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Essential Graduate Physics

Lecture Notes and Problems

Exercise Problems with Model Solutions

Part SM: Statistical Mechanics

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Chapter 1. Review of Thermodynamics

Problem 1.1. Two bodies, with temperature-independent heat capacities $C_{1,2}$ and initial temperatures $T_{1,2}$ are placed into a weak thermal contact. Calculate the change of the total entropy of the system before it reaches thermal equilibrium.

Solution: Due to the thermal contact's weakness, the temperature-equilibration process is relatively slow, so each body is close to its internal thermal equilibrium at any given time. As a result, we may use Eq. (1.19) of the lecture notes to describe the change of the body's entropy during the transfer of an elementary heat dQ_j to it:

$$dS_j = \frac{dQ_j}{T_j'}, \quad \text{with} \quad j = 1, 2\,. \qquad (*)$$

(In this solution, the prime signs mark intermediate, instant temperatures of the bodies, to distinguish them from the initial values specified in the assignment.) On the other hand, by the definition of the heat capacity, for the same dQ_j, we may also write

$$dQ_j = C_j dT_j'\,.$$

Plugging this expression into Eq. (*) and integrating the result through the whole temperature equilibration process, we get

$$\Delta S = \int_{\text{ini}}^{\text{fin}} (dS_1 + dS_2) = C_1 \int_{T_1}^{T_{\text{fin}}} \frac{dT_1'}{T_1'} + C_2 \int_{T_2}^{T_{\text{fin}}} \frac{dT_2'}{T_2'} = C_1 \ln\frac{T_{\text{fin}}}{T_1} + C_2 \ln\frac{T_{\text{fin}}}{T_2}, \qquad (**)$$

where T_{fin} is the final, common temperature of the system. This temperature may be calculated from the energy conservation law:

$$dQ_1 + dQ_2 = 0, \quad \text{i.e.} \quad C_1 dT_1' + C_2 dT_2' = 0\,.$$

The integration of the last relation through the whole process yields

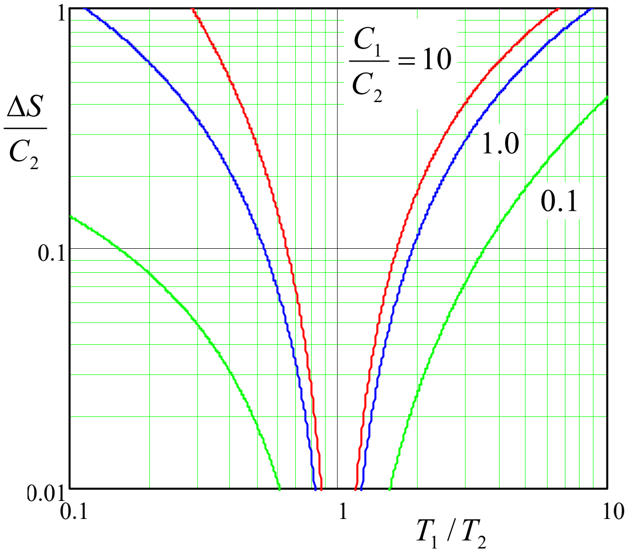
$$C_1(T_{\text{fin}} - T_1) + C_2(T_{\text{fin}} - T_2) = 0\,.$$

From here,

$$T_{\text{fin}} = \frac{C_1T_1 + C_2T_2}{C_1 + C_2},$$

so, finally, Eq. (**) yields

$$\Delta S = C_1 \ln\frac{C_1T_1 + C_2T_2}{(C_1 + C_2)T_1} + C_2 \ln\frac{C_1T_1 + C_2T_2}{(C_1 + C_2)T_2}\,.$$



Typical results given by this formula are shown in the figure on the right. (Notice its log-log scale.) An elementary analysis of the result shows that if $C_{1,2} > 0$, the change of entropy is positive for any parameters of the system – besides the trivial case $T_1 = T_2$ when there is no heat flow at all, and hence $\Delta S = 0$.

Problem 1.2. A gas portion has the following properties:

(i) its heat capacity $C_V = aT^b$, and

(ii) the work $\mathscr{W}_T$ necessary for its isothermal compression from V_2 to V_1 equals $cT\ln(V_2/V_1)$,

where a, b, and c are some constants. Find the equation of state of the gas and calculate the temperature dependences of its entropy S and thermodynamic potentials E, H, F, G, and Ω.

Solution: By plugging condition (ii) of the problem's assignment into Eq. (1.1) of the lecture notes, we get

$$P(T,V_1) = -\frac{\partial \mathscr{W}_T}{\partial V_1} = \frac{cT}{V_1},$$

so the equation of state coincides with that of an ideal gas (see Eq. (1.44) of the lecture notes) with $N = c$. Hence we may use Eqs. (1.45)-(1.50), with that substitution, to finalize the solution. In particular, comparing Eq. (1.50) and condition (i) of the assignment, we obtain

$$\frac{d^2 f}{dT^2} = -\frac{1}{NT} C_V = -\frac{a}{c} T^{b-1}.$$

Integrating this equality twice, we get

$$\frac{df}{dT} = -\frac{a}{bc} T^b + d, \qquad f = -\frac{a}{b(b+1)c} T^{b+1} + dT + g, \qquad \text{i.e. } f - T\frac{df}{dT} = \frac{a}{(b+1)c} T^{b+1} + g,$$

where d and g are some new constants. With that, Eqs. (1.45)-(1.49) give

$$S = N\left(\ln\frac{V}{N} - \frac{df}{dt}\right) = c\ln\frac{V}{c} + \frac{a}{b}T^b - cd\,,$$

$$F = -NT\ln\frac{V}{N} + Nf(T) = -cT\ln\frac{V}{c} - \frac{a}{b(b+1)}T^{b+1} + c(dT + g),$$

$$E = N\left(f - T\frac{df}{dT}\right) = \frac{a}{b+1}T^{b+1} + cg, \qquad H \equiv E + PV = \frac{a}{b+1}T^{b+1} + c(g + T),$$

$$G \equiv F + PV = -cT\ln\frac{V}{c} - \frac{a}{b(b+1)}T^{b+1} + c\left[(d+1)T + g\right], \qquad \Omega = -PV = -cT.$$

Note that all thermodynamic potentials (besides Ω) are still determined up to some arbitrary constants.

Problem 1.3. A volume with an ideal classical gas of similar molecules is separated into two parts with a partition so that the number N of molecules in each part is the same but their volumes are different. The gas is initially in thermal equilibrium with the environment, and its pressure in one part is P_1, and in the other part, P_2. Calculate the change of entropy resulting from a fast removal of the partition.

Solution: Before the removal of the partition, the total entropy (as an extensive parameter) is the sum of entropies of its independent parts, $S_{\text{ini}} = S_1 + S_2$, so Eq. (1.46) of the lecture notes yields

$$S_{\text{ini}} = N\left[\ln\frac{V_1}{N} - \frac{df}{dT}\right] + N\left[\ln\frac{V_2}{N} - \frac{df}{dT}\right] = N\left[\ln\frac{T^2}{P_1P_2} - 2\frac{df}{dT}\right],$$

where the last expression is obtained by using the equation of state, $V/N = T/P$, for each part of the volume, and T is the initial temperature of the system. At a fast gas expansion, we may neglect the thermal exchange of the gas with its environment. Also, at a fast removal of the partition (say, sideways), the gas cannot perform any mechanical work on it. As a result, the gas' total energy is conserved during the removal. According to Eq. (1.47) of the lecture notes, this means that the gas temperature T is conserved as well. As a result, the partition removal does not cause any heat flow to/from the environment, so this result for temperature is valid for all times after it. In addition, the total number of molecules ($2N$) is also conserved. Because of that, we may use Eq. (1.44) to calculate the final pressure of the gas, after the partition's removal, as

$$P_{\text{fin}} = \frac{2NT}{V_1 + V_2} \equiv \frac{2T}{V_1/N + V_2/N} = \frac{2T}{T/P_1 + T/P_2} \equiv 2\frac{P_1P_2}{P_1 + P_2}. \qquad (*)$$

Now applying Eq. (1.46) again and then using Eq. (*), we may calculate the final entropy as

$$S_{\text{fin}} = 2N\left[\ln\frac{V_1 + V_2}{2N} - \frac{df}{dT}\right] = 2N\left[\ln\frac{T}{P_{\text{fin}}} - \frac{df}{dT}\right] = 2N\left[\ln\frac{(P_1 + P_2)T}{2P_1P_2} - \frac{df}{dT}\right]$$
$$\equiv N\left[\ln\frac{(P_1 + P_2)^2}{4P_1P_2} + \ln\frac{T^2}{P_1P_2} - 2\frac{df}{dT}\right].$$

Hence, its change during the expansion,

$$\Delta S \equiv S_{\text{fin}} - S_{\text{ini}} = N\ln\frac{(P_1 + P_2)^2}{4P_1P_2} \geq 0,$$

does not depend on temperature – at least explicitly.

As a sanity check, our result shows that if $P_1 = P_2$, the entropy does not change. (This is natural because, in this case, the partition's removal has no macroscopic consequences.) For any other relation of the initial pressures, the irreversible process caused by the partition removal results in a growth of the entropy – as it should.

Problem 1.4. An ideal classical gas of N particles is initially confined to volume V, and is in thermal equilibrium with a heat bath of temperature T. Then the gas is allowed to expand to volume $V' > V$ in one of the following ways:

(i) The expansion is slow, so due to the sustained thermal contact with the heat bath, the gas temperature remains equal to T.

(ii) The partition separating the volumes V and $(V' - V)$ is removed very fast, allowing the gas to expand rapidly.

For each case, calculate the changes of pressure, temperature, energy, and entropy of the gas during its expansion, and compare the results.

Solutions:

(i) The first process is isothermal, at temperature T, so for the initial pressure P of the gas and its final pressure P', the equation of state (see Eq. (1.44) of the lecture notes) gives

$$P = \frac{NT}{V}, \qquad P' = \frac{NT}{V'}, \qquad \text{i.e. } \Delta P \equiv P' - P = NT\left(\frac{1}{V'} - \frac{1}{V}\right). \tag{*}$$

Since there is no change in temperature, the energy of the gas (which, according to Eq. (1.47), is a function of temperature alone) does not change either. However, at the expansion, the gas performs a nonvanishing mechanical work (for example, upon the piston that moderates the expansion speed to keep the process isothermal):

$$-\mathscr{W} = \int_V^{V'} P(V'')dV'' = \int_V^{V'} \frac{NT}{V''}dV'' = NT\ln\frac{V'}{V} > 0\,.$$

Since the gas energy does not change, this energy loss has to be exactly compensated by the heat $\Delta Q = -\mathscr{W} > 0$ transferred from the heat bath. This enables us to calculate the change of the entropy during the process by using Eq. (1.20) with $T = \text{const}$:

$$\Delta S = \frac{\Delta Q}{T} = \frac{-\mathscr{W}}{T} = N\ln\frac{V'}{V} > 0\,. \tag{**}$$

(The same expression follows from Eq. (1.46) because df/dT is a function of T alone and hence does not change at the process.)

(ii) The fast expansion is irreversible, without time for any heat transfer, so $\Delta Q = 0$, and without performing any mechanical work, $\mathscr{W} = 0$. (At a free expansion, there is no piston to move.) Hence, per Eq. (1.18), the internal energy E of the gas cannot change: $\Delta E = 0$. Now using Eq. (1.47) again, we may conclude that the gas temperature cannot change either, $\Delta T = 0$.[1] On the other hand, according to Eqs. (1.44) and (1.46), the gas pressure and its entropy are determined by the current state of the gas rather than by the way it has been reached, so their changes are described by the same relations (*) and (**).

Note, however, that in contrast to the first (slow and reversible) process, at which the total entropy of the system (the gas + the heat bath) does not change, the second, fast process is irreversible, with the total entropy of the system rising by the ΔS given by Eq. (**). Note also that since the gas temperature does not change in either of these cases, all the above results are valid regardless of whether the heat capacity of the gas depends on T or not.

Problem 1.5. For an ideal classical gas with temperature-independent specific heat, derive the relation between P and V at its adiabatic expansion/compression.

Solution: Per Eq. (1.50) of the lecture notes,

$$\frac{d^2 f}{dT^2} = -\frac{c_V}{T}\,.$$

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[1] Note that this result is only valid for an ideal gas, while for real gases (discussed in Chapters 3 and 4 of the lecture notes), this process may lead to either heating or cooling – see, e.g., Problem 4.3.

where $c_V \equiv C_V/N$ is the specific heat – namely the heat capacity per unit particle. If C_V is temperature-independent, so is c_V, and integrating both sides of the above equation over temperature, we get

$$\frac{df}{dT} = -c_V \ln T + a ,$$

where a is another temperature-independent constant. As was discussed in Sec. 1.3 of the lecture notes, at an adiabatic process, the entropy has to be constant, and hence Eq. (1.46) yields

$$\ln\frac{V}{N} - \frac{df}{dT} \equiv \ln\frac{V}{N} + c_V \ln T - a \equiv \ln\left(\frac{V}{N}T^{c_V}\right) - a = \text{const}.$$

(Here and below, the expressions "const" mean various amounts remaining constant during the adiabatic expansion/compression.) So we get the following relation between temperature and volume:

$$\frac{V}{N}T^{c_V} = \text{const}.$$

Now by using the equation of state (1.44), rewritten as $T = PV/N$, we get the required relation,

$$P^{c_V}\left(\frac{V}{N}\right)^{c_V+1} = \text{const}.$$

Traditionally, this relation is represented in the form

$$PV^{\gamma} = \text{const},$$

where the constant $\gamma \equiv (c_V + 1)/c_V$, per Eq. (1.51), is the specific heat (and hence heat capacity) ratio:

$$\gamma \equiv \frac{c_V + 1}{c_V} \equiv \frac{C_V + N}{C_V} = \frac{C_P}{C_V}.$$

Please remember that this result is only valid if C_V, and hence $C_P = C_V + N$, are temperature-independent.

Problem 1.6. Calculate the speed and the wave impedance of acoustic waves propagating in an ideal classical gas with temperature-independent specific heat, in the limits when the propagation may be treated as:

(i) an isothermal process, and
(ii) an adiabatic process.

Which of these limits is achieved at higher wave frequencies?

Solution: As classical mechanics shows,[2] the speed v and the wave impedance $\mathscr{Z}$ of a longitudinal acoustic wave in a fluid (i.e., a medium with a negligible shear modulus μ) are

$$v = \left(\frac{K}{\rho}\right)^{1/2}, \qquad \mathscr{Z} = (K\rho)^{1/2},$$

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[2] See, e.g., CM Sec. 7.7, in particular Eq. (7.114), and Eq. (7.120) with $\mu = 0$.

where ρ is the volumic mass density of the fluid: $\rho \equiv M/V = mN/V$ (where m is the mass of one particle), and K is its *bulk modulus* (reciprocal compressibility) defined as

$$K \equiv -V\left(\frac{\partial P}{\partial V}\right)_X ,$$

where X is the parameter remaining constant at the fluid's expansion/compression. In typical liquids, K is very high and does not depend much on what X is; however, in gases the difference is substantial.

(i) At an *isothermal* process, we may take $X = T$, so using Eq. (1.44) of the lecture notes in the form $P = NT/V$, so

$$K = -V\left(-\frac{NT}{V^2}\right) = P, \qquad v = \left(\frac{P}{\rho}\right)^{1/2} = \left(\frac{T}{m}\right)^{1/2}, \qquad \mathcal{Z} = (P\rho)^{1/2} = (mT)^{1/2} n ,$$

where $n \equiv N/V$ is the particle density. Note that v does not depend on the density, and hence on the static compression of the gas. Also, as will be discussed in Chapter 2, this v coincides with the r.m.s. velocity of the gas particles in any fixed direction.

(ii) As was discussed in the model solution of the previous problem, at an *adiabatic* process (where we may take $X = S =$ const), the pressure depends on volume differently: $P = fV^{-\gamma}$, where $\gamma \equiv C_P/C_V = (c_V + 1)/c_V$, while the factor f does not depend on V, so the differentiation yields

$$K = -V\left(-\gamma f V^{-\gamma-1}\right) = \gamma P, \qquad v = \left(\frac{\gamma P}{\rho}\right)^{1/2} = \left(\frac{\gamma T}{m}\right)^{1/2}, \qquad \mathcal{Z} = (\gamma P\rho)^{1/2} = (\gamma mT)^{1/2} n .$$

Since $\gamma > 1$ by definition, these results show that the acoustic wave velocity and impedance in the adiabatic case are always larger than those in the isothermal case. Practically, the isothermal limit may be reached only at very low frequencies, where the wave's time period is long enough to enable temperature to constantly equilibrate over the whole size of the system. At the usual (say, audible) sound frequencies, ambient conditions, and for human-scale gas volumes, only the adiabatic result is realistic.

Problem 1.7. As will be discussed in Sec. 3.5 of the lecture notes, the so-called "hardball" models of classical particle interaction yield the following equation of state of a gas of such particles:

$$P = T\varphi(n),$$

where $n = N/V$ is the particle density, while the function $\varphi(n)$ is generally different from that ($\varphi_{\text{ideal}}(n) = n$) of the ideal gas, but still independent of temperature. For such a gas, with a temperature-independent c_V, calculate:

(i) the energy of the gas, and
(ii) its pressure as a function of n at an adiabatic compression.

Solutions:

(i) First of all, let us notice that at $N =$ const,

$$dn \equiv d\left(\frac{N}{V}\right) = -N\frac{dV}{V^2}, \qquad \text{so } dV = -\frac{V^2}{N}dn \equiv -N\frac{dn}{n^2} .$$

Now, just as it was done in Sec. 1.4 of the lecture notes for the ideal gas, we can start with the calculation of the free energy:

$$F = -\int PdV\Big|_{N,T=\text{const}} = -T\int \varphi(n)dV\Big|_{N,T=\text{const}} = TN\Phi(n) + Nf(T), \quad \text{where } \Phi(n) \equiv \int \frac{\varphi(n)dn}{n^2},$$

and then proceed to the calculation of the entropy and then the internal energy:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = -N\left[\Phi(n) + \frac{df}{dT}\right], \qquad \text{so } E = F + TS = N\left(f - T\frac{df}{dT}\right).$$

(ii) The last relation between E and $f(T)$ is the same as for the ideal gas – see Eq. (1.47) of the lecture notes. As a result, c_V is also expressed by the same Eq. (1.50), giving

$$\frac{d^2 f}{dT^2} = -\frac{c_V}{T}.$$

Since, per the assignment, c_V is temperature-independent, the integration of this relation over T yields

$$\frac{df}{dT} = -c_V \ln T + \text{const}.$$

Now, just as it was done in the solution of Problem 5, the requirement of the entropy's constancy at the adiabatic compression (at constant N) yields

$$\Phi(n) + \frac{df}{dt} \equiv \Phi(n) - c_V \ln T \equiv \ln\frac{\exp\{\Phi(n)\}}{T^{c_V}} = \text{const}, \qquad \text{i.e. } T^{c_V} = \text{const}\times\exp\{\Phi(n)\}.$$

Now by using the T expressed from the given equation of state, $T = P/\varphi(n)$, we get

$$P = \text{const}\times\varphi(n)\left[\exp\{\Phi(n)\}\right]^{1/c_V} \equiv \text{const}\times\varphi(n)\left[\exp\left\{\int\frac{\varphi(n)dn}{n^2}\right\}\right]^{1/c_V}.$$

As a sanity check, for an ideal gas where $\varphi(n) = n$, so $\Phi(n) = \ln n + \text{const}$, i.e. $\exp\{\Phi(n)\} \propto n$, the above result is reduced to

$$P \propto n(n)^{1/c_V} \propto n^{(1 + 1/c_V)} \equiv (N/V)^{(c_V+1)/c_V},$$

i. e. to the solution of Problem 5.

Problem 1.8. For an arbitrary thermodynamic system with a fixed number of particles, prove the four *Maxwell relations* (mentioned in Sec. 1.4 of the lecture notes):

$$\text{(i)}: \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \qquad \text{(ii)}: \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S,$$

$$\text{(iii)}: \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \qquad \text{(iv)}: \left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S,$$

and also the following formula:

$$\text{(v)}: \quad \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P.$$

Solution: The mixed partial second derivative of the free energy $F(T, V)$ may be represented in two equivalent forms:

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right]_V.$$

But according to Eqs. (1.35) of the lecture notes, the internal derivative on the left-hand side of this equality is just $(-S)$, while that on the right-hand side is just $(-P)$, thus proving Eq. (i). The remaining three Maxwell relations may be proved absolutely similarly, applying similar arguments to the partial derivatives of the following thermodynamic potentials:

(ii) $H(P, S)$ – see Eqs. (1.31);

(iii) $G(P, T)$ – see Eqs. (1.39); and

(iv) $E(S,V)$ – see Eqs. (1.9) and (1.15).

In order to prove Eq. (v), let us divide all terms of the general Eq. (1.17),

$$dE = TdS - PdV,$$

by dV, and apply it to the particular case when all these elementary changes are performed at a constant temperature. The result is

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P.$$

Now using Eq. (i), we get Eq. (v) proved.

Note that there are quite a few other similar thermodynamic equalities for E and other thermodynamic potentials, which may be proved similarly.[3]

Problem 1.9. Express the difference $(C_P - C_V)$ between the heat capacities difference of a system via its equation of state $P = P(V, T)$.

Solution: Subtracting the two expressions derived at the end of Section 1.3 of the lecture notes, we get

$$C_P - C_V = T\left[\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V\right], \qquad (*)$$

so we only need to express the right-hand side of this relation via the equation of state. The entropy S of a system with a fixed number N of particles is completely determined by its volume V and temperature T, and hence may be considered a function of these two independent arguments. Hence its full differential may be expressed as

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[3] See, e.g., Eqs. (16.6)-(16.8) in L. Landau and E. Lifshitz, *Statistical Physics, Part 1*, 3rd ed., Pergamon, 1980.

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT . \qquad (**)$$

On the other hand, the same arguments V and T uniquely determine pressure P via the equation of state. Hence we may alternatively consider the entropy as a function of P and T, and represent the same differential in another form:

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT . \qquad (***)$$

The three differentials dV, dP, and dT participating in Eqs. (**) and (***) are not fully independent, but are related by the equation of state $P = P(V, T)$, whose differentiation gives

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT .$$

Plugging this expression for dP into Eq. (***), and then requiring the dS given by the resulting relation to be equal to that given by Eq. (**), we get

$$\left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT = \left(\frac{\partial S}{\partial P}\right)_T \left[\left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT\right] + \left(\frac{\partial S}{\partial T}\right)_P dT .$$

This equality has to be satisfied for arbitrary elementary changes dV and dT of the two independent arguments V and T. This requirement yields the following two equalities for the partial derivatives:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T, \qquad \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial S}{\partial T}\right)_P .$$

Eliminating $(\partial S/\partial P)_T$ from the system of these two relations, we get the following expression for the difference inside the square brackets in Eq. (*):

$$\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T \frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T} .$$

Now using the Maxwell relation whose proof was the first task of the previous problem,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V ,$$

to eliminate the entropy from the right-hand side, we finally get

$$C_P - C_V = -T \frac{(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T} . \qquad (****)$$

As a sanity check: for the ideal classical gas, the equation of state is given by Eq. (1.44) of the lecture notes, $P = NT/V$, and hence

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{N}{V}, \qquad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{NT}{V^2},$$

so Eq. (****) is reduced to the same result,

$$C_P - C_V = N ,$$

that was obtained differently in the lecture notes – see Eq. (1.51).

More generally, the derivative $(\partial P/\partial V)_T$ has to be negative for the mechanical stability of the system,[4] so Eq. (****) confirms the inequality $C_P - C_V > 0$, which was already mentioned in Sec. 1.3 of the lecture notes. Note also that according to the same formula, for materials with very low *compressibility* $-(\partial V/\partial P)/V$, such as most solids and liquids, the difference between the two heat capacities is much lower than any of C_V and C_P, thus justifying the frequent usage of the term "heat capacity C" without specifying the conditions of its measurement – as this was done, for example, in Problem 1.1 and will be done on other occasions in this course.

Note also that if we represented the equation of state in the alternative form $V = V(P, T)$, and then acted absolutely as above, we would get an equivalent expression:[5]

$$C_P - C_V = -T\frac{(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T},$$

but conceptually, the equality $P = P(V, T)$ and hence Eq. (****) have a more direct physical sense.

Let me finish by challenging the reader to streamline the above derivation of Eq. (****) by using the well-known chain rule

$$\left(\frac{\partial X}{\partial Y}\right)_Z\left(\frac{\partial Y}{\partial Z}\right)_X\left(\frac{\partial Z}{\partial X}\right)_Y = -1,$$

which is valid for any three variables X, Y, and Z that are related as $f(X, Y, Z) = 0$, where f is a differentiable function of all its arguments.

Problem 1.10. Prove that the *isothermal compressibility*[6] of a system of N similar particles,

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$$

may be expressed in two different ways:

$$\kappa_T = \frac{V^2}{N^2}\left(\frac{\partial^2 P}{\partial \mu^2}\right)_T = \frac{V}{N^2}\left(\frac{\partial N}{\partial \mu}\right)_{T,V}.$$

Solution: By combining Eq. (1.60) of the lecture notes for the grand canonical potential, $\Omega = -PV$, and Eq. (1.61) for its full differential, for the case of constant temperature ($dT = 0$), we get

$$d(-PV) = -PdV - Nd\mu, \qquad \text{for } T = \text{const}.$$

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[4] This condition, virtually evident from Fig. 1.4, will be further discussed in Sec. 4.1 of the lecture notes.

[5] The derivative in the numerator of this expression is proportional to the system's *thermal expansion coefficient* α, while that in the denominator, is to its *isothermal compressibility* κ_T – see the next problem.

[6] Note that the compressibility is just the reciprocal bulk modulus, $\kappa = 1/K$ – see, e.g., CM Sec. 7.3.

After spelling out the derivative on the left-hand side and the cancellation of $-PdV$, we get simply

$$VdP = Nd\mu, \qquad \text{for } T = \text{const}.$$

This relation[7] means that we may write

$$\left(\frac{\partial P}{\partial \mu}\right)_T = \frac{N}{V}, \tag{*}$$

regardless of whether the volume V of the system or the number N of particles in it (or maybe some combination of the two) is fixed.

Now let us use Eq. (*) to transform the second derivative participating in the first equality to be proved:

$$\left(\frac{\partial^2 P}{\partial \mu^2}\right)_T \equiv \left[\frac{\partial}{\partial \mu}\left(\frac{\partial P}{\partial \mu}\right)_T\right]_T = \frac{\partial}{\partial \mu}\left(\frac{N}{V}\right)_T. \tag{**}$$

In the particular case when the number of particles is fixed, we may continue as

$$\left(\frac{\partial^2 P}{\partial \mu^2}\right)_T = N\frac{\partial}{\partial \mu}\left(\frac{1}{V}\right)_{T,N} \equiv -\frac{N}{V^2}\left(\frac{\partial V}{\partial \mu}\right)_{T,N}.$$

In a system with fixed T and N, the state of the system (in particular both V and μ) is uniquely defined by pressure P, we may continue even further as

$$\left(\frac{\partial^2 P}{\partial \mu^2}\right)_T = -\frac{N}{V^2}\left(\frac{\partial V}{\partial P}\right)_{T,N}\left(\frac{\partial P}{\partial \mu}\right)_{T,N} = -\frac{N}{V^2}\left(\frac{\partial V}{\partial P}\right)_{T,N}\frac{N}{V} \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}\frac{N^2}{V^2},$$

where at the second step, Eq. (*) was used again. But the last expression, besides the last fraction, by definition, is the isothermal compressibility, thus giving us the first relation we had to prove:

$$\kappa_T = \frac{V^2}{N^2}\left(\frac{\partial^2 P}{\partial \mu^2}\right)_T.$$

Now let us transform this expression by using Eq. (**) again:

$$\kappa_T = \frac{V^2}{N^2}\frac{\partial}{\partial \mu}\left(\frac{N}{V}\right)_T.$$

Performing the differentiation for the case when the volume rather than the number of particles is fixed, we get the second relation in question:

$$\kappa_T = \frac{V}{N^2}\left(\frac{\partial N}{\partial \mu}\right)_{T,V}.$$

This formula may be useful, in particular, for a convenient representation of statistical fluctuations of the number of particles in systems with fixed T, V, and μ – see Chapter 5 below.

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[7] It may be also obtained, for $dT = 0$, from Eq. (1.53c), $dG = -SdT + VdP + \mu dN$, after using Eq. (1.56), $G = \mu N$.

Finally, an additional exercise for the reader: use a calculation similar to that carried out in the previous problem's solution to prove the following relation,

$$\kappa_T - \kappa_S = \frac{TV\alpha^2}{C_P},$$

where κ_S is the *adiabatic compressibility* defined similarly to κ_T:

$$\kappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,N},$$

and α is the *thermal expansion* coefficient:

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}.$$

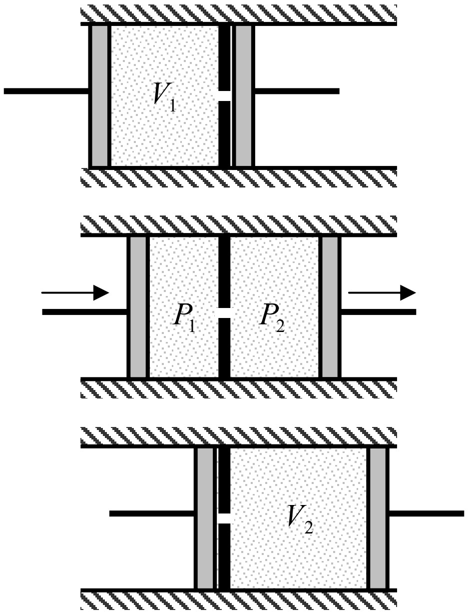
Problem 1.11. *Throttling*[8] is an expansion of gas by driving it through either a small hole (called the *throttling valve*) or a porous partition, using an externally sustained difference of pressure values on two sides of such an obstacle.

(i) Prove that in the absence of heat exchange with the environment, the enthalpy of the transferred gas does not change.

(ii) Express the *Joule-Thomson coefficient* $(\partial T/\partial P)_H$, which characterizes the gas temperature change at throttling, via its thermal expansion coefficient $\alpha \equiv (\partial V/\partial T)_P/V$.

Solutions:

(i) The figure on the right shows a simple system that can sustain constant pressure values P_1 and $P_2 < P_1$ on two sides of a throttling valve through the throttling process. (The top panel shows the beginning of the process, while the bottom one, its end.) The total work performed by the two pistons on the gas during the process is obviously



$$\Delta \mathscr{W} = P_1V_1 - P_2V_2.$$

In the absence of heat transfer to/from the gas ($dQ = 0$), the integration of the basic Eq. (1.18) through the process yields

$$\Delta E = \Delta \mathscr{W} = P_1V_1 - P_2V_2,$$

so the gas' enthalpy (1.27) indeed does not change:

$$\Delta H \equiv H_2 - H_1 \equiv (E_2 + P_2V_2) - (E_1 + P_1V_1) = \Delta E + P_2V_2 - P_1V_1 = 0.$$

(ii) For an arbitrary slow process in a system with a fixed number of particles, we may use Eq. (1.30) of the lecture notes:

$$dH = TdS + VdP. \qquad (*)$$

---

[8] Sometimes it is called the *Joule-Thomson process*, though more typically, the latter term refers to the possible gas cooling at the throttling.

Assuming that entropy S is expressed as a function of pressure P and temperature T, we may continue as

$$dH = T\left[\left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT\right] + VdP \equiv T\left(\frac{\partial S}{\partial T}\right)_P dT + \left[T\left(\frac{\partial S}{\partial P}\right)_T + V\right]dP.$$

As was discussed in Sec. 1.3 of the lecture notes, the coefficient before dT in the last expression is just the heat capacity at a fixed pressure, so for a process with $H = \text{const}$ (i.e. $dH = 0$), we get

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[-T\left(\frac{\partial S}{\partial P}\right)_T - V\right].$$

However, according to the solution of Problem 8(iii), the partial derivative on the right-hand side of this result may be expressed via the thermal expansion coefficient α:

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \equiv \frac{V}{C_P}\left[T\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P - 1\right] \equiv \frac{V}{C_P}(T\alpha - 1).$$

In Chapter 4, this expression will be used for the evaluation of the inversion point (i.e. the point where the Joule-Thomson coefficient changes sign) of the van der Waals gas.

Note also that the throttling always leads to the entropy's increase, i.e. is irreversible. Indeed, from Eq. (*), we see that at $dH = 0$, $dS = -(V/T)dP$, and since the expression in the parentheses is always positive, the drop of pressure during this process always leads to $dS > 0$.

Problem 1.12. A system with a fixed number of particles is in thermal and mechanical contact with its environment of temperature T_0 and pressure P_0. Assuming that the internal relaxation of the system is sufficiently fast, derive the conditions of stability of its equilibrium with the environment with respect to small perturbations.

Solution: The above assumption means that even if the volume V and energy E of the system deviate from their equilibrium values imposed by the environment, its parts are in a virtual mutual equilibrium, so we may apply to the system all the results discussed in Chapter 1 of the lecture notes. In particular, the system's equilibrium should correspond to the minimum of the Gibbs energy (1.37), with $T = T_0$ and $P = P_0$:

$$G = E - T_0 S + P_0 V\ . \qquad (*)$$

Let us expand G into the Taylor series in small deviations $\tilde{S}$ and $\tilde{V}$ from the equilibrium,[9]

$$\tilde{G} = \frac{\partial G}{\partial S}\tilde{S} + \frac{\partial G}{\partial V}\tilde{V} + \frac{1}{2}\frac{\partial^2 G}{\partial^2 S}\tilde{S}^2 + \frac{\partial^2 G}{\partial S \partial V}\tilde{S}\tilde{V} + \frac{1}{2}\frac{\partial^2 G}{\partial^2 V}\tilde{V}^2 + \dots$$

Besides the borderline cases when the displayed terms give an uncertain result, the higher-order terms of the expansion do not affect the stability and may be ignored. Hence, by using Eq. (*), we get

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[9] Here, each partial derivative is taken at the condition that the counterpart variable of our set $\{S, V\}$ is fixed, for example, $\partial G/\partial S \equiv (\partial G/\partial S)_V$, etc. For brevity, I will spell out this common notation only in the final result.

$$\tilde{G} = \left(\frac{\partial E}{\partial S} - T_0\right)\tilde{S} + \left(\frac{\partial E}{\partial V} + P_0\right)\tilde{V} + \frac{1}{2}\frac{\partial^2 E}{\partial^2 S}\tilde{S}^2 + \frac{\partial^2 E}{\partial S \partial V}\tilde{S}\tilde{V} + \frac{1}{2}\frac{\partial^2 E}{\partial^2 V}\tilde{V}^2 .$$

Here all the derivatives have to be taken at the equilibrium point. According to Eqs. (1.9) and (1.15), at this point, both parentheses in the last expression vanish, and we are left with the quadratic form

$$\tilde{G} = \frac{1}{2}\frac{\partial^2 E}{\partial^2 S}\tilde{S}^2 + \frac{\partial^2 E}{\partial S \partial V}\tilde{S}\tilde{V} + \frac{1}{2}\frac{\partial^2 E}{\partial^2 V}\tilde{V}^2 . \tag{**}$$

For the equilibrium to be stable, this form has to be positive for any $\tilde{S}$ and $\tilde{V}$, so that in its trend to minimize *G*, the system would "try" to reduce the magnitudes of these deviations.[10] Mathematics tells us that this is the case if the following three conditions are satisfied:[11]

$$\frac{\partial^2 E}{\partial^2 S} > 0, \qquad \frac{\partial^2 E}{\partial^2 V} > 0, \qquad \frac{\partial^2 E}{\partial^2 S}\frac{\partial^2 E}{\partial^2 V} > \left(\frac{\partial^2 E}{\partial S \partial V}\right)^2 .$$

Now using Eqs. (1.9) and (1.15) again, we may represent these conditions as

$$\left(\frac{\partial T}{\partial S}\right)_V \equiv \frac{T}{C_V} > 0, \qquad -\left(\frac{\partial P}{\partial V}\right)_S \equiv \frac{1}{V\kappa_S} > 0, \qquad \frac{T}{C_V}\frac{1}{V\kappa_S} > \left(\frac{\partial T}{\partial V}\right)_S^2 \equiv \frac{1}{V^2\alpha_S^2},$$

where $\kappa_S \equiv -(\partial V/\partial T)_S/V$ is the adiabatic compressibility and $\alpha_S \equiv -(\partial V/\partial T)_S/V$ is the adiabatic thermal expansion coefficient – see also the model solution of the previous problem.

As will be shown in Chapter 5 of the lecture notes, at appropriate conditions, the left-hand sides of the first two inequalities provide the scales of spontaneous fluctuations of, respectively, the thermal energy and the volume of the system.

<u>Problem 1.13</u>. Derive the analog of the relation for the difference ($C_P - C_V$), whose derivation was the task of Problem 9, for a fixed-volume sample with a uniform magnetization $\mathscr{M}$ parallel to the uniform external field $\mathscr{H}$. Spell out this result for a paramagnet that obeys the *Curie law* $\mathscr{M} \propto \mathscr{H}/T$ – the relation to be derived and discussed later in this course.

Solution: For a fixed-volume system, the contribution of the variables *V* and *P* into the thermodynamic potentials, and hence to the observable properties, is negligible. Instead, in a magnetic material, their roles are played by the Cartesian components of, respectively, the magnetization $\mathscr{M}$ and the external magnetic field $\mathscr{H}$. For our current case of parallel and space-independent vectors $\mathscr{M}$ and $\mathscr{H}$, one of the coordinate axes may be directed along them, so each of these vectors would have just one Cartesian component. In this case, according to Eqs. (1.1) and (1.3) of the lecture notes, all formulas of thermodynamics are valid with the replacements

$$V \to \mathscr{M}V, \qquad P \to -\mu_0 \mathscr{H} . \tag{*}$$

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[10] This condition, similar to that for the potential energy's minimum in mechanics, is a particular case of what is called *Le Châtelier' principle*.

[11] These inequalities may be readily derived: it is sufficient to take, in Eq. (**), $\tilde{S} = \lambda\tilde{V}$, getting $\tilde{G} = f(\lambda)\tilde{V}^2$, and then require the coefficient $f(\lambda)$ to be positive for all values of λ.

In particular, instead of the difference ($C_P - C_V$), we may consider the difference ($C_{\mathscr{H}} - C_{\mathscr{M}}$) between the heat capacities at fixed magnetization and at fixed field. Making this substitution and also the replacements (*) in the last result[12] of the model solution of Problem 9:

$$C_P - C_V = -T\frac{(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T},$$

we get

$$C_{\mathscr{H}} - C_M = V\mu_0 T\frac{(\partial \mathscr{M}/\partial T)_{\mathscr{H}}^2}{(\partial \mathscr{M}/\partial \mathscr{H})_T} \equiv V\mu_0\frac{T}{\chi_T}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}}^2, \qquad (**)$$

where the partial derivative

$$\chi \equiv \frac{\partial \mathscr{M}}{\partial \mathscr{H}}$$

is called the *magnetic susceptibility* of the material – in Eq. (**), the one taken at a fixed temperature.

In particular, for a Curie-law paramagnet with $\mathscr{M} = a\mathscr{H}/T$ with a constant a, we get $\chi_T = a/T$, $(\partial\mathscr{M}/\partial T)_{\mathscr{H}} = -a\mathscr{H}/T^2$, and Eq. (**) yields

$$C_{\mathscr{H}} - C_M = V\mu_0 a\left(\frac{\mathscr{H}}{T}\right)^2,$$

so $C_{\mathscr{H}} \to C_{\mathscr{M}}$ at either $\mathscr{H} \to 0$ or $T \to \infty$.

Problem 1.14. Two bodies have equal temperature-independent heat capacities C but different initial temperatures, $T_1 > T_2$. Calculate the largest mechanical work obtainable from this system by using a heat engine.

Solution: The largest work may be extracted by using the bodies as the hot and cold heat baths of a Carnot heat engine, with each cycle taking just a small heat portion, $dQ_H << CT_H$, from the hotter body and releasing an even smaller amount of heat, $dQ_L < dQ_H$, into the colder body – while turning the difference $dQ_H - dQ_L$ into the mechanical work $-d\mathscr{W}$. Each engine cycle cools the former body and heats the latter body just a bit:

$$dT_H = -\frac{dQ_H}{C}, \qquad dT_L = \frac{dQ_L}{C}.$$

Since each such change is small, we may also use Eq. (1.66) of the lecture notes,

$$\frac{dQ_H}{dQ_L} = \frac{T_H}{T_L},$$

which has been derived for constant T_H and T_L. Combining these three relations, we see that the temperature changes obey the rule

$$\frac{dT_H}{dT_L} = -\frac{T_H}{T_L}.$$

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[12] The magnetic analog of the first of those results, which is given by Eq. (****) of that solution, includes partial derivatives at fixed $\mathscr{M}$ and is less useful because, in practice, it is easier to fix the external magnetic field rather than the material's magnetization.

Integrating this relation, rewritten as

$$\frac{dT_H}{T_H}+\frac{dT_L}{T_L}=0, \qquad \text{i.e. as} \quad d\left(\ln T_H+\ln T_L\right)\equiv d\left[\ln(T_H T_L)\right]=0,$$

we see that through the process, the product $T_H T_L$ remains constant, so using the initial values of temperature, T_1 and T_2, we get

$$T_H T_L = T_1 T_2 = \text{const.}$$

This formula means, in particular, that the temperatures tend to $T_{\text{fin}} = (T_1T_2)^{1/2}$. Note that this final temperature is always lower than the $T'_{\text{fin}} = (T_1 + T_2)/2$ that we would get at direct thermal contact of the bodies, with no mechanical work done at all. To find the total work in our case, we may apply Carnot's relation (1.68) to the work on a single cycle:

$$-d\mathscr{W}=\left(1-\frac{T_L}{T_H}\right)dQ_H,$$

and then integrate this result through the whole process:

$$-\mathscr{W}=\int_{\text{ini}}^{\text{fin}}\left(1-\frac{T_L}{T_H}\right)dQ_H=\int_{T_1}^{T_{\text{fin}}}\left(1-\frac{T_1T_2}{T_H^2}\right)\left(-CdT_H\right)=C\left(T_1+T_2-2T_{\text{fin}}\right)=C\left(T_1^{1/2}-T_2^{1/2}\right)^2.$$

The result shows that only in the limit $T_1/T_2 \to \infty$, the work tends to CT_1, i.e. to the full initial heat contents of the hotter body.

Another (shorter but also more formal and hence less transparent) way to derive the same results is to note that the heat does not leave the (two bodies + engine) system, so the mechanical work has to be equal to the sum of the changes of the thermal energies of the bodies:

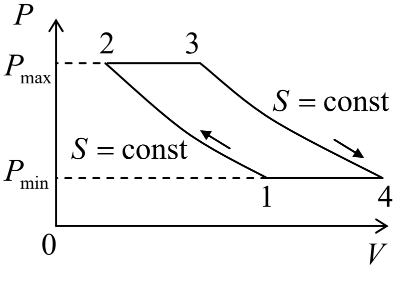
$$-\mathscr{W}=C\left(T_1-T_{\text{fin}}\right)+C\left(T_2-T_{\text{fin}}\right)\equiv C\left(T_1+T_2-2T_{\text{fin}}\right),$$

and then calculate T_{fin} from the requirement for the total entropy of the system to remain constant – as it has to be at a reversible process such as the Carnot cycle:

$$\Delta S=\Delta S_1+\Delta S_2=\int_{T_1}^{T_{\text{fin}}}\frac{dQ_1}{T}+\int_{T_2}^{T_{\text{fin}}}\frac{dQ_2}{T}=C\int_{T_1}^{T_{\text{fin}}}\frac{dT}{T}+C\int_{T_2}^{T_{\text{fin}}}\frac{dT}{T}=C\left(\ln\frac{T_{\text{fin}}}{T_1}+\ln\frac{T_{\text{fin}}}{T_2}\right)\equiv C\ln\frac{T_{\text{fin}}^2}{T_1T_2}=0,$$

giving the same $T_{\text{fin}} = (T_1T_2)^{1/2}$, and hence the same final result for $\mathscr{W}$.

Problem 1.15. Express the efficiency η of a heat engine that uses the so-called *Joule* (or "Brayton") *cycle* consisting of two adiabatic and two isobaric processes (see the figure on the right), via the highest and lowest values of pressure, and compare the result with η_{Carnot}. Assume an ideal classical working gas with temperature-independent C_P and C_V.



Solution: Let us number the process junction points as shown in the figure above. Since at any adiabatic process (in our case, at the stages 1→2 and 3→4 of the cycle), $\Delta Q = 0$, the work ($-\Delta\mathscr{W}$) performed by the gas at any of these segments equals $-\Delta E$. Since for an ideal classical gas of a fixed number of particles, the internal energy is a function of temperature alone (see Eq. (1.47) of the lecture notes), we may calculate its change just as

$$\Delta E = \int \frac{dE(T)}{dT} dT \equiv \int C_V dT ,$$

regardless of the volume change. So, if C_V is temperature-independent as in our case, then $-\Delta\mathscr{W} = -\Delta E = -C_V\Delta T$. Next, the work at any isobaric process, with $P = \text{const}$ (such as the stages denoted 2→3 and 4→1 in the figure above) is simply $P\Delta V$. As a result, the total mechanical work performed during the cycle is

$$-\mathscr{W} = -C_V(T_2 - T_1) + P_{\max}(V_3 - V_2) - C_V(T_4 - T_3) + P_{\min}(V_1 - V_4).$$

After using the equation of state, $PV = NT$ (which gives, in particular, $P_{\max}V_{2,3} = NT_{2,3}$ and $P_{\min}V_{1,4} = NT_{1,4}$) and applying Eq. (1.51) in the form $C_V = C_P - N$, this expression becomes

$$-\mathscr{W} = C_P\left[(T_3 - T_2) - (T_4 - T_1)\right].$$

The heat intake Q_H from the hot bath takes place only at the isobaric process 2→3 and is equal to $C_P(T_3 - T_2)$, so the engine's efficiency

$$\eta \equiv \frac{|\mathscr{W}|}{Q_\text{H}} = 1 - \frac{T_4 - T_1}{T_3 - T_2}. \qquad (*)$$

In order to express the efficiency via the given values P_1 and P_2, we may first combine the result of Problem 5 ($PV^\gamma = \text{const}$) and the equation of state ($PV = NT$) to get the general relation between temperature and pressure at an adiabatic process:

$$T = \text{const} \times P^{(\gamma-1)/\gamma}, \qquad \text{with } \gamma \equiv \frac{C_P}{C_V} = \frac{c_V + 1}{c_V}, \quad \text{i.e. } \frac{\gamma - 1}{\gamma} = \frac{c_V}{c_V + 1}.$$

Applying this result to the two adiabatic stages of the Joule cycle (3→4 and 1→2), and using the relations $P_1 = P_4 = P_{\min}$ and $P_2 = P_3 = P_{\max}$ again, we get

$$T_1 = T_2\left(\frac{P_{\min}}{P_{\max}}\right)^{(\gamma-1)/\gamma}, \qquad T_4 = T_3\left(\frac{P_{\min}}{P_{\max}}\right)^{(\gamma-1)/\gamma}.$$

Now plugging these relations into the right-hand side of Eq. (*), we see that the differences ($T_3 - T_2$) in the numerator and denominator cancel, giving us a very simple final result,

$$\eta = 1 - \left(\frac{P_{\min}}{P_{\max}}\right)^{(\gamma-1)/\gamma} \equiv 1 - \left(\frac{P_{\min}}{P_{\max}}\right)^{c_V/(c_V+1)}. \qquad (**)$$

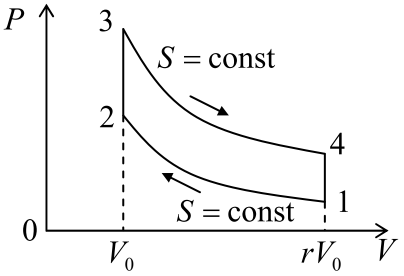
In order to compare this formula with Eq. (1.68) for the Carnot cycle, it is better to use the above relation between P and T at the adiabatic process again to recast Eq. (**) in two other temperature forms:

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{T_4}{T_3}.$$

Of the four junction points of the cycle (see the figure above), T_3 is the largest one ($T_{\max}$), while T_1 is the lowest one ($T_{\min}$), so the fractions in these two formulas are always larger than $T_{\min}/T_{\max}$, and hence

$$\eta \leq 1 - \frac{T_{\min}}{T_{\max}} = \eta_{\text{Carnot}},$$

as it should be for any cycle.



Problem 1.16. Calculate the efficiency of a heat engine using the *Otto cycle*[13] that consists of two adiabatic and two isochoric (constant-volume) reversible processes – see the figure on the right. Explore how the efficiency depends on the *compression ratio* $r \equiv V_{\max}/V_{\min}$, and compare it with the Carnot cycle's efficiency. Assume an ideal classical working gas with temperature-independent heat capacity.

Solution: Let us number the process junction points as shown in the figure above. At the adiabatic stages 3→4 and 1→2, there is no heat flow to/from the working gas. The thermal exchange takes place only during the isochoric stages 2→3 and 4→1, so due to the assumed specific heat's constancy, we may write

$$Q_{\text{H}} = C_V(T_3 - T_2), \qquad Q_{\text{L}} = C_V(T_4 - T_1).$$

As a result, so for the cycle's efficiency as a function of junction point temperatures, we immediately get the same expression as for the Joule cycle (see the previous problem):

$$\eta \equiv \frac{Q_{\text{H}} - Q_{\text{L}}}{Q_{\text{H}}} = 1 - \frac{T_4 - T_1}{T_3 - T_2}. \qquad (*)$$

Now plugging the equation of state of an ideal gas in the form $P = NT/V$ into the result of Problem 5 for the adiabatic process, $PV^{\gamma} = \text{const}$ (where $\gamma \equiv C_P/C_V$), we get $TV^{(\gamma-1)} = \text{const}$. Applying this relation to stages 3→4 and 1→2 (with the same volume ratio r), we get similar results for their temperature ratios:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{rV_0}{V_0}\right)^{\gamma-1} = r^{\gamma-1}, \qquad \frac{T_3}{T_4} = \left(\frac{V_4}{V_3}\right)^{\gamma-1} = \left(\frac{rV_0}{V_0}\right)^{\gamma-1} = r^{\gamma-1}. \qquad (**)$$

Using these relations to eliminate T_3 and T_2 from Eq. (*), we get the following very simple result:

$$\eta = 1 - \frac{T_4 - T_1}{T_4 r^{\gamma-1} - T_1 r^{\gamma-1}} \equiv 1 - \frac{1}{r^{\gamma-1}}. \qquad (***)$$

Since by definition, $\gamma > 1$, i.e. $\gamma - 1 > 0$, and $r > 1$ (see the figure above), the denominator in the last form of the result is always positive and larger than one, so the efficiency is between 0 and 1 – as it should be. In particular, at $r \to 1$ (a very "narrow" cycle) the denominator tends to 1 as well, so $\eta \to 0$.

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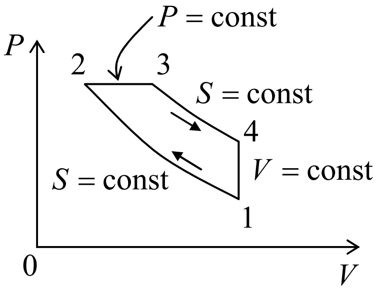
[13] This name stems from the fact that the cycle is an approximate model of operation of the four-stroke internal combustion ("petrol") engine, which was improved and made practicable by N. Otto in 1876 – though its idea had been conceived earlier (in 1860) by É. Lenoir.

This is natural because the useful work, proportional to the cycle's area on the [P, V] plane, tends to zero in this limit. On the other hand, as r grows, so does the denominator, so $\eta \to 1$.

In order to understand whether this efficiency increase can make it higher than that of the Carnot cycle with the same minimal and maximal temperatures, we may use Eqs. (**) to recast our result in two other forms:

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{T_4}{T_3}.$$

Since temperature drops at the adiabatic expansion, the figure above shows that $T_2 < T_3 = T_{\max}$ and $T_1 = T_{\min} < T_4$. As a result, either of these two expressions for η shows that, for any r, the Otto cycle's efficiency is always lower than $\eta_{\text{Carnot}} = 1 - T_{\max}/T_{\min}$.



Problem 1.17. The *Diesel cycle* (an approximate model of the Diesel internal combustion engine's operation) consists of two adiabatic processes, one isochoric process, and one isobaric process – see the figure on the right. Assuming an ideal working gas with temperature-independent C_V and C_P, express the cycle's efficiency η via its two dimensionless parameters: the so-called *cutoff ratio* $\alpha \equiv V_3/V_2 > 1$ and the compression ratio $r \equiv V_1/V_2 > \alpha$.

Solution: In this cycle, the working gas picks up heat from the hot bath only during the isobaric 2→1 stage,[14] so $Q_\text{H} = C_P(T_3 - T_2)$, and drains heat to the cold bath only during the isochoric 4→1 stage, so $Q_\text{L} = C_V(T_4 - T_1)$. As a result, the cycle's efficiency is

$$\eta \equiv \frac{Q_\text{H} - Q_\text{L}}{Q_\text{H}} \equiv 1 - \frac{Q_\text{L}}{Q_\text{H}} = 1 - \frac{C_V}{C_P}\frac{T_4 - T_1}{T_3 - T_2} \equiv 1 - \frac{1}{\gamma}\frac{T_4 - T_1}{T_3 - T_2}, \qquad (*)$$

where, as usual, $\gamma \equiv C_P/C_V > 1$. In order to express this result via the parameters α and r, let us use the conservation of the product $TV^{(\gamma-1)}$ at the adiabatic process in an ideal gas – see the previous problem's solution. Applying it to each of the adiabatic stages of the Diesel cycle, we get

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} \equiv \frac{1}{r^{\gamma-1}}, \qquad \frac{T_4}{T_3} = \left(\frac{V_3}{V_4}\right)^{\gamma-1} \equiv \left(\frac{V_3}{V_1}\right)^{\gamma-1}.$$

One more temperature ratio we need follows directly from the equation of state $PV = NT$, applied to the 2→3 stage (where P = const):

$$\frac{T_3}{T_2} = \frac{V_3}{V_2} \equiv \alpha .$$

Combining these ratios, we get

$$\frac{T_4}{T_1} \equiv \frac{T_4}{T_3}\frac{T_3}{T_2}\frac{T_2}{T_1} = \left(\frac{V_3}{V_1}\right)^{\gamma-1} \alpha\, r^{\gamma-1} \equiv \left(\frac{V_2}{V_1}\frac{V_3}{V_2}\right)^{\gamma-1} \alpha\, r^{\gamma-1} = \frac{1}{r^{\gamma-1}}\alpha^{\gamma-1}\alpha\, r^{\gamma-1} \equiv \alpha^{\gamma}.$$

---

[14] In practical Diesel engines, this is the stage of fuel combustion inside the engine's cylinder, and the role of the hot bath is played by the hot gas formed as the result.

Now, plugging the calculated ratios into Eq. (*), rewritten as

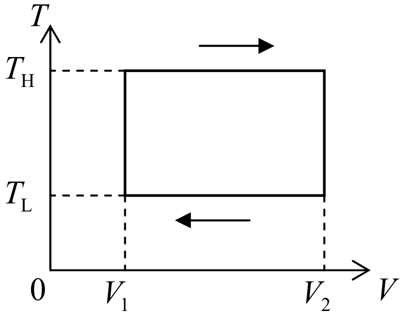
$$\eta = 1 - \frac{1}{\gamma}\frac{T_1}{T_2}\frac{T_4/T_1 - 1}{T_3/T_2 - 1},$$

we bring the result to the requested form:

$$\eta = 1 - \frac{1}{\gamma r^{\gamma-1}}\frac{\alpha^{\gamma} - 1}{\alpha - 1}.$$

Since, by definition, $\gamma > 1$ and $\alpha > 1$, the last fraction is larger than 1. As a result, at the same compression ratio r, the efficiency of the Diesel cycle is lower than not only that of the Carnot efficiency but also that of the Otto cycle – see Eq. (***) in the previous problem's solution. However, in practical Diesel engines, a larger compression ratio r (up to 20) may be reached, so their efficiency may be higher than that of the typical four-stroke engines (where $r \sim 10$).

Problem 1.18. A heat engine's cycle consists of two isothermal (T = const) and two isochoric (V = const) processes – see the figure below.[15]



(i) Assuming that the working gas is an ideal classical gas of N particles, calculate the mechanical work performed by the engine during one cycle.

(ii) Are the specified conditions sufficient to calculate the engine's efficiency? (Justify your answer.)

Solutions:

(i) In this cycle, mechanical work is performed only at the isothermal processes, in which $P = NT/V$ with NT = const, so the total work

$$-\mathscr{W} = \oint PdV = \int_{V_1}^{V_2} PdV\Big|_{T_\text{H}} + \int_{V_2}^{V_1} PdV\Big|_{T_\text{L}} = NT_\text{H}\int_{V_1}^{V_2}\frac{dV}{V} + NT_\text{L}\int_{V_2}^{V_1}\frac{dV}{V} = N(T_\text{H} - T_\text{L})\ln\frac{V_2}{V_1}.$$

(ii) To calculate the cycle's efficiency $\eta \equiv -\mathscr{W}/Q_\text{H}$, we would need to know also the heat Q_H taken from the hot bath. The heat consists of the isothermal-stage part ΔQ_T, which may be expressed by the first of Eqs. (1.65) of the lecture notes, and the isochoric-stage part ΔQ_V. Let us assume that during the isochoric heating (from T_L to T_H), the working gas is in brought contact only with the hot bath (which is a smart thing to do to avoid the direct transfer of heat between two heat baths); then $\Delta Q_V = \Delta E$. Then we may use Eqs. (1.46) and (1.47) to write

$$Q_\text{H} = \Delta Q_T + \Delta E = T_\text{H}(S_2 - S_1) + \left[E(T)\right]_{T_\text{L}}^{T_\text{H}} = NT_\text{H}\ln\frac{V_2}{V_1} + N\left[f(T) - T\frac{df(T)}{dT}\right]_{T_\text{L}}^{T_\text{H}}.$$

Hence, the calculation of the efficiency η would require, besides the given assumptions and parameters, the function $f(T)$ that characterizes the internal degrees of freedom of the gas, or

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[15] The reversed cycle of this type is a reasonable approximation for the operation of the *Stirling* and *Gifford-McMahon* (GM) refrigerators broadly used for *cryocooling* – for a review, see, e.g., A. de Waele, *J. Low Temp. Phys*. **164**, 179 (2011).

alternatively, the heat capacity $C_V(T)$ – which have not been given in the assignment. The only certain fact is that without the second term in the last expression, i.e. at $\Delta Q_V = 0$, η would be equal to η_{Carnot}, but in the presence of this term (which is never negative), the actual Q_H is higher, i.e. the cycle's efficiency is lower than this limit. For example, for the ideal classical gas with no thermally-activated internal degrees of freedom, we may borrow Eq. (3.19), to be derived in Sec. 3.1 of the lecture notes, to get

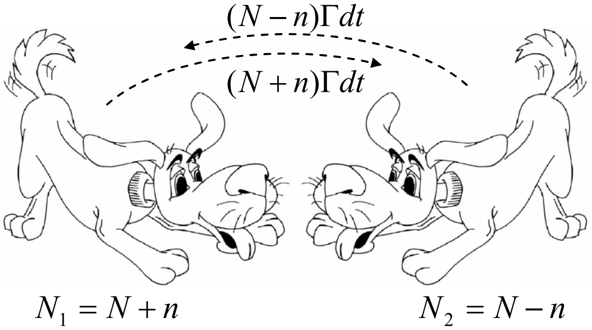
$$Q_H = NT_H \ln\frac{V_2}{V_1} + \frac{3}{2}N\left(T_H - T_L\right),$$

$$\eta \equiv -\frac{\mathscr{W}}{Q_H} = \frac{\left(T_H - T_L\right)\ln\left(V_2/V_1\right)}{T_H \ln\left(V_2/V_1\right) + \left(3/2\right)\left(T_H - T_L\right)} \equiv \frac{1}{1/\eta_{\text{Carnot}} + \left(3/2\right)/\ln\left(V_2/V_1\right)} \le \eta_{\text{Carnot}}\,.$$

Chapter 2. Principles of Physical Statistics

Problem 2.1. A famous example of macroscopic irreversibility was suggested in 1907 by P. Ehrenfest. Two dogs share $2N >> 1$ fleas. Each flea may jump onto another dog, and the rate Γ of such events (i.e. the probability of jumping per unit time) does not depend either on time or on the location of other fleas. Find the time evolution of the average number of fleas on a dog, and of the flea-related part of the total dogs' entropy (at arbitrary initial conditions), and prove that the entropy can only grow.[16]

Solution: Due to the conservation of the total flea number $2N$, we may represent the number of fleas on each dog, averaged over the statistical ensemble of many similar two-dog pairs (but not over time!), as $N_{1,2} = N \pm n$ – see the figure on the right.[17] Let us consider a time interval dt so small that during it, the flea numbers $N_{1,2}$ do not change significantly. Subtracting the "flea flows" shown in the figure, we get the following expression for elementary change of, say, N_1:



$$dN_1 \equiv d(N+n) \equiv dn = N_2\Gamma dt - N_1\Gamma dt \equiv (N-n)\Gamma dt - (N+n)\Gamma dt \equiv -2n\Gamma dt \,,$$

i.e. the following ordinary differential equation for the function $n(t)$:

$$\frac{dn}{dt} = -2n\Gamma dt \,. \qquad (*)$$

The equation may be easily solved for arbitrary initial conditions:

$$n(t) = n(0)\exp\{-2\Gamma t\}.$$

So, as we could expect, regardless of the initial distribution of the fleas, eventually $n(t) \to 0$, i.e. the *average* number of fleas on each dog becomes the same – a typical irreversible process.

To calculate the entropy, we may apply Eq. (2.29) of the lecture notes to two different positions of a flea, with probabilities $W_{1,2} = (N \pm n)/2N$, so the average entropy per flea is

$$\frac{S}{2N} = -W_1 \ln W_1 - W_2 \ln W_2 = -\frac{N+n}{2N}\ln\frac{N+n}{2N} - \frac{N-n}{2N}\ln\frac{N-n}{2N},$$

and the entropy of the whole system (i.e. of the set of $2N$ fleas on both dogs) is

$$S = -(N+n)\ln(N+n) - (N-n)\ln(N-n) + \text{const}\,.$$

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[16] This is essentially a simpler (and funnier :-) version of the particle scattering model used by L. Boltzmann to prove his famous *H-theorem* (1872). Besides the historical significance of that theorem, the model used in it (see Sec. 6.2 of the lecture notes) is as cartoonish, and hence not more general.

[17] The dog image is adapted from http://home.howstuffworks.com.

(Another way to get the same result for S is to use the microcanonical distribution (2.24), $S = \ln M$, with M being the number of different ways to place $N_1 = N + n$ indistinguishable fleas on one dog, of $2N$ total:[18]

$$M = {}^{N_1}C_{2N} \equiv \frac{(2N)!}{N_1!(2N-N_1)!} \equiv \frac{(2N)!}{(N+n)!(N-n)!}, \qquad \text{so } S = \ln\frac{(2N)!}{(N+n)!(N-n)!},$$

and then apply the Stirling formula to the last expression.)

In order to analyze the entropy's evolution, we may differentiate the function $S[n(t)]$ over time:,

$$\frac{dS}{dt} = \frac{dS}{dn}\frac{dn}{dt} = \ln\left(\frac{N-n}{N+n}\right)\frac{dn}{dt},$$

and then use Eq. (*) to rewrite this result as

$$\frac{dS}{dt} = -2n\Gamma\ln\left(\frac{N-n}{N+n}\right).$$

Within the meaningful interval $n \in [-N, +N]$, the last logarithm is negative at $n > 0$ and positive if $n < 0$, so in either case, at $\Gamma > 0$, the right-hand side of the last relation is a non-negative function of n. Hence the exponential *reduction* of the average flea imbalance $2n$ is accompanied by a *growth* of the entropy – i.e. of disorder.

Problem 2.2. Use the microcanonical distribution to calculate thermodynamic properties (including the entropy, all relevant thermodynamic potentials, and the heat capacity) of a two-level system in thermodynamic equilibrium with its environment, at a temperature T that is comparable with the energy gap Δ. For each variable, sketch its temperature dependence and find its asymptotic values (or trends) in the low-temperature and high-temperature limits.

Hint: The two-level system is any system with just two different stationary states, whose energies (say, E_0 and E_1) are separated by a gap $\Delta \equiv E_1 - E_0$. Its popular (but by no means the only!) example is the spin-½ of a particle, e.g., an electron, in an external magnetic field.[19]

Solution: Let us consider a microcanonical ensemble consisting of many similar sets of $N >> 1$ non-interacting, distinguishable[20] two-level systems, taking (just for the notation simplicity) the lowest state energy E_0 for the energy origin, so $E_0 = 0$ and $E_1 = \Delta \geq 0$. Just as in the case of quantum oscillators analyzed in Sec. 2.2 of the lecture notes, the number Σ_N of states with the total energy of the set below a certain value E_N increases, with the growth of E_N, by discrete steps at $E_N = N'\Delta$, where $N' = 1, 2,\ldots, N$. The height $\Delta\Sigma_N$ of such a step is equal to the number of different ways to distribute N' indistinguishable energy increments ("excitations", or "quanta") Δ among N distinct systems. This number is equal to the number of ways to select N' similar objects (in combinatorics, traditionally called "balls") of the total number of N, in an arbitrary order, and hence it is just the binomial coefficient[21]

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[18] See MA Eq. (2.2).

[19] See, e.g., QM Secs. 4.6 and 5.1, in particular, Eq. (4.167).

[20] Say, by their fixed spatial positions.

[21] See, e.g., MA Eq. (2.2).

$$\Delta\Sigma_N = {}^{N'}C_N \equiv \frac{N!}{N'!(N-N')!}.$$

Taking the energy spread ΔE of the microcanonical ensemble equal to Δ (which is legitimate if N, N', and $(N-N')$ are much larger than 1, i.e. if $\Delta\Sigma_N >> 1$ and $\Delta E << E$), for the average entropy per system we get

$$S = \lim\Big|_{N,N'\to\infty} \frac{\ln \Delta\Sigma_N}{N} = \lim\Big|_{N,N'\to\infty} \frac{1}{N}\left\{\ln(N!) - \ln(N'!) - \ln[(N-N')!]\right\}.$$

The application of the Stirling formula (in its simplest form given by Eq. (2.27) of the lecture notes) reduces this relation to[22]

$$S = -n\ln n - (1-n)\ln(1-n), \qquad (*)$$

where $n \equiv N'/N = E_N/N\Delta \leq 1$ is the average number of the energy quanta Δ per two-level system, so the average energy per system is $E = E_N/N = n\Delta$.[23]

Now we can use the definition of temperature, given by Eq. (1.9), to calculate

$$\frac{1}{T} \equiv \frac{dS}{dE} = \frac{1}{\Delta}\frac{dS}{dn} = \frac{1}{\Delta}\ln\left(\frac{1}{n}-1\right) \equiv \frac{1}{\Delta}\ln\left(\frac{\Delta}{E}-1\right).$$

Solving this equation for E, we get the following equilibrium value of the average energy:

$$E = \frac{\Delta}{e^{\Delta/T}+1}.$$

Plugging this result for $n = E/\Delta$ back into Eq. (*) yields the equilibrium value of the entropy:

$$S = \ln\left(1+e^{-\Delta/T}\right) + \frac{\Delta}{T}\frac{1}{e^{\Delta/T}+1}.$$

Now that we know the energy and the entropy as functions of temperature, we are on the thermodynamics autopilot – see Chapter 1:

$$F \equiv E - TS = -T\ln\left(1+e^{-\Delta/T}\right),$$

$$C \equiv \left(\frac{\partial E}{\partial T}\right)_V = \frac{\Delta^2}{T^2}\frac{e^{\Delta/T}}{\left(1+e^{\Delta/T}\right)^2} \equiv \left[\frac{(\Delta/2T)}{\cosh(\Delta/2T)}\right]^2.$$

(As in the harmonic-oscillator problem discussed in Sec. 2.2, the notion of volume, and hence of pressure P, is not defined for this system, so there are no differences between C_V and C_P, between E and H, and between F and G.)

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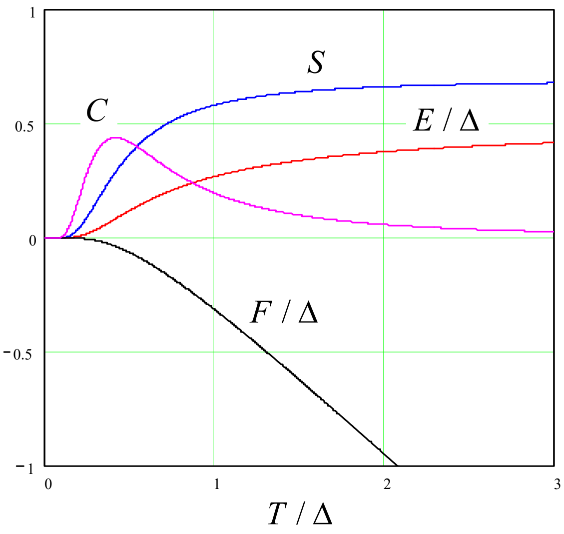
[22] We will run into a similar expression again in Sec. 2.8 of the lecture notes, at the discussion of ensembles of identical Fermi-Dirac particles out of equilibrium – see Eq. (2.123).

[23] Note that this derivation of Eq. (*) has followed the derivation of more general Eq. (2.29) in the lecture notes, so alternatively, we might just use that formula with $M = 2$, $W_1 = n$ and $W_2 = 1 - W_1 \equiv 1 - n$.

The figure on the right shows the temperature behavior of the calculated thermodynamic variables. In the low-temperature limit ($T << \Delta$), all of them approach zero. (For E and F, this value is conditional, but for the heat capacity, it is measurable.) On the other hand, in the high-temperature limit ($\Delta << T$), the behavior of each variable is specific: $E \to \Delta/2 = \text{const}$,[24] $F \to -T\ln 2 \to -\infty$, $S \to \ln 2 \approx 0.693 = \text{const}$, while $C \to 0$. It is interesting that the heat capacity is vanishing in both low-temperature and high-temperature limits, and has a maximum ($C_{\max} \approx 0.45$) at a finite temperature ($T \approx 0.43\ \Delta$). An interpretation of this behavior will become easy after the energy level occupancies have been calculated using the Gibbs distribution – see the next problem.



Problem 2.3. Solve the previous problem using the Gibbs distribution. Also, calculate the probabilities of the energy level occupation, and give physical interpretations of your results, in both temperature limits.

Solution: Let us apply the Gibbs distribution to a canonical ensemble of many similar two-level systems. Each system has just two energy states, $E_0 = 0$ and $E_1 = \Delta$, so the probabilities of finding the system in each of them obey the Gibbs distribution (2.58),

$$W_m = \frac{1}{Z}\exp\left\{-\frac{E_m}{T}\right\},$$

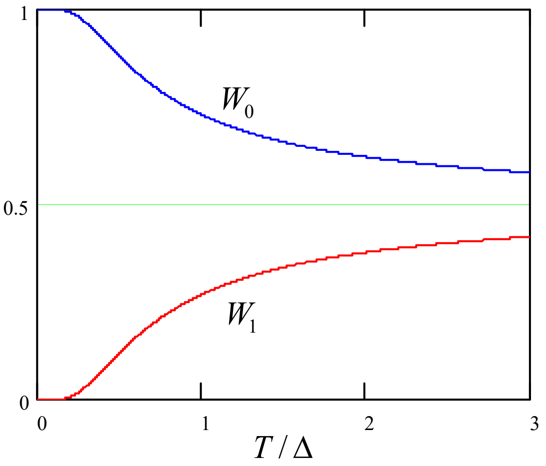
with the index m taking only two values, $m = 0, 1$. As a result, the statistical sum (2.59) equals

$$Z \equiv \sum_{m=0,1}\exp\left\{-\frac{E_m}{T}\right\} = 1 + \exp\left\{-\frac{\Delta}{T}\right\}, \qquad (*)$$

so

$$W_0 = \frac{1}{Z}\exp\left\{-\frac{E_0}{T}\right\} = \frac{1}{1+e^{-\Delta/T}},$$

$$W_1 = \frac{1}{Z}\exp\left\{-\frac{E_1}{T}\right\} = \frac{e^{-\Delta/T}}{1+e^{-\Delta/T}} \equiv \frac{1}{e^{\Delta/T}+1}.$$



The figure on the right shows these probabilities as functions of temperature. At $T \to 0$, the system is almost certainly in its ground state, $W_0 \to 1$, while the probability of finding the system on the upper energy level is exponentially low: $W_1 \to \exp\{-\Delta/T\} \to 0$. On the contrary, at high temperatures, $T >> \Delta$, both probabilities are

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[24] This fact means that for two-level systems the equipartition theorem (2.48) is not valid even at high temperatures. One may say that in contrast to the harmonic oscillators or rotators with their infinite energy spectra, two-level (and more generally, any finite-energy-level) systems are never classical!

virtually equal, $W_0 \approx W_1 \approx ½$. This "equilibration" of the energy level population at $T \to \infty$ is typical for systems with a finite number of quantized energy levels – but not for systems such as quantum oscillators or rotators, whose energy level "ladders" are infinite.[25]

Now plugging Eq. (*) into the main formula (2.63) relating the Gibbs distribution with thermodynamics, we readily get the free energy (per system)

$$F = T \ln \frac{1}{Z} = -T \ln\left(1 + e^{-\Delta/T}\right).$$

This formula coincides with the result following from the microcanonical distribution – see the previous problem. Now we may use Eq. (1.35), $S = -(\partial F/\partial T)$, to find the entropy, and then Eq. (1.33), rewritten as $E = F + TS$, to find the average energy E. Alternatively, the energy may be found using Eq. (2.61a):

$$E = \sum_{m=0,1} W_m E_m = W_0 E_0 + W_1 E_1 = W_1 \Delta = \frac{\Delta}{e^{\Delta/T} + 1}.$$

(Note that the parameter $n \equiv N'/N = E/N\Delta$ used in the model solution of the previous problem is nothing else than W_1.) Now we can use Eq. (1.24), $C = \partial E/\partial T$, to find the heat capacity per system. All these results coincide with those obtained from the microcanonical ensemble – see the model solution of the previous problem for formulas and plots.

The above results for W_0 and W_1 enable an easy interpretation of the temperature behavior of the thermodynamic variables. In particular, at low temperatures ($T << \Delta$), the system is effectively confined to the lowest level, so if this energy is taken as the reference, the average E tends to zero. Also, the system's state choice in this limit is virtually certain, so there is almost no disorder, and entropy approaches zero as well. In the opposite limit, at $T >> \Delta$, i.e. at $W_1 \approx W_0 \approx ½$, the average energy naturally tends to the average between levels. Also, in this limit, the choice between two possible states of each particular system of the ensemble is random; hence the entropy tends to the value ln2, which corresponds to one lost bit of information about the particular choice.

Finally, by its definition, the heat capacity of a system is substantial only if a small variation of temperature causes a noticeable redistribution of the energy level probabilities – and hence of the average energy. As the formulas and plots above show, in our current problem, such redistribution takes place only at $T \sim \Delta/2$; hence the peak of the function $C(T)$ at these intermediate temperatures.

Problem 2.4. A quantum spin-½ particle with a gyromagnetic ratio γ is placed into an external magnetic field $\mathscr{H} = \mathscr{H}\mathbf{n}_z$. Neglecting the possible orbital motion of the particle, calculate its average magnetization $\langle m_z \rangle$ as a function $\mathscr{H}$, and in particular its low-field magnetic susceptibility χ, in thermal equilibrium at temperature T. Calculate the same characteristics for a classical magnetic dipole $\boldsymbol{m}$ of a fixed magnitude m_0, free to change its direction in space, and compare the results.

Hint: The low-field magnetic susceptibility of a single particle is defined[26] as

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[25] See, e.g., QM Secs. 5.4 and 5.6.

[26] This "atomic" (or "molecular") susceptibility χ should not be confused with the "volumic" susceptibility $\chi_m \equiv \partial \mathscr{M}_z/\partial \mathscr{H}$, where $\mathscr{M}$ is the magnetization, i.e. the magnetic moment of a unit volume of a system – see, e.g., EM Eq. (5.111). For a uniform medium with $n \equiv N/V$ non-interacting dipoles per unit volume, $\chi_m = n\chi$.

$$\chi = \frac{\partial\langle \mathscr{m}_z\rangle}{\partial\mathscr{H}}\Big|_{\mathscr{H}\to 0}\,.$$

Solution: According to quantum mechanics,[27] the interaction of a magnetic dipole with an external magnetic field $\mathscr{B}$ is described by the following Hamiltonian operator:[28]

$$\hat{H} = -\hat{\boldsymbol{\mathscr{m}}}\cdot\boldsymbol{\mathscr{B}}\,. \qquad (*)$$

If the magnetic moment vector $\boldsymbol{\mathscr{m}}$ of a particle is entirely due to its spin (as it is assumed in our assignment), then its operator is related to that of the spin as $\hat{\boldsymbol{\mathscr{m}}} = \gamma\hat{\mathbf{S}}$, where γ is the particle's gyromagnetic ratio. For a spin-½ particle, $\hat{\mathbf{S}} = (\hbar/2)\hat{\boldsymbol{\sigma}}$, where $\hbar$ is the Planck's constant, and $\hat{\boldsymbol{\sigma}}$ is the vector operator whose Cartesian components, in the standard z-basis, are represented by 2×2 Pauli matrices; in particular,

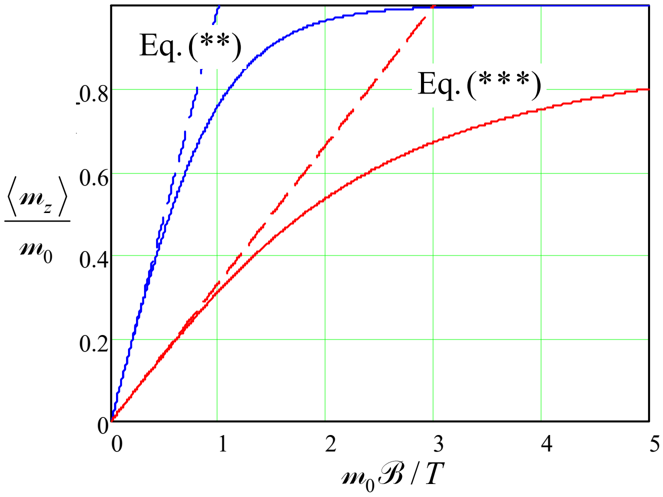
$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

As a result, we may represent the field-aligned z-component $\mathscr{m}_z$ of the magnetic moment by the diagonal matrix

$$\mathscr{m}_z = \gamma\frac{\hbar}{2}\sigma_z \equiv \mathscr{m}_0\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \text{where } \mathscr{m}_0 \equiv \gamma\frac{\hbar}{2}.$$

(The scalar constant $\mathscr{m}_0$ may be classically interpreted as the magnitude of a discrete dipole moment that may be directed only either along or against the external field.) The corresponding eigenvalues of the Hamiltonian (*) are the eigenenergies, $E_\uparrow$ and $E_\downarrow$, separated by the energy gap

$$\Delta \equiv E_\uparrow - E_\downarrow = 2\mathscr{m}_0\mathscr{B} \equiv \hbar\gamma\mathscr{B}\,.$$



But this is just a particular case of the two-level systems that were discussed in two previous problems, so we may use their results. In particular, the average z-component of the magnetic moment is

$$\begin{aligned}\langle\mathscr{m}_z\rangle &= (+\mathscr{m}_0)W_1 + (-\mathscr{m}_0)W_0 \\ &= \mathscr{m}_0\tanh\frac{\mathscr{m}_0\mathscr{B}}{T}.\end{aligned} \qquad (**)$$

This function is shown with the solid blue curve in the figure on the right.[29] In the high-field (low-temperature) limit $\mathscr{m}_0\mathscr{B} >> T$, it describes the magnetic moment's saturation as its highest possible value $\mathscr{m}_0$ corresponding to the definite

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[27] See, e.g., QM Eqs. (4.105), (4.115)-(4.116), and (4.163).

[28] Let me hope that the operator "hat" above the letter H clearly distinguishes the Hamiltonian from the enthalpy – which is not used in this solution.

[29] According to Eq. (**), $\langle\mathscr{m}_z\rangle$ is an odd function of $\mathscr{B}$, so the plot is only shown for $\mathscr{B} \geq 0$.

orientation of the dipole along the field – "spin polarization". In the opposite, low-field limit, the tanh function may be well approximated by its argument, so assuming that the dipole is located in free space, i.e. (in the SI units) $\mathscr{B} = \mu_0\mathscr{H}$, we get

$$\langle m_z \rangle \approx m_0 \frac{m_0 \mathscr{B}}{T} = \mu_0 \frac{m_0^2}{T}\mathscr{H}, \quad \text{at} \quad m_0\mathscr{B} << T,$$

so

$$\chi_{\text{m}} = \mu_0 \frac{m_0^2}{T}.$$

This $\chi_{\text{m}} \propto 1/T$ dependence of the paramagnetic (positive) magnetic susceptibility is called the *Curie law*; in this course, its limitations and extensions will be discussed in the context of the Ising model of phase transitions – see Secs. 4.4-4.5.

Now let us consider the classical model outlined in the assignment,[30] in which the orientation of the magnetic dipole vector $\boldsymbol{m}$, of a fixed magnitude m_0, is arbitrary. The system's isotropy implies that possible dipole orientations (but not their occupations!) are uniformly distributed over all the full solid angle $\Omega = 4\pi$.[31] Hence the Gibbs distribution (2.58), applied to a canonical ensemble of such dipoles, may be recast into that for the probability density $w \equiv dW/d\Omega$:

$$w = \frac{1}{Z}\exp\left\{-\frac{E}{T}\right\}, \quad \text{with } Z = \oint_{4\pi} \exp\left\{-\frac{E}{T}\right\} d\Omega,$$

and the average of m_z calculated as

$$\langle m_z \rangle = \oint_{4\pi} m_z w \, d\Omega.$$

The magnetic dipole's energy in an external magnetic field $\mathscr{B}$ is just the classical version of Eq. (*),[32]

$$E = -\boldsymbol{m}\cdot\boldsymbol{\mathscr{B}} \equiv -m_z\mathscr{B},$$

so

$$\langle m_z \rangle = \oint_{4\pi} m_z \exp\left\{\frac{m_z\mathscr{B}}{T}\right\} d\Omega \Big/ \oint_{4\pi} \exp\left\{\frac{m_z\mathscr{B}}{T}\right\} d\Omega.$$

In the spherical coordinates, with the polar axis directed along the magnetic field, we have $m_z = m_0\cos\theta$, so since $d\Omega = \sin\theta \, d\theta \, d\varphi$, both integrals over the azimuthal angle φ are equal to 2π and cancel, and we get

$$\langle m_z \rangle = m_0 \int_0^\pi \cos\theta \exp\left\{\frac{m_z\mathscr{B}}{T}\cos\theta\right\} \sin\theta \, d\theta \Big/ \int_0^\pi \exp\left\{\frac{m_z\mathscr{B}}{T}\cos\theta\right\} \sin\theta \, d\theta.$$

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[30] This is an ultimately simple (no-interaction) version of the so-called *classical Heisenberg model*, which follows from quantum mechanics for particles with very large spins, $s >> 1$.

[31] This (virtually self-evident) assumption is confirmed by the quantum theories of both orbital and spin angular momenta, in their classical limits – see, e.g., QM Secs. 3.6 and 5.6.

[32] See, e.g., EM Eq. (5.100). Note that this formula is valid only if the magnitude m_0 of the magnetic moment is independent of the applied field, i.e. if the field just orients the dipole rather than induces it.

Introducing a convenient dimensionless variable $\xi \equiv (\mathscr{m}_0\mathscr{B}/T)\cos\theta$, so $\cos\theta = (T/\mathscr{m}_0\mathscr{B})\xi$ and $\sin\theta d\theta = -(T/\mathscr{m}_0\mathscr{B})d\xi$, we may reduce this formula to a ratio of two simple integrals, of which one (in the denominator) is elementary, while the other one may be readily worked out by parts:

$$\begin{aligned}\langle \mathscr{m}_z \rangle &= \frac{T}{\mathscr{B}}\left(\int_{-\mathscr{m}_0\mathscr{B}/T}^{+\mathscr{m}_0\mathscr{B}/T} e^{\xi}\xi\, d\xi \Bigg/ \int_{-\mathscr{m}_0\mathscr{B}/T}^{+\mathscr{m}_0\mathscr{B}/T} e^{\xi}\, d\xi \right) = \frac{T}{\mathscr{B}}\Big[(\xi-1)e^{\xi}\Big]_{-\mathscr{m}_0\mathscr{B}/T}^{+\mathscr{m}_0\mathscr{B}/T} \Big/ \Big[e^{\xi}\Big]_{-\mathscr{m}_0\mathscr{B}/T}^{+\mathscr{m}_0\mathscr{B}/T} \\ &= \mathscr{m}_0\, L\left(\frac{\mathscr{m}_0\mathscr{B}}{T}\right), \qquad \text{where } L(\xi) \equiv \coth\xi - \frac{1}{\xi}.\end{aligned} \qquad (***)$$

The red curve in the figure above shows this *Langevin function*.[33] In the high-field limit ($\mathscr{m}_0|\mathscr{B}| >> T$, i.e. at $|\xi| >> 1$), its first term tends to $\text{sgn}\xi$, while the second one is negligible, so the dipole is reliably polarized: $\langle \mathscr{m}_z\rangle \to \mathscr{m}_0\,\text{sgn}\mathscr{B}$. On the other hand, in the low-field limit, we may use the Taylor expansion of $\coth\xi$ at $\xi \to 0$, truncated to two leading terms: $\coth\xi \equiv \cosh\xi/\sinh\xi \approx (1 + \xi^2/2!)/(\xi + \xi^3/3!) \approx 1/\xi + \xi/3$, to reduce Eq. (***) to

$$\langle \mathscr{m}_z \rangle \approx \mathscr{m}_0 \frac{\mathscr{m}_0\mathscr{B}}{3T} = \mu_0 \frac{\mathscr{m}_0^2\mathscr{H}}{3T},$$

so the low-field susceptibility, in this model, is

$$\chi = \mu_0 \frac{\mathscr{m}_0^2}{3T}.$$

The comparison of Eqs (**) and (***), illustrated with the blue and red lines in the figure above, shows that the field dependence of the average magnetic moment of a quantum spin-½ is qualitatively similar to but quantitatively different from that in the classical magnetic dipole. In particular, in terms of $\mathscr{m}_0$ (which gives the moment's saturation value in both models), the low-field susceptibility of spin-½ particles is three times higher.

One more remark: an alternative way to calculate $\langle \mathscr{m}_z\rangle$ (for both models) is to use the analogy between the usual pair $\{-P, V\}$ of the generalized coordinates/forces, participating in Eq. (1.1) of the lecture notes and hence in all formulas of Chapter 1, and the pair $\{\mu_0\mathscr{H}_z, \mathscr{m}_z\}$. Indeed, the expression $E = -\mathscr{m}_z\mathscr{B} \approx -\mathscr{m}_z\mu_0\mathscr{H}$ used above for the potential energy of a dipole means that the elementary work of a fixed external magnetic field $\mathscr{H}_z\mathbf{n}_z$ on a changing magnetic moment is $d\mathscr{W} = \mu_0\mathscr{H}_z d\mathscr{m}_z$.[34] Comparing it with Eq. (1.1), $d\mathscr{W} = -PdV$, we see that for the average properties of a particle in the magnetic field $\mathscr{H}_z\mathbf{n}_z$, we may use all the thermodynamic equalities discussed in Chapter 1, with the replacements $P \to -\mu_0\mathscr{H}$, $V \to \langle \mathscr{m}_z\rangle$. In particular, the second of Eqs. (1.39) becomes

$$\langle \mathscr{m}_z \rangle = \left(\frac{\partial G}{\partial(-\mu_0\mathscr{H})} \right)_T,$$

where G is the Gibbs energy per particle. However, since in our approach, the product $-\mu_0\mathscr{H}_z\langle \mathscr{m}_z\rangle$ (i.e. the analog of the product PV) that gives the difference between the thermodynamic potentials G and F

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[33] Named after Paul Langevin who was the first to derive Eq. (***) but is much more famous for suggesting the *Langevin equation* – see Sec. 5.5 below.

[34] See also Eq. (1.3b) for the case of just one particle.

(see, e.g., the last of Eqs. (1.37) of the lecture notes) is already taken into account in the expression for E,[35] we may identify G with F, and calculate this thermodynamic potential using Eq. (2.63):

$$G = F = -T \ln Z .$$

It is straightforward to verify that for both parts of our current problem, this approach yields the same results (*)-(***) – see also the solution of Problem 7.

Problem 2.5.* Calculate the weak-field magnetic susceptibility of a hydrogen atom, at room temperature. Is this response to the field paramagnetic or diamagnetic? Compare the result with the estimated susceptibility of a hydrogen *molecule* H_2.

Solution: The response of the hydrogen atom to a weak magnetic field $\mathscr{B}$ includes, first of all, a contribution from its electron's spin-½,[36] leading to the splitting of its energy into two levels separated by the gap $\Delta E = 2m_0\mathscr{B}$, where m_0 is the effective magnetic moment, with

$$\left| m_0 \right| = \mu_B \equiv \frac{e}{m_e}\frac{\hbar}{2} \approx 0.927\times 10^{-23}\ \frac{\text{J}}{\text{T}} .$$

Plugging this value into the corresponding result of the previous problem for the weak-field susceptibility of a spin-½, we get

$$\chi_{\text{spin}} = \mu_0 \frac{\mu_B^2}{T} \equiv \mu_0 \frac{\hbar^2 e^2}{4m_e^2 T} > 0 . \qquad (*)$$

This susceptibility is positive, i.e. this part of the response to the field is paramagnetic.

The second, orbital component of the magnetic response is given by the well-known formula[37]

$$\chi_{\text{orbit}} = -\mu_0 \frac{e^2}{6m_e}\left\langle r^2 \right\rangle , \qquad (**)$$

valid for an arbitrary single-electron system. At room temperatures T, which are much lower than the Hartree energy unit $E_H \approx 27$ eV (corresponding to $T_K = E_H/k_B \sim 3\times10^5$ K), thermal excitation of the atom is negligible, so the $\langle r^2\rangle$ participating in Eq. (**) may be calculated directly from the quantum-mechanical description of the atom's ground state. For the hydrogen atom, such calculation is straightforward,[38] giving $\langle r^2\rangle = 3r_B^2$, where $r_B \equiv 4\pi\varepsilon_0\hbar^2/e^2m_e$ is the Bohr radius, so Eq. (**) yields

$$\chi_{\text{orbit}} = -\mu_0 \frac{e^2 r_B^2}{2m_e} .$$

By using the well-known relation between r_B and E_H,[39]

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[35] In terms of the discussion in Sec. 1.4, this means that we are using the first option for the description of the system of particles in the external field.

[36] The contribution to the response from the spin-½ of the atomic nucleus (proton) is very small, due to its much lower gyromagnetic ratio: $\gamma_p/\gamma_e \sim m_e/m_p \sim 10^{-3} << 1$.

[37] See, e.g., the model solutions of EM Problem 5.18 and QM Problem 6.15.

[38] See, e.g., the model solution of QM Problem 8.2.

[39] See, e.g., QM Eq. (1.13).

$$r_{\mathrm{B}}^2 = \frac{\hbar^2}{m_{\mathrm{e}} E_{\mathrm{H}}},$$

this result may be rewritten as

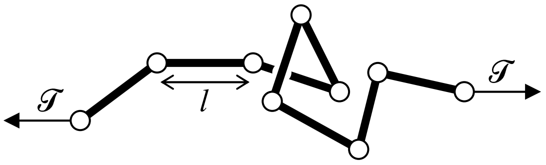
$$\chi_{\text{orbit}} \equiv -\mu_0 \frac{\hbar^2 e^2}{2 m_{\mathrm{e}}^2 E_{\mathrm{H}}}. \qquad (***)$$

Comparing this formula with Eq. (**), we see that

$$\frac{|\chi_{\text{orbit}}|}{\chi_{\text{spin}}} = \frac{2T}{E_{\mathrm{H}}}.$$

For room temperatures, this ratio is of the order of 10^{-3}, so the magnetic susceptibility of the hydrogen *atom* is dominated by the paramagnetic response of its electron's spin.

On the contrary, in the ground state of the hydrogen *molecule*, its two electrons are in the singlet spin state with zero total spin,[40] so its response to the weak magnetic field is dominated by the orbital diamagnetism: $\chi = \chi_{\text{orbit}} < 0$. Since the effective size $\langle r^2 \rangle^{1/2}$ of this molecule is of the order of r_{B}, this susceptibility χ is of the order of that given by Eq. (***), i.e. its magnitude is much smaller than the paramagnetic susceptibility of a single hydrogen atom.



Problem 2.6. N similar stiff rods of length l are connected with the joints that allow for free 3D rotation, to form a chain – see the figure on the right. The chain, in thermal equilibrium at temperature T, is stretched with a fixed force $\mathscr{F}$. Calculate the spring constant κ of the chain in the elastic limit $\mathscr{F} \to 0$.

Solution: Since the force $\mathscr{F}$ is fixed,[41] the chain's potential energy U may be expressed as the scalar product $-\mathscr{F}\cdot\mathbf{R}$, where $\mathbf{R}$ is the vector connecting its ends.[42] Evidently, $\mathbf{R}$ may be represented as the vector sum of such vectors $\mathbf{l}_n$ for each rod (all with the same length $|\mathbf{l}_n| = l$), so

$$\Delta U \equiv -\mathscr{F} \cdot \sum_{n=1}^{N} \mathbf{l}_n \equiv \sum_{n=1}^{N} \Delta U_n, \qquad \text{with } \Delta U_n \equiv -\mathscr{F} \cdot \mathbf{l}_n = -\mathscr{F} l \cos\theta_n, \qquad (*)$$

where θ_n is the angle between the n^{th} rod and the direction of the force $\mathscr{F}$ (which is shown horizontal in the figure above).

Due to the unrestricting joints, the system does not impose any relationship between the angles θ_n. Thus (a bit counter-intuitively) the energy of each rod does not depend on those of its counterparts, so the statistics of its position may be calculated from the above expression for ΔU_n, and is similar for all rods. Moreover, this statistics is exactly the same as for a classical magnetic dipole in the magnetic

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[40] See, e.g., QM Secs. 2.6 and 8.2.

[41] Note that for sufficiently long chains of $N >> 1$ units, this assumption is not essential because, for each unit, other $(N - 1) >> 1$ units sustain a nearly constant average tension at any boundary conditions at its ends.

[42] In order for the sign in this expression to be correct, the end of the vector $\mathbf{R}$ has to be at the point of application of the force $\mathscr{F}$.

field, which was calculated in the second part of the solution of Problem 4, with the replacement $\mathscr{m}_0\mathscr{B} \to \mathscr{F}l$. As a result, Eq. (***) of that solution may be immediately used to write

$$\langle \cos\theta_n \rangle = L\left(\frac{\mathscr{F}l}{T}\right) \equiv \coth\frac{\mathscr{F}l}{T} - \frac{T}{\mathscr{F}l}. \qquad (**)$$

The average full extension of the chain in the direction of the force is $Nl\langle\cos\theta_n\rangle$, so to calculate the spring constant in the elastic limit, we only need the asymptotic form of the Langevin function at $\mathscr{T} \to 0$ (which was also calculated in the solution of Problem 4):

$$\langle \cos\theta_n \rangle \to \frac{\mathscr{F}l}{3T}, \qquad \text{so } \kappa \equiv \left(\frac{\partial}{\partial\mathscr{F}} Nl\langle\cos\theta_n\rangle\right)^{-1}_{\mathscr{F}=0} = \frac{3T}{Nl^2}.$$

The growth of κ with T may be explained as follows: at a fixed tension $\mathscr{T}$, growing thermal agitation "tries" to keep the orientation of each unit completely random, and hence to keep its average extension along the direction of the force equal to a fixed value (zero).

Problem 2.7. Calculate the low-field magnetic susceptibility of a particle with an arbitrary (either integer or semi-integer) spin s, neglecting its orbital motion. Compare the result with the solution of Problem 4.

Hint: Quantum mechanics[43] tells us that the Cartesian component $\mathscr{m}_z$ of the magnetic moment of such a particle, in the direction of the applied field, has $(2s + 1)$ stationary values:

$$\mathscr{m}_z = \gamma\hbar m_s, \qquad \text{with } m_s = -s, -s+1, \ldots, +s-1, +s,$$

where γ is the gyromagnetic ratio of the particle, s is its spin, and $\hbar$ is Planck's constant.

Solution: Let us consider a canonical ensemble of many such particles. The spin energy in an external magnetic field of magnitude $\mathscr{B}$ is $E = -\mathscr{m}_z\mathscr{B} = -\gamma\hbar m_s\mathscr{B}$, so the statistical sum is

$$Z = \sum_{m_s=-s}^{+s} \exp\left\{\frac{\gamma\hbar\mathscr{B}m_s}{T}\right\} \equiv \sum_{m_s=-s}^{+s} \lambda^{m_s} \equiv \lambda^{-s}\sum_{k=0}^{2s}\lambda^k, \quad \text{where } \lambda \equiv \exp\left\{\frac{\gamma\hbar\mathscr{B}}{T}\right\}, \text{ while } k \equiv m_s + s.$$

Since s may be only either an integer or a half-integer, $2s$ is always an integer, so the last sum is just the well-known finite geometric progression,[44] and we get a very simple result:

$$Z = \lambda^{-s}\,\frac{1-\lambda^{2s+1}}{1-\lambda} \equiv \frac{\lambda^{-(s+1/2)} - \lambda^{s+1/2}}{\lambda^{-1/2} - \lambda^{1/2}} \equiv \sinh\frac{\gamma\hbar\mathscr{B}(2s+1)}{2T}\Big/\sinh\frac{\gamma\hbar\mathscr{B}}{2T}. \qquad (*)$$

Now we could calculate the average $\mathscr{m}_z$ just as was done in the model solution of Problem 4,[45] but just for practice, let us use the alternative approach that was discussed but not used at the end of that solution:

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[43] See, e.g., QM Sec. 5.7, in particular Eq. (5.197).

[44] See, e.g., MA Eq. (2.8a).

[45] Calculating the resulting full dependence of $\langle m_z\rangle$ on $\mathscr{H}$, frequently called the *Brillouin function*, is a simple but useful additional exercise, highly recommended to the reader. Plotted for the growing values of s, it gives a family

$$\langle \mathscr{m}_z \rangle = \left(\frac{\partial F}{\partial(-\mu_0 \mathscr{H})} \right)_T = -\left(\frac{\partial F}{\partial \mathscr{B}} \right)_T, \quad \text{where } F = -T \ln Z .$$

For the statistical sum given by Eq. (*),

$$F = -T \left\{ \ln[\sinh b(2s+1)] - \ln[\sinh b] \right\}, \qquad \text{where } b \equiv \frac{\gamma\hbar\mathscr{B}}{2T} .$$

For our purposes, we need only the low-field limit of this expression, at $b \to 0$, so we may approximate each of the involved sinh functions using only two leading terms of their Taylor expansions:

$$\sinh \xi \approx \xi + \frac{\xi^3}{3!} \equiv \xi \left(1 + \frac{\xi^2}{6} \right) \cdot$$

This approximation yields

$$F \approx -T \left\{ \ln b(2s+1) + \ln\left[1 + \frac{b^2(2s+1)^2}{6} \right] - \left[\ln b + \ln\left(1 + \frac{b^2}{6} \right) \right] \right\} \approx -T \ln(2s+1) - \frac{2}{3} T b^2 s(s+1)$$

$$\equiv -T \ln(2s+1) - \frac{2}{3} T \left(\frac{\gamma\hbar\mathscr{B}}{2T} \right)^2 s(s+1), \qquad \text{for } \frac{\gamma\hbar\mathscr{B}}{2T} << 1,$$

so

$$\langle \mathscr{m}_z \rangle = -\left(\frac{\partial F}{\partial \mathscr{B}} \right)_T = \frac{\gamma^2 \hbar^2 \mathscr{B}}{3T} s(s+1),,$$

and hence the low-field atomic susceptibility is

$$\chi_\text{m} \equiv \frac{\partial \langle \mathscr{m}_z \rangle}{\partial \mathscr{H}} \Big|_{\mathscr{H} \to 0} = \frac{\partial \langle \mathscr{m}_z \rangle}{\partial (\mathscr{B}/\mu_0)} = \mu_0 \frac{\gamma^2 \hbar^2}{3T} s(s+1).$$

With the notation $\mathscr{m}_0 \equiv \max[\mathscr{m}_z] = \gamma\hbar s$, compatible with those accepted in both parts of Problem 4, this result reads

$$\chi_\text{m} = \mu_0 \frac{\mathscr{m}_0^2}{3T} \frac{s+1}{s},$$

showing a gradual transition from the results for the spin-½ model considered in the first part of that problem, to those for the classical model analyzed in its second part, at s is increased from ½ to ∞.

<u>Problem 2.8</u>. Analyze the possibility of using a system of non-interacting spin-½ particles placed into a controllable external magnetic field, for refrigeration.

Solution: Combining the results of Problem 2 with the relation $\Delta = 2\mathscr{m}_0\mathscr{B} = 2(\gamma\hbar/2)\mathscr{B} \equiv \gamma\hbar\mathscr{B}$ (see the solution of Problem 4), we get the following formula for the average entropy per spin:

$$\frac{S}{N} = \ln\left(1 + e^{-\hbar\gamma\mathscr{B}/T} \right) + \frac{\hbar\gamma\mathscr{B}}{T} \frac{1}{e^{\hbar\gamma\mathscr{B}/T} + 1} .$$

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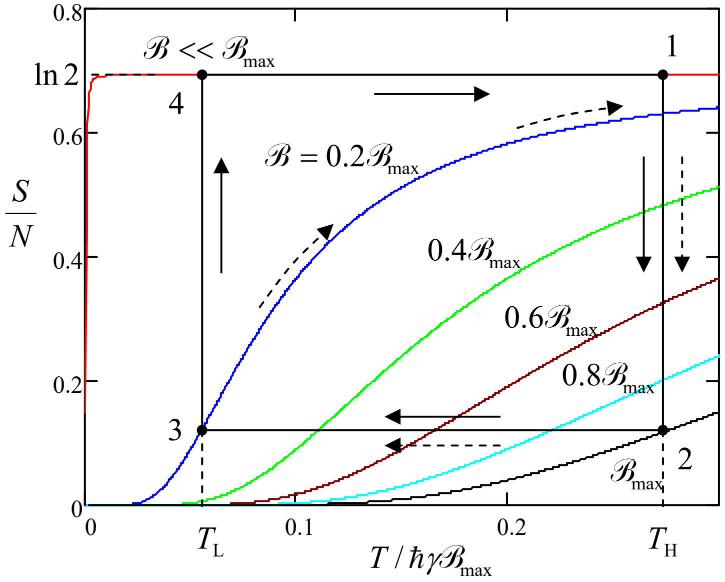
of uneventful saturation curves that gradually bridge those for s = ½ and for the classical magnetic dipole (corresponding to $s \to \infty$) – see, e.g., the plots in the model solution of Problem 4.



Note that the entropy depends on only one dimensionless combination of parameters, $T/\hbar\gamma\mathscr{B}$, so an increase of the applied field just stretches the plot of the function $S(T)$ along the horizontal axis – see the figure on the right. These plots imply the following possible way to organize the Carnot cooling cycle using the spin system as a "working gas".[46]

Starting, for example, from point 1 (at a negligible magnetic field when the spins are in both possible eigenstates with equal probability, i.e. completely disordered, so the entropy per spin is largest, $S/N = \ln 2$), the field is slowly increased to some value $\mathscr{B}_{\max} \sim T_H/\hbar\gamma$, while keeping the refrigerant in contact with the "hot bath" of temperature T_H.[47] Since during this process, the entropy decreases (physically because almost all spins condense onto the lowest energy level, thus decreasing the spin disorder to almost zero), heat $-Q_H = T_H\Delta S > 0$ is being transferred to the hot bath. Then (at point 2) the refrigerant is thermally insulated from both baths and then the external field is decreased. In this adiabatic process, the refrigerant's entropy cannot change, so the product $T/\hbar\gamma\mathscr{B}$ (whose unique function S is) cannot change either. This means that the refrigerant's temperature drops proportionally to the decreasing field.[48]

At point 3 where T is decreased to the temperature T_L of the "cold bath" (practically, the object being cooled), the refrigerant is brought into thermal contact with that bath, and then the field's decrease is continued isothermally until point 4, in which the energy level splitting becomes negligible, so the spin energy levels get equally populated again, and the entropy per spin approaches its maximum value ln2. At this point, the refrigerant is thermally disconnected from the cold bath, and the cycle is completed adiabatically using a small field increase until the spin temperature rises to T_H again.[49]

Practical cycles of such "adiabatic magnetic refrigeration" somewhat differ from (and hence have somewhat lower $\text{COP}_{\text{cooling}}$) than the Carnot cycle described above, mostly because of the technical difficulty of changing the thermal contacts between the refrigerant and the heat baths fast – typically this

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[46] In most practical applications of this concept, the spins are those of atoms in a solid sample of a certain material (see below), which is called either more formally, the *refrigerant*, or in the technical slang, the *salt pill*.

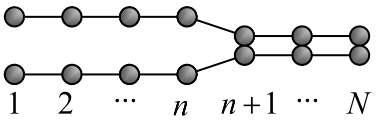
[47] For a typical application of this technique, with T_H corresponding to ~4 K, the term "hot bath" is pretty awkward, and practitioners prefer the term "cooling source" – which is of course wrong from the point of view of physics.

[48] This stage (2 → 3) of *adiabatic demagnetization* renders its name to this refrigeration technique, which is alternatively called *magnetic refrigeration*. It was suggested independently by P. Debye in 1926 and W. Giauque in 1927, and implemented experimentally by several research groups in the early 1930s, enabling them, for the first time, to reach temperatures well below 1 K in laboratory.

[49] Comparing this cycle with those shown in Fig. 1.9b of the lecture notes, one should take into account that the S and T axes are now swapped, so the clockwise circulation of the point representing the system's state in the figure above corresponds to a refrigerator rather than to a heat engine.

is done by letting in and pumping out small portions of gaseous helium. The most popular modification of the cycle is skipping its isothermal part (3→4), by allowing a slow heating of the refrigerant together with the cooled object in a fixed magnetic field, due to unavoidable unintentional heat leaks – see, for example, dashed arrows in the figure above. In carefully designed systems, such heat-up may last for up to a week; in such cases, engineers speak about *single-shot* adiabatic cooling.

Another difference between experimental implementations of this technique and the simplest scheme described above is that in some used materials,[50] the applied magnetic field splits energy levels of atoms into $M > 2$ rather than just two sublevels,[51] making the maximum entropy per atom ($\ln M$) larger than ln2, and hence decreasing the necessary amount of the refrigerant.



Problem 2.9. A rudimentary "zipper" model of DNA replication is a chain of N links that may be either open or closed – see the figure on the right. Opening a link increases the system's energy by $\Delta > 0$; and a link may change its state (either open or closed) only if all links to the left of it are open, while all those on the right, are closed. Calculate the average number of open links in thermal equilibrium, and analyze its temperature dependence, especially for the case $N >> 1$.

Solution: According to the model described in the assignment, the chain may have only (N + 1) different states, each with some number n ($0 \leq n \leq N$) of left links open and all other links closed (see the figure above), so the total link-related energy is $E_n = n\Delta$. Hence the Gibbs distribution (see Eqs. (2.58)-(2.59) of the lecture notes) gives the following probability of the state with n open links:

$$W_n = \frac{1}{Z}\exp\left\{-\frac{n\Delta}{T}\right\}, \qquad \text{with } Z = \sum_{n=0}^{N}\exp\left\{-\frac{n\Delta}{T}\right\}.$$

From here and the general Eq. (2.7), the average number of open links may be calculated as

$$\langle n\rangle = \sum_{n=1}^{N} nW_n = \sum_{n=1}^{N} n\exp\left\{-\frac{n\Delta}{T}\right\}\Big/\sum_{n=0}^{N}\exp\left\{-\frac{n\Delta}{T}\right\}.$$

The sum in the denominator is the well-known finite geometric progression:[52]

$$\sum_{n=0}^{N}\exp\left\{-\frac{n\Delta}{T}\right\} \equiv \sum_{n=0}^{N}\lambda^n = \frac{1-\lambda^{N+1}}{1-\lambda}, \qquad \text{where } \lambda \equiv e^{-\Delta/T} \leq 1, \tag{*}$$

while that in the numerator may be readily calculated via its derivative over the parameter λ. Indeed,

$$\sum_{n=0}^{N} n\exp\left\{-\frac{n\Delta}{T}\right\} \equiv \sum_{n=0}^{N} n\lambda^n = \lambda\frac{\partial}{\partial\lambda}\sum_{n=0}^{N}\lambda^n ,$$

so by using Eq. (*), we get

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[50] The initially used materials were paramagnetic salts, such as Mg_3N_2. The current materials of choice include such alloys as $Gd_5(Si_2Ge_2)$ and $PrNi_5$; they allow to reach temperatures below 10^{-3} K using modest applied fields of a few teslas. For more on the adiabatic refrigeration see, e.g., Secs. 8.2-8.5 in G. White and P. Meeson, *Experimental Techniques in Low-Temperature Physics*, 4th ed., Oxford Sci. Publications, 2002.

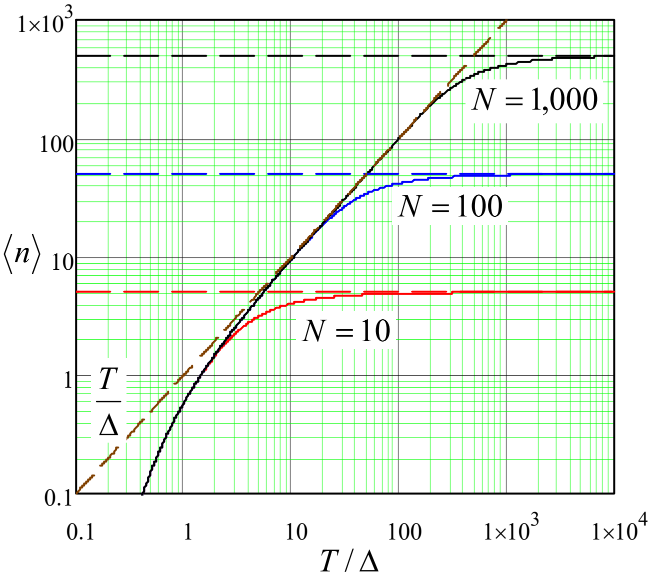
[51] A quantitative discussion of this *Zeeman effect* may be found, e.g., in QM Sec. 6.4.

[52] See, e.g., MA Eq. (2.8a).

$$\sum_{n=0}^{N} n \exp\left\{-\frac{n\Delta}{T}\right\} = \lambda \frac{\partial}{\partial\lambda}\frac{1-\lambda^{N+1}}{1-\lambda} = \lambda \frac{\left(1-\lambda^{N+1}\right)-(N+1)\lambda^{N}(1-\lambda)}{(1-\lambda)^2},$$

and, finally,

$$\langle n\rangle = \frac{\lambda}{1-\lambda} - (N+1)\frac{\lambda^{N+1}}{1-\lambda^{N+1}} \equiv \frac{1}{e^{\Delta/T}-1} - \frac{N+1}{e^{(N+1)\Delta/T}-1}. \qquad (**)$$



As the figure on the right shows, this result is not quite trivial, especially at $N >> 1$. Let us start from the obvious: if the temperature is low, $T << \Delta$, the probability of having even one (the leftmost) link open is exponentially low. Indeed, in this limit, both exponents participating in Eq. (**), $\exp\{\Delta/T\}$ and $\exp\{(N+1)\Delta/T\}$, are much larger than 1. Moreover, for any $N > 1$, the latter exponent is much larger than the former one. As a result, despite the additional multiplier $(N+1)$, the second term in Eq. (**) is negligible in comparison with the first one, and the formula is reduced to

$$\langle n\rangle \approx e^{-\Delta/T} << 1, \qquad \text{for } T << \Delta,$$

independently of N. (As the figure shows, this approximation actually works pretty well all the way up to $T \approx \Delta$.)

The opposite, high-temperature limit is also readily predictable. If T is much larger than both Δ and $(N+1)\Delta$, both exponents $\exp\{\Delta/T\}$ and $\exp\{(N+1)\Delta/T\}$ approach 1, and the denominators in both terms of Eq. (**) become small – approximately equal to, respectively, Δ/T and $(N+1)\Delta/T$, so the magnitudes of both terms become large. Due to the additional factor $(N+1)$ in the numerator of the second term, it nearly cancels the first one, with the remaining balance

$$\langle n\rangle \approx \frac{N}{2}, \qquad \text{for } T >> \Delta, (N+1)\Delta,$$

due to the quadratic terms in the Taylor expansions

$$\exp\left\{\frac{\Delta}{T}\right\} \approx 1 + \frac{\Delta}{T} + \frac{1}{2}\left(\frac{\Delta}{T}\right)^2, \qquad \exp\left\{(N+1)\frac{\Delta}{T}\right\} \approx 1 + (N+1)\frac{\Delta}{T} + \frac{1}{2}(N+1)^2\left(\frac{\Delta}{T}\right)^2.$$

The physics of this result is also pretty simple: at very high temperatures, the energy gain Δ is negligible, and each link has an equal chance to be open or closed.

Perhaps less obvious is one more simple behavior of very long chains ($N >> 1$) within a broad range of intermediate temperatures:

$$\langle n\rangle \approx \frac{T}{\Delta}, \qquad \text{for } \Delta << T << (N+1)\Delta$$

– see the sloped dashed straight line in the figure above. (Mathematically, it follows from Eq. (**) when its first term has already reached its high-temperature limit T/Δ, while the second term is still in its low-temperature limit, and hence is negligible.) The physical interpretation of this simple formula is that the thermal agitation with the characteristic energy $T >> \Delta$ is sufficient to open, on average, $T/\Delta >> 1$ left links of the chain, but not more than that.

Problem 2.10. Use the microcanonical distribution to calculate the average entropy, energy, and pressure of a classical 3D particle of mass m, with no internal degrees of freedom, free to move in volume V, at temperature T.

Hint: Try to make a more accurate calculation than has been done in Sec. 2.2 for the system of N harmonic oscillators. For that, you would need to know the volume V_d of a d-dimensional hypersphere of a unit radius. To avoid being too cruel, I am providing it:

$$V_d = \pi^{d/2} \Big/ \Gamma\left(\frac{d}{2}+1\right),$$

where $\Gamma(\xi)$ is the gamma function.[53]

Solution: Let us consider a microcanonical ensemble of many sets of $N >> 1$ distinct particles.[54] An evident generalization of the quantum state counting rule (see, e.g., Eq. (2.82) of the lecture notes), with $\mathbf{k} = \mathbf{p}/\hbar$, shows that the number of different quantum states of the particle set, with the total energy below a certain value E_N, is

$$\Sigma_N = \frac{1}{(2\pi\hbar)^{3N}} \int\limits_{\Sigma_j (p_j^2/2m) < E_N} d^{3N}q\, d^{3N}p = \frac{V^N}{(2\pi\hbar)^{3N}} p_E^{3N} V_{3N},$$

where $1 \leq j \leq 3N$, $p_E \equiv (2mE_N)^{1/2}$ is the momentum of a particle with energy E_N, i.e. the radius of the hypersphere in the $3N$-dimensional momentum space, containing the states we are counting. Using the formula provided in the *Hint*, with $d = 3N$, we get

$$\Sigma_N = \frac{V^N}{(2\pi\hbar)^{3N}} (2mE_N)^{3N/2} \frac{\pi^{3N/2}}{\Gamma(3N/2+1)},$$

$$g(E_N) \equiv \frac{d\Sigma}{dE_N} = \frac{3N}{2} \frac{V^N}{\Gamma(3N/2+1)} \left(\frac{m}{2\pi\hbar^2}\right)^{3N/2} E_N^{3N/2-1},$$

$$S_N \equiv \ln[g(E_N)] + \text{const} = N \ln V + \left(\frac{3N}{2} - 1\right) \ln E_N + \frac{3N}{2} \ln\left(\frac{m}{2\pi\,\hbar^2}\right) + \ln N - \ln\left[\Gamma\left(\frac{3N}{2}+1\right)\right] + \text{const.}$$

In the limit $N \to \infty$, we may apply the Stirling formula to $\ln[\Gamma(3N/2 + 1)] \approx \ln[(3N/2)!]$, getting

$$S_N \to N \ln V + \frac{3N}{2} \ln E_N + \frac{3N}{2} \ln\left(\frac{m}{2\pi\hbar^2}\right) - \frac{3N}{2}\left(\ln \frac{3N}{2} - 1\right) + \text{const}$$

$$= N \ln\left[V \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} \left(\frac{2E_N}{3N}\right)^{3/2}\right] + \frac{3}{2} N + \text{const.}$$

---

[53] For its definition and main properties, see, e.g., MA Eqs. (6.6)-(6.9).

[54] Please note that even though a single classical particle has an essentially continuous energy spectrum, the application of this method to $N = 1$ would give substantial errors (in particular, $E = T/2$ instead of the correct $E = 3T/2$) – explain why.

Now we can use the definition (1.9) of temperature to get

$$\frac{1}{T} \equiv \left(\frac{\partial S_N}{\partial E_N}\right)_V = \frac{3N}{2E_N}, \qquad \text{i.e. } E_N = \frac{3N}{2}T,$$

so the average energy per particle is[55]

$$E \equiv \frac{E_N}{N} = \frac{3}{2}T.$$

Now by expressing E_N via T, the entropy S per particle may be recast as a function of T and V:

$$S \equiv \frac{S_N}{N} = \ln\left[V\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} T^{3/2}\right] + \frac{3}{2} + \text{const},$$

and then used to calculate the free energy (per particle) as a function of these two arguments:

$$F \equiv E - TS = -T\ln\left[V\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right] = -T\ln V + f(T), \qquad (*)$$

$$f(T) \equiv -T\ln\left[\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right]. \qquad (**)$$

The result (*) is exactly Eq. (1.45) of the lecture notes (derived there from the equation of state $PV = NT$) for the particular case $N = 1$. This is why all other thermodynamic relations for the particle, with this specific form of $f(T)$, coincide with Eqs. (1.44)-(1.51) of the lecture notes, again with $N = 1$. However, Eq. (**) for the function $f(T)$ is new, specific for a particle with no internal degrees of freedom; its generalization will be discussed in Sec. 3.1 of the lecture notes – see, in particular Eq. (3.16b).

Problem 2.11. Solve the previous problem using the Gibbs distribution.

Solution: Combining Eqs. (2.59) and (2.82) of the lecture notes, we get

$$Z \equiv \sum_n e^{-E_n/T} \to \int e^{-E_n/T} dn = \frac{V}{(2\pi\hbar)^3}\int e^{-E(p)/T} d^3p = \frac{V}{(2\pi\hbar)^3}\int e^{-p^2/2mT} d^3p$$

$$= \frac{V}{(2\pi\hbar)^3}\int_{-\infty}^{+\infty} e^{-p_x^2/2mT} dp_x \int_{-\infty}^{+\infty} e^{-p_y^2/2mT} dp_y \int_{-\infty}^{+\infty} e^{-p_z^2/2mT} dp_z = \frac{V}{(2\pi\hbar)^3}\left(2\pi mT\right)^{3/2},$$

so

$$F = -T\ln Z = -T\ln\left[V\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right],$$

i.e. we have arrived (much faster) at the same result as using the microcanonical distribution in the previous problem.

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[55] This result passes a sanity check: for a 3D particle, with its three "half-degrees of freedom", this equality corresponds to the equipartition theorem.

In Sec. 3.1 of the lecture notes, this calculation will be generalized to a classical gas of N particles, with a nontrivial difference of the so-called "correct Boltzmann counting", which does not contribute to the equation of state but affects the entropy of the gas.

Problem 2.12. Calculate the average energy, entropy, free energy, and the equation of state of a classical 2D particle (without internal degrees of freedom), free to move within area A, at temperature T, starting from:

(i) the microcanonical distribution, and
(ii) the Gibbs distribution.

Hint: For the equation of state, make the appropriate modification of the notion of pressure.

Solutions:

(i) Rewriting the solution of Problem 10 with the appropriate replacement of volume V with area A, and the change of phase space dimensionality from (3+3)N to (2+2)N (so that $1 \leq j \leq 2N$), we get

$$\Sigma_N = \frac{1}{(2\pi\hbar)^{2N}} \int_{\Sigma_j (p_j^2/2m) < E_N} d^{2N}q\, d^{2N}p = \frac{A^N}{(2\pi\hbar)^{2N}} p_E^{2N} V_{2N} = \frac{A^N}{(2\pi\hbar)^{2N}} (2mE_N)^N \frac{\pi^N}{\Gamma(N+1)},$$

$$g(E_N) = \frac{d\Sigma_N}{dE_N} = \frac{NA^N}{N!} \left(\frac{m}{2\pi\hbar^2} \right)^N E_N^{N-1},$$

$$S_N = \ln[g(E_N)] + \text{const} = N \ln A + (N-1) \ln E_N + N \ln\left(\frac{m}{2\pi\hbar^2} \right) + \ln N - \ln(N!) + \text{const},$$

$$S_N \to_{N\to\infty} N \ln\left(A \frac{m}{2\pi\hbar^2} \frac{E_N}{N} \right) + \text{const}, \qquad \frac{1}{T} \equiv \left(\frac{\partial S_N}{\partial E_N} \right)_A = \frac{N}{E_N},$$

so the average energy $E \equiv E_N/N$ per particle equals T (in agreement with the equipartition theorem for two "half-degrees of freedom"), and

$$S \equiv \frac{S_N}{N} = \ln\left(A \frac{mT}{2\pi\hbar^2} \right) + \text{const}\,.$$

From here,

$$F \equiv E - TS = -T \ln\left(A \frac{mT}{2\pi\hbar^2} \right) = -T \ln A + f(T), \quad \text{with} \quad f(T) = -T \ln\left(\frac{mT}{2\pi\hbar^2} \right). \qquad (*)$$

In our 2D system, the usual conjugate pair of variables $\{-P, V\}$ has to be replaced with the pair $\{-\sigma, A\}$, where $(-\sigma)$ is the surface "anti-tension", i.e. the average normal force exerted by the particle per unit length of the contour limiting the area A. As a result, the second of Eqs. (1.35) of the lecture notes has to be replaced with

$$\sigma = -\left(\frac{\partial F}{\partial A} \right)_T,$$

together with Eq. (*) giving us essentially the same equation of state as in the 3D case:

$$\sigma A = T\,.$$

(ii) Applying the Gibbs distribution to a single classical particle, we have

$$Z \equiv \sum_n e^{-E_n/T} \rightarrow \frac{A}{(2\pi\hbar)^2}\int e^{-p^2/2mT} d^2p = \frac{A}{(2\pi\hbar)^2}\int_{-\infty}^{+\infty} e^{-p_x^2/2mT} dp_x \int_{-\infty}^{+\infty} e^{-p_y^2/2mT} dp_y = \frac{A}{(2\pi\hbar)^2} 2\pi mT,$$

so

$$F = -T\ln Z = -T\ln\left(A\frac{mT}{2\pi\hbar^2}\right),$$

i.e. the same formula as obtained by the first approach. It triggers the thermodynamics autopilot enabling us to re-calculate all other results, including the equation of state.

Problem 2.13. A quantum particle of mass m is confined to free motion along a 1D segment of length a. Using any approach you like, calculate the average force the particle exerts on the "walls" (ends) of such "1D potential well" in thermal equilibrium, and analyze its temperature dependence, focusing on the low-temperature and high-temperature limits.

Hint: You may consider the series $\Theta(\xi) \equiv \sum_{n=1}^{\infty} \exp\left\{-\xi n^2\right\}$ a known function of ξ.[56]

Solution: The well-known eigenenergies of this problem are[57]

$$E_n = \frac{p_n^2}{2m} = \frac{(\hbar k_n)^2}{2m} = E_1 n^2, \qquad \text{where } E_1 \equiv \frac{\pi^2\hbar^2}{2ma^2} \quad \text{and } n = 1, 2, 3, \ldots.$$

Hence the statistical sum of the Gibbs distribution for this system, in thermal equilibrium at temperature T, is

$$Z \equiv \sum_{n=1}^{\infty} e^{-E_n/T} = \sum_{n=1}^{\infty} e^{-E_1 n^2/T} \equiv \Theta\left(\frac{E_1}{T}\right),$$

where $\Theta(\xi)$ is the function mentioned in the *Hint*, so the free energy is

$$F = T\ln\frac{1}{Z} = -T\ln\left[\Theta\left(\frac{E_1}{T}\right)\right].$$

Since the elementary external work $d\mathscr{W}$ of slowly moving walls on our 1D system may be represented as $-\mathscr{F}da$, where $\mathscr{F}$ is the average force exerted by the particle on the walls, the usual canonical pair of mechanical variables $\{-P, V\}$ has to be replaced with the pair $\{-\mathscr{F}, a\}$. Hence the second of Eqs. (1.35) of the lecture notes has to be replaced with

$$\mathscr{F} = -\left(\frac{\partial F}{\partial a}\right)_T.$$

Combining the above formulas, we get

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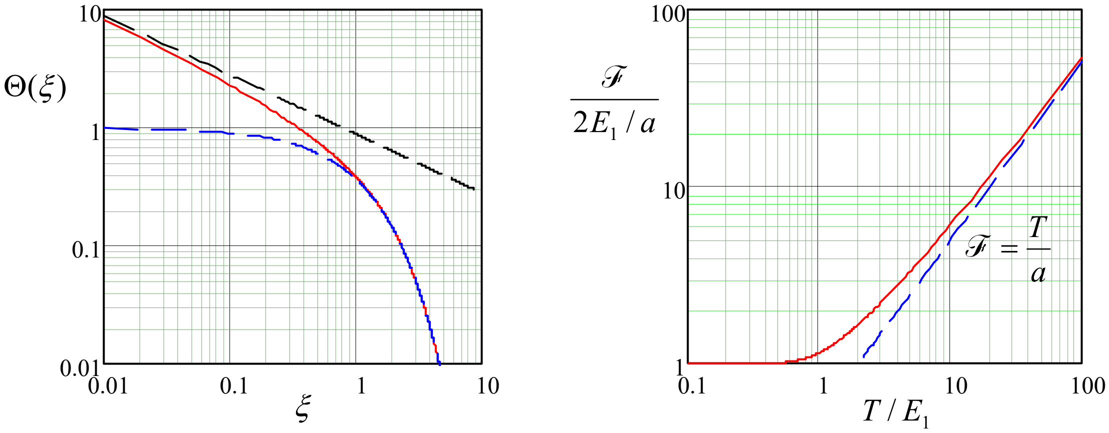
[56] It may be reduced to the so-called elliptic theta-function $\theta_3(z, \tau)$ for a particular case $z = 0$ – see, e.g., Sec. 16.27 in the Abramowitz-Stegun handbook cited in MA Sec. 16(ii). However, you do not need that (or any other) handbook to solve this problem.

[57] See, e.g., QM Sec. 1.4 – or any undergraduate text on quantum mechanics.

$$\mathscr{F} = T\left[\frac{\partial}{\partial a}\ln\Theta\left(\frac{E_1}{T}\right)\right]_T = T\left[\frac{\partial}{\partial E_1}\ln\Theta\left(\frac{E_1}{T}\right)\right]_T\frac{\partial E_1}{\partial a} = -\frac{2E_1}{a}\left[\frac{d}{d\xi}\ln\Theta(\xi)\right]_{\xi=E_1/T}.$$

Log-log plots of the function $\Theta(\xi)$ and its asymptotes are shown on the left panel of the figure below, while its right panel shows the resulting temperature dependence of the force $\mathscr{F}$, and its high-temperature asymptote.



At $\xi \to \infty$, the series defining the function $\Theta(\xi)$ is dominated by its first term, so

$$\Theta(\xi) \approx e^{-\xi}, \quad \ln\Theta(\xi) \approx -\xi, \quad \frac{d}{d\xi}\ln\Theta(\xi) \approx -1, \qquad \text{i.e. } \mathscr{F} \approx \frac{2E_1}{a} \equiv \frac{\pi^2\hbar^2}{ma^3}, \quad \text{at } T << E_1.$$

This is exactly the (temperature-independent) result we would get from a purely quantum-mechanical analysis of the particle's ground state – in that it resides at $T \to 0$.

On the other hand, at $\xi \to 0$, the series is converging very slowly and hence may be well approximated with a Gaussian integral:[58]

$$\Theta(\xi) \equiv \sum_{n=1}^{\infty} e^{-\xi n^2} \approx \int_0^{\infty} e^{-\xi n^2} dn = \frac{\pi^{1/2}}{2\xi^{1/2}} \to \infty, \quad \text{at } \xi \to 0.$$

As a result, in this (classical) limit we get

$$\ln\Theta(\xi) \approx -\frac{1}{2}\ln\xi + \text{const}, \qquad \frac{d}{d\xi}[\ln\Theta(\xi)] \approx -\frac{1}{2\xi}, \qquad \text{i.e. } \mathscr{F} \to \frac{T}{a}, \quad \text{at } T >> E_1.$$

The last result may be also obtained from elementary arguments: according to the equipartition theorem, the average energy of a free classical 1D particle, $p^2/2m = mv^2/2$, is equal to $T/2$, so its r.m.s. momentum is $(mT)^{1/2}$, and the r.m.s. velocity is $(T/m)^{1/2}$. Since each elastic reflection from the wall transfers to it twice the momentum of the incident particle, and the time interval Δt between particle's collisions with the same wall is twice the segment length a divided by the particle's velocity, we get

$$\mathscr{F} = \left\langle\frac{2p}{\Delta t}\right\rangle = \left\langle\frac{2p}{2a/v}\right\rangle \equiv \frac{1}{a}\langle pv\rangle = \frac{m}{a}\langle v^2\rangle = \frac{m}{a}\frac{T}{m} \equiv \frac{T}{a}.$$

---

[58] See, e.g., MA Eq. (6.9b).

Note that per the solutions of Problems 10-12, the equation of state of a free classical particle is essentially the same for any dimensionality.

Problem 2.14. Rotational properties of diatomic molecules (such as N_2, CO, etc.) may be reasonably well described by the so-called *dumbbell model*: two point particles, of masses m_1 and m_2, with a fixed distance d between them. Ignoring the translational motion of the molecule as a whole, use this model to calculate its heat capacity, and spell out the result in the limits of low and high temperatures. Is your solution valid for the so-called *homonuclear* molecules consisting of two similar atoms, such as H_2, O_2, N_2, etc.?

Solution: As we know from classical mechanics,[59] the motion of a two-particle system may be considered as a superposition of the translation motion of their center of mass as a point particle of mass $M = m_1 + m_2$, located at $\mathbf{R} = (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/M$, and the mutual rotation of particles 1 and 2 about this point, equivalent to the rotation of a *single* particle with the so-called *reduced mass*

$$\mathcal{m} = \frac{m_1 m_2}{M} = \frac{m_1 m_2}{m_1 + m_2} \qquad \left(\text{so } \mathcal{m}^{-1} = m_1^{-1} + m_2^{-1}\right),$$

about an immobile point. This reduction of two-particle motion to that of a single particle is valid in quantum mechanics as well.[60] In our case of a fixed distance d, this means that the rotational properties of the molecule are equivalent to those of the so-called *spherical rotator* – a particle free to move on the surface of a sphere – in our case, with the radius d.

According to quantum mechanics,[61] the eigenfunctions of such a rotator are the *spherical harmonics* indexed by two integer quantum numbers: $l = 0, 1,\ldots$, and m with possible values within the limits $-l \leq m \leq +l$. In the absence of an external field affecting the rotation, the corresponding eigenenergies depend only on the "orbital" quantum number l:

$$E_l = \frac{\hbar^2}{2I} l(l+1),$$

where $I \equiv \mathcal{m}d^2$ is the effective particle's moment of inertia. Hence the l^{th} energy level is $(2l + 1)$-degenerate, with different stationary wavefunctions corresponding to different values of the "magnetic" quantum number m. This means that the Gibbs distribution is

$$W_l = Z^{-1}\exp\{-E_l / T\}, \quad \text{with } Z = \sum_{l=0}^{\infty}(2l+1)\exp\left\{-\frac{\hbar^2}{2IT}l(l+1)\right\}. \qquad (*)$$

From here, the average energy may be found as[62]

$$E = \sum_{l=0}^{\infty} E_l W_l = \frac{\hbar^2}{2I}\frac{1}{Z}\sum_{l=0}^{\infty} l(l+1)(2l+1)\exp\left\{-\frac{\hbar^2}{2IT}l(l+1)\right\}, \qquad (**)$$

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[59] See, e.g., CM Sec. 3.4.

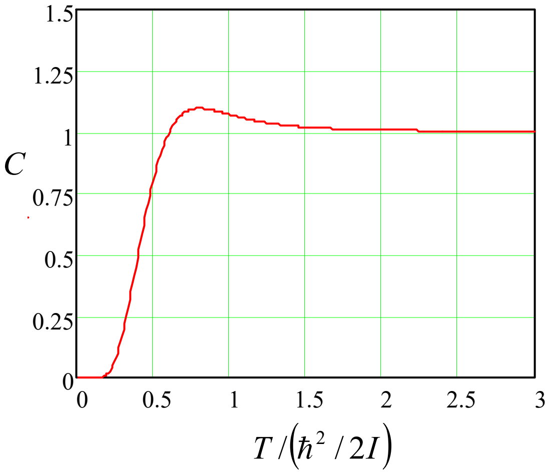
[60] See, e.g., the model solution of QM Problem 8.11.

[61] See, e.g., QM Secs. 3.6 and 5.6.

[62] The same result may be obtained by using Eq. (2.61b) of the lecture notes: $E = \partial(\ln Z)/\partial(-\beta)$, where $\beta \equiv 1/T$.

and the heat capacity as $C(T) = \partial E/\partial T$.

In the general case, the sums in Eqs. (*) and (**) may be calculated only numerically. The resulting function $C(T) = dE/dT$ has a weak maximum, $C_{\max} \approx 1.1$ at the temperature $T \approx 0.8\,(\hbar^2/2I)$ – see the figure on the right. (The physical origin of this maximum is similar to that in two-level systems – see the discussion in the model solution of Problem 3. However, notice that in our current case, $C(T)$ does not vanish at $T \to \infty$, because the energy spectrum of the rotator is infinite, so the probability re-distribution among its values continues even at high temperatures – see below.)



In the high- and low-temperature limits these results may be simplified. In the former (classical) limit, $T >> \hbar^2/2I$, the sum (*) is converging at $l >> 1$, and hence may be well approximated with an integral:

$$Z \approx \int_{l=0}^{\infty} 2l \exp\left\{-\frac{\hbar^2}{2IT} l^2\right\} dl = \int_{l=0}^{\infty} \exp\left\{-\frac{\hbar^2}{2IT} l^2\right\} d(l^2) = \frac{2IT}{\hbar^2}\int_0^{\infty} e^{-\xi} d\xi = \frac{2IT}{\hbar^2},$$

and the average energy (**) is

$$E = \frac{1}{Z}\int_{l=0}^{\infty} E_l\, 2l \exp\left\{-\frac{\hbar^2}{2IT} l^2\right\} dl = \frac{\hbar^2}{2IT}\int_{l=0}^{\infty} \frac{\hbar^2}{2I} l^2 \exp\left\{-\frac{\hbar^2}{2IT} l^2\right\} d(l^2) = T\int_0^{\infty} \xi e^{-\xi} d\xi = T,$$

giving the heat capacity $C \to 1$ – see the figure above again. This result is natural because, in the inertial reference frame of the system's center of mass, the classical rotator's energy may be expressed as

$$E = \frac{p^2}{2m} = \frac{p_1^2 + p_2^2}{2m},$$

with the linear momentum vector **p** having two Cartesian components $p_{1,2}$ – in any two directions perpendicular to each other and the sphere's radius. According to the equipartition theorem discussed in Sec. 2.2 (and valid in this classical limit), the average energy of each of these two "half-degrees of freedom" is $T/2$.

In the opposite, low-temperature limit $T << \hbar^2/2I$, the terms of the statistical sum (*) drop fast (exponentially) with l, and we may keep only two first terms – with $l = 0$ and $l = 1$:

$$Z \approx 1 + 3\exp\left\{-\frac{\hbar^2}{IT}\right\} \equiv 1 + 3\exp\left\{-\frac{\hbar^2\beta}{I}\right\}, \qquad \text{so that } \ln Z \approx 3\exp\left\{-\frac{\hbar^2\beta}{I}\right\},$$

where $\beta \equiv 1/T$. From here and Eq. (2.61b), the average energy becomes[63]

$$E = \frac{\partial(\ln Z)}{\partial(-\beta)} \approx 3\frac{\hbar^2}{I}\exp\left\{-\frac{\hbar^2\beta}{I}\right\} \equiv 3\frac{\hbar^2}{I}\exp\left\{-\frac{\hbar^2}{IT}\right\} \to 0,$$

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[63] Alternatively, this result may be obtained either from Eq. (**) or as $\langle E\rangle \approx W_0E_0 + 3E_1W_1 \approx 3E_1\exp\{-E_1/T\}$.

and the heat capacity

$$C = \frac{\partial E}{\partial T} \approx 3\left(\frac{\hbar^2}{IT}\right)^2 \exp\left\{-\frac{\hbar^2}{IT}\right\} << 1, \qquad \text{for } T << \frac{\hbar^2}{I}. \tag{***}$$

Hence, at $T \to 0$, the heat capacity is exponentially small – the property common for all systems with a finite energy gap between the ground state and the lowest excited state(s). Note also that the degeneracy of the excited states of the system does affect its thermodynamic properties, in particular being responsible for the front numerical factor in the last result. (This 3 is just $2l + 1$ for $l = 1$.)

However, this solution may need revision in the case when two atoms of the molecule are similar, i.e. for homonuclear molecules, because if such atoms are in the similar quantum states of their internal degrees of freedom (including electronic, vibrational, and nuclear-spin ones), they are *indistinguishable* and have to satisfy specific permutation rules of quantum mechanics.[64] A discussion of such revision is the task of the next problem.

Problem 2.15.* Modify the solution of the previous problem for homonuclear molecules. Specifically, consider the cases of molecules H_2, D_2, and N_2. For the first of them, compute the equilibrium ratio of the number of the ortho- and parahydrogen molecules as a function of temperature.

Hint: Use the value of d that gives the experimentally observed difference of 1.455 kJ/mol between the ground state energies of these two hydrogen species ("spin isomers").

Solution: At ambient conditions, two atoms of most homonuclear molecules are in the same (ground) quantum state of their electronic and vibrational degrees of freedom, because the energies of their excitation are well above T (~ 26 meV at T_K = 300K). As a result, their rotational quantum state may be *either symmetric or antisymmetric* with respect to the nuclei permutation, depending on the nuclear spin state of their system.

In particular, if the state is *antisymmetric*, with zero total spin, as it is in the singlet spin state of the hydrogen molecule (in this case, it is common to speak about *parahydrogen*), its rotational wavefunction has to be *symmetric* with respect to the permutation of such fermions as the hydrogen nuclei.[65] But such a nuclear swap is equivalent to the replacement $\mathbf{r} \to -\mathbf{r}$, and the spherical harmonics with odd values of l are antisymmetric with respect to this replacement.[66] As a result, only the rotational states with even values $l = 2p$ (with $p = 0, 1, 2,\ldots$) are permitted, and we have to review the calculations in the previous problem's solution by keeping only contributions from these states:

$$Z_\text{s} = \sum_{l=2p} \exp\{-E_l / T\} = \sum_{p=0}^{\infty} (4p+1)\exp\left\{-\frac{\hbar^2}{IT}p(2p+1)\right\}. \tag{*}$$

In the low-temperature limit, this formula yields

$$Z_\text{s} \approx 1 + 5\exp\left\{-\frac{3\hbar^2}{IT}\right\}, \qquad \ln Z_\text{s} \approx 5\exp\left\{-\frac{3\beta\hbar^2}{I}\right\}, \qquad E_\text{s} \approx 15\frac{\hbar^2}{I}\exp\left\{-\frac{3\hbar^2}{IT}\right\},$$

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[64] See, e.g., QM Sec. 8.1.

[65] See, e.g., QM Eqs. (8.15) and (8.18).

[66] See, e.g., QM Eqs. (3.168) and (3.171), and/or Fig. 3.20 of that course.

so at $T \to 0$, $E_s \to E_0 = 0$. Note that in this limit, the heat capacity is much lower than that calculated in the previous problem:

$$C_\mathrm{s} \approx 45\left(\frac{\hbar^2}{IT}\right)^2 \exp\left\{-\frac{3\hbar^2}{IT}\right\} << 1, \qquad \text{for } T << \frac{\hbar^2}{I},$$

(At $T \to 0$, the change of the exponent is much more important than that of the pre-exponential factor.)

Superficially, it may look like the quantum ban on the population of each other level (with odd values of l) should affect even the high-temperature results. However, this is not so; indeed, because of this level decimation, the statistical sum becomes twice smaller:

$$Z_\mathrm{s} \approx \frac{IT}{\hbar^2}, \qquad \text{for } \frac{\hbar^2}{I} << T,$$

but since this constant factor changes $\ln Z_\mathrm{s}$ only by an additive constant, it does not affect the average energy and heat capacity: $E_\mathrm{s} \approx T$, so $C_\mathrm{s} \approx 1$.

On the contrary, in the *orthohydrogen* molecules, that are in the triplet spin state of their nuclear spins (with the total spin equal to $\hbar$), and hence are *symmetric* with respect to nuclear swap, the fermionic permutation rule permits only *antisymmetric* rotational wavefunctions, i.e. only the odd values $l = 2p + 1$. For these states, Eq. (*) should be replaced with

$$Z_\mathrm{a} = 3\sum_{l=2p+1} \exp\{-E_l / T\} = 3\sum_{p=0}^{\infty}(4p+3)\exp\left\{-\frac{\hbar^2}{IT}(p+1)(2p+1)\right\}, \qquad (**)$$

where the front factor of 3 is due to the nuclear spin degeneracy of the triplet state. In the low-temperature limit, this gives an even lower heat capacity:

$$Z_\mathrm{a} \approx 3\left(3\exp\left\{-\frac{\hbar^2}{IT}\right\} + 7\exp\left\{-\frac{6\hbar^2}{IT}\right\}\right) \equiv 9\exp\left\{-\frac{\beta\hbar^2}{I}\right\}\left(1 + \frac{7}{3}\exp\left\{-\frac{5\beta\hbar^2}{I}\right\}\right),$$

$$\ln Z_\mathrm{a} \approx \ln 9 - \frac{\beta\hbar^2}{I} + \frac{7}{3}\exp\left\{-\frac{5\beta\hbar^2}{I}\right\}, \qquad E_\mathrm{a} \approx \frac{\hbar^2}{I} + \frac{35}{3}\frac{\hbar^2}{I}\exp\left\{-\frac{5\hbar^2}{IT}\right\},$$

$$C_\mathrm{a} \approx \frac{175}{3}\left(\frac{\hbar^2}{IT}\right)^2 \exp\left\{-\frac{5\hbar^2}{IT}\right\} << 1, \qquad \text{for } T << \frac{\hbar^2}{I}.$$

Note that in this limit, E_a tends to the non-zero value E_1,[67] so there is a final energy gap between the ground state energies of the hydrogen spin isomers:

$$E_\mathrm{a} - E_\mathrm{s} \to E_1 - E_0 = \frac{\hbar^2}{I}, \qquad \text{for } T \to 0. \qquad (***)$$

(In the high-temperature limit, E and C are again not affected by the quantum symmetry effects.)

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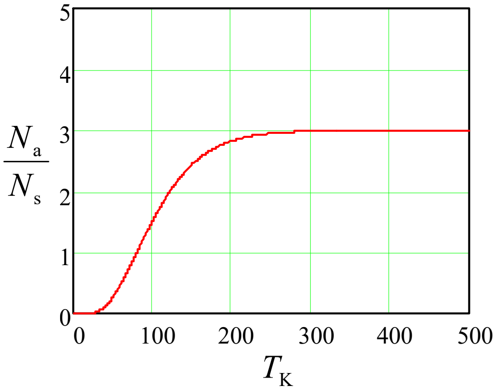
[67] Note that rather counter-intuitively, this means that the ground state of such molecule, with $l = 1$, corresponds to its nonvanishing rotation, with the energy $E_l = E_1 = \hbar^2/I$. Even more amazingly, this rotation is imposed on the molecule by its nuclear spin system, whose coupling with other degrees of freedom of the molecule is much weaker than E_1!

Another readily measurable characteristic of the H_2 gas is the ratio of the numbers N_a and N_s of its ortho- and parahydrogen molecules. If they are in equilibrium,[68] it is helpful to merge Eqs. (*) and (**) into the total statistical sum $Z_s + Z_a$, and use the above selection rules to write

$$\frac{N_s}{N_s+N_a}=\sum_{l=2p}W_l=\frac{1}{Z_a+Z_s}\sum_{p=0}^{\infty}(4p+1)\exp\left\{-\frac{\hbar^2}{IT}p(2p+1)\right\},$$
$$\frac{N_a}{N_s+N_a}=3\sum_{l=2p+1}W_l=\frac{3}{Z_a+Z_s}\sum_{p=0}^{\infty}(4p+3)\exp\left\{-\frac{\hbar^2}{IT}(p+1)(2p+1)\right\},$$

where the front factor of 3 in the expression for N_a again represents the triplet state's spin degeneracy.

The figure on the right shows the ratio N_a/N_s calculated numerically from these expressions, by using the values $m_1 = m_2 = 1.672\times10^{-27}$ kg ($\approx m_p$) and d = 74 pm. (The latter value makes the energy gap (***) between the ground states of the ortho- and parahydrogen isomers close to its experimental value of 1.455 kJ/mol ≈ 15 meV.) The figure shows that at low temperatures, the parahydrogen, with its lower ground state energy E_s, dominates. However, as the temperature is increased, the higher ground state energy becomes less important than its three-fold spin degeneracy in the orthohydrogen, so above ~80 K this isomer dominates the mixture, and at room temperature, the ratio N_a/N_s is already very close to its high-temperature limit of 3.



The deuterium molecule D_2 and the nitrogen molecule N_2 (with atoms of the prevailing ^{14}N isotope) are also examples of spin isomers – however, with a major difference. The net nuclear spin of their atoms equals 1, so the nucleus is a boson, and as a result, the total quantum state of their molecules has to be *symmetric* with respect to the permutation of its nuclei, equivalent to the coordinate inversion $\mathbf{r} \leftrightarrow -\mathbf{r}$. Since the ground electronic and vibrational states of these covalent-bound molecules are *symmetric* with respect to this inversion, its rotational wavefunction has to be *symmetric* for the symmetric nuclear spin state, and vice versa.

According to the quantum rules of spin addition,[69] the system of two spins-1 may be in any of six symmetric states (with the net spin equal to either 0 or 2) and three antisymmetric states (with the net spin equal to 1). As a result, at $T << \hbar^2/I$, the total statistical sum $Z = Z_s + Z_a$ is dominated by that of the symmetric states (more particularly, by the ground-state: $Z_s \approx 1$), so the molecules are predominantly in that state. On the other hand, at high temperatures $T >> \hbar^2/I$, $Z_s \approx Z_a$,[70] and the ratio of probabilities for a molecule to be in the symmetric/antisymmetric orbital state is determined by the relative number of the corresponding nuclear spin states:

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[68] Note that because of the extreme weakness of nuclear spin interactions, the time of such equilibration may be as long as a few days, though it may be sped up using certain catalysts.

[69] See, e.g., QM Sec. 8.1 and the model solutions of Problems 8.10 and 8.14 of that course.

[70] Due to higher vales of $d \approx 110$ pm, and especially of $m_{1,2} \approx 14\, m_p$ in comparison with hydrogen, the transition to this limit for nitrogen takes place well below the room temperature.

$$\frac{N_s}{N_a} = \frac{6}{3} \equiv 2 .$$

Just as in the case of hydrogen, in this limit, $C_s \approx C_a \approx 1$, so this composition of the molecular ensemble does not affect its total heat capacity. However, the ratio N_s/N_a still may be experimentally measured because the rotational symmetry of the wavefunctions affects the probability of externally induced quantum transitions from different initial states to a higher excited state. In the late 1920s, i.e. before the experimental discovery of neutrons in 1932, measurements of such probabilities of the N_2 molecules (carried out by L. Ornstein) have helped to establish the fact that the spin of the nucleus ^{14}N is indeed equal to 1, and hence to discard the then-plausible model in that the nucleus would consist of 14 protons and 7 electrons, giving it the observed values of the mass: $m \approx 14m_p$, and of the net electric charge $Q = 7e$. (In that model, the ground-state value of the nuclear spin had to be semi-integer rather than integer, so it would be a fermion rather than the boson.)

Problem 2.16. Calculate the heat capacity of a heteronuclear diatomic molecule by using the simple model described in Problem 14, but now assuming that the rotation is confined to one plane.[71]

Solution: Repeating the arguments given in the model solution of the previous problem, the system's Hamiltonian may be reduced to that of the so-called *planar rotator* – a particle with the reduced mass $\mathscr{m}$, free to move on a plane circle of the radius equal to d. The Hamiltonian consists only of the 1D kinetic energy,

$$\hat{H} = \frac{\hat{p}^2}{2\mathscr{m}} \equiv \frac{\hat{L}_z^2}{2\mathscr{m}d^2},$$

where $\hat{L}_z = d\hat{p}$ is the angular momentum's component normal to the rotation plane. Quantum mechanics tells us[72] that the eigenvalues L_z of this system are equal to $m\hbar$, where m is an integer (the "magnetic quantum number"). As a result, the rotator's energy levels are described by the relation

$$E_m = \frac{\hbar^2 m^2}{2I} \equiv E_1 m^2, \quad \text{where } E_1 \equiv \frac{\hbar^2}{2I}, \quad \text{with } I \equiv \mathscr{m}d^2 .$$

This spectrum is similar to that studied in Problem 13. However, in contrast to that problem, the rotator's ground state corresponds to $m = 0$ (and has the energy $E_0 = 0$), while all its excited energy levels (with $m \neq 0$) are doubly degenerate – corresponding to two possible signs of m, because the rotator's stationary functions,

$$\psi_m(\varphi) = \frac{1}{(2\pi)^{1/2}} e^{im\varphi},$$

corresponding to these signs, are different. As a result, the statistical sum of the system is

$$Z = e^{-E_0/T} + 2\sum_{m=1}^{\infty} e^{-E_m/T} \equiv 1 + 2\Theta\left(\frac{E_1}{T}\right) \equiv 1 + 2\Theta(\beta E_1), \quad \text{with } \beta \equiv \frac{1}{T},$$

---

[71] This is an approximate but reasonable model of the constraints imposed on small atomic groups (e.g., ligands) by their atomic environment inside some large molecules.

[72] See, e.g., QM Sec. 3.5.

where $\Theta(\xi)$ is the same function,

$$\Theta(\xi) \equiv \sum_{m=1}^{\infty} e^{-\xi m^2},$$

as was discussed (and plotted) in the model solution of Problem 13. For the average energy of the particle, from this expression and Eq. (2.61b) of the lecture notes, we get

$$E = \frac{\partial(\ln Z)}{\partial(-\beta)} = -E_1 \left\{ \frac{d}{d\xi} \ln[1 + 2\Theta(\xi)] \right\}_{\xi = E_1/T},$$

so its heat capacity

$$C \equiv \frac{\partial E}{\partial T} = \xi^2 \left\{ \frac{d^2}{d\xi^2} \ln[1 + 2\Theta(\xi)] \right\}_{\xi = E_1/T}. \qquad (*)$$

In the low-temperature limit ($T/E_1 \to 0$), the largest contribution to C is provided by the first term of the sum $\Theta(\xi)$:

$$Z \to 1 + 2e^{-\beta E_1}, \quad \ln Z \to 2e^{-\beta E_1}, \quad E \to 2E_1 e^{-\beta E_1} \equiv 2E_1 e^{-E_1/T}, \quad C \to 2\left(\frac{E_1}{T}\right)^2 e^{-E_1/T},$$

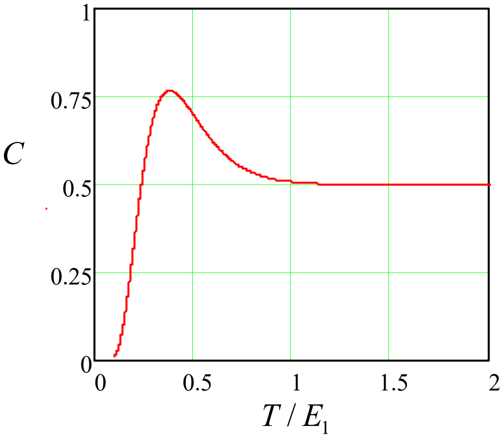
so the heat capacity is exponentially low. In the opposite (essentially, classical) limit of high temperatures, $\beta E_1 << 1$, the function $\Theta(\beta E_1)$ is reduced to a standard Gaussian integral:

$$\Theta(\xi) \approx \int_0^{\infty} e^{-\xi m^2} dm = \frac{\pi^{1/2}}{2\xi^{1/2}},$$

so

$$Z \to \left(\frac{\pi}{\beta E_1}\right)^{1/2}, \quad \ln Z \to \frac{1}{2} \ln \frac{\pi}{\beta E_1}, \quad E \to \frac{T}{2}, \quad C \to \frac{1}{2}.$$

This result is natural because, at $T >> E_1$, the system is essentially classical, with its Hamiltonian function being a quadratic function of one "half-degree of freedom", so the classical equipartition theorem predicts that $E = T/2$. As a plot of Eq. (*) shows (see the figure on the right), between these two limits, the heat capacity as a function of temperature has a maximum at $T \approx 0.4\ E_1$, whose origin is similar to that for two-level systems – see the discussions in the model solution of Problem 3.



<u>Problem 2.17</u>. A classical, rigid, strongly elongated body (such as a thin needle) is free to rotate about its center of mass and is in thermal equilibrium with its environment. Are the angular velocity vector **ω** and the angular momentum vector **L**, on average, directed along the elongation axis of the body, or normal to it?

Solution: According to classical mechanics,[73] the energy of free rotation of a rigid body may be expressed as

$$E=\sum_{j=1}^{3}\frac{I_j\omega_j^2}{2}, \qquad (*)$$

where I_j are the principal moments of inertia, and ω_j are the Cartesian components of the angular velocity vector $\boldsymbol{\omega}$ along the corresponding principal axes. Each ω_j may be considered as a generalized velocity, i.e. a "half-degree of freedom", giving a quadratic contribution to the energy (*). Hence, according to the equipartition theorem, the statistical average of each quadratic component of E is equal to $T/2$, so

$$I_1\left\langle\omega_1^2\right\rangle=I_2\left\langle\omega_2^2\right\rangle=I_3\left\langle\omega_3^2\right\rangle. \qquad (**)$$

In a strongly elongated body, one of the moments I_j (say, I_3), corresponding to the rotation along the elongation axis, is much smaller than two other ones ($I_{1,2}$), so

$$\left\langle\omega_3^2\right\rangle=\frac{I_1}{I_3}\left\langle\omega_1^2\right\rangle=\frac{I_2}{I_3}\left\langle\omega_2^2\right\rangle>>\left\langle\omega_{1,2}^2\right\rangle.$$

This means that the axis of the random thermally agitated rotations of the body is, on average, very close to the elongation axis.

On the other hand, when rewritten for the Cartesian components $L_j = I_j\omega_j$ of the angular momentum vector $\mathbf{L}$, Eq. (**) takes the form

$$\frac{\left\langle L_1^2\right\rangle}{I_1}=\frac{\left\langle L_2^2\right\rangle}{I_2}=\frac{\left\langle L_3^2\right\rangle}{I_3},$$

so these components are in the opposite relation:

$$\left\langle L_3^2\right\rangle=\frac{I_3}{I_1}\left\langle L_1^2\right\rangle=\frac{I_3}{I_2}\left\langle L_2^2\right\rangle<<\left\langle L_{1,2}^2\right\rangle,$$

i.e. the vector $\mathbf{L}$ is, on average, directed almost normally to the elongation axis.

Note that the generalization of these results to the low-temperature (essentially quantum) case requires caution, because classical mechanics does not have the notion of particle indistinguishability, and the above formulas follow from an implicit assumption that the turn of the body by any angle is distinguishable. This is not true, for example, for diatomic molecules, whose rotation about the axis passing through the atomic nuclei is (at all realistic temperatures) purely quantum; this is the reason why their rotational dynamics is different – see the solutions of Problems 14-16.

Problem 2.18. Two similar classical electric dipoles, of a fixed magnitude d, are separated by a fixed distance r. Assuming that each dipole moment vector $\mathbf{d}$ may point in any direction and that the system is in thermal equilibrium, write general expressions for its statistical sum Z, average interaction energy E, heat capacity C, and entropy S, and calculate them explicitly in the high-temperature limit.

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[73] See, e.g., CM Sec. 4.2, in particular Eq. (4.25).

Solution: According to the basic electrostatics,[74] the energy of interaction of two independent dipoles is

$$U = \frac{1}{4\pi\varepsilon_0}\frac{\mathbf{d}_1\cdot\mathbf{d}_2 r^2 - 3(\mathbf{r}\cdot\mathbf{d}_1)(\mathbf{r}\cdot\mathbf{d}_2)}{r^5} \equiv \frac{1}{4\pi\varepsilon_0}\frac{d_{1x}\cdot d_{2x} + d_{1y}\cdot d_{2y} - 2d_{1z}\cdot d_{2z}}{r^3},$$

where in the last expression, the z-axis is directed along the vector $\mathbf{r}$ connecting the dipoles. Plugging the expressions for Cartesian components of dipole moments via the polar and azimuthal angles of their orientation,

$$d_{jx} = d\sin\theta_j\cos\varphi_j, \qquad d_{jy} = d\sin\theta_j\sin\varphi_j, \qquad d_{jz} = d\cos\theta_j, \qquad \text{where } j = 1,2,$$

into the last form of U, we may rewrite it as

$$U = af, \qquad \text{with } a \equiv \frac{d^2}{4\pi\varepsilon_0 r^3},$$

$$f \equiv \sin\theta_1\cos\varphi_1\sin\theta_2\cos\varphi_2 + \sin\theta_1\sin\varphi_1\sin\theta_2\sin\varphi_2 - 2\cos\theta_1\cos\theta_2 \qquad (*)$$
$$\equiv \sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2) - 2\cos\theta_1\cos\theta_2.$$

At $T << a$, when thermal effects are very small, the system stays very close to one of its potential energy minima. According to Eq. (*), there are two of them;[75] in both cases, the dipole moments **d** are aligned with each other and with the line connecting them:

$$U_{\min} = af_{\min}, \qquad f_{\min} = -2, \quad \text{at} \quad \theta_1 = \theta_2 = \begin{cases} 0, \\ \pi. \end{cases}$$

(In any of these positions, the angles φ_1 and φ_2 are uncertain, and do not affect $f_{\min}$.) In this limit,

$$E \approx U_{\min} = af_{\min} \equiv -2\frac{1}{4\pi\varepsilon_0}\frac{d^2}{r^3}.$$

The negative sign of the energy and the growth of its magnitude at $r \to 0$ indicate that the dipoles, in a stable equilibrium, attract each other.

Since each dipole is free to take any direction, possible states of its orientation are uniformly distributed over the full solid angle $\Omega_j = 4\pi$. (If necessary, please revisit the discussion of this point in the model solution of Problem 4.) As a result, the probability density $w \equiv dW/d\Omega_1 d\Omega_2$ to find the system at a certain point $\{\theta_1, \varphi_1; \theta_2, \varphi_2\}$ may be calculated using the Gibbs distribution in the form

$$w = \frac{1}{Z}\exp\left\{-\frac{U}{T}\right\} \equiv \frac{1}{Z}e^{-\beta U},$$

where $\beta \equiv 1/T$ is the reciprocal temperature, and Z is the following statistical sum:

$$Z = \oint_{4\pi} d\Omega_1 \oint_{4\pi} d\Omega_2 e^{-\beta U}.$$

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[74] See, e.g., EM Eq. (3.16), with the notation replacement $\mathbf{p}_{1,2} \to \mathbf{d}_{1,2}$.

[75] If an explanation of this point is needed, see, e.g., the model solution of EM Problem 3.5.

As we know from Eq. (2.61b) of the lecture notes, the average interaction energy may be calculated from this Z as

$$E = \oint_{4\pi} d\Omega_1 \oint_{4\pi} d\Omega_2 U w \equiv \frac{1}{Z} \oint_{4\pi} d\Omega_1 \oint_{4\pi} d\Omega_2 U e^{-\beta U} \equiv \frac{1}{Z}\frac{\partial Z}{\partial(-\beta)} \equiv -\frac{\partial(\ln Z)}{\partial \beta}.$$

From these Z and E, two other variables of our interest may be readily calculated using the general relations (1.22) and (2.62):

$$C \equiv \frac{\partial E}{\partial T}, \qquad S = \frac{E}{T} + \ln Z.$$

Thus, we need to calculate only one integral, namely

$$Z = \oint_{4\pi} d\Omega_1 \oint_{4\pi} d\Omega_2 e^{-\beta U} = \int_0^{\pi} \sin\theta_1 d\theta_1 \int_0^{2\pi} d\varphi_1 \int_0^{\pi} \sin\theta_2 d\theta_2 \int_0^{2\pi} d\varphi_2\, e^{-\beta U}.$$

Due to the 2π-periodicity of the function under the integral with respect to both arguments φ_j, the integral would not change if we replace the integration interval $[0, 2\pi]$ for one of these angles, say φ_1, with any 2π-long interval, for example $[\varphi_2, \varphi_2 + 2\pi]$. Now in this integral, to be worked out at fixed φ_2, we may write $d\varphi_1 = d\varphi$, where $\varphi \equiv \varphi_1 - \varphi_2$. Since, according to Eq. (*), the function under the integral depends only on φ but not on φ_2, we may first take the integral over φ_2, giving us the factor 2π, so the general expression for Z is reduced to

$$Z = 2\pi \int_0^{\pi} \sin\theta_1 d\theta_1 \int_0^{\pi} \sin\theta_2 d\theta_2 \int_0^{2\pi} d\varphi\, e^{-\beta a f}, \quad \text{with } f = \sin\theta_1 \sin\theta_2 \cos\varphi - 2\cos\theta_1 \cos\theta_2.$$

This is as far as we can go analytically for arbitrary temperatures, so let us explore the high- and low-temperature limits. Since $|f| \sim 1$, in the high-temperature limit $T >> a$, i.e. $\beta a << 1$, the argument of the exponent in the expression for Z is small for any dipole orientations, and we may expand it into the Taylor series in this parameter, keeping only three leading terms:

$$e^{-\beta a f} \approx 1 - \beta a f + \frac{1}{2}(\beta a f)^2.$$

The integration of the first term yields a β-independent contribution, $(4\pi)^2$, into Z. The second term, proportional to f, has two parts. The integral of the part proportional to $\cos\varphi$ vanishes because of the integral over φ, while that of the remaining part is a product of two similar integrals of the type

$$\int_0^{\pi} \sin\theta_j d\theta_j \cos\theta_j = \int_{-1}^{+1} \cos\theta_j\, d(\cos\theta_j) = \int_{-1}^{+1} \xi\, d\xi = 0.$$

This is exactly why we needed to keep the last, quadratic term in the above Taylor expansion: it does give the largest nonvanishing β-dependent contribution to Z. Indeed, in this approximation

$$Z - (4\pi)^2 = \pi(\beta a)^2 \int_0^{\pi} \sin\theta_1 d\theta_1 \int_0^{\pi} \sin\theta_2 d\theta_2 \int_0^{2\pi} d\varphi (\sin\theta_1 \sin\theta_2 \cos\varphi - 2\cos\theta_1 \cos\theta_2)^2.$$

Opening the parentheses, we see that the mixed term proportional to $\cos\varphi$ gives no contribution to the integral over φ, so we may continue as follows:

$$Z-(4\pi)^2 = \pi(\beta a)^2 \int_0^{\pi} \sin\theta_1 d\theta_1 \int_0^{\pi} \sin\theta_2 d\theta_2 \int_0^{2\pi} d\varphi \left(\sin^2\theta_1 \sin^2\theta_2 \cos^2\varphi + 4\cos^2\theta_1 \cos^2\theta_2\right)$$

$$\equiv (\pi\beta a)^2 \int_0^{\pi} \sin\theta_1 d\theta_1 \int_0^{\pi} \sin\theta_2 d\theta_2 \left(\sin^2\theta_1 \sin^2\theta_2 + 8\cos^2\theta_1 \cos^2\theta_2\right)$$

$$\equiv (\pi\beta a)^2 \int_0^{\pi} d(\cos\theta_1) \int_0^{\pi} d(\cos\theta_2) \left[\left(1-\cos^2\theta_1\right)\left(1-\cos^2\theta_2\right) + 8\cos^2\theta_1 \cos^2\theta_2\right].$$

Introducing the variables $\xi_j \equiv \cos\theta_j$ again, we get

$$\frac{Z-(4\pi)^2}{(\pi\beta a)^2} = \int_{-1}^{+1} d\xi_1 \int_{-1}^{+1} d\xi_2 \left[\left(1-\xi_1^2\right)\left(1-\xi_2^2\right) + 8\xi_1^2\xi_2^2\right] \equiv \int_{-1}^{+1} d\xi_1 \int_{-1}^{+1} d\xi_2 \left(1-\xi_1^2-\xi_2^2+9\xi_1^2\xi_2^2\right)$$

$$\equiv \left[4-4\int_{-1}^{+1}\xi^2 d\xi + 9\left(\int_{-1}^{+1}\xi^2 d\xi\right)^2\right] = \left[4-4\cdot\frac{2}{3}+9\cdot\left(\frac{2}{3}\right)^2\right] \equiv \frac{16}{3},$$

so, finally,

$$Z = (4\pi)^2 + \frac{16}{3}\pi^2\beta^2 a^2 .$$

This high-temperature approximation is valid only if $\beta a << 1$, so we may take

$$\ln Z = \ln\left[(4\pi)^2\left(1+\frac{1}{(4\pi)^2}\frac{16}{3}\pi^2\beta a^2\right)\right] \approx \ln(4\pi)^2 + \frac{1}{(4\pi)^2}\frac{16}{3}\pi^2\beta^2 a^2 \equiv 2\ln(4\pi) + \frac{1}{3}\beta^2 a^2 .$$

With that result, we get

$$E = -\frac{\partial(\ln Z)}{\partial\beta} \approx -\frac{2}{3}a^2\beta \equiv -\frac{2a^2}{3T} . \qquad (**)$$

Now we may use this expression to calculate

$$C = \frac{\partial E}{\partial T} = \frac{2a^2}{3T^2}, \qquad S = \frac{E}{T} + \ln Z = -\frac{2a^2}{3T^2} + 2\ln(4\pi) + \frac{1}{3}\beta^2 a^2 \equiv \text{const} - \frac{a^2}{3T^2} ,$$

where, in the last expression, "const" means a term independent of the dipole-dipole interaction.

These results show that in the high-temperature limit, all effects of dipole interaction are relatively small – proportional to $a^2/T^2 << 1$. This is natural because in this case, the probability density w is almost uniformly distributed over all dipole orientations, thus nearly averaging out the interaction energy. In particular, Eq. (**) shows that while the dipoles still attract each other even in this limit, the attraction is much weaker than at low temperatures, and drops much faster with distance:

$$E = -\frac{2}{3T}\left(\frac{d^2}{4\pi\varepsilon_0 r^3}\right)^2 \propto -\frac{1}{r^6} .$$

Note that such distance dependence is typical for one of molecular ("van der Waals") forces – the so-called *London dispersion force*, which dominates the long-range interaction of electroneutral atoms and molecules.[76] This similarity is natural because the London force is also due to the statistically averaged interaction of electric dipoles. However, in contrast to the fixed-magnitude dipole model that was the subject of this problem, the London dispersion force between most molecules (having no such spontaneous electric dipole moments) is due to the weak mutual induction of randomly fluctuating dipoles. These fluctuations have not only the classical but also a quantum contribution, so the force has the same dependence on r even at $T \to 0$, while becoming temperature–independent in that limit.[77]

Problem 2.19. A classical 1D particle of mass m, residing in the potential well

$$U(x) = \alpha |x|^{\gamma}, \qquad \text{with } \gamma > 0,$$

is in thermal equilibrium with its environment, at temperature T. Calculate the average values of its potential energy U and the full energy E:

(i) directly from the Gibbs distribution, and
(ii) by using the virial theorem of classical mechanics[78] and the equipartition theorem.

Solutions:

(i) The continuous-spectrum version of the Gibbs distribution (2.58) for such a particle is

$$w(x,p) = \frac{1}{Z}\exp\left\{-\frac{E(x,p)}{T}\right\}, \qquad \text{with } Z = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dp \; \exp\left\{-\frac{E(x,p)}{T}\right\},$$

where E is the particle's full energy:

$$E(x,p) = \frac{p^2}{2m} + U(x),$$

so the exponent participating in the expressions for w and Z may be represented as a product:

$$\exp\left\{-\frac{E(x,p)}{T}\right\} = \exp\left\{-\frac{p^2}{2mT}\right\} \times \exp\left\{-\frac{U(x)}{T}\right\}.$$

Due to such factoring, the integrals over p, participating in Z and in Eq. (2.11) applied to U,

$$\langle U \rangle = \frac{1}{Z}\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dp \; U(x) \exp\left\{-\frac{E(x,p)}{T}\right\},$$

are exactly the same and cancel.[79] Also, due to the symmetry of the given function $U(x)$, both integrals over x may be limited to $x > 0$, so we may write

---

[76] Note that the traditional form, $1/r^{12}$, of the second term in the van der Waals formula, describing molecular/atomic repulsion at small distances, does not have a similarly quantitative physical foundation – see its discussion in Sec. 4.1 of the lecture notes.

[77] See, e.g., the solutions of QM Problems 3.20, 5.20, and 7.6, and also of Problem 5.19 in this course.

[78] See, e.g., CM Problem 1.12.

[79] A similar cancellation will lead us, in Sec. 3.1 of the lecture notes, to a more general result, the so-called *Boltzmann distribution* – see Eq. (3.26).

$$\langle U \rangle = \int_0^{+\infty} U(x) \exp\left\{-\frac{U(x)}{T}\right\} dx \bigg/ \int_0^{+\infty} \exp\left\{-\frac{U(x)}{T}\right\} dx, \quad \text{with } U(x) = \alpha x^\gamma. \qquad (*)$$

The integral in the denominator, for our particular form of the function $U(x)$, may be worked out by its reduction to the usual definition of the gamma function[80] by the following variable replacement: $\xi \equiv \alpha x^\gamma/T$, giving $x = (T\xi/\alpha)^{1/\gamma}$, and hence $dx = (T/\alpha)^{1/\gamma}\xi^{1/\gamma - 1}d\xi/\gamma$:

$$\int_0^{+\infty} \exp\left\{-\frac{U(x)}{T}\right\} dx = \int_0^{+\infty} \exp\left\{-\frac{\alpha x^\gamma}{T}\right\} dx = \left(\frac{T}{\alpha}\right)^{\frac{1}{\gamma}} \frac{1}{\gamma} \int_0^{+\infty} e^{-\xi} \xi^{\frac{1}{\gamma}-1} d\xi = \left(\frac{T}{\alpha}\right)^{\frac{1}{\gamma}} \frac{1}{\gamma} \Gamma\left(\frac{1}{\gamma}\right) \equiv \left(\frac{1}{\alpha\beta}\right)^{\frac{1}{\gamma}} \frac{1}{\gamma} \Gamma\left(\frac{1}{\gamma}\right),$$

where $\beta \equiv 1/T$ is the reciprocal temperature. Now the integral in the numerator of Eq. (*) may be calculated by differentiation of the above expression over β:

$$\int_0^{+\infty} U(x) \exp\left\{-\frac{U(x)}{T}\right\} dx = -\frac{\partial}{\partial\beta} \int_0^{+\infty} \exp\{-\beta U(x)\} dx = -\frac{\partial}{\partial\beta}\left[\left(\frac{1}{\alpha\beta}\right)^{\frac{1}{\gamma}} \frac{1}{\gamma} \Gamma\left(\frac{1}{\gamma}\right)\right] = \frac{1}{\beta\gamma}\left(\frac{1}{\alpha\beta}\right)^{\frac{1}{\gamma}} \frac{1}{\gamma} \Gamma\left(\frac{1}{\gamma}\right),$$

so Eq. (*), after the cancellation of common factors (including the gamma function), yields a very simple result independent of the coefficient α, i.e. of the potential's scale:

$$\langle U \rangle = \frac{1}{\beta\gamma} \equiv \frac{T}{\gamma}. \qquad (**)$$

For the kinetic energy, the partition function's factoring yields the same result as for a free particle (see Eq. (2.48) of the lecture notes):

$$\left\langle \frac{p^2}{2m} \right\rangle = \int_0^{+\infty} \frac{p^2}{2m} \exp\left\{-\frac{p^2}{2mT}\right\} dp \bigg/ \int_0^{+\infty} \exp\left\{-\frac{p^2}{2mT}\right\} dp = \frac{T}{2}, \qquad (***)$$

so the average total energy is

$$\langle E \rangle = \left\langle \frac{p^2}{2m} \right\rangle + \langle U \rangle = \left(\frac{1}{2} + \frac{1}{\gamma}\right) T. \qquad (****)$$

(ii) Applied to a single particle, the virial theorem reads

$$\frac{\overline{p^2}}{2m} = -\frac{\overline{\mathbf{F}\cdot\mathbf{r}}}{2},$$

relating the *temporal* (time) averages of its kinetic energy and the scalar force-by-position product. Since we may represent the thermalization of the particle as the eventual result of its very weak interaction with a heat bath, not perturbing each motion period noticeably, the statistical averages of both sides of this relation are also equal:

$$\frac{\left\langle \overline{p^2} \right\rangle}{2m} = -\frac{\left\langle \overline{\mathbf{F}\cdot\mathbf{r}} \right\rangle}{2}.$$

---

[80] See, e.g., MA Eq. (6.7a).

From Eq. (***) (or just from the equipartition theorem), in thermal equilibrium, the left-hand side of this relation equals $T/2$, while the scalar product on the right-hand side is just $Fx = (-\partial U/\partial x)\,x$, so

$$\left\langle \overline{x\frac{\partial U}{\partial x}} \right\rangle = T \cdot$$

For our (time-independent) potential,

$$x\frac{\partial U(x)}{\partial x} \equiv x\frac{d}{dx}\left(\alpha |\,x\,|^{\gamma}\right) = \alpha\gamma x\,\mathrm{sgn}(x)|\,x\,|^{\gamma-1} \equiv \alpha\gamma |\,x\,|^{\gamma} \equiv \gamma U(x),$$

so[81]

$$\gamma\langle \overline{U} \rangle = T, \qquad \text{i.e. } \langle \overline{U} \rangle = \frac{T}{\gamma}; \qquad \langle E \rangle = \langle \overline{E} \rangle = \left\langle \overline{\frac{p^2}{2m} + U} \right\rangle = \frac{T}{2} + \frac{T}{\gamma} \equiv T\left(\frac{1}{2} + \frac{1}{\gamma}\right).$$

So we got, in a much simpler way, the same results as were obtained by the first, direct approach – see Eqs. (**) and (****).

For the particular case $\gamma = 2$, i.e. for the quadratic confining potential $U = \alpha\,|\,x\,|^2 \equiv \alpha x^2$, when the particle is just a harmonic oscillator, this result returns us to Eq. (2.48). However, it shows that generally, $\langle E \rangle \neq T$; for example, for very soft confining potentials ($\gamma \to 0$), the average energy may be much larger than T. This fact sheds additional light on the reasons why the general notion of temperature has to be defined differently than the average energy per particle and gives a good pretext to have one more thoughtful look at Eq. (1.9).

Problem 2.20. For a slightly anharmonic classical 1D oscillator with mass m and potential energy

$$U(x) = \frac{\kappa}{2}x^2 + \alpha x^3$$

with a small coefficient α, in thermal equilibrium with its environment, calculate:

(i) the statistical average of the coordinate x, and

(ii) the deviation of the heat capacity from its basic value $C = 1$,

in the first (linear) approximation in low temperature T.

Solution: According to the basic Eq. (2.11) of the lecture notes, for this 1D system

$$\langle x \rangle = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dp\; x w(x,p), \qquad \langle U \rangle = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dp\; U(x) w(x,p),$$

where $w(x, p)$ is the probability density. In thermal equilibrium (i.e. for the canonical ensemble), this density may be calculated from the continuous-spectrum version of the Gibbs distribution (2.58):

$$w(x,p) = \frac{1}{Z}\exp\left\{-\frac{E(x,p)}{T}\right\}, \qquad \text{with } Z = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dp\; \exp\left\{-\frac{E(x,p)}{T}\right\},$$

where E is the oscillator's full energy:

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[81] Since in this Hamiltonian system, the total energy E is conserved, the time averaging sign over it may be either dropped or added at will.

$$E(x,p)=\frac{p^2}{2m}+U(x), \qquad \text{so } \exp\left\{-\frac{E(x,p)}{T}\right\}=\exp\left\{-\frac{p^2}{2mT}\right\}\times\exp\left\{-\frac{U(x)}{T}\right\}.$$

Due to this factoring of the exponent, the integrals over p in the expressions for $\langle x\rangle$, $\langle U\rangle$, and Z are exactly the same and cancel, so (similarly to Eq. (*) in the solution of the previous problem):

$$\langle x\rangle=\int_{-\infty}^{+\infty}x\exp\left\{-\frac{U(x)}{T}\right\}dx\Big/\int_{-\infty}^{+\infty}\exp\left\{-\frac{U(x)}{T}\right\}dx, \quad \langle U\rangle=\int_{-\infty}^{+\infty}U(x)\exp\left\{-\frac{U(x)}{T}\right\}dx\Big/\int_{-\infty}^{+\infty}\exp\left\{-\frac{U(x)}{T}\right\}dx. \quad (*)$$

According to the equipartition theorem (2.48), in a classical harmonic oscillator, the characteristic scale of x is $\langle x^2\rangle^{1/2} = (T/\kappa)^{1/2}$, so at low temperatures, we may treat the ratio $\alpha x^3/T \sim \alpha T^{1/2}/\kappa^{3/2}$ as a dimensionless small parameter, and Taylor-expand the exponent participating in Eqs. (*) as

$$\begin{aligned}\exp\left\{-\frac{U(x)}{T}\right\}&=\exp\left\{-\frac{\kappa x^2}{2T}\right\}\exp\left\{-\frac{\alpha x^3}{T}\right\}\approx\exp\left\{-\frac{\kappa x^2}{2T}\right\}\left(1-\frac{\alpha x^3}{T}+\frac{\alpha^2x^6}{2T^2}\right)\\&\equiv\exp\left\{-\frac{\kappa x^2}{2T}\right\}-\frac{\alpha x^3}{T}\exp\left\{-\frac{\kappa x^2}{2T}\right\}+\frac{\alpha^2x^6}{2T^2}\exp\left\{-\frac{\kappa x^2}{2T}\right\}.\end{aligned} \quad (**)$$

The second term of this expansion is an odd function of x, and hence gives no contribution to the integral in the denominator of Eqs. (*), so in our approximation, we get

$$\begin{aligned}\int_{-\infty}^{+\infty}\exp\left\{-\frac{U(x)}{T}\right\}dx&\approx\int_{-\infty}^{+\infty}\exp\left\{-\frac{\kappa x^2}{2T}\right\}dx+\int_{-\infty}^{+\infty}\frac{\alpha^2x^6}{2T^2}\exp\left\{-\frac{\kappa x^2}{2T}\right\}dx\\&=\left(\frac{2T}{\kappa}\right)^{1/2}\int_{-\infty}^{+\infty}\exp\{-\xi^2\}d\xi+\frac{\alpha^2}{2T^2}\left(\frac{2T}{\kappa}\right)^{7/2}\int_{-\infty}^{+\infty}\xi^6\exp\{-\xi^2\}d\xi\\&=\left(\frac{2\pi T}{\kappa}\right)^{1/2}\left(1+\frac{15\alpha^2T}{2\kappa^3}\right),\end{aligned} \quad (***)$$

where the last step used the values of two standard Gaussian integrals.[82]

At the integration in the numerator of Eq. (*) for $\langle x\rangle$, the first and the third terms of the expansion (**), which are even functions of x, give no contributions, while the second one yields

$$\int_{-\infty}^{+\infty}x\exp\left\{-\frac{U(x)}{T}\right\}dx\approx-\frac{\alpha}{T}\int_{-\infty}^{+\infty}x^4\exp\left\{-\frac{\kappa x^2}{2T}\right\}dx\equiv-\frac{\alpha}{T}\left(\frac{2T}{\kappa}\right)^{5/2}\int_{-\infty}^{+\infty}\xi^4\exp\{-\xi^2\}d\xi=-\frac{\alpha}{T}\left(\frac{2T}{\kappa}\right)^{5/2}\frac{3}{4}\pi^{1/2},$$

where, at the last step, one more Gaussian integral[83] has been used. Since this factor is already proportional to our small parameter, we may keep only the leading term of the expansion (***) in the denominator of Eq. (*) for $\langle x\rangle$, finally getting[84]

$$\langle x\rangle=-\frac{\alpha}{T}\left(\frac{2\pi T}{\kappa}\right)^{5/2}\frac{3}{4}\pi^{1/2}\Big/\left(\frac{2\pi T}{\kappa}\right)^{1/2}\equiv-\frac{3\alpha T}{\kappa^2}. \quad (****)$$

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[82] See, e.g., MA Eq. (6.9b) and the second of MA Eqs. (6.9d).

[83] See, e.g., the first of MA Eqs. (6.9d)

[84] Eqs. (***) and (****) are quantitatively only if the calculated $|\langle x\rangle|$ is much smaller than $\langle x^2\rangle^{1/2} \sim (T/\kappa)^{1/2}$.

The last result conceptually explains the fact of thermal expansion of most liquids and solids, because at interatomic interactions, the effective coefficient α is typically negative – see, e.g., Fig. 3.7 of the lecture notes. However, for a quantitative comparison with experiment, the theory has to be duly generalized to phonon modes – see, e.g., the discussion in Sec. 2.6(ii).

In order to calculate $\langle U\rangle$ from the second of Eqs. (*), we could use the expansion (**) in both integrals. However, it is easier to notice that this average may be calculated by directly using Eq. (***):[85]

$$\langle U\rangle = \frac{\partial}{\partial(-1/T)}\ln\int_{-\infty}^{+\infty}\exp\left\{-\frac{U(x)}{T}\right\}dx \equiv T^2\frac{\partial}{\partial T}\ln\int_{-\infty}^{+\infty}\exp\left\{-\frac{U(x)}{T}\right\}dx$$

$$\approx T^2\frac{\partial}{\partial T}\ln\left[\left(\frac{2\pi T}{\kappa}\right)^{1/2}\left(1+\frac{15\alpha^2 T}{2\kappa^3}\right)\right] \approx T^2\frac{\partial}{\partial T}\left[\ln\left(\frac{2\pi T}{\kappa}\right)^{1/2}+\frac{15\alpha^2 T}{2\kappa^3}\right] = \frac{T}{2}+\frac{15\alpha^2 T^2}{2\kappa^3}.$$

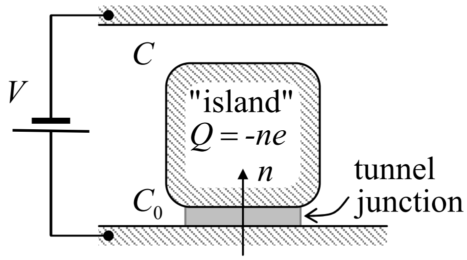
The contribution of this potential energy to the heat capacity of the oscillator is

$$C_U = \frac{\partial}{\partial T}\langle U\rangle = \frac{1}{2}+\frac{15\alpha^2 T}{\kappa^3}.$$

On the other hand, the kinetic energy of the system is a quadratic form of the momentum p, so according to the equipartition theorem, its contribution to the heat capacity is not affected by the weak anharmonicity and still equals ½. Hence its deviation from the base value is

$$C - 1 = \frac{15\alpha^2 T}{\kappa^3} << 1,$$

explaining *a posteriori* why we needed to keep the third term, proportional to α^2, in the expansion (**).



Problem 2.21. A small conductor (in this context, usually called the *single-electron island*) is placed between two conducting electrodes, with voltage V applied between them. The gap between one of the electrodes and the island is so narrow that electrons may tunnel quantum-mechanically through this gap (the "weak tunnel junction") – see the figure on the right. Calculate the average charge of the island as a function of V at temperature T.

Hint: The quantum-mechanical tunneling of an electron electrons through a weak junction[86] between two macroscopic conductors and its subsequent energy relaxation may be treated as a single inelastic (energy-dissipating) event, so the only energy essential for the thermal equilibrium of the system is its electrostatic potential energy.

Solution: The calculation of the relevant electrostatic energy of this system U as a function of the net charge $Q = -ne$ of the island (where n, the difference between the total numbers of electrons and

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[85] This is exactly the same as what Eq. (2.61b) of the lecture notes does for the full energy.

[86] In this particular context, the adjective "weak" denotes a junction with a tunneling transparency so low that the tunneling electron's wavefunction loses its quantum-mechanical coherence before the electron has a chance to tunnel back. In a typical junction of a macroscopic area this condition is fulfilled if its effective resistance is much higher than the quantum unit of resistance (see, e.g., QM Sec. 3.2), $R_Q \equiv \pi\hbar/2e^2 \approx 6.5\ \text{k}\Omega$.

protons in the island, may take only integer values) is elementary – see, e.g., the solution of EM Problem 2.32. Its result is

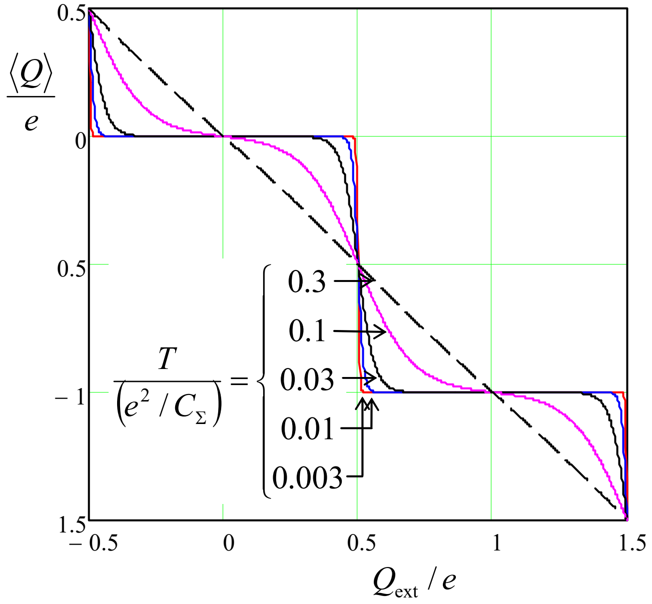
$$U(n)=\frac{(Q+Q_{\text{ext}})^2}{2C_\Sigma}+\text{const}\equiv\frac{(Q_{\text{ext}}-ne)^2}{2C_\Sigma}+\text{const},$$

where $Q_{\text{ext}} \equiv CV$ is the effective polarization charge of the island ([87]), and $C_\Sigma \equiv C + C_0$ is its total capacitance. Applying the Gibbs distribution (2.58)-(2.59) to this system, we get

$$\langle Q\rangle=\frac{1}{Z}\sum_{n=-\infty}^{+\infty}(-ne)\exp\left\{-\frac{(Q_{\text{ext}}-ne)^2}{2C_\Sigma T}\right\},\qquad \text{with } Z=\sum_{n=-\infty}^{+\infty}\exp\left\{-\frac{(Q_{\text{ext}}-ne)^2}{2C_\Sigma T}\right\},$$

so introducing the dimensionless external charge $n_{\text{ext}} \equiv Q_{\text{ext}}/e \equiv CV/e$ and the normalized temperature $\tau \equiv T/(e^2/C_\Sigma)$, we get[88]

$$\frac{\langle Q\rangle}{e}=-\frac{\sum_{n=-\infty}^{+\infty} n\ \exp\left\{-(n_{\text{ext}}-n)^2/2\tau\right\}}{\sum_{n=-\infty}^{+\infty}\exp\left\{-(n_{\text{ext}}-n)^2/2\tau\right\}}.$$



This result is plotted in the figure on the right for several values of the normalized temperature. At $T << e^2/C_\Sigma$, the dependence of $\langle Q\rangle$ on Q_{ext} (i.e. on the applied voltage V) follows the vertical-step *Coulomb staircase* pattern – for a discussion of its physics, see, e.g., the model solution of EM Problem 2.32. However, non-zero temperatures even as low as $\sim 0.3e^2/C_\Sigma$ result in almost complete smearing of the pattern. Because of a similar smearing, most single-electron devices (such as *single-electron transistors*, *single-electron traps*, etc.[89]) also require temperatures to be lower than $\sim 0.03e^2/C_\Sigma$ for their proper operation. This requirement presents one of two major challenges[90] for the development of digital single-electronics, because for their operation at room temperature ($T \sim 25$ meV), it demands e^2/C_Σ to be of the order of 1 eV, corresponding to single-electron islands of just a few nanometers in size.

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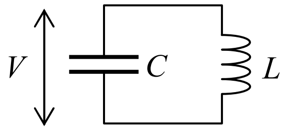
[87] Note that since the applied voltage V is a continuous variable, the values of Q_{ext}, in contrast to those of $Q \equiv -ne$, are *not* limited to the multiples of the fundamental charge e. If this important conceptual point is not clear, please review its discussion in EM Sec. 2.6.

[88] Let me emphasize again that the validity of this Gibbs distribution is not affected by the fact that electrons obey the Fermi-Dirac statistics, because here we deal with the energy U of the whole system, rather than one of its (indistinguishable) components.

[89] For a review, see, e.g., K. Likharev, *Proc. IEEE* **87**, 606 (1999).

[90] The second major challenge is the randomness of the so-called *background* (or "offset") *charges* – see the just-cited review paper.



Problem 2.22. A lumped LC circuit (see the figure on the right) is in thermodynamic equilibrium with its environment. Calculate the r.m.s. fluctuation $\delta V \equiv \langle V^2\rangle^{1/2}$ of the voltage across it, for an arbitrary ratio $T/\hbar\omega$, where $\omega = (LC)^{-1/2}$ is the resonance frequency of this "tank circuit".

Solution: The expression for the classical energy of the LC circuit is well known from undergraduate physics, but we want the result that would describe its quantum properties as well, so let us derive its Hamiltonian carefully, first using the basic notions of classical analytical mechanics.[91] At negligible energy losses, the circuit may be described by a Lagrangian function $\mathscr{L}$, which is the difference between the kinetic and potential energies of the system. For example, we may write

$$\mathscr{L} = \frac{LI^2}{2} - \frac{Q^2}{2C},$$

where the electric charge Q of the capacitor and the current $I = \dot{Q}$ through the inductive coil may be considered, respectively, a generalized coordinate and the corresponding generalized velocity of the system. The corresponding generalized momentum is

$$p_Q \equiv \frac{\partial \mathscr{L}}{\partial \dot{Q}} = LI \equiv \Phi .$$

(Physically, $\Phi = LI$ is the total magnetic flux through the inductive coil.) Hence the Hamiltonian function of the system is

$$\mathscr{H} \equiv p_Q I - \mathscr{L} = \frac{\Phi^2}{2L} + \frac{Q^2}{2C}.$$

Now we may perform the transfer to quantum mechanics just by the replacement of I and Q with the operators representing these observables.[92] The resulting Hamiltonian operator,

$$\hat{\mathscr{H}} = \frac{\hat{\Phi}^2}{2L} + \frac{\hat{Q}^2}{2C},$$

is similar to that of a mechanical harmonic oscillator – see, e.g., Eq. (2.46) of the lecture notes, with the following replacements: $q \to Q$, $p \to p_Q = \Phi$, $m \to L$, $\kappa \to 1/C$ (giving, in particular, $\omega^2 = \kappa/m \to 1/LC$ – a well-known result). With these replacements, Eq. (2.78) of the lecture notes yields

$$\langle Q^2 \rangle = \frac{\hbar\omega C}{2} \coth\frac{\hbar\omega}{2T}.$$

The voltage we are interested in is just $V = Q/C$, so

$$\langle V^2 \rangle = \frac{\langle Q^2 \rangle}{C^2} = \frac{\hbar\omega}{2C} \coth\frac{\hbar\omega}{2T},$$

and the r.m.s. fluctuation δV is just the square root of this expression. The physics of this result and its implications will be discussed in detail in Chapter 5 of the lecture notes.

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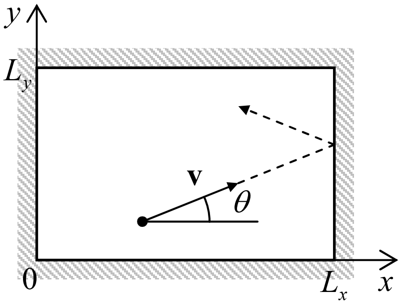
[91] See, e.g., CM Secs. 2.1 and 2.3.

[92] See, e.g., CM Sec. 10.1 and/or QM Sec. 1.2.

Problem 2.23. Derive Eq. (2.92) of the lecture notes from simplistic arguments, by representing the blackbody radiation as an ideal gas of photons treated as classical ultra-relativistic particles. What do similar arguments give for an ideal gas of classical but non-relativistic particles?



Solution: Let us consider a rectilinear cavity of volume $V = L_x \times L_y \times L_z$, containing N photons being elastically reflected from the walls, but otherwise empty. Each reflection from the wall that is perpendicular to the x-axis transfers the momentum $\Delta p_x = 2p_x$ to it. For a free ultra-relativistic particle, the full momentum magnitude p and the energy ε are related as $\varepsilon = cp$, where c is the speed of light,[93] so the transferred momentum may be expressed as

$$\Delta p_x = 2p_x = \frac{2\varepsilon}{c}\cos\theta, \qquad (*)$$

where θ is the incidence angle – see the figure on the right. Since photons in free space move with velocity c, the reflected photon will return to the same wall again (after being reflected by the opposite wall) after the ballistic flight time

$$\Delta t_x = \frac{2L_x}{v_x} = \frac{2L_x}{c\cos\theta}, \qquad (**)$$

so the (time-) average force exerted by this particular photon on the wall is

$$\overline{\mathscr{F}}_x = \frac{\Delta p_x}{\Delta t_x} = \frac{\varepsilon}{L_x}\cos^2\theta,$$

corresponding to its average pressure

$$\overline{P} = \frac{\overline{\mathscr{F}}_x}{A_x} = \frac{\overline{\mathscr{F}}_x}{L_y L_z} = \frac{\varepsilon}{L_x L_y L_z}\cos^2\theta \equiv \frac{\varepsilon}{V}\cos^2\theta.$$

Now summing up the pressure contributions by all N photons, we get

$$P = \frac{E}{V}\langle\cos^2\theta\rangle$$

where E is the sum of all ε, i.e. the full energy of the photon gas, and $\cos^2\theta$ is averaged over the statistical ensemble of random directions of photon propagation:

$$\langle\cos^2\theta\rangle = \frac{1}{4\pi}\oint_{4\pi} d\Omega\cos^2\theta = \frac{1}{4\pi}\int_0^{2\pi} d\varphi \int_0^{\pi}\cos^2\theta\sin\theta d\theta = \frac{1}{4\pi}2\pi\int_{-1}^{+1}\xi^2 d\xi = \frac{1}{3}.$$

As a result, we get Eq. (2.92) of the lecture notes:

$$P = \frac{1}{3}\frac{E}{V}. \qquad (***)$$

Now let us make a similar calculation for a non-relativistic gas, with just one (but significant!) change. Namely, the momentum of such a particle is $\mathbf{p} = m\mathbf{v}$, so instead of Eq. (*) we should write

$$\Delta p_x = 2p_x = 2mv_x.$$

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[93] If this relation is not evident, please see, for example, EM Sec. 9.3, in particular Eq. (9.79).

Using the middle form of Eq. (**) for the time interval, $\Delta t_x = 2L_x/v_x$, we get

$$\overline{\mathscr{F}}_x = \frac{\Delta p_x}{\Delta t_x} = \frac{m}{L_x} v_x^2, \qquad \text{so } \overline{P} = \frac{\overline{\mathscr{F}}_x}{L_y L_z} = \frac{m}{L_x L_y L_z} v_x^2 = \frac{m}{V} v_x^2 .$$

Again, summing the pressure contributions by all particles, while assuming the gas' isotropy (so $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle = \langle v^2\rangle/3 = (2/3)\langle \varepsilon \rangle/m$),[94] we get a result,

$$P = N\frac{m}{V}\langle v_x^2 \rangle = \frac{2}{3}\frac{N}{V}\langle \varepsilon \rangle = \frac{2}{3}\frac{E}{V}, \qquad (****)$$

which differs from Eq. (***) by a factor of 2 – as was already discussed in Sec. 2.6 of the lecture notes.

Now note that while the above derivations of Eqs. (***) and (****) had required the assumption of the isotropy of particle flight directions, they did *not* require the gas to be in full thermal equilibrium. If this condition is added, we may use the equipartition theorem (2.48), valid for non-relativistic particles only, to recast Eq. (****) as

$$P = N\frac{m}{V}\langle v_x^2 \rangle = 2\frac{N}{V}\left\langle \frac{mv_x^2}{2} \right\rangle = 2\frac{N}{V}\frac{T}{2} \equiv \frac{NT}{V},$$

thus recovering the equation of state of the ideal classical gas, Eq. (1.44) – which will be derived in a different, more general way in Sec. 3.1.

Problem 2.24. Calculate the enthalpy, the entropy, and the Gibbs energy of blackbody electromagnetic radiation in thermal equilibrium with temperature T inside volume V, and then use these results to find the law of temperature and pressure drop at an adiabatic expansion.

Solution: Plugging Eq. (2.88) of the lecture notes for the energy, Eq. (2.91) for the free energy, and Eq. (2.92) for the PV product of the blackbody radiation,

$$E = \frac{\pi^2}{15\hbar^3 c^3} VT^4, \qquad F = -\frac{E}{3}, \qquad PV = \frac{E}{3}, \qquad (*)$$

into the general thermodynamic relations (1.27), (1.33), and (1.37), we readily get

$$H \equiv E + PV = \frac{4}{3}E = \frac{4\pi^2}{45\hbar^3 c^3} VT^4, \qquad S = \frac{E-F}{T} = \frac{4}{3}\frac{E}{T} = \frac{4\pi^2}{45\hbar^3 c^3} VT^3, \qquad G \equiv F + PV = 0 .$$

Actually, the last result was already given (in a different form) in the lecture notes – see Eq. (2.93). Its simplest physical interpretation is that the thermally-equilibrium radiation may be considered as a gas of ultra-relativistic, massless particles (photons), which may be created "from nothing", i.e. may be formally considered as coming from (and going to) some external source with a vanishing chemical potential $\mu \propto G$.

As was discussed in Sec. 1.3 of the lecture notes (and mentioned several times after that), at an adiabatic expansion of a system, its entropy stays constant, so the above expression for S yields

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[94] Here ε is generally the kinetic energy of the particle and may be associated with its total energy only if its internal degrees of freedom are in some fixed (e.g., ground) states – see Sec. 3.1 for more discussion of this point.

$$VT^3 = \text{const}, \quad \text{i.e. } T \propto \frac{1}{V^{1/3}}, \tag{**}$$

i.e. at an isotropic expansion, the radiation temperature is inversely proportional to the linear size of the region it occupies. Next, according to Eqs. (*), the radiation's pressure,

$$P = \frac{E}{3V} = \frac{\pi^2}{45\hbar^3 c^3} T^4, \tag{***}$$

is independent of V, so plugging the reciprocal relation, $T \propto P^{1/4}$, into Eq. (**), we get

$$P \propto \frac{1}{V^{4/3}}.$$

This relation may be rewritten in a form similar to that for the adiabatic expansion of the "usual" (non-relativistic) ideal gas:[95]

$$PV^{\gamma} = \text{const},$$

if we take $\gamma = 4/3$. Note, however, that in our current case of the photon (and any ultra-relativistic) gas, the coefficient γ cannot be interpreted as the C_P/C_V ratio, because, according to Eq. (1.23) of the lecture notes, the notion of C_P is undefined if the pressure is a unique function of T, as it is in this case – see Eq. (***) again.

Problem 2.25. As was mentioned in Sec. 2.6(i) of the lecture notes, the relation between the temperature $T_\oplus$ of the visible Sun's surface and that (T_o) of the Earth's surface follows from the balance of the thermal radiation they emit. Prove that the experimentally observed relation indeed follows, with good precision, from a simple model in which the surfaces radiate as perfect black bodies with constant temperatures.

Hint: You may pick up the experimental values you need from any reliable source.

Solution: According to the Stefan radiation law (see Eq. (2.89) of the lecture notes), the full radiation power of the Sun, within this model, is

$$\mathscr{P}_\oplus = 4\pi R_\oplus^2 \sigma T_\oplus^4, \tag{*}$$

where $R_\oplus$ is the Sun's radius. At the Earth's distance r_o from the Sun, this radiation is uniformly distributed over a spherical surface with the area

$$A = 4\pi r_\text{o}^2,$$

so the Earth, visible from the Sun as a plane round disk of the radius $R_\text{o} << r_\text{o}$, absorbs power

$$\mathscr{P}_\text{in} = \mathscr{P}_\oplus \frac{\pi R_\text{o}^2}{A} = \frac{\pi R_\text{o}^2 R_\oplus^2 \sigma T_\oplus^4}{r_\text{o}^2}.$$

If the power radiated by the Earth's surface to space is expressed similarly to Eq. (*):

$$\mathscr{P}_\text{out} = 4\pi R_\text{o}^2 \sigma T_\text{o}^4,$$

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[95] See, e.g., the solution of Problem 1.5.

Then, from the radiation balance $\mathscr{P}_{\text{in}} = \mathscr{P}_{\text{out}}$, we get the following result:

$$T_{\text{o}} = T_{\oplus}\left(\frac{R_{\oplus}}{2r_{\text{o}}}\right)^{1/2},$$

independent of both the Earth radius R_{o} and the Stefan-Boltzmann constant σ – and hence of the Planck constant and the speed of light – see Eq. (2.89b) of the lecture notes.

Plugging in the experimental values $T_{\oplus} \approx 5{,}778$ K, $R_{\oplus} \approx 0.6958\times10^6$ km, and $r_{\text{o}} \approx 149.6\times10^6$ km, for the temperature of Earth's surface, we get the number $T_{\text{o}} \approx 278.6$ K (i.e. ~6°C), which differs from the average actual temperature of 288 K by just ~3%. This surprisingly good agreement is due to the high values of emissivity (see the next problem), $\varepsilon \sim 99\%$, of both the Sun's photosphere and the Earth's oceans (covering most of our planet's surface), at the relevant radiation frequencies.

Problem 2.26. If the surface of a body is not perfectly radiation-absorbing ("black"), the power of its thermal radiation differs from the value given by the Planck radiation law by a factor $\varepsilon < 1$, called *emissivity*. Prove that such a surface reflects the $(1 - \varepsilon)$ fraction of the incident radiation.

Solution: Consider a surface in thermal equilibrium with a large surrounding volume, at some temperature T. According to the discussion in Sec. 2.6(i) of the lecture notes, the power incident on the surface from the volume is described by Planck's law: $\mathscr{P}_{\text{in}} = \mathscr{P}_{\text{Planck}}$. However, in thermal equilibrium, the total power flowing from the surface,

$$\mathscr{P}_{\text{out}} = \mathscr{P}_{\text{rad}} + r\mathscr{P}_{\text{in}},$$

where r is the reflection coefficient we need to find, has to equal $\mathscr{P}_{\text{in}}$, because at thermal equilibrium, there should be no net heat flow into the interior of the body – if it is not transparent. This balance, using the definition of ε given in the assignment: $\mathscr{P}_{\text{rad}} = \varepsilon\mathscr{P}_{\text{Planck}}$, yields

$$\mathscr{P}_{\text{Planck}} = \varepsilon\mathscr{P}_{\text{Planck}} + r\mathscr{P}_{\text{Planck}},$$

i.e. proves the stated result for the reflection coefficient:

$$r = 1 - \varepsilon.$$

This simple relation is sometimes called the *Kirchhoff law of radiation*. (Such a long name is probably justified to avoid confusion with the famous two laws, or "rules",[96] governing lumped electric circuits, that were formulated by the same Gustav Robert Kirchhoff.) This law looks less elementary when it is applied to frequency-dependent $\varepsilon(\omega)$ and $r(\omega)$. (Please review the above solution to get convinced that it is valid even in this case, for each radiation frequency ω.) In particular, in application to discrete spectral lines, it says that if any body/material absorbs strongly on the frequencies where it emits intensively – as it does at quantum transitions between energy levels – see, e.g., QM Sec. 9.3. This fact explains, in particular, the so-called *dark lines* (also called "Fraunhofer lines") of light absorption by relatively cold gases, first discovered in the solar light spectrum in the early 19th century.

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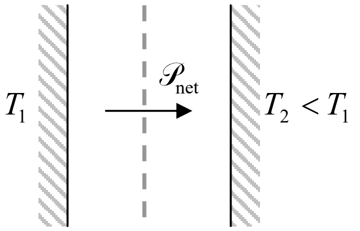
[96] See, e.g., EM Secs. 4.1 and 6.6.

Note also that in this solution, ε was treated as an angle-averaged parameter, hiding, in particular, the (sometimes essential) dependence of the so-called *directional emissivity* ε_Ω on the radiation's direction.



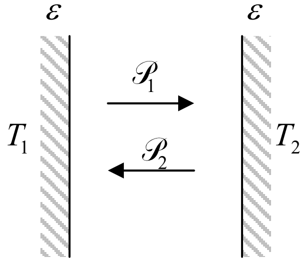
Problem 2.27. If two black surfaces, facing each other, have different temperatures (see the figure on the right), then according to the Stefan radiation law (2.89), there is a net flow of thermal radiation from the hotter surface to the colder one:

$$\frac{\mathscr{P}_{\text{net}}}{A} = \sigma\left(T_1^4 - T_2^4\right).$$

For many applications, notably including most low-temperature experiments, this flow is detrimental. One way to suppress it is to reduce the emissivity ε (for its definition, see the previous problem) of both surfaces – say by covering them with shiny metallic films. An alternative way toward the same goal is to place, between the surfaces, a thin layer (usually called the *thermal shield*), with a low emissivity of both surfaces – see the dashed line in the figure above. Assuming that the emissivity is the same in both cases and neglecting its possible dependence on the angle and frequency, find out which way is more efficient.

Solution: If $\varepsilon < 1$, the power $\mathscr{P}_{\text{rad}}$ of radiation by a surface is lower than the value $\mathscr{P}(T) \equiv \sigma T^4$ following from the Stefan law: $\mathscr{P}_{\text{rad}} = \varepsilon\mathscr{P}(T)$, but the total power flowing from it also includes that of the reflected wave: $\mathscr{P}_{\text{ref}} = r\mathscr{P}_{\text{in}}$, where $\mathscr{P}_{\text{in}}$ is the power incident on this surface from outside, and r is the reflectivity. As was proved in the solution of the previous problem, the reflectivity r is related to the emissivity ε of the same surface by the Kirchhoff radiation law:

$$r = 1 - \varepsilon .$$



Applying these arguments to the power $\mathscr{P}_1$ flowing from surface 1 to surface 2, and to its counterpart $\mathscr{P}_2$, for the first approach discussed in the assignment (see the figure on the right), we may write two similar relations:

$$\begin{aligned} \mathscr{P}_1 &= \varepsilon\mathscr{P}(T_1) + (1-\varepsilon)\mathscr{P}_2, \\ \mathscr{P}_2 &= \varepsilon\mathscr{P}(T_2) + (1-\varepsilon)\mathscr{P}_1. \end{aligned} \qquad (*)$$

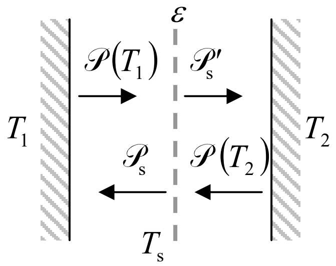
Solving this simple system of two linear equations, we get

$$\mathscr{P}_1 = \frac{\mathscr{P}(T_1) + (1-\varepsilon)\mathscr{P}(T_2)}{2-\varepsilon}, \qquad \mathscr{P}_2 = \frac{\mathscr{P}(T_2) + (1-\varepsilon)\mathscr{P}(T_1)}{2-\varepsilon},$$

so the net power flow from surface 1 to surface 2 is

$$\mathscr{P}_{\text{net}} \equiv \mathscr{P}_1 - \mathscr{P}_2 = \left[\mathscr{P}(T_1) - \mathscr{P}(T_2)\right]\frac{\varepsilon}{2-\varepsilon} \equiv \sigma\left(T_2^4 - T_1^4\right)\frac{\varepsilon}{2-\varepsilon}. \qquad (**)$$

As a sanity check, in the limit $\varepsilon \to 0$ (perfectly reflecting surfaces) the net power tends to zero, while for $\varepsilon = 1$ (perfectly absorbing surfaces) we get the blackbody formula quoted in the assignment.



For the second method described in the assignment (see the figure on the right), the powers radiated by surfaces 1 and 2, which are considered perfectly black, follow the unmodified Stefan law, but we need to write equations similar to Eqs. (*) for the powers flowing from each surface of the thermal shield, assigning to it some (so far, unknown) temperature T_s:

$$\mathscr{P}_s = \varepsilon\mathscr{P}(T_\text{s}) + (1-\varepsilon)\mathscr{P}(T_1),$$
$$\mathscr{P}'_s = \varepsilon\mathscr{P}(T_\text{s}) + (1-\varepsilon)\mathscr{P}(T_2).$$

Since the shield is not connected directly to any external objects, in thermal equilibrium, the net radiation power $\mathscr{P}_\text{net}$ flowing from the left to the right should be the same on the left and the right sides of the shield:

$$\mathscr{P}(T_1) - \mathscr{P}_\text{s} = \mathscr{P}'_\text{s} - \mathscr{P}(T_2).$$

Solving this system of four equations, we get, in particular,

$$\mathscr{P}(T_\text{s}) = \frac{\mathscr{P}(T_1) + \mathscr{P}(T_2)}{2}, \qquad \text{giving } T_\text{s} = \left(\frac{T_1^4 + T_2^4}{2}\right)^{1/4};$$
$$\mathscr{P}_\text{net} \equiv \mathscr{P}(T_1) - \mathscr{P}_\text{s} = [\mathscr{P}(T_1) - \mathscr{P}(T_2)]\frac{\varepsilon}{2} \equiv \sigma(T_2^4 - T_1^4)\frac{\varepsilon}{2}.$$

Comparing the last result with Eq. (**), we see that both methods are very efficient, with the second method yielding a somewhat better result, i.e. a lower net power flow. However, for typical well-reflecting surfaces, with ε of the order of 1%, this difference is minor. Still, the thermal shield method is more convenient practically and may be further improved by using several thin layers, separated by gaps from each other and both surfaces.[97] (Calculating $\mathscr{P}_\text{net}$ for such a system, with N similar shields, is an additional exercise, highly recommended to the reader.)

Problem 2.28. Two perfectly reflecting parallel plates of area A are separated by a free-space gap of a constant thickness $t << A^{1/2}$. Calculate the energy of the thermally-induced electromagnetic field inside the gap in thermal equilibrium, with temperature T in the range

$$\frac{\hbar c}{A^{1/2}} << T << \frac{\hbar c}{t}.$$

Does the field push the plates apart?

Solution: Electrodynamics tells us that within a broad frequency range,

$$\frac{c}{A^{1/2}} << \omega << \frac{c}{t}, \qquad \text{in which } t << \lambda \equiv \frac{2\pi}{k} \equiv \frac{2\pi c}{\omega} << A^{1/2},$$

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[97] Perhaps the most impressive recent example is the huge (~25×15m^2) sunshield of NASA's James Webb Space Telescope launched in 2021, with 5 layers of plastic (polyimide) thin film, each only 25 microns thick, with 50-nm silicon and 100-nm aluminum coatings.

such a system supports transverse electromagnetic (TEM) waves of speed c.[98] Hence if the temperature is within the range specified in the assignment, we may just reproduce the calculations carried in Sec. 2.6(i) of the lecture notes, by replacing the 3D density of states in Eqs. (2.82)-(2.83) with the 2D density, and the degeneracy factor $g = 2$ with $g = 1$:

$$dN = \frac{gA}{(2\pi)^2} d^2k = \frac{A}{(2\pi)^2} 2\pi k dk = \frac{A}{2\pi c^2} \omega d\omega .$$

With this replacement, Eq. (2.84) becomes

$$u(\omega) \equiv \frac{E}{A}\frac{dN}{d\omega} = \frac{\hbar\omega^2}{2\pi c^2} \frac{1}{e^{\hbar\omega/T} - 1},$$

so the total energy of the radiation in the gap is[99]

$$E = A\int_0^\infty u(\omega) d\omega = \frac{A\hbar}{2\pi c^2} \int_0^\infty \frac{\omega^2 d\omega}{e^{\hbar\omega/T} - 1} \equiv \frac{A\hbar}{2\pi c^2}\left(\frac{T}{\hbar}\right)^3 \int_0^\infty \frac{\xi^2 d\xi}{e^{\xi} - 1} = \frac{A\hbar}{2\pi c^2}\left(\frac{T}{\hbar}\right)^3 \Gamma(3)\zeta(3) \approx 0.383\frac{AT^3}{c^2\hbar^2}.$$

Note that the energy scales as T^3, rather than as T^4 in the Stefan law, because of a different dimensionality of the system. (If T is increased beyond $\sim\hbar c/t$, some non-TEM modes may be excited in the gap as well,[100] and we may expect a gradual crossover to the Stephan law.)

Next, since the calculated average energy E of the spontaneous radiation, and hence its free energy F, are independent of the gap thickness t, it does not apply any normal pressure to the conducting plates. This (perhaps, rather counterintuitive) result is due to the fact that the wave vectors $\mathbf{k}$ (and hence the photon momenta $\mathbf{p} = \hbar\mathbf{k}$) of these waves are parallel to the plate surfaces.[101] (Note that an account of the ground-state energy of the TEM modes would not change the situation.) Moreover, since the pressure of the unavoidable 3D (non-TEM) electromagnetic waves outside of the plates is not compensated, at the frequencies $\omega < \pi c/t$, by the TEM waves between them, the plates are effectively *attracted* to each other, even at $T \to 0$ – the so-called *Casimir effect*.[102]

On the other hand, our calculation shows that the energy of the TEM waves inside the gap is proportional to the system area A, just as in the 3D case it is proportional to the containing volume V – see Eq. (2.88) of the lecture notes. As a result, the thermally-induced TEM radiation between the plates does apply outward stress to the system's edges, "trying" to stretch the plates. This effect may be interpreted as a result of the reflection of the just discussed photons, with the momenta $\mathbf{p} = \hbar\mathbf{k}$, from the plate border.

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[98] See, e.g., EM Sec. 7.6. In the TEM waves, the electric field $\mathscr{E}$ is normal to the plate surfaces, while the magnetic field $\mathscr{B}$ is normal to both $\mathscr{E}$ and the wave vector $\mathbf{k}$, i.e. is parallel to the plate surfaces.

[99] For the last two steps of this calculation, we may use MA Eq. (6.8b) with $s = 3$, and then MA Eqs. (2.7b) and (6.7c).

[100] According to electrodynamics, all such modes have frequencies exceeding the critical value $\omega_c = \pi c/t$.

[101] In the electromagnetic field language, due to the universal relation $\mathscr{B} = \mathscr{E}/c \equiv (\varepsilon_0\mu_0)^{1/2}\mathscr{E}$ between the electric and magnetic field magnitudes in the TEM waves, the attraction force $F_e/A = -\varepsilon_0\mathscr{E}^2/2$ due to the electric field normal to the plate surfaces, is exactly compensated by the repulsive force $F_m/A = \mathscr{B}^2/2\mu_0$ due to the magnetic field parallel to the surfaces – see, e.g., EM Sec. 9.8, in particular Eqs. (9.240) and (9.242).

[102] For its discussion, see, e.g., QM Sec. 9.1.

Problem 2.29. Use the Debye theory to estimate the specific heat of aluminum at room temperature (say, 300 K) and express the result in the following popular units:

(i) eV/K per atom,
(ii) J/K per mole, and
(iii) J/K per gram.

Compare the last number with the experimental value (from a reliable source).

Solution: As was mentioned in Sec. 2.6(ii) of the lecture notes, the Debye temperature of aluminum is close to 430 K (with an uncertainty smaller than 1%), so at room temperatures, $T/T_D \approx 300/430 \approx 0.700$. Using Eqs. (2.97)-(2.98), or just reading out the value from one of the plots in Fig. 2.11, we get[103]

$$\frac{C}{nV} \equiv \frac{C}{N} \approx 2.71. \qquad (*)$$

This result is valid literally only if the specific heat is defined by Eq. (1.22), $C \equiv \partial Q/\partial T$, with temperature T expressed in energy units – say, joules. With the temperature expressed in kelvins, $T_K \equiv T/k_B$, the specific heat becomes

$$C_{\text{in J/K}} = \frac{\partial Q}{\partial T_K} = \frac{\partial Q}{\partial (T/k_B)} \equiv k_B \frac{\partial Q}{\partial T} = k_B C,$$

so Eq. (*) yields

$$\left(\frac{C}{N}\right)_{\text{in J/K·atom}} \approx 2.71 k_B \approx 2.71 \times \left(1.38 \times 10^{-23}\right) \frac{\text{J}}{\text{K} \cdot \text{atom}} \approx 3.74 \times 10^{-23} \frac{\text{J}}{\text{K} \cdot \text{atom}}.$$

Now let us express this number in the requested units:

$$\text{(i)} \quad \left(\frac{C}{N}\right)_{\text{in eV/K·atom}} \approx \left(\frac{C}{N}\right)_{\text{in J/K·atom}} \frac{1}{e} \approx \frac{3.74 \times 10^{-23}}{1.60 \times 10^{-19}} \frac{\text{eV}}{\text{K} \cdot \text{atom}} \approx 0.233 \frac{\text{meV}}{\text{K} \cdot \text{atom}},$$

$$\text{(ii)} \quad \left(\frac{C}{N}\right)_{\text{in J/K·mole}} \approx \left(\frac{C}{N}\right)_{\text{in J/K·atom}} N_A \approx 3.74 \times 10^{-23} \times \left(6.02 \times 10^{23}\right) \frac{\text{J}}{\text{K} \cdot \text{mole}} \approx 22.5 \frac{\text{J}}{\text{K} \cdot \text{mole}},$$

$$\text{(iii)} \quad \left(\frac{C}{N}\right)_{\text{in J/K·g}} \approx \left(\frac{C}{N}\right)_{\text{in J/K·mole}} \frac{1}{\mu} \approx \frac{22.5}{27.0} \frac{\text{J}}{\text{K} \cdot \text{g}} \approx 0.833 \frac{\text{J}}{\text{K} \cdot \text{g}},$$

where $\mu \approx 26.98 \approx 27.0$ is the average atomic weight of the natural aluminum (dominated by the ^{27}Al isotope), i.e. the average mass (expressed in grams) of its mole.

For the last of the values, a linear interpolation of the experimental values given in the classical tables by Kaye and Laby[104] (0.880 J/K·g for 273 K and 0.937 J/K·g for 373 K) to 300 K gives 0.895 J/K·g. Another respectable source[105] gives just a ~1% higher value, 0.904 J/K·g, for the same 300 K. Finally, Wikipedia's article *Aluminium* (the metal's name in British English) lists, without an explicit

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[103] As was mentioned in Sec. 2.6, for solids (like aluminum at room temperature), with their very small expansion coefficient, the difference between C_V and C_P is negligible, so the index "V" in Eq. (2.97) may be dropped.

[104] G. Kaye and T. Laby, *Tables of Physical and Chemical Constants*, 16th ed., Longman, 1995.

[105] R. Hultgren *et al., Selected Values of Thermodynamic Properties of the Elements*, ASM, 1973.

reference and temperature specification, the number 24.20 J/K·mole, equivalent to 0.897 J/K·g, i.e. just in-between these two references. So, the average experimental value is ~7.5% higher than our estimate. This deviation demonstrates a limited accuracy of the Debye theory but is still surprisingly small for such a simple and universal model.

Problem 2.30. Low-temperature specific heat of some solids has a considerable contribution from the thermal excitation of spin waves, whose dispersion law.[106] Neglecting anisotropy, calculate the temperature dependence of this contribution to C_V at low temperatures, and discuss conditions of its experimental observation.

Hint: Just as the photons and phonons discussed in Sec. 2.6 of the lecture notes, the quantum excitations of spin waves (called *magnons*) may be considered non-interacting bosonic quasiparticles with zero chemical potential, whose statistics obeys Eq. (2.72).

Solution: Acting exactly as in Sec. 2.6(ii), for isotropic 3D waves of any kind, we may calculate the number of different modes within a small interval $d\omega$ of frequencies as

$$dN = \frac{gV}{(2\pi)^3} 4\pi k^2 dk = \frac{gV}{(2\pi)^3} 4\pi k^2 \frac{dk}{d\omega} d\omega .$$

Since the wave excitation statistics obeys Eq. (2.72), we may calculate the corresponding energy as

$$dE = \frac{\hbar\omega}{e^{\hbar\omega/T}-1} dN = \frac{gV}{(2\pi)^3} \frac{\hbar\omega}{e^{\hbar\omega/T}-1} 4\pi k^2 \frac{dk}{d\omega} d\omega ,$$

so the total energy of the excitations at temperature T is

$$E = 4\pi \frac{gV}{(2\pi)^3} \int_0^\infty \frac{\hbar\omega}{e^{\hbar\omega/T}-1} k^2 \frac{dk}{d\omega} d\omega ,$$

giving the following contribution to the heat capacity:

$$C_V \equiv \frac{\partial E}{\partial T} = 4\pi \frac{gV}{(2\pi)^3} \int_0^\infty \frac{\partial}{\partial T}\left(\frac{\hbar\omega}{e^{\hbar\omega/T}-1}\right) k^2 \frac{dk}{d\omega} d\omega = 4\pi \frac{gV}{(2\pi)^3} \int_0^\infty \left(\frac{\hbar\omega}{T}\right)^2 \frac{e^{\hbar\omega/T}}{\left(e^{\hbar\omega/T}-1\right)^2} k^2 \frac{dk}{d\omega} d\omega . \quad (*)$$

At sufficiently low temperatures, $T << \hbar\omega$, the second fraction under the last integral tends to $\exp\{-\hbar\omega/T\}$, so for any plausible dispersion relation $\omega(k)$, the integral converges at frequencies $\omega_{\max} \sim T/\hbar$. Hence, for such temperatures, we may use the low-frequency approximation for the dispersion law $k(\omega)$; in the specific case of spin waves, $k^2 = \alpha\omega$, where α is a constant, so $dk/d\omega = (\alpha/\omega)^{-1/2}/2$. With these substitutions, Eq. (*) becomes

$$C_V = 4\pi \frac{gV}{(2\pi)^3} \alpha^{3/2} \int_0^\infty \left(\frac{\hbar\omega}{T}\right)^2 \frac{e^{\hbar\omega/T}}{\left(e^{\hbar\omega/T}-1\right)^2} \omega^{1/2} d\omega \equiv 4\pi \frac{gV}{(2\pi)^3} \frac{1}{2} \left(\frac{\alpha T}{\hbar}\right)^{3/2} \int_0^\infty \frac{e^{\xi}}{\left(e^{\xi}-1\right)^2} \xi^{5/2} d\xi ,$$

where $\xi \equiv \hbar\omega/T$. The last integral is just a dimensionless constant, and does not affect the temperature dependence of the heat capacity:

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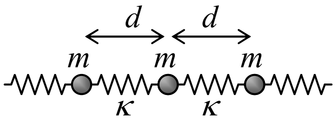
[106] Note that the same dispersion law is typical for bending waves in thin elastic rods – see, e.g., CM Sec. 7.8.

$$C_V = \text{const} \times T^{3/2}. \qquad (**)$$

As Eq. (2.99) of the lecture notes shows, the *phonon* contribution to C_V at low temperatures is proportional to T^3, i.e. drops, at $T \to 0$, much *faster* than Eq. (**) predicts. On the other hand, as will be shown in Sec. 3.3 of the lecture notes, the *free-electron* contribution to specific heat in conductors is proportional to T, i.e. decreases much *slower* than that by magnons. Hence, there is a chance to observe the full specific heat being proportional to $T^{3/2}$ in insulators with atomic spin ordering at low temperatures. (The spin waves are collective deviations of the magnetic moments from such an ordered state.) Indeed, a classical example of a material with such behavior of C_V is europium oxide (EuO); the very substantial ($\sim 7\mu_B$) spontaneous magnetic moments of its Eu atoms lead to their ferromagnetic ordering below the Curie temperature $T_C \approx 69$ K.

More generally, reviewing the above solution for any excitations with the dispersion law $\omega \propto k^n$, we may conclude that in a 3D continuum, they provide a low-temperature specific heat contribution scaling as $T^{3/n}$.

Problem 2.31. Derive a general expression for the specific heat of a very long straight chain of similar particles of mass m, confined to move only in the direction of the chain and elastically interacting with effective spring constants κ – see the figure on the right. Spell out the result in the limits of very low and very high temperatures. Would using the Debye approximation change these results?



Hint: You may like to use the following integral:[107] $\int_0^{+\infty} \frac{\xi^2 d\xi}{\sinh^2 \xi} = \frac{\pi^2}{6}$.

Solution: According to classical mechanics,[108] small longitudinal oscillations in this system may be represented as a sum of N independent standing waves with frequencies

$$\omega_n = \omega_{\max} \left| \sin \frac{k_n d}{2} \right|, \qquad \text{with } \omega_{\max} = 2\left(\frac{\kappa}{m}\right)^{1/2}, \quad n = 1, 2, \ldots, N, \qquad (*)$$

where k_n are equidistant wave numbers separated by intervals $k_{n+1} - k_n \equiv \Delta k = \pi/l = \pi/Nd$. Here N is the number of the particles in the chain, and d is its spatial period, so $l = Nd$ is the total length of the chain. In both classical and quantum mechanics, each of these standing waves may be treated as an independent harmonic oscillator, so per Eq. (2.75) of the lecture notes, the total heat capacity of the chain is

$$C = \sum_{n=1}^{N} C_n = \sum_{n=1}^{N} \left[\frac{\hbar\omega_n / 2T}{\sinh(\hbar\omega_n / 2T)} \right]^2, \qquad (**)$$

where the summation has to be limited to N physically distinguishable wave modes.

If $N >> 1$ (as the assignment implies), the summation may be replaced with integration:

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[107] It may be reduced, via integration by parts, to the table integral MA Eq. (6.8d) with $n = 1$.

[108] See, e.g., CM Sec. 6.3, in particular Eq. (6.30).

$$C=\int_0^N\left[\frac{\hbar\omega_n/2T}{\sinh(\hbar\omega_n/2T)}\right]^2 dn=\frac{N}{\pi}\int_0^{\pi}\left[\frac{\hbar\omega_n/2T}{\sinh(\hbar\omega_n/2T)}\right]^2 d(k_n d),$$

so the requested general expression for the heat capacity per particle is

$$\frac{C}{N}=\frac{1}{\pi}\int_0^{\pi}\left[\frac{\hbar\omega_n/2T}{\sinh(\hbar\omega_n/2T)}\right]^2 d(k_n d), \qquad (***)$$

with ω_n given by Eq. (*).

The function under the integral drops very fast (exponentially) as soon as $\hbar\omega_n$ becomes substantially larger than T, so at temperatures much lower than $\hbar(\kappa/m)^{1/2}$, i.e. than $\hbar\omega_{\max}$, the integral is cut off at frequencies much smaller than $\omega_{\max}$. For these frequencies, Eq. (*) may be simplified,[109]

$$\omega_n=\omega_{\max}\frac{k_n d}{2}, \quad \text{so that } d(k_n d)=\frac{2d\omega_n}{\omega_{\max}}, \quad \text{for } 0\le\omega_n<<\omega_{\max}, \qquad (****)$$

and Eq. (***) is reduced to

$$\frac{C}{N}=\frac{2}{\pi\omega_{\max}}\int_0^{\infty}\left[\frac{\hbar\omega_n/2T}{\sinh(\hbar\omega_n/2T)}\right]^2 d\omega_n\equiv\frac{4T}{\pi\hbar\omega_{\max}}\int_0^{+\infty}\frac{\xi^2 d\xi}{\sinh^2\xi},$$

where $\xi\equiv\hbar\omega_n/2T$. This is exactly the integral mentioned in the *Hint*, so we get

$$\frac{C}{N}=\frac{4T}{\pi\hbar\omega_{\max}}\frac{\pi^2}{6}\equiv\frac{2\pi}{3}\frac{T}{\hbar\omega_{\max}}<<1, \qquad \text{for } T<<\hbar\omega_{\max}.$$

Note that in the 1D system, the specific heat increases with T much faster than in similar 3D systems – cf. Eq. (2.99) of the lecture notes.[110]

In the opposite limit, when the temperature is much higher than $\hbar\omega_{\max}$, according to Eq. (**), $C_n = 1$ for each of the N elementary oscillators of the system, so

$$\frac{C}{N}=1, \qquad \text{for } T>>\hbar\omega_{\max},$$

in agreement with the classical equipartition theorem – which in this limit should be applied to each of the N oscillation modes.

As was discussed in Sec. 2.6(ii) of the lecture notes, the Debye approximation replaces the genuine dispersion law, in our current case given by Eq. (*), with its acoustic asymptote, in our case Eq. (****), for all N oscillation modes of the system. In order to keep this number intact, the summation/integration over the modes should be carried out up to a frequency ω_D different from $\omega_{\max}$:

$$N=\int_{\omega=0}^{\omega=\omega_D}dn=\int_{\omega=0}^{\omega=\omega_D}\frac{dk}{\Delta k}=\frac{l}{\pi}\int_{\omega=0}^{\omega=\omega_D}dk=\frac{l}{\pi}\int_0^{\omega_D}\frac{d\omega_n}{d\omega_n/dk_n}=\frac{l}{\pi}\int_0^{\omega_D}\frac{d\omega_n}{\omega_{\max}d/2}=\frac{l}{\pi}\frac{2}{\omega_{\max}d}\omega_D=N\frac{2\omega_D}{\pi\omega_{\max}},$$

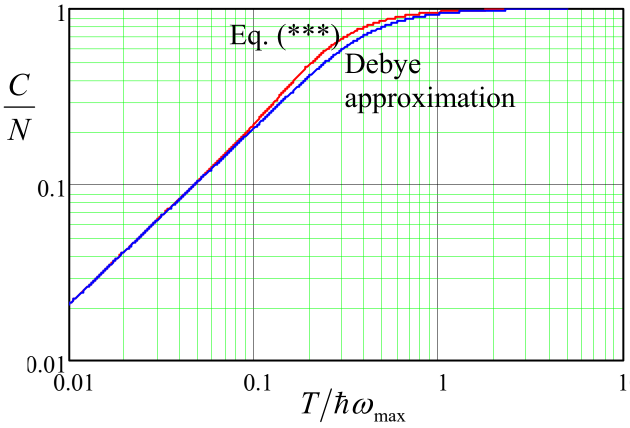
---

[109] Physically this means that at such temperatures, only acoustic waves give a substantial contribution to heat capacity.

[110] Historically, the 1D character of atomic motion in some organic materials was revealed exactly by experimental observations of this temperature dependence.

so $\omega_D = (\pi/2)\omega_{\max}$. Since Eq. (****) describing this approximation yields $d\omega_n = \omega_{\max}d(k_nd/2) = (\pi/2)\omega_{\max}(dn/N)$, i.e. $dn = (2/\pi)Nd\omega_n/\omega_{\max}$, instead of Eq. (***), we have to write

$$\frac{C_D}{N} = \frac{1}{N}\int_0^N \left[\frac{\hbar\omega_n/2T}{\sinh(\hbar\omega_n/2T)}\right]^2 dn = \frac{2}{\pi\omega_{\max}}\int_0^{(\pi/2)\omega_{\max}} \left[\frac{\hbar\omega_n/2T}{\sinh(\hbar\omega_n/2T)}\right]^2 d\omega_n .$$



The figure on the right shows the result of a numerical calculation using this formula (blue line), as well as that using the exact Eq. (***). It shows that the Debye approximation slightly (by ~10%) affects the results at intermediate temperatures $T \sim \hbar\omega_{\max}$, but does not change them in the limits explored above. Indeed, in the high-temperature limit, only the total number of oscillation modes is important (and the Debye approximation always counts them correctly), while in the low-temperature case, the acoustic approximation (****) may be accepted for all thermally-activated modes even at the virtually exact numerical integration of Eq. (***).

So, if the dispersion law of elastic oscillations is as simple as Eq. (*), there is no real motivation to use the Debye approximation. Still, the above exercise is very useful because it gives a good idea of the approximation's accuracy. By the way, the plots above show that at $T/T_D \equiv T/\hbar\omega_D \approx 0.7$, i.e. $T/\hbar\omega_{\max} \approx 0.7(\pi/2) \approx 1.1$, the Debye theory underestimates the specific heat by ~7% – the number very close to the deviation (for a 3D model) discussed in the solution of Problem 19.

Problem 2.32. Use the Debye approximation to obtain a general expression for the longitudinal phonon contribution to the specific heat of a stand-alone monatomic layer of an elastic material (such as graphene). Find its explicit temperature dependence at $T \to 0$.

Solution: According to the general wave theory, in an isotropic 2D continuum, Eq. (2.82) of the lecture notes for the number of oscillation modes has to be modified as[111]

$$dN = \frac{gA}{(2\pi)^2}d^2k = \frac{gA}{(2\pi)^2}2\pi kdk \equiv \frac{gA}{2\pi}kdk , \qquad (*)$$

where A is the layer's area. Here g is the degeneracy factor, i.e. the number of different wave types with the same wave vector $\mathbf{k}$; in this problem, we are asked to account for longitudinal waves only,[112] so we may take $g = 1$. The Debye approximation assumes that their dispersion relation is linear, $k = \omega/v_l$, for

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[111] In most monatomic layers, the longitudinal waves are only slightly anisotropic, so the isotropy assumed by the last form of Eq. (*) is very reasonable.

[112] *Transverse* elastic waves in monatomic layers are highly anisotropic and their properties depend on many factors including the layer placement (suspended or substrate-supported) and its background tension (see, e.g., CM Sec. 7.8). As a result, in contrast with 3D solids, the transverse wave treatment on the same footing as the longitudinal waves makes little sense.

all frequencies below certain ω_D that has to be calculated from the equality of the total number of modes calculated from Eq. (*),

$$N = \int_{\omega=0}^{\omega=\omega_\text{D}} dN = \frac{A}{2\pi} \int_{\omega=0}^{\omega=\omega_\text{D}} k dk = \frac{A}{2\pi}\frac{1}{v_l^2} \int_0^{\omega_\text{D}} \omega d\omega = \frac{A\omega_\text{D}^2}{4\pi v_l^2},$$

to the universal number $N = An$ of the 1D oscillation modes in a layer with n atoms per unit area. From this relation,

$$\omega_\text{D} = 2(\pi n)^{1/2} v_l .$$

Each of these modes may be treated as an independent 1D harmonic oscillator whose heat capacity C_ω is given by Eq. (2.75) of the lecture notes. As a result, we get the following general expression for the total contribution of longitudinal phonons to the heat capacity of the layer:

$$C = \int_{\omega=0}^{\omega=\omega_\text{D}} C_\omega dN = \int_0^{\omega_\text{D}} C_\omega \frac{dN}{d\omega} d\omega = \frac{A}{2\pi}\frac{1}{v_l^2} \int_0^{\omega_\text{D}} \left[\frac{\hbar\omega/2T}{\sinh(\hbar\omega/2T)}\right]^2 \omega d\omega \equiv \frac{4A}{\pi}\frac{T^2}{\hbar^2 v_l^2} \int_0^{\xi_\text{D}} \frac{\xi^3 d\xi}{\sinh^2\xi},$$

where $\xi \equiv \hbar\omega/2T$ and $\xi_\text{D} \equiv \hbar\omega_\text{D}/2T$.

In the low-temperature limit $T << \hbar\omega_\text{D}$, i.e. $\xi_\text{D} >> 1$, while the last (dimensionless) integral converges at $\xi \sim 1$, due to the exponentially growing denominator. As a result, this integral becomes independent of its upper limit ξ_D, and hence of T, so the specific heat (per unit atom) is[113]

$$\frac{C}{N} = \frac{4A}{\pi}\frac{T^2}{\hbar^2 v_l^2} I \Big/ \frac{A\omega_\text{D}^2}{4\pi v_l^2} \equiv \left(\frac{4T}{\hbar\omega_D}\right)^2 I, \qquad \text{where } I \equiv \int_0^\infty \frac{\xi^3 d\xi}{\sinh^2\xi} \approx 1.8031 .$$

Thus, for this 2D system, the low-temperature specific heat is proportional to T^2 – the result we could expect from Eq. (2.99) of the lecture notes for a 3D continuum and from the solution of the previous problem for a 1D system.

Problem 2.33. Calculate the r.m.s. thermal fluctuation of an arbitrary point of a uniform guitar string of length l, stretched by force $\mathscr{T}$, at temperature T. Evaluate your result for $l = 0.7$ m, $\mathscr{T} = 10^3$ N, and room temperature.

Hint: You may like to use the following series: $\sum_{n=1}^{\infty} \frac{\sin^2(\pi n\xi)}{(\pi n)^2} = \frac{\xi(1-\xi)}{2}$, for $0 \leq \xi \leq 1$.

Solution: Basic classical mechanics tells us[114] that a small transverse displacement $q(z, t)$ of a thin (flexible) string stretched along the z-axis gives it the following energy per unit length:

$$\frac{dE}{dz} = \frac{\mu}{2}\left(\frac{\partial q}{\partial t}\right)^2 + \frac{\mathscr{T}}{2}\left(\frac{\partial q}{\partial z}\right)^2, \qquad (*)$$

and obeys the usual 1D wave equation

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[113] Just for the reader's reference, $I = (3/2)\zeta(3)$, where $\zeta(s)$ is the Riemann zeta function – see MA Eq. (2.7).

[114] See, e.g., CM Sec. 6.3 and the solution of Problem 6.10 of that course.

$$\mu \frac{\partial^2 q}{\partial t^2} = \mathscr{T} \frac{\partial^2 q}{\partial z^2},$$

where μ is the string's linear density, i.e. its mass per unit length, while $\mathscr{T}$ is its tension's magnitude (equal to the stretching force). This equation, together with the boundary conditions at the string's ends,

$$q(0,t) = q(l,t) = 0, \qquad (**)$$

is satisfied with the sum of variable-separated terms, each describing a standing-wave mode:

$$q(z,t) = \sum_{n=1}^{\infty} q_n(z,t), \quad \text{with } q_n = Z_n(z)T_n(t).$$

Here $Z_n(z)$ are the sinusoidal standing-wave profiles that comply with the boundary conditions (**),

$$Z_n = \sin\frac{\pi n z}{l}, \quad \text{with } n = 1, 2, 3, \ldots,$$

and each function $T_n(t)$ obeys the same ordinary differential equation as the usual harmonic oscillator, but with the mode-specific frequency ω_n:

$$\ddot{T}_n + \omega_n^2 T_n = 0, \qquad \text{where } \omega_n^2 \equiv \frac{\mathscr{T}}{\mu}\left(\frac{\pi n}{l}\right)^2, \qquad (***)$$

with the well-known solution

$$T_n = A_n \cos(\omega_n t + \varphi_n).$$

The fact that each of these standing waves obeys its individual equation of motion, i.e. is uncoupled from other oscillation modes, means that its energy E_n is conserved. Since, with time, the energy is periodically and fully "re-pumped" between its potential and kinetic forms, we may calculate it, for example, as the maximum value of the potential energy, given by the second term of Eq. (*):

$$E_n = \max_t \left[\int_0^l \frac{\mathscr{T}}{2}\left(\frac{\partial q_n}{\partial z}\right)^2 dz\right] = \max_t \left[T_n^2(t)\right]\frac{\mathscr{T}}{2}\left(\frac{\pi n}{l}\right)^2 \int_0^l Z_n^2(z)dz = A_n^2 \frac{\mathscr{T}}{2}\left(\frac{\pi n}{l}\right)^2 \frac{l}{2}.$$

Now we may use either the equipartition theorem (2.48) or Eq. (2.80) in the thermal limit ($T >> \hbar\omega_n$), to write

$$\langle A_n^2 \rangle \frac{\mathscr{T}}{2}\left(\frac{\pi n}{l}\right)^2 \frac{l}{2} = T, \qquad \text{giving } \langle A_n^2 \rangle = \frac{4lT}{\mathscr{T}} \frac{1}{(\pi n)^2}.$$

From this, we can calculate the variance of fluctuations at an arbitrary point z as follows:

$$\langle q^2 \rangle = \left\langle \left[\sum_{n=1}^{\infty} A_n \cos(\omega_n t + \varphi_n)\sin\frac{\pi n z}{l}\right]^2 \right\rangle = \left\langle \sum_{n,n'=1}^{\infty} A_n A_{n'} \cos(\omega_n t + \varphi_n)\cos(\omega_{n'} t + \varphi_{n'})\sin\frac{\pi n z}{l}\sin\frac{\pi n z}{l} \right\rangle.$$

Due to the randomicity of the mode phases φ_n, the averages of all cross-terms vanish, so

$$\langle q^2 \rangle = \left\langle \sum_{n=1}^{\infty} A_n^2 \cos^2(\omega_n t + \varphi_n)\sin^2\frac{\pi n z}{l} \right\rangle = \frac{1}{2}\sum_{n=1}^{\infty} \langle A_n^2 \rangle \sin^2\frac{\pi n z}{l} = \frac{2lT}{\mathscr{T}} \sum_{m=0}^{\infty} \frac{\sin^2 \pi n \xi}{(\pi n)^2},$$

where $\xi \equiv z/l$. Using the series provided in the *Hint*, we finally get

$$\langle q^2 \rangle = \frac{T}{\mathscr{T} l} z(l-z), \qquad \text{i.e. } \delta q = \left[\frac{T}{\mathscr{T} l} z(l-z)\right]^{1/2}.$$

Note that the calculated variance formally does not depend on μ, though in practice, the string's mass affects the result because usually its tension $\mathscr{T}$ is adjusted to obtain the desired value of the fundamental mode frequency, $\omega_1 = (\pi/l)(\mathscr{T}/\mu)^{1/2}$ – see Eq. (***).

Now plugging in the (quite realistic) parameters given in the assignment, in particular, $T = k_B T_K \approx (1.38\times10^{-23}\times300)$ J, for the r.m.s. fluctuation of the middle point ($z = l/2$), we get $\delta q \approx 0.85\times10^{-12}$ m. On the human scale, such displacements are not too large, but they still may be readily measured even with inexpensive lab equipment – for example, a simple capacitive sensor followed by a low-noise electronic amplifier. (Sensors of gravitational wave observatories, such as the now-famous LIGO, can measure displacements about eight orders of magnitude smaller, though at frequencies much lower than the typical guitar tune.)

Problem 2.34. Use the general Eq. (2.123) of the lecture notes to re-derive the Fermi-Dirac distribution (2.115) for a system in equilibrium.

Solution: As discussed in Sec. 2.8 of the lecture notes, Eq. (2.123),

$$S_k = -\langle N_k \rangle \ln\langle N_k \rangle - (1-\langle N_k \rangle)\ln(1-\langle N_k \rangle), \tag{*}$$

expresses the entropy related to the k^{th} quantum state of Fermi particles as a function of its average occupancy $\langle N_k \rangle$, and is valid even out of equilibrium. For the thermal and chemical equilibrium, we may require the total entropy,

$$S = \sum_k S_k,$$

of a system of N particles with a fixed total energy E, considered as a function of all $\langle N_k \rangle$, to reach its maximum, with two constraints:

$$\sum_k \langle N_k \rangle = N = \text{const}, \qquad \sum_k \varepsilon_k \langle N_k \rangle = E = \text{const}. \tag{**}$$

As was discussed in Sec. 2.2, this requirement demands all conditional derivatives to vanish:

$$\left[\frac{\partial S}{\partial \langle N_k \rangle}\right]_{\text{cond}} \equiv \frac{\partial S}{\partial \langle N_k \rangle} + \sum_{k' \neq k} \frac{\partial S}{\partial \langle N_{k'} \rangle}\frac{\partial \langle N_{k'} \rangle}{\partial \langle N_k \rangle} = 0. \tag{***}$$

The system of such equations for all k, as well as the first of the conditions (**), may be satisfied by taking $\partial S/\partial\langle N_k \rangle = \lambda = \text{const}$. However, this form would leave the second of the conditions (**) unsatisfied, so we may try to look for the solution in a more general form:

$$\frac{\partial S}{\partial \langle N_k \rangle} = \lambda + \lambda' \varepsilon_k, \tag{****}$$

with the Lagrange multipliers λ and λ' independent of k. Plugging this form into the right-hand part of Eq. (***), we get

$$\left[\frac{\partial S}{\partial\langle N_k\rangle}\right]_{\text{cond}} = \lambda + \lambda'\varepsilon_k + \sum_{k'\neq k}\left(\lambda + \lambda'\varepsilon_{k'}\right)\frac{\partial\langle N_{k'}\rangle}{\partial\langle N_k\rangle} \equiv \lambda\frac{\partial}{\partial\langle N_k\rangle}\sum_{k'}\langle N_{k'}\rangle + \lambda'\frac{\partial}{\partial\langle N_k\rangle}\sum_{k'}\varepsilon_{k'}\langle N_{k'}\rangle,$$

so with the additional conditions (**), the conditional derivatives indeed vanish, thus satisfying the system of equations (***). In the particular case (*) of the fermionic entropy, Eq. (***) gives

$$-\ln\langle N_k\rangle + \ln(1-\langle N_k\rangle) = \lambda + \lambda'\varepsilon_k.$$

Solving this equation for the average occupancy, we get

$$\langle N_k\rangle = \frac{1}{\exp\{\lambda + \lambda'\varepsilon_k\}+1}.$$

In order to express the Lagrange multipliers λ and λ' participating in this result via the standard thermodynamic notions, let us use our intermediate result (****) to spell out the change of S at a small, reversible variation of the system's parameters, which changes the average occupancies $\langle N_k\rangle$ but keeps the system's volume (and hence the particles' energy spectrum ε_k) intact:

$$dS = \sum_k \frac{\partial S}{\partial\langle N_k\rangle}d\langle N_k\rangle = \sum_k\left(\lambda + \lambda'\varepsilon_k\right)d\langle N_k\rangle \equiv \lambda\sum_k d\langle N_k\rangle + \lambda'\sum_k \varepsilon_k d\langle N_k\rangle.$$

Comparing this expression with the corresponding changes of N and E given by Eq. (**),

$$dN = \sum_k d\langle N_k\rangle, \qquad dE = \sum_k \varepsilon_k d\langle N_k\rangle,$$

we see that they are related as

$$dS = \lambda dN + \lambda' dE.$$

Now comparing this equality with the thermodynamics relation (1.52) with $dV = 0$,

$$dE = TdS + \mu dN, \qquad \text{i.e. } dS = -\frac{\mu}{T}dN + \frac{dE}{T},$$

we get $\lambda = -\mu/T$, $\lambda' = 1/T$, so the above result for $\langle N_k\rangle$ indeed coincides with Eq. (2.115).

Absolutely similarly, the general Eq. (2.126) may be used for an alternative calculation of the Bose-Einstein distribution (2.118) valid in equilibrium.

Problem 2.35. Each of two identical particles, not interacting directly, may be in any of two quantum states, with the single-particle energies ε equal to 0 and Δ. Write down the statistical sum Z of the system, and use it to calculate its average total energy E at temperature T, for the cases when the particles are:

(i) distinguishable (say, by their spatial positions);
(ii) indistinguishable fermions;
(iii) indistinguishable bosons.

Analyze and interpret the temperature dependence of $\langle E\rangle$ for each case, assuming that $\Delta > 0$.

Solutions: Let us denote the possible states of the system by a set of two arrows that code the single-particle states: ↓ for the state of energy 0, and ↑ for the state of energy Δ. Then the possible states and their total energies are as follows:

$$\{\downarrow\downarrow\}: E = 0; \qquad \{\downarrow\uparrow\}: E = \Delta; \qquad \{\uparrow\downarrow\}: E = \Delta; \qquad \{\uparrow\uparrow\}: E = 2\Delta. \qquad (*)$$

Now we are ready to address the problem's tasks.

(i) For distinguishable particles, all states (*) are possible and different, so

$$Z \equiv \sum_m \exp\left\{-\frac{E_m}{T}\right\} = 1 + 2e^{-\Delta/T} + e^{-2\Delta/T}.$$

(As a useful detour: note that this expression may be rewritten as

$$Z = \left(1 + e^{-\Delta/T}\right)^2, \qquad (**)$$

and derived, in this form, from the following general arguments:[115] since for a system of two non-interacting particles, the energy is $E = \varepsilon_1 + \varepsilon_2$, then if all its states are different, we may write

$$Z \equiv \sum_m \exp\left\{-\frac{E_m}{T}\right\} = \sum_m \exp\left\{-\frac{(\varepsilon_1 + \varepsilon_2)_m}{T}\right\} \equiv \sum_m \exp\left\{-\frac{(\varepsilon_1)_m}{T}\right\}\exp\left\{-\frac{(\varepsilon_2)_m}{T}\right\}.$$

For distinguishable particles, the possible states of each particle are independent, and we get

$$Z = \sum_{m_1, m_2} \exp\left\{-\frac{(\varepsilon_1)_{m_1}}{T}\right\}\exp\left\{-\frac{(\varepsilon_2)_{m_2}}{T}\right\} \equiv \sum_{m_1} \exp\left\{-\frac{(\varepsilon_1)_{m_1}}{T}\right\}\sum_{m_2} \exp\left\{-\frac{(\varepsilon_2)_{m_2}}{T}\right\}.$$

But each of these partial sums is just the partial statistical sum of a single particle, so we get a very simple result:

$$Z = Z_1 Z_2,$$

which is reduced to an even simpler form, $Z = Z_1^2$, if the partial sums are equal, for our simple system immediately giving Eq. (**) – the end of the detour.)

Now returning to Eq. (**) and plugging it, in the form

$$Z = \left(1 + e^{-\beta\Delta}\right)^2, \qquad \text{where } \beta \equiv \frac{1}{T},$$

into Eq. (2.61b) of the lecture notes,

$$\langle E \rangle = -\frac{\partial(\ln Z)}{\partial \beta} \equiv -\frac{1}{Z}\frac{\partial Z}{\partial \beta}, \qquad (***)$$

we readily get

$$\langle E \rangle = \frac{2\Delta}{e^{\beta\Delta} + 1} \equiv \frac{2\Delta}{e^{\Delta/T} + 1}.$$

According to this expression, the average energy tends to $2\Delta\exp\{-\Delta/T\} \to 0$ at $T/\Delta \to 0$, and to Δ at $T/\Delta \to \infty$. Both asymptotic behaviors are natural because at $T << \Delta$, each of the particles resides on

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[115] These arguments will be used in Sec. 3.1 of the lecture notes for an analysis of an ideal gas of N particles.

the lower single-particle energy level with an almost 100% probability, while at $T >> \Delta$, they have an equal probability to be on the lower and the higher energy levels, each giving an average contribution of $\Delta/2$ to the total energy of the system.

(ii) In the case of indistinguishable fermions, the first and the last states of the list (*) are impossible due to the Pauli principle, while the remaining two combinations, ↓↑ and ↑↓, are possible only as entangled components of one antisymmetric state, the *singlet*, with energy $E = \Delta$. (In the standard quantum shorthand notation, the normalized ket-vector of the state is[116]

$$|a\rangle = \frac{\exp\{i\varphi\}}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right),$$

where φ is an arbitrary real phase.) This means that Z is reduced to just one term:

$$Z = \exp\left\{-\frac{\Delta}{T}\right\} \equiv \exp\{-\beta\Delta\}, \qquad \text{i.e. } \ln Z = -\beta\Delta,$$

so Eq. (***) immediately yields a very natural result,

$$\langle E\rangle = \Delta,$$

for any temperature. (Note that due to the entangled nature of the singlet state, it is incorrect to prescribe this energy to any particular particle.)

(iii) In the case of indistinguishable bosons, all states (*) are possible but, again, the middle two combinations exist only as entangled components of one quantum state – now a symmetric one,

$$|s\rangle = \frac{\exp\{i\varphi\}}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right),$$

with the same energy $E = \Delta$. As a result, the statistical sum is

$$Z = 1 + e^{-\Delta/T} + e^{-2\Delta/T} \equiv 1 + e^{-\beta\Delta} + e^{-2\beta\Delta},$$

and Eq. (***) yields

$$\langle E\rangle = \Delta\frac{e^{-\beta\Delta}\left(1+2e^{-\beta\Delta}\right)}{1+e^{-\beta\Delta}+e^{-2\beta\Delta}} \equiv \Delta\frac{e^{-\Delta/T}\left(1+2e^{-\Delta/T}\right)}{1+e^{-\Delta/T}+e^{-2\Delta/T}} \to \begin{cases} \Delta e^{-\Delta/T} \to 0, & \text{for } T/\Delta \to 0, \\ \Delta = \text{const}, & \text{for } T/\Delta \to \infty. \end{cases}$$

Besides the loss of the factor of two (reflecting the only state available for low-energy excitations) in the low-temperature limit, these asymptotes and their interpretations are the same as in case (i) for distinguishable particles.

Problem 2.36. Each of $N >> 1$ indistinguishable fermions has two non-degenerate energy levels separated by gap Δ. Calculate the chemical potential of their system in thermal equilibrium at temperature T, if the direct interaction of the particles is negligible.

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[116] See, e.g., QM Sec. 8.1, in particular Eq. (8.11).

Solution: If we dealt with the *grand canonical* ensemble, i.e. if the chemical potential μ was exactly fixed, we could readily calculate the exact average numbers of particles on the lower level (whose energy ε_0 we may take for 0) and on the higher level (of energy $\varepsilon_1 = \Delta$) by applying, to each level, the Fermi-Dirac distribution (2.115):

$$\langle N_0 \rangle = \frac{\langle N \rangle}{e^{(\varepsilon_0 - \mu)/T} + 1} \equiv \frac{\langle N \rangle}{e^{-\mu/T} + 1}, \qquad \langle N_1 \rangle = \frac{\langle N \rangle}{e^{(\varepsilon_1 - \mu)/T} + 1} \equiv \frac{\langle N \rangle}{e^{(\Delta - \mu)/T} + 1}.$$

Now we may use the very common trick, which was discussed in Sec. 2.8 of the lecture notes.[117] If the total number of particles is so large that $\langle N_{0,1} \rangle >> 1$, the relative fluctuations of these numbers are negligibly small, and we may use the above formulas even for the *canonical* (Gibbs) ensemble, in whose member systems, the total number $N = \langle N_0 \rangle + \langle N_1 \rangle$ of particles is exactly fixed:

$$\frac{N}{e^{-\mu/T} + 1} + \frac{N}{e^{(\Delta - \mu)/T} + 1} = N, \qquad \text{i.e.} \quad \frac{1}{e^{-\mu/T} + 1} + \frac{1}{e^{(\Delta - \mu)/T} + 1} = 1,$$

to calculate the *average* value of the chemical potential, whose relative fluctuations, at $N >> 1$, are very small. The last equation may be easily solved, giving

$$\mu = \Delta / 2.$$

Note that this result may be used as a toy model of the electron/hole statistics in undoped ("intrinsic") semiconductors, to be discussed in Sec. 6.4 of the lecture notes – cf. Fig. 6.6 and Eq. (6.60).

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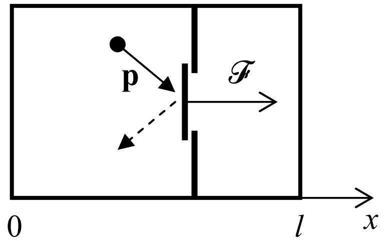
[117] This way of calculation of the (average) chemical potential will be repeatedly used, for other systems, in Chapters 3 and 6 of this course.

Chapter 3. Ideal and Not-So-Ideal Gases

Problem 3.1. Use the Maxwell distribution for an alternative (statistical) calculation of the mechanical work performed by the Szilard engine discussed in Sec. 2.3 of the lecture notes.

Hint: You may assume the simplest geometry of the engine – see Fig. 2.4.



Solution: Let us assume that initially, the partition with a door in it was in the middle of the cylinder (in the figure on the right, at $x = l/2$) and that the information provided by the Maxwell demon has enabled us to close the door when the molecule was in the left part of the cylinder. Then the repeated hits by the molecule provide an average force pushing the partition to the right. The momentum transferred from the particle to the partition at a single elastic hit is $2p_x$, where p_x is the momentum's component normal to the partition. Time-averaging the 2nd Newton law (or rather its x-component),

$$\frac{dp_x}{dt} = \mathscr{F}_x ,$$

over the interval τ between the hits, we see that the average force $\overline{\mathscr{F}_x}$ acting on the partition is equal to the ratio $2p_x/\tau$. At an arbitrary position x of the partition (with $l/2 \leq x \leq l$), the interval τ equals $2x/v_x$, where $v_x = p_x/m$ is the x-component of the particle's velocity. Thus,

$$\overline{\mathscr{F}_x} = \frac{2p_x}{\tau} = \frac{2mv_x}{2x/v_x} \equiv \frac{mv_x^2}{x} .$$

To average this result over a statistical ensemble of similar experiments, we may use the Maxwell distribution (or alternatively the equipartition theorem) giving $m\langle v_x^2\rangle/2 = T/2$, so

$$\left\langle \overline{\mathscr{F}_x} \right\rangle = \frac{T}{x} .$$

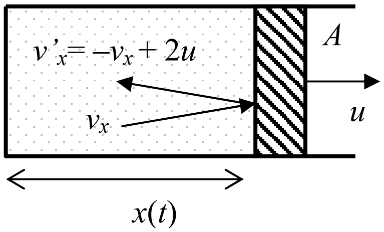
Now we can calculate the work done by the molecule during a slow motion of the partition from $x_{\text{ini}} = l/2$ to $x_{\text{fin}} = l$, at a constant temperature:

$$\mathscr{W} = \int_{l/2}^{l} \left\langle \overline{\mathscr{F}_x} \right\rangle dx = \int_{l/2}^{l} \frac{T}{x} dx = T \ln 2.$$

This is exactly the work that was calculated in Sec. 2.3 from the thermodynamic relation $dQ = TdS$.

One more way to get the same result is to use the equation of state of the ideal classical gas with just one molecule, $PV = T$, and calculate the same work by integration over an isothermal two-fold expansion of the containing volume V:

$$\mathscr{W} = \int_{V/2}^{V} P(V')dV' = \int_{V/2}^{V} \frac{T}{V'} dV' = T \ln 2.$$



Problem 3.2. Use the Maxwell distribution to calculate the *drag coefficient* $\eta \equiv -\partial\langle\mathscr{F}\rangle/\partial u$, where $\mathscr{F}$ is the force exerted by an ideal classical gas on a piston moving with a low velocity u, in the simplest geometry shown in the figure on the right, assuming that collisions of the gas particles with the piston are elastic.

Solution: This problem is essentially a refinement of the previous one: now we have to take into account a low but nonvanishing velocity u of the piston. Let us first consider a particle with an initial velocity with a positive horizontal component v_x (in the cylinder's reference frame) – see the figure above. In the piston's reference frame, this component equals $(v_x - u)$. Since the collision is elastic, in the piston's frame, the component's modulus is conserved, so after the collision, it equals $-(v_x - u) \equiv -v_x + u$, so in the cylinder's frame, it is $v_x' = (-v_x + u) + u \equiv -v_x + 2u$. Hence the momentum transferred to the piston is $-\Delta(mv_x) = -m[(-v_x + 2u) - v_x] = 2m(v_x - u) \equiv 2mv_x(1 - u/v_x)$. This momentum should be attributed to the appropriate time interval Δt around the hit moment t, namely, to the sum of the intervals $\Delta t_- = x/v_x$ and $\Delta t_+ = x/|v_x'|$ between that moment and the instances of the previous and the next reflections of the particle from the opposite (immobile) end of the cylinder – see the figure above:

$$\Delta t = \Delta t_- + \Delta t_+ = \frac{x}{v_x} + \frac{x}{|v_x'|} = \frac{x}{v_x} + \frac{x}{v_x(1-2u/v_x)} \equiv \frac{2x(1-u/v_x)}{v_x(1-2u/v_x)}.$$

Hence the time-averaged force exerted on the piston by one particle is

$$\overline{\mathscr{F}_x} = \frac{-\Delta(mv_x)}{\Delta t} = \frac{mv_x^2}{x}\left(1 - \frac{2u}{v_x}\right) \equiv \frac{m}{x}\left(v_x^2 - 2uv_x\right).$$

(As the simplest sanity check: at $u = 0$, this expression is reduced to the one derived in the solution of the previous problem.) Since a particle moving initially in the opposite direction but with the same velocity, much higher than u, exerts on the piston an equal average force, we can generalize this formula as

$$\overline{\mathscr{F}_x} = \frac{m}{x}(v_x^2 - 2u|v_x|), \qquad \text{for } |u| << |v_x|.$$

Now this force should be averaged over the 1D Maxwell distribution of the velocity component v_x, following from Eqs. (3.5)-(3.8) of the lecture notes:

$$dW = \frac{1}{\sqrt{2\pi}\sigma}\exp\left\{-\frac{v_x^2}{2\sigma^2}\right\}dv_x, \quad \text{with } \sigma^2 \equiv \langle v_x^2\rangle = \frac{T}{m}.$$

The resulting average force exerted by N molecules on the piston is

$$\langle\mathscr{F}\rangle \equiv N\langle\overline{\mathscr{F}_x}\rangle = \frac{Nm}{x}\langle v_x^2\rangle - 2\frac{Nm}{x}\langle|v_x|\rangle u \equiv A\frac{NT}{V} - \eta u, \qquad (*)$$

where A is the piston area, $V = Ax$ is the current volume occupied by the gas (see the figure above), and

$$\eta \equiv 2A\frac{Nm}{V}\langle|v_x|\rangle = 2A\frac{Nm}{V}\frac{1}{\sqrt{2\pi}\sigma}2\int_0^\infty v_x\exp\left\{-\frac{v_x^2}{2\sigma^2}\right\}dv_x = A\frac{N}{V}\left(\frac{8mT}{\pi}\right)^{1/2}. \qquad (**)$$

The largest, first term on the right-hand side of Eq. (*) is the usual static pressure force of the ideal classical gas, while the second one is the linear approximation for the drag (viscous-friction) force $\mathscr{F}_{\text{drag}} = -\eta\mathbf{u}$, always directed against the body's velocity, and hence dissipating its mechanical energy.[118]

The particular expression (**) for the drag coefficient η will be used in Chapter 5 to illustrate the fundamental relation between fluctuations and dissipation.

<u>Problem 3.3</u>. Derive the equation of state of an ideal classical gas from the grand canonical distribution.

Solution: According to Eq. (2.109) of the lecture notes, in the grand canonical ensemble, i.e. in the statistical ensemble with fixed temperature T and chemical potential μ but variable number N of particles (see Fig. 2.13 and its discussion), the grand thermodynamic potential Ω equals

$$\Omega = -T\ln\sum_{m,N}\exp\left\{\frac{\mu N - E_{m,N}}{T}\right\} \equiv -T\ln\sum_N e^{\mu N/T}\sum_m \exp\left\{-\frac{E_{m,N}}{T}\right\}. \qquad (*)$$

However, per Eq. (2.59), the last sum is just the partition function Z_N of the canonical (Gibbs) distribution, for a particular value of N. As was discussed in detail in Sec. 3.1, for the ideal classical gas of indistinguishable particles, this function is given by Eq. (3.15):

$$Z_N = \frac{1}{N!}\left[gV\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right]^N,$$

so the last form of Eq. (*) reduces to

$$\Omega = -T\ln\sum_{N=0}^{\infty} e^{\mu N/T}\frac{1}{N!}\left[gV\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right]^N \equiv -T\ln\sum_{N=0}^{\infty}\frac{1}{N!}\left[e^{\mu/T}gV\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right]^N. \qquad (**)$$

According to the Taylor expansion of the exponential function at the origin,

$$e^{\xi} = \sum_{k=0}^{\infty}\frac{1}{k!}\frac{d^k\left(e^{\xi}\right)}{d\xi^k}\Big|_{\xi=0}\xi^k = \sum_{k=0}^{\infty}\frac{1}{k!}\xi^k,$$

the sum in the last form of Eq. (**) is just the exponent of the product in the square brackets, so we get

$$\Omega = -T\,e^{\mu/T}gV\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}. \qquad (***)$$

Now we can calculate the *average* number of particles in the gas, by using the last of Eqs. (1.62):[119]

$$\langle N\rangle = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = -\left(\frac{\partial}{\partial\mu}\left[-Te^{\mu/T}gV\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right]\right)_{T,V} = e^{\mu/T}gV\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}.$$

---

[118] For a discussion of various effects of this force, see, e.g., CM Chapters 5 and 8.

[119] Note that with the replacements $\langle N\rangle \to N$ and $\mu \to \langle\mu\rangle$ (justified for $N >> 1$), this expression coincides with Eq. (3.32) of the lecture notes, which was derived there from the Gibbs distribution.

Plugging this relation, read backward, back to Eq. (***), we get a very simple result,

$$\Omega = -T\langle N\rangle ,$$

so the thermodynamic relation (1.60), $\Omega = -PV$, immediately yields the equation of state of the gas,

$$PV = \langle N\rangle T .$$

In the thermodynamic limit $N \to \infty$, when the difference between $\langle N\rangle$ and N is negligible, this expression coincides with Eq. (3.18), which was derived in Sec. 3.1 of the lecture notes from the Gibbs (canonical) distribution – valid for a statistical ensemble with fixed T and N rather than μ.

Problem 3.4. Prove that Eq. (3.22) of the lecture notes,

$$\Delta S = N_1 \ln\frac{V_1+V_2}{V_1} + N_2 \ln\frac{V_1+V_2}{V_2} ,$$

derived for the change of entropy at the mixing of two ideal classical gases of completely distinguishable particles (that initially had equal densities N/V and temperatures T), is also valid if the particles in each of the gases are indistinguishable from each other but different from those in the counterpart gas. For simplicity, you may assume that the masses and internal degeneracy factors of all the particles are equal.

Solution: For each of the gases before mixing, we may use Eq. (3.20) of the lecture notes,

$$S_{1,2} = N_{1,2}\left[\ln\frac{V_{1,2}}{N_{1,2}} - \frac{df(T)}{dT}\right],$$

which results from Eq. (3.12) with the correct Boltzmann counting. (Due to the equality of m and g of all particles, their function $f(T)$ is the same, so it does not need an index.) For the gas after mixing, we have to modify the counting in the following way:

$$Z = \frac{1}{N_1!N_2!}\left(\sum_k \exp\left\{-\frac{\varepsilon_k}{T}\right\}\right)^{N_1+N_2} ,$$

in order to account for the internal indistinguishability of particles of each type. Now carrying out the calculations similar to those done in Sec. 3.1, for the entropy of the mixed gas we get

$$S = N_1 \ln\frac{V_1+V_2}{N_1} + N_2 \ln\frac{V_1+V_2}{N_2} - \left(N_1+N_2\right)\frac{df(T)}{dT} .$$

From here, we see that the mixing entropy,

$$\Delta S \equiv S - \left(S_1+S_2\right) = N_1 \ln\frac{V_1+V_2}{V_1} + N_2 \ln\frac{V_1+V_2}{V_2} ,$$

is indeed described by the same expression as for all-distinguishable particles. This result is natural because the mixing does not change the internal disorder (i.e. the entropy) of each component of the gas.

Problem 3.5. A round cylinder of radius R and length L, containing an ideal classical gas of $N >> 1$ particles of mass m each, is rotated about its symmetry axis with an angular velocity ω. Assuming that the gas as a whole rotates with the cylinder, and is in thermal equilibrium at temperature T,

(i) calculate the gas pressure distribution along the cylinder's radius, and

(ii) neglecting the internal degrees of freedom of the particles, calculate the total energy of the gas and its heat capacity.

Analyze the results in the high- and low-temperature limits.

Solutions:

(i) From classical mechanics[120] we know that in the non-inertial reference frame rotating with the cylinder (in which the gas as a whole rests), we have to add, to all real forces exerted on a particle, the centrifugal "inertial force"

$$\mathscr{F}_{\text{centrifugal}} = -m\boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r}) \equiv m\omega^2\boldsymbol{\rho},$$

where $\boldsymbol{\rho}$ is the radius vector's component in the plane normal to the rotation axis. This force may be represented as $-\nabla U$, where U is the effective potential energy

$$U(\mathbf{r}) = -\frac{m\omega^2\rho^2}{2} + \text{const}\,.$$

With this specification, Eq. (3.26) of the lecture notes yields the following gas density (the number of its particles per unit volume):

$$n(\mathbf{r}) = n_0 \exp\left\{\frac{m\omega^2\rho^2}{2T}\right\}.$$

The constant n_0 (physically, the particle density at $\rho = 0$, i.e. on the cylinder's axis) may be calculated from the condition that the total number of particles in the cylinder is equal to the given N:

$$\int_V n(\mathbf{r})d^3r \equiv 2\pi L n_0 \int_0^R \exp\left\{\frac{m\omega^2\rho^2}{2T}\right\}\rho d\rho \equiv n_0\frac{2\pi LT}{m\omega^2}\left(\exp\left\{\frac{m\omega^2R^2}{2T}\right\}-1\right) = N\,.$$

This condition yields

$$n_0 = \frac{N}{L}\frac{m\omega^2}{2\pi T}\frac{1}{\exp\{m\omega^2R^2/2T\}-1}, \quad \text{so } n(\mathbf{r}) = \frac{N}{L}\frac{m\omega^2}{2\pi T}\frac{\exp\{m\omega^2\rho^2/2T\}}{\exp\{m\omega^2R^2/2T\}-1}\,.$$

Now applying the equation of state of an ideal gas locally, in the form $P(\mathbf{r}) = n(\mathbf{r})T$, we get[121]

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[120] See, e.g., CM Sec. 4.6. Note that the other (Coriolis) "inertial force" due to rotation with a constant angular velocity, $\mathscr{F}_{\text{Coriolis}} = -2m\boldsymbol{\omega}\times\mathbf{v}$, is perpendicular to particle's velocity $\mathbf{v}$ and hence cannot do any work on the particle, so it does not contribute to the effective potential energy. True, that force *does* contribute to the canonical moment and hence the total energy of each particle (see, e.g., CM Eqs. (4.98) and (4.100)), but these contributions are linear in $\mathbf{v}$ and hence are averaged out at the statistical averaging over all particles.

[121] Note that according to Eq. (*), $P(R)/P(0) = \exp\{m\omega^2R^2/2T\}$, so at $m\omega^2R^2 >> T$, even a minor difference in the mass m of the particle may lead to a considerable difference of this pressure ratio. This is exactly the effect employed for the separation of isotopes (in particular, of ^{238}U from ^{235}U, in the form of the hexafluoride gas UF_6) in centrifuges used in the nuclear fuel enrichment technology.

$$P(\mathbf{r}) = n(\mathbf{r})T = \frac{N}{L}\frac{m\omega^2}{2\pi}\frac{\exp\{m\omega^2\rho^2/2T\}}{\exp\{m\omega^2R^2/2T\}-1}. \qquad (*)$$

If the temperature T is relatively high (and/or the rotation is relatively slow), then both exponents in this expression may be Taylor-expanded, with only leading terms kept. The result gives only a minor correction to the static value $P = NT/V$:

$$P \approx \frac{NT}{\pi R^2 L}\left[1+\frac{m\omega^2(\rho^2 - R^2/2)}{2T}\right] \equiv \frac{NT}{V}\left[1+\frac{m\omega^2(\rho^2 - R^2/2)}{2T}\right] \to \frac{NT}{V}, \quad \text{for } m\omega^2R^2 << T.$$

In the opposite, low-temperature/high-ω limit, $T << m\omega^2R^2$, the exponent in the denominator of Eq. (*) is much larger than 1, and the formula is reduced to the following relation:

$$P \approx \frac{Nm\omega^2}{2\pi L}\exp\left\{\frac{\rho^2 - R^2}{\rho_0^2}\right\}, \qquad \text{where } \rho_0 \equiv \left(\frac{2T}{m\omega^2}\right)^{1/2} << R, \qquad (**)$$

showing that all the gas is compressed into a layer, of thickness $\sim\rho_0 << R$, at the cylinder's wall and that the pressure at the very wall (at $\rho = R$) is temperature-independent, determined just by the rotation.

(ii) In the lab reference frame, the particle's velocity $\mathbf{v}$ is the vector sum of the velocity $\mathbf{v}_{\text{rel}}$ of its thermal motion in the rotating reference frame, and the average local rotation velocity $\mathbf{v}_{\text{rot}} = \boldsymbol{\omega}\times\mathbf{r}$, so its total kinetic energy is

$$\frac{mv^2}{2} = \frac{m(\mathbf{v}_{\text{rel}}+\mathbf{v}_{\text{rot}})^2}{2} = \frac{mv_{\text{rel}}^2}{2} + m\mathbf{v}_{\text{rel}}\cdot\mathbf{v}_{\text{rot}} + \frac{mv_{\text{rot}}^2}{2} = \frac{mv_{\text{rel}}^2}{2} + m\mathbf{v}_{\text{rel}}\cdot(\boldsymbol{\omega}\times\mathbf{r}) + \frac{m\omega^2\rho^2}{2}.$$

Since the thermal velocity $\mathbf{v}_{\text{rel}}$ is random, with the isotropic distribution of its directions, the statistical average of the second term vanishes, while the average of the first term (according to the equipartition theorem) is $3T/2$. As a result, the total energy of the gas[122] may be calculated as

$$\begin{aligned} E &= \frac{3T}{2}N + \int_V n(\mathbf{r})\frac{m\omega^2\rho^2}{2}d^3r = \frac{3T}{2}N + \frac{m\omega^2}{2}2\pi L n_0\int_0^R \exp\left\{\frac{m\omega^2\rho^2}{2T}\right\}\rho^2\rho d\rho \\ &= \frac{3T}{2}N + \frac{2\pi LT^2}{m\omega^2}n_0\left[\left(\frac{m\omega^2R^2}{2T}-1\right)\exp\left\{\frac{m\omega^2R^2}{2T}\right\}+1\right] \qquad (***) \\ &\equiv TN\left[\frac{3}{2}+\frac{(m\omega^2R^2/2T-1)\exp\{m\omega^2R^2/2T\}+1}{\exp\{m\omega^2R^2/2T\}-1}\right]. \end{aligned}$$

In the high-temperature limit, $T >> m\omega^2R^2$, the Taylor expansion of the exponents, with only two leading terms kept, yields the usual thermal energy $(3/2)NT$ plus a small correction describing the kinetic energy of rotation of the gas (which, in this limit, is distributed virtually uniformly over the cylinder's bulk) as the whole:

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[122] Note that in the inertial lab frame, the centrifugal "inertial force" and the associated effective potential $U(\mathbf{r})$ do not exist, so the full energy of the gas is just the sum of the kinetic energies $mv^2/2$ of its particles.

$$E \approx TN\left(\frac{3}{2}+\frac{m\omega^2R^2}{4T}\right)\equiv\frac{3}{2}NT+N\frac{m\omega^2R^2}{4}=\frac{3}{2}NT+\frac{I_1\omega^2}{2},\qquad \text{where } I_1\equiv\frac{MR^2}{2},$$

and $M \equiv mN$ is the total mass of the gas, so I_1 is the usual moment of inertia of a uniform round cylinder of mass M. Since this rotation-related correction is temperature-independent, it does not affect the heat capacity of the gas, $C \equiv dE/dT = 3N/2$.

In the opposite, low-temperature limit, the exponents in the numerator and denominator in the final form of Eq. (***) are much larger than 1. As a result, they cancel and we get a result very similar in form:

$$E \approx TN\left[\frac{3}{2}+\left(\frac{m\omega^2R^2}{2T}-1\right)\right]\equiv\frac{m\omega^2R^2}{2}N+\frac{NT}{2}=\frac{I_2\omega^2}{2}+\frac{NT}{2}\qquad \text{where } I_2\equiv MR^2.$$

However, here the first, temperature-independent term, which describes the kinetic energy of rotation of the gas as a whole (now compressed to the cylinder's wall, and hence having a larger moment of inertia, $I_2 = 2I_1$), is much larger than the second, temperature-dependent term. Moreover, somewhat counter-intuitively, the second term is three times smaller than that of a stationary gas, so the heat capacity of the system is also three times lower: $C = N/2$. As the full result (***) shows, this reduction is due to the increase, with growing temperature, of the thickness scale ρ_0 of the gas layer near the wall – see Eq. (**). This increase, pushing the gas a bit farther from the cylinder's wall, reduces the kinetic energy of its rotation, and thus slows the growth of the full energy of the gas.

Problem 3.6. $N >> 1$ classical, non-interacting, indistinguishable particles of mass m are confined in a parabolic, spherically-symmetric 3D potential well $U(\mathbf{r}) = \kappa r^2/2$. Use two different approaches to calculate all major thermodynamic characteristics of the system, including its heat capacity, in thermal equilibrium at temperature T. Which of the results should be changed if the particles are distinguishable?

Hint: Suggest a replacement of the notions of volume and pressure, appropriate for this system.

Solution: First of all, let us calculate the characteristics that do not require the notions of volume and pressure, starting from the statistical sum. The sum may be calculated in (at least :-) two different ways.

Approach 1 is to rely on the system's classicity from the very beginning. This makes the Cartesian coordinates and momenta independent arguments, and allows us to use Eq. (3.24) of the lecture notes, which may be rewritten as a product:

$$w(\mathbf{r},\mathbf{p}) = \text{const}\times\exp\left\{-\frac{p^2}{2mT}\right\}\times\exp\left\{-\frac{U(\mathbf{r})}{T}\right\}.$$

Since the first of these operands is the probability density of a free particle, we may generalize Eq. (3.14) (valid for indistinguishable particles) as follows:

$$Z=\frac{1}{N!}\left(z_p\int\exp\left\{-\frac{U(\mathbf{r})}{T}\right\}d^3r\right)^N, \qquad (*)$$

where the momentum-related factor z_p is the same as for a free-particle gas and may be calculated by Gaussian integration – exactly as this was done at the derivation of Eq. (3.15):

$$z_p = \frac{g}{(2\pi\hbar)^3}\left[\int_{-\infty}^{+\infty}\exp\left\{-\frac{p_j^2}{2mT}\right\}dp_j\right]^3 = g\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}.$$

The coordinate factor in Eq. (*), for our quadratic potential, may be also represented as a product of three similar, simple Gaussian integrals, which may be calculated similarly:

$$\int\exp\left\{-\frac{U(\mathbf{r})}{T}\right\}d^3r = \int\exp\left\{-\kappa\frac{r_1^2+r_2^2+r_3^2}{T}\right\}d^3r \equiv \left[\int_{-\infty}^{+\infty}\exp\left\{-\frac{\kappa r_j^2}{2T}\right\}dr_j\right]^3 = \left(\frac{2\pi T}{\kappa}\right)^{3/2},$$

so, finally,

$$Z = \frac{1}{N!}\left[g\left(\frac{m}{\hbar^2\kappa}\right)^{3/2}T^3\right]^N. \qquad (**)$$

Now we may calculate the free energy by using Eq. (2.63) and the given condition $N >> 1$, which enables the application of the Stirling formula to simplify $\ln(N!)$:

$$F = -T\ln Z = -NT\ln\left(N\kappa^{3/2}\right) + Nf(T), \qquad \text{with } f(T) \equiv -T\left\{\ln\left[g\left(\frac{mT^2}{\hbar^2}\right)^{3/2}\right]+1\right\}.$$

The reason why N is grouped with $\kappa^{3/2}$ under the first logarithm (just as it is grouped with $1/V$ at the usual, rigid confinement within volume V – see Eq. (3.16a) of the lecture notes) is that our current soft-well system does not have any clearly defined volume, and the only parameter that characterizes the confinement is the effective spring constant κ. The comparison with Eq. (3.16) shows that in this case, the closest analog of the fixed volume V is the following fixed parameter:

$$\mathscr{V} \equiv \frac{1}{\kappa^{3/2}},$$

despite its different dimensionality (m^3/J$^{3/2}$). In this notation, the expression for the free energy becomes formally similar to Eq. (3.16a) for the rigidly confined gas,

$$F = -NT\ln\frac{N}{\mathscr{V}} + Nf(T), \qquad (***)$$

so the remaining calculations are similar until we need to spell out the function $f(T)$ – which is now different. In particular, using Eq. (1.35) to calculate the system's entropy, at fixed $\mathscr{V}$, we get

$$S = -\left(\frac{\partial F}{\partial T}\right)_{\mathscr{V}} = N\ln\left[\frac{N}{\mathscr{V}}\right] - N\frac{df(T)}{dT},$$

so, according to Eq. (1.47), the internal energy of the system is

$$E = F + TS = N\left[f(T) - T\frac{df(T)}{dT}\right] = 3NT.$$

Mercifully, E is again strictly proportional to N, so we may readily calculate the average energy per particle, $E/N = 3T$, and the heat capacity per particle, also at a fixed "volume" $\mathscr{V}$, i.e., at fixed potential's profile:

$$\frac{C_{\mathscr{V}}}{N} \equiv \frac{1}{N}\left(\frac{\partial E}{\partial T}\right)_{\mathscr{V}} = 3 .$$

This simple result is in agreement with the equipartition theorem (2.48) because, in contrast with the rigidly confined gas, each of the three degrees of freedom of each particle provides it with not only a quadratic kinetic energy but also a quadratic potential energy. Finally, from the analogy of Eq. (***) and Eq. (3.16) for the "usual" (rigidly confined) ideal classical gas, it is clear that if we introduce the corresponding analog of pressure using the second of Eqs. (1.35), the resulting equation of state is also the same:

$$\mathscr{P} = -\left(\frac{\partial F}{\partial \mathscr{V}}\right)_T = \frac{NT}{\mathscr{V}} . \qquad (****)$$

At this point, we have to notice that the effective volume of the well's part occupied by the particles may be defined by the natural relation

$$V_{\text{ef}} \equiv \frac{N}{n(0)} = \frac{1}{n(0)}\int n(\mathbf{r})\, d^3 r ,$$

where $n(\mathbf{r})$ is the particle density at the point $\mathbf{r}$. Since, according to Eq. (3.26), the density $n(\mathbf{r})$ is equal to $n(0)\exp\{-U(\mathbf{r})/T\}$, the necessary integral has been essentially calculated above, giving

$$V_{\text{ef}} \equiv \frac{1}{n(0)}\int n(\mathbf{r})\, d^3 r = \int \exp\left\{-\frac{U(\mathbf{r})}{T}\right\} d^3 r = \left(\frac{2\pi T}{\kappa}\right)^{3/2} \equiv (2\pi T)^{3/2}\mathscr{V} .$$

As this result shows, the effective volume V_{ef} (which, in contrast to $\mathscr{V}$, has the usual physical dimensionality, m^3), depends on temperature, and hence cannot be employed in the basic relations of thermodynamics without modification.

Approach 2. Let us notice that Eq. (**) may be rewritten as

$$Z = \frac{1}{N!}\left[g\left(\frac{T}{\hbar\omega}\right)^3\right]^N ,$$

where $\omega \equiv (\kappa/m)^{1/2}$ has the physical sense of the frequency of oscillations of a single particle of the gas in our harmonic potential. This unsolicited appearance of the oscillation frequency shows that this expression may be also obtained differently. In this, more quantum-mechanics-based approach, let us first treat each gas particle as a 3D harmonic oscillator, and use the well-known result for its energy spectrum:[123]

$$\varepsilon_k = \hbar\omega\left(n_1 + n_2 + n_3 + \frac{3}{2}\right), \qquad \text{with } n_j = 0, 1, 2, \ldots,$$

so, with the inconsequential temperature-independent shift of the particle energy reference to the ground-state energy $(3/2)\hbar\omega$, Eq. (3.12) of the lecture notes becomes

$$Z = \frac{1}{N!}\left[g\sum_{n_1,n_2,n_3=0}^{\infty}\exp\left\{-\frac{\hbar\omega}{T}(n_1+n_2+n_3)\right\}\right]^N = \frac{1}{N!}\left[g\left(\sum_{n_j=0}^{\infty}\exp\left\{-\frac{\hbar\omega}{T}n_j\right\}\right)^3\right]^N .$$

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[123] See, e.g., QM Sec. 3.5, in particular, Eq. (3.124).

This sum is just the geometric progression and may be spelled out exactly (see Eqs. (2.67)-(2.68) of the lecture notes), but for our current purposes, we may use just its classical limit valid at $\hbar\omega << T$:

$$Z \to \frac{1}{N!}\left[g\left(\int_0^\infty \exp\left\{-\frac{\hbar\omega}{T}n_j\right\}dn_j\right)^3\right]^N = \frac{1}{N!}\left[g\left(\frac{T}{\hbar\omega}\right)^3\right]^N,$$

immediately returning us to Eq. (**) and all the following results obtained by Approach 1. Moreover, we may obtain some of these results directly from Eqs. (2.73)-(2.75) in the classical limit, with proper multiplications by the factor of 3 to acknowledge the 3D nature of our current problem.

Finally, the above results show that just as in the "usual" gas, the distinguishability of the particles, which kills the "correct Boltzmann counting" factor $1/N!$ in Eq. (**), does not affect the equation of state of the system and its energy and heat capacity, but does affect its free energy and entropy – just as in the rigidly confined gas – as was discussed in Sec. 3.1 of the lecture notes.

Problem 3.7. In the simplest model of thermodynamic equilibrium between the liquid and gas phases of the same molecules, temperature and pressure do not affect the molecule's condensation energy Δ. Calculate the density and pressure of such *saturated vapor*, assuming that it behaves as an ideal gas of classical particles.

Solution: In this model, from the point of view of the gas/vapor, the liquid is an unlimited source of molecules with energy $(-\Delta)$, i.e. an environment with a constant chemical potential, just as in the grand canonical ensemble – see Sec. 2.7 of the lecture notes. Referring the molecule's energy to that at rest in the gaseous phase, we may write $\mu = -\Delta$. Hence we may apply to this phase all the formulas derived from the grand canonical distribution; in particular, for non-interacting classical particles, we may use Eq. (3.32) of the lecture notes. For the molecule density $n \equiv N/V$ in the gaseous phase, it immediately yields

$$n = g\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} \exp\left\{-\frac{\Delta}{T}\right\}.$$

Since the gas itself remains classical, it obeys the Maxwell distribution (3.5) and hence the equation of state (3.18) in its last form:

$$P = nT.$$

Note, however, that since now the number of gas particles is *not* fixed (they may go to, and come from the liquid as necessary for the chemical and thermal equilibrium), in this model, the pressure is a function of temperature only and is independent of the volume:

$$P = P(T) = nT = g\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} T^{5/2} \exp\left\{-\frac{\Delta}{T}\right\}. \qquad (*)$$

As will be discussed in Chapter 4, such nearly – exponential dependence (dominated by the Arrhenius factor $\exp\{-\Delta/T\}$) is a common feature of most phenomenological models of real gases – including the famous van der Waals model, though it is frequently not immediately apparent from the equation of state of the gaseous phase alone.

Finally, just for the reader's reference: Eq. (*) with the particular value $\Delta \approx 0.71\times 10^{-19}$ J ≈ 0.44 eV (corresponding to $\Delta/k_B \approx 5{,}130$ K) gives a surprisingly reasonable approximation for the temperature dependence of the partial pressure of the saturated water vapor at all temperatures not too close to water's critical point of 647 K – see the same Chapter 4. With the water molecule's mass of $m \approx 3.00\times 10^{-26}$ kg, this value of Δ is in good agreement with the water's experimentally measured latent heat of vaporization Λ (~2.27 MJ/kg at ambient conditions). Note also a simple mnemonic rule valid near the room temperature: the partial pressure of the saturated water vapor nearly doubles at the temperature's increase by every 10 K. This rule enables a simple if approximate calculation of the air's relative humidity from its temperature and the dew point (the temperature at which the vapor, of the given density, saturates).

Problem 3.8. An ideal classical gas of $N >> 1$ particles is confined in a container of volume V and wall surface area A. The particles may condense on the walls, releasing energy Δ per particle and forming an ideal 2D gas on their surfaces. Calculate the number of condensed particles and the gas pressure, and discuss their temperature dependences, in thermodynamic equilibrium.

Solution: Since the surface condensate and the volume gas may exchange particles at will, their chemical potentials μ have to be equal. To calculate μ of the gaseous phase, we may use Eq. (3.32) of the lecture notes, with N replaced with $(N - N_0)$, where N_0 is the number of condensed particles:[124]

$$\mu_{\text{volume}} = T\ln\frac{N-N_0}{N_V(T)}, \qquad \text{where } N_V(T) \equiv g_V V\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}.$$

On the other hand, since the surface condensate is an ideal 2D gas, we need to review the calculations of Sec. 3.1 using the 2D density of states. Using the evident modification of Eq. (3.13),[125]

$$\sum_k (...) \to \frac{gA}{(2\pi\hbar)^2}\int (...)d^2p,$$

for an isotropic surface (with $d^2p = 2\pi p dp$, and $d\varepsilon = d(p^2/2m) \equiv pdp/m$), we get

$$dN_2 = \frac{gA}{(2\pi\hbar)^2}d^3p = \frac{gA}{(2\pi\hbar)^2}2\pi p dp, \qquad g_2(\varepsilon) \equiv \frac{dN_2}{d\varepsilon} = \frac{gA}{(2\pi\hbar)^2}\frac{2\pi p dp}{pdp/m} \equiv \frac{gAm}{2\pi\hbar^2}. \qquad (*)$$

(Note that in contrast to the 3D density of states given by Eq. (3.43) of the lecture notes, $g_3(\varepsilon) \propto \varepsilon^{1/2}$, the function $g_2(\varepsilon)$ is actually a constant.) One more necessary modification is that in accordance with the problem assignment, all energies of particles on the surface, including μ, should be shifted down by the energy Δ. Taking into account also that the degeneracy g_S of surface states may be different from that, g_V, of the gaseous states, we get[126]

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[124] As evident from this expression, $N_V(T)$ has the physical meaning of the effective number of states available for occupation in the gaseous phase at the given temperature. Similar notions are used in the discussion of electrons and holes in semiconductors – see, e.g., Sec. 6.4.

[125] If in doubt, please consult QM Secs. 1.7-1.8, in particular Eq. (1.99). For the particular case of electromagnetic waves, this expression was already used in the solution of Problem 2.28.

[126] Similarly to N_V, the N_A introduced this way has the physical sense of the effective number of the surface states available for occupation at temperature T.

$$\mu_{\text{surface}} = -\Delta + T\ln\frac{N_0}{N_S(T)}, \qquad \text{where } N_S(T) \equiv g_S A\frac{mT}{2\pi\hbar^2}.$$

Equating these two expressions for μ to describe the chemical equilibrium between the two phases, we get the following equation:

$$T\ln\frac{N-N_0}{N_V(T)} = -\Delta + T\ln\frac{N_0}{N_S(T)},$$

which readily yields

$$\frac{N_0}{N} = \frac{1}{1+(N_V/N_S)\exp\{-\Delta/T\}} \equiv \frac{1}{1+\kappa(T/\Delta)^{1/2}\exp\{-\Delta/T\}} \leq 1, \quad \text{where } \kappa \equiv \frac{g_V V}{g_S A}\left(\frac{m\Delta}{2\pi\hbar^2}\right)^{1/2}. \quad (**)$$

Hence the number of particles in the gaseous phase is

$$N - N_0 = N\frac{\kappa(T/\Delta)^{1/2}\exp\{-\Delta/T\}}{1+\kappa(T/\Delta)^{1/2}\exp\{-\Delta/T\}},$$

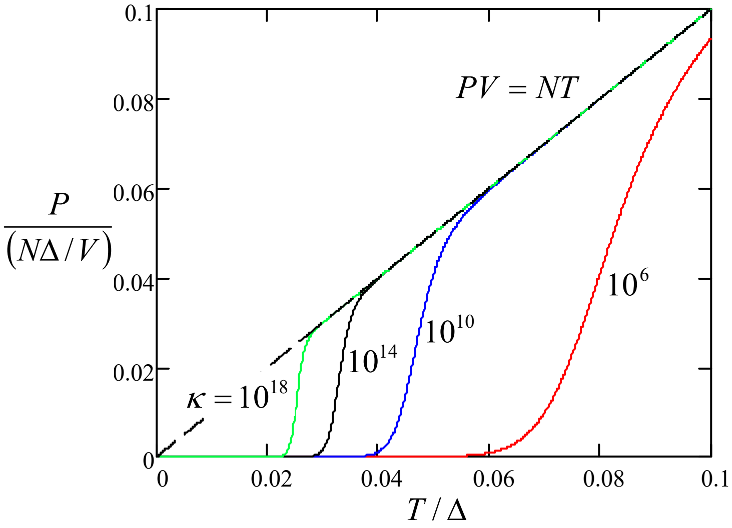
and since they obey the ideal-gas equation of state, their pressure is

$$P = \frac{N-N_0}{V}T = \frac{\kappa(T/\Delta)^{1/2}\exp\{-\Delta/T\}}{1+\kappa(T/\Delta)^{1/2}\exp\{-\Delta/T\}}\frac{NT}{V} \equiv \frac{1}{1+\kappa^{-1}(\Delta/T)^{1/2}\exp\{\Delta/T\}}\frac{NT}{V}. \qquad (***)$$

This result, plotted in the figure on the right for several values of the dimensionless constant κ (which is typically very large[127]) shows that the temperature dependence of P is very much different at temperatures below and above some value T_c that has to be calculated from the transcendental equation

$$\left(\frac{\Delta}{T_c}\right)^{1/2} = \kappa\exp\left\{-\frac{\Delta}{T_c}\right\}. \qquad (****)$$

(In the typical cases when $\kappa >> 1$, the temperature T_c is somewhat lower than Δ, but for all reasonable values of that parameter, it is not much lower.)



In particular, if the temperature is well below T_c, virtually all particles are condensed at the surface: $N_0 \approx N$, so the pressure provided by the few particles remaining in the gaseous phase is exponentially low:

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[127] Indeed, according to Eq. (**), the parameter κ is of the order of $V/Ar_c(\Delta)$ where $r_c(T)$ is the temperature-dependent correlation length that was discussed in Sec. 3.2 of the lecture notes – see Eq. (3.37). As it follows from the estimates made during that discussion, r_c is microscopic even at very low temperatures, while the ratio V/A is of the order of the linear size of the container, so for all "macroscopic" (human-scale) containers, κ is very large.

$$P = \frac{NT}{V}\kappa\left(\frac{T}{\Delta}\right)^{1/2}\exp\left\{-\frac{\Delta}{T}\right\} << \frac{NT}{V}, \qquad \text{at } T << T_{\text{c}}.$$

This function $P(T)$, which also includes the Arrhenius factor $\exp\{-\Delta/T\}$, is close to, but still different from the one obtained in the solution of the previous problem – which is closer to experiment for typical liquids. On the other hand, for some systems, our current model of the liquid/vapor equilibrium is more realistic in that it does describe the condensate's full evaporation at temperatures well above T_{c}, when $N_0 << N$, and the pressure in the gaseous phase obeys the equation of state of the usual ideal gas, $P = NT/V$.

Note also that in contrast to genuine phase transitions (to be discussed in Chapter 4), the temperature dependences of all variables at $T \sim T_{\text{c}}$ are smooth even at $N \to \infty$. Such smooth temperature borderlines are frequently called *crossovers*; they are typical for systems whose particles (or other elementary components) do not interact.[128]

Problem 3.9. The inner surfaces of the walls of a closed container of volume V, filled with $N >> 1$ particles, have $N_{\text{S}} >> 1$ similar particle traps (small potential wells). Each trap can hold only one particle, at a potential energy $-\Delta < 0$ relative to that in the volume. Assuming that the gas of the particles in the volume is ideal and classical, derive an equation for the chemical potential μ of the system in equilibrium, and use it to calculate this potential and the gas pressure in the limits of small and large values of the N/N_{S} ratio.

Solution: The total number of particles, N, is the sum of some number N_0 of the particles condensed on the surface (localized at the surface traps), and the number $(N - N_0)$ of the particles thermally activated into the gas phase. Due to the given conditions that the gas is classical and that the number $(N - N_0)$ of these particles is large, it may be calculated (just as was done in the solutions of two previous problems) from Eq. (3.32) of the lecture notes:

$$N - N_0 = N_{\text{V}}(T)\exp\left\{\frac{\mu}{T}\right\}, \qquad \text{where } N_{\text{V}}(T) \equiv \frac{g_{\text{V}}V}{\hbar^3}\left(\frac{mT}{2\pi}\right)^{3/2} >> 1. \qquad (*)$$

In order to obtain one more relation between the unknown variables μ and N_0, we may consider a statistical ensemble of single traps, and apply to it the grand canonical distribution with $(1 + g_{\text{S}})$ different states: one empty-trap state, of a certain (inconsequential) energy ε_0, and g_{S} different possible states with one trapped molecule, each with the energy $(\varepsilon_0 - \Delta)$. As a result, Eqs. (2.106)-(2.107) yield the following probabilities of these states:

$$W_0 = \frac{1}{Z_{\text{S}}}\exp\left\{-\frac{\varepsilon_0}{T}\right\}, \qquad W_1 = \frac{1}{Z_{\text{S}}}\exp\left\{\frac{\mu + \Delta - \varepsilon_0}{T}\right\},$$

with

$$Z_{\text{S}} = \exp\left\{-\frac{\varepsilon_0}{T}\right\} + g_{\text{S}}\exp\left\{\frac{\mu + \Delta - \varepsilon_0}{T}\right\},$$

so the average number of filled traps (with the trapped molecule in any of g_{S} possible states) is

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[128] Such smooth transitions are also common for virtually all systems with a finite number of particles –see, for example, the solution of Problem 26 below and also the discussion of this issue in Sec. 4.5 of the lecture notes.

$$N_0 = N_S g_S W_1 = N_S \frac{g_S \exp\{(\mu+\Delta)/T\}}{1+g_S \exp\{(\mu+\Delta)/T\}},$$

where in the thermodynamic equilibrium, μ and T have to be the same as in Eq. (*). Combining these expressions, we get

$$N_V(T)\exp\left\{\frac{\mu}{T}\right\} + N_S \frac{g_S \exp\{(\mu+\Delta)/T\}}{1+g_S \exp\{(\mu+\Delta)/T\}} = N\,. \qquad (**)$$

Unfortunately, for this model of the condensate/gas equilibrium (which is more realistic than those discussed in the two previous problems), Eq. (**) for μ defies an exact analytical solution for arbitrary parameters. However, it may be readily solved in the limits of low and high values of the N/N_S ratio. Indeed, since N_0 cannot be larger than N_S, in the limit $N >> N_S$, most particles have to be in the gaseous phase, so in the 0th approximation, the second term in Eq. (**) may be ignored, and this equation is reduced to Eq. (3.32) of the ideal classical gas of N particles, giving

$$\mu = -T\ln\frac{N_V(T)}{N}, \qquad P = \frac{NT}{V} \propto T, \qquad \text{for } N >> N_S\,.$$

Now we may use this value of μ to calculate, in the 1st approximation, the (relatively small) number of condensed particles:

$$N_0 = \frac{N_S}{[N_V(T)/g_S N]\exp\{-\Delta/T\}+1} << N\,. \qquad (***)$$

According to Eq. (*) and Eq. (3.35) of the lecture notes, the ratio $N_V(T)/N$ in the denominator is close to $(T/T_0)^{3/2}$ and has to be much larger than 1 to keep the gas classical. However, since the exponent is such a steep function at large values of its argument, the ratio N_0/N_S depends mostly on the condensation energy Δ: if it is much larger than the crossover value[129]

$$\Delta_c \equiv T\ln\frac{N_V(T)}{g_S N}, \qquad (****)$$

the first term in the denominator of Eq. (***) is negligibly small, and $N_0 \approx N_S$. In the opposite limit, $\Delta << \Delta_c$, the ratio N_0/N_S is exponentially small.

In the opposite limit of a relatively large number of traps, $N << N_S$, Eq. (**) may be satisfied only if the fraction in its second term is much smaller than 1, i.e. if $\exp\{-(\Delta+\mu)/T\} >> g_S \sim 1$, so the equation is reduced to

$$N_V(T)\exp\left\{\frac{\mu}{T}\right\} + N_S g_S \exp\left\{\frac{\Delta+\mu}{T}\right\} = N,$$

and may be readily solved for μ:

$$\exp\left\{\frac{\mu}{T}\right\} = \frac{N}{N_V(T)+N_S g_S \exp\{\Delta/T\}}, \quad \text{i.e. } \mu = -T\ln\left[\frac{N_V(T)}{N} + \frac{N_S g_S}{N}\exp\left\{\frac{\Delta}{T}\right\}\right].$$

With this, Eq. (*) gives a result functionally almost similar to Eq. (***) of the previous problem:

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[129] See the discussion of this notion in the solution of the previous problem.

$$N - N_0 = \frac{N}{1 + [N_S g_S / N_V(T)] \exp\{\Delta / T\}}, \qquad P = \frac{(N - N_0)T}{V} = \frac{NT}{V} \frac{1}{1 + [N_S g_S / N_V(T)] \exp\{\Delta / T\}},$$

just with a different pre-exponential coefficient in the denominator.

Again, the ratio $N_V(T)/N$ is of the order of $(T/T_0)^{3/2}$ and has to be large for the gas to stay classical. However, since in our limit, the ratio N_S/N is also large, and the $\exp\{\Delta/T\}$ is a very steep function, the gas pressure depends mostly on the condensation energy Δ. If this energy is much larger than the crossover value Δ_c given by Eq. (****), the number of particles in the gas phase is exponentially small,

$$N - N_0 = N_V(T) \frac{N}{N_S g_S} \exp\left\{-\frac{\Delta}{T}\right\} \propto T^{3/2} \exp\left\{-\frac{\Delta}{T}\right\},$$

(virtually all particles are condensed on the surface traps), and so is its pressure:

$$P = \frac{NT}{V} \frac{N_V(T)}{N_S g_S} \exp\left\{-\frac{\Delta}{T}\right\} \propto NT^{5/2} \exp\left\{-\frac{\Delta}{T}\right\} .$$

As in the results of the two previous problems, the pressure in this limit is dominated by the Arrhenius activation factor $\exp\{-\Delta/T\}$. Note also a very natural trend, $P \propto 1/N_S$, though the condition $N_S >> N$ used for the derivation of this result does not allow us to use it for following up the no-trap limit $N_S \to 0$. In the opposite limit of a low condensation energy $\Delta << \Delta_c$, our result is again reduced to the pressure of an ideal classical gas of N particles, $P = NT/V$. This is natural because, in this limit, virtually all particles are thermally activated into the gas phase.

To summarize the above analysis, the particle condensation on the surface affects the gas properties substantially only if the number N_S of traps is of the order of N (or higher) *and* the condensation energy is larger than the temperature-dependent crossover value (****).[130]

Problem 3.10. Calculate the magnetic response (the *Pauli paramagnetism*) of a degenerate ideal gas of spin-½ particles to a weak external magnetic field, due to a partial spin alignment with the field.

Solution: According to basic quantum mechanics,[131] a spin-½ particle placed into magnetic field $\mathscr{B}$ may have only two stationary spin states, with energies

$$\Delta\varepsilon = -\mathbf{m}_0 \cdot \boldsymbol{\mathscr{B}} = \pm m_0 \mathscr{B}, \qquad (*)$$

where $\mathbf{m}_0$ is the effective magnetic moment associated with the spin.[132] Hence, we may represent the Fermi gas of non-interacting particles as two independent gases with different particle spin orientations, with shifted particle energies

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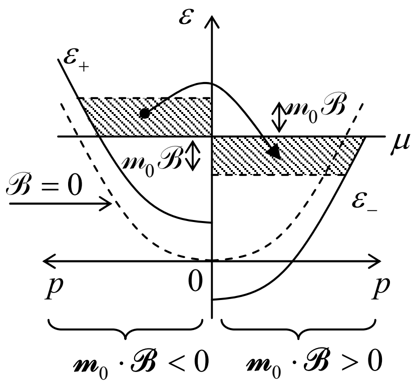
[130] Note also that the solved problem maps very closely onto the statistics of charge carriers in doped semiconductors – see Sec. 6.4 of the lecture notes and the associated problems.

[131] See, e.g., QM Secs. 4.4-4.6 and 5.1.

[132] As was already discussed in the solution of Problem 2.4, $m_0 = \gamma\hbar/2$, where γ is the gyromagnetic ratio of the particle.

$$\varepsilon_\pm = \frac{p^2}{2m} \pm \mathscr{m}_0\mathscr{B}\,.$$



(Let me hope that different fonts leave a very little chance of confusion between the particle's mass m and its magnetic moment $\mathscr{m}_0$).

If $\mathscr{B} = 0$, the number of particles in each partial gas is the same, but after the field has been applied, the spins of some particles flip to align with the field to reduce their energies, i.e. transfer from one partial gas to another. Such a transfer continues until the chemical potentials μ of both partial gases become equal – see the schematic figure on the right. As this scheme shows, at relatively small fields and temperatures ($\mathscr{m}_0\mathscr{B},\ T << \varepsilon_F$), the number of transferred particles, in the linear approximation in the field, is

$$\Delta N = \frac{g_3(\mu)}{2}\mathscr{m}_0\mathscr{B}\,, \qquad (**)$$

where $g_3(\varepsilon) \propto g$ is the density of states given by Eq. (3.43) of the lecture notes, which counts particles of all spin states,[133] while in Eq. (**) we need to count only one of them – hence the extra factor ½.

Superficially, it may look that this result is valid only at extremely low temperatures, $T << \mathscr{m}_0\mathscr{B}$, when the thermal smearing of the Fermi surface (see Fig. 3.2a of the lecture notes and its discussion) is much smaller than the energy shift caused by the applied field – as pictured, for the sake of simplicity, in the figure above. However, this is not so. Indeed, we might derive Eq. (**) by subtracting two Eqs. (3.65) of the lecture notes, with the appropriate substitution $g(\mu) \to g_3(\mu)/2$, written for two values of μ that differ by $m_0\mathscr{B}$, and keeping only the leading term, linear in $\mathscr{m}_0\mathscr{B}$. Since Eq. (3.65), by its derivation, is valid for any chemical potential shifts and temperatures much lower than ε_F, so is Eq. (**).

Each flipped spin changes the total magnetic moment of the gas by $2\mathscr{m}_0$, so the net magnetization (the magnetic moment of a unit volume) becomes

$$\mathscr{M} = \frac{2\mathscr{m}_0\Delta N}{V} = \mathscr{m}_0^2\,\frac{g_3(\mu)}{V}\mathscr{B}\,,$$

with the vector $\boldsymbol{\mathscr{M}}$ directed along the vector $\boldsymbol{\mathscr{B}}$ and hence describing a *paramagnetic* response of the gas to the applied field. As the figure above shows, in this linear approximation in $\mathscr{B}$, we may take $g_3(\mu) = g_3(\mu)|_{\mathscr{B}=0} \equiv g_3(\varepsilon_F)$, so the magnetization is proportional to the field, and hence may be characterized by the following positive magnetic susceptibility:[134]

$$\chi_m \equiv \frac{\mathscr{M}}{\mathscr{H}} = \mu_0\,\frac{\mathscr{M}}{\mathscr{B}} = \mu_0\mathscr{m}_0^2\,\frac{g_3(\varepsilon_F)}{V}\,. \qquad (***)$$

The result in this form is convenient for applications because it is to some extent stable with respect to deviations of the Fermi surface from the spherical shape, typical for conduction electrons in

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[133] In our case of spin-½ particles, the spin degeneracy $g = 2s + 1 = 2$.

[134] See, e.g., EM Eq. (5.111). Note that such a simple transfer from $\mathscr{H}$ to $\mathscr{B}$ is only valid at $|\chi_m| << 1$.

most metals.[135] If these deviations are negligible, and the Fermi surface is indeed virtually spherical (as it is, e.g., in alkali metals), we may use Eq. (3.55b) of the lecture notes to recast it in another form:

$$\chi_\mathrm{m} = \frac{3}{2}\mu_0 \mathscr{m}_0^2 \frac{N}{V\varepsilon_\mathrm{F}} \equiv \frac{3}{2}\mu_0 \frac{n\mathscr{m}_0^2}{\varepsilon_\mathrm{F}},$$

where $n \equiv N/V$ is the particle density. Comparing this expression with that for a similar but non-degenerate gas, following from the solution of Problem 2.4,

$$\chi_\mathrm{m} = \mu_0 \frac{n\mathscr{m}_0^2}{T},$$

we may conclude that cooling of an ideal Fermi gas results in the Curie-law growth of its paramagnetic susceptibility only until it saturates at $T \sim \varepsilon_\mathrm{F}$, i.e. at the onset of the gas' degeneracy.

For the particular case of electrons, we may use the expression $\mathscr{m}_0 = \mu_\mathrm{B} = e\hbar/2m_\mathrm{e}$. Together with the general relation $\varepsilon_\mathrm{F} = \hbar^2 k_\mathrm{F}^2/2m_\mathrm{e}$ and Eq. (3.54) in the form $n = 2(4\pi/3)k_\mathrm{F}^3/(2\pi)^3$, it enables us to rewrite our result in its more common form:

$$\chi_\mathrm{m} = \frac{\mu_0}{4\pi^2}\frac{e^2 k_\mathrm{F}}{m_\mathrm{e}}.$$

In order to facilitate a comparison of Eq. (***) for the Pauli paramagnetism with the *Landau diamagnetism* resulting from the orbital motion of particles of the same degenerate Fermi gas (whose calculation will be the subject of the next problem), let us re-derive the same result in a slightly different way. According to Eq. (*), the reversal of the magnetic moment $\mathscr{m}$ of one particle, from the direction against the field to the direction along it, changes its energy by $\Delta\varepsilon(\mathscr{B}) = -2\mathscr{m}_0\mathscr{B}$. Hence the transfer of $\Delta N >> 1$ particles, caused by a gradually growing field (see the arrow in the figure above), results in the following magnetic energy change:[136]

$$\begin{aligned}\Delta E \equiv E(\mathscr{B}) - E(0) &= \int_0^{\Delta N} \Delta\varepsilon(\mathscr{B}')dN' \equiv \int_0^{\mathscr{B}} \Delta\varepsilon(\mathscr{B}')\frac{dN'}{d\mathscr{B}'}d\mathscr{B}' \\ &= \int_0^{\mathscr{B}} (-2\mathscr{m}_0\mathscr{B}')\frac{g_3(\varepsilon_\mathrm{F})}{2}\mathscr{m}_0\, d\mathscr{B}' = -\frac{g_3(\varepsilon_\mathrm{F})}{2}\mathscr{m}_0^2\mathscr{B}^2.\end{aligned} \qquad (****)$$

But, according to basic magnetostatics,[137] the magnetization-related part of the total magnetic field energy $V\mathscr{B}^2/2\mu$ in volume V of a weakly polarizable linear medium (with $\chi_\mathrm{m} << 1$) is

$$\Delta E = V\left(\frac{\mathscr{B}^2}{2\mu} - \frac{\mathscr{B}^2}{2\mu_0}\right) \equiv V\left[\frac{\mathscr{B}^2}{2\mu_0(1+\chi_\mathrm{m})} - \frac{\mathscr{B}^2}{2\mu_0}\right] \approx -V\frac{\mathscr{B}^2}{2\mu_0}\chi_\mathrm{m}.$$

Comparing this expression with Eq. (****), we arrive at Eq. (***) again.

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[135] These deviations are due, mostly, to the interaction of the electrons with the crystal lattice – see, e.g., QM Secs. 2.7 and 3.4.

[136] Note that the simple multiplication of $\Delta\varepsilon(\mathscr{B}) = -2\mathscr{m}_0\mathscr{B}$ by the ΔN given by Eq. (**) would not give the correct factor ½, which reflects the induced character of the magnetization, proportional to the field. (If this issue is not absolutely clear, you may like to review the derivation of Eq. (1.60) in EM Sec. 1.3.)

[137] See, e.g., EM Secs. 5.5 and 6.2.

Problem 3.11. Calculate the magnetic response (the *Landau diamagnetism*) of a degenerate ideal gas of electrically charged fermions to a weak external magnetic field, due to their orbital motion.

Solution: According to basic quantum mechanics,[138] an external magnetic field causes the quantization of the motion of a free particle of mass m and electric charge q, in the plane normal to the field. The spectrum of the corresponding component $\varepsilon_\perp$ of its orbital energy is a set of *Landau levels*:

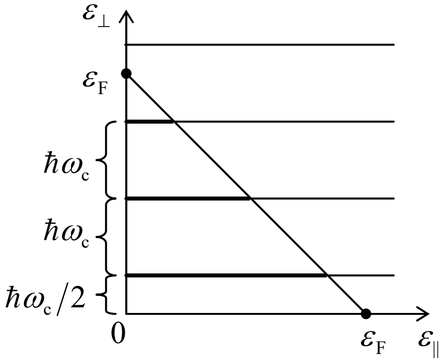
$$\varepsilon_n = \hbar\omega_\mathrm{c}\left(n+\frac{1}{2}\right), \qquad \text{where } \omega_\mathrm{c} = \frac{q\mathscr{B}}{m}, \quad n = 0,1,2,\ldots. \tag{*}$$

The orbital degeneracy of each level, on a plane of area A, is $g_2/\hbar\omega_\mathrm{c}$, where g_2 is the of 2D density states in the absence of the field,[139] so the magnetic field does not affect the state density averaged over the Landau levels. The magnetic field does not affect the motion of the particle along its direction, including its energy $\varepsilon_{||} = p_{||}^2/2m$; as a result, the total energy of the particle is

$$\varepsilon = \varepsilon_n + \varepsilon_{||} = \hbar\omega_\mathrm{c}\left(n+\frac{1}{2}\right) + \frac{p_{||}^2}{2m}, \tag{**}$$

with the average 3D density of states $g_3(\varepsilon)$ the same as at $\mathscr{B} = 0$ – see Sec. 3.3 of the lecture notes.

If the $N >> 1$ fermions confined in volume V do not directly interact, the above expressions enable the calculation of the magnetic response of the system, using (at least :-) three different approaches. The first, most general approach[140] is to sum up the contributions (2.114) from all quantum states of the system to calculate the total grand canonical potential Ω of the system as a function of μ, T, and $\mathscr{B}$. This expression naturally includes a sum over all Landau levels (i.e. over the index n), which may be explicitly calculated in the limit $\mathscr{B} \to 0$ using the Euler-Maclaurin formula.[141] The resulting expression for Ω may then be used to calculate the magnetic response using the second of Eqs. (1.62), and the analogy between the canonical pairs of variables $\{-P, V\}$ and $\{\mu_0\mathscr{H}_j, \mathscr{M}_j\}$, discussed in Sec. 1.1. The advantage of this approach is that its full form (i.e. before following the limit $\mathscr{B} \to 0$) is valid for arbitrary temperatures and fields, in particular at $\hbar\omega_\mathrm{c} \sim \varepsilon_\mathrm{F}$ where its results describe the so-called *de Haas-van Alphen effect* – periodic oscillations of the magnetization as a function of $1/\mathscr{B}$, as the Landau levels (*) sequentially cross the Fermi surface.[142]



For our limited goal of analysis of a *degenerate* Fermi gas with $T/\varepsilon_\mathrm{F} \to 0$, this general approach is, however, somewhat excessive because, in this limit, the susceptibility χ_m tends to a finite value, which may be more readily calculated by taking $T = 0$ from the very beginning. In this case, the level-filling diagram shown in the figure on the right may be readily used to calculate

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[138] See, e.g., QM Sec. 3.2.

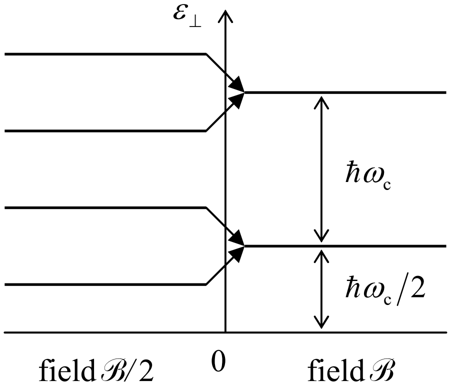
[139] See, e.g., Eq. (*) in the model solution of Problem 8.

[140] It is followed, for example, in Sec. 59 of L. Landau and L. Lifshitz, *Statistical Physics, Part 1*, 3rd ed., Pergamon, 1980.

[141] See, e.g., MA Eq. (2.12a).

[142] These oscillations are closely related to the *Shubnikov-de Haas effect* – the accompanying oscillations of the electric conductivity, and its extreme 2D form – the *quantum Hall effect* (see QM Sec. 3.2).

the total energy E of the system as a function of the magnetic field and the Fermi energy ε_F, i.e. the largest value of the single-particle energy (**).[143] From this function, we may calculate the difference $\Delta E \equiv E(\mathscr{B}) - E(0) \propto \mathscr{B}^2 \to 0$ and use it to find χ_m, exactly as this was done at the end of the previous problem's solution. This approach is quite straightforward and is highly recommended to the reader as an additional exercise.



However, here I would like to describe an even shorter, very elegant alternative calculation, which partly re-uses the previous problem's solution.[144] Let us consider the systems of Landau levels in fields $\mathscr{B}$ and $\mathscr{B}/2$ – see the figure on the right. Since we are only pursuing the limit $\mathscr{B} \to 0$, we may consider the level splitting on a scale $\hbar\omega_c$ that is much smaller than T (which is in turn much lower than ε_F), so the full number of states on adjacent Landau levels is virtually the same. The diagram shows that at the field's increase from $\mathscr{B}/2$ to $\mathscr{B}$, the energy of states on each other level, and hence of half of all states of the system, goes up the energy by $\hbar\omega_c/4$, while another half goes down by the same amount. But this is exactly the effect analyzed in the previous problem (see, in particular, the figure in its solution), with the replacement

$$\mathscr{m}_0\mathscr{B} \to \frac{\hbar\omega_c}{4} \equiv \frac{\hbar q}{4m}\mathscr{B}, \qquad \text{i.e. } \mathscr{m}_0 \to \frac{\hbar q}{4m}.$$

Hence the expression for the energy change ΔE due to the resulting redistribution of particles over the energy levels with ε close to ε_F, derived in that solution, becomes

$$\Delta E \equiv E\left(\frac{\mathscr{B}}{2}\right) - E(\mathscr{B}) = -\frac{1}{2} g_3(\varepsilon_F)\left(\frac{\hbar q}{4m}\right)^2 \mathscr{B}^2.$$

Now reproducing this result for the series of sequential two-fold increases of the field, we get

$$E(\mathscr{B}) - E(0) \equiv \left[E(\mathscr{B}) - E\left(\frac{\mathscr{B}}{2}\right)\right] + \left[E\left(\frac{\mathscr{B}}{2}\right) - E\left(\frac{\mathscr{B}}{4}\right)\right] + \left[E\left(\frac{\mathscr{B}}{4}\right) - E\left(\frac{\mathscr{B}}{8}\right)\right] + ...$$

$$= \frac{1}{2} g_3(\mu)\left(\frac{\hbar q}{4m}\right)^2 \mathscr{B}^2\left(1 + \frac{1}{4} + \frac{1}{16} + ...\right).$$

The last sum is just the geometric series,[145] equal to 4/3, so we finally get

$$E(\mathscr{B}) - E(0) = \frac{1}{2} g_3(\mu)\left(\frac{\hbar q}{4m}\right)^2 \mathscr{B}^2 \frac{4}{3} \equiv \frac{1}{6} g_3(\mu)\left(\frac{\hbar q}{2m}\right)^2 \mathscr{B}^2.$$

---

[143] This intermediate result also describes the de Haas-van Alphen oscillations, which at $T = 0$ are very sharp.

[144] To the best of my knowledge, this trick was invented only recently – see E. Batyev, *Physics-Uspekhi* **52**, 1245 (2009).

[145] See, e.g., MA Eq. (2.8b), with $\lambda = 1/4$.

This expression, for $q = -e$ and $m = m_e$, differs only by the factor (–1/3) from Eq. (****) of the solution of the previous problem, provided that in the latter formula, we take $m_0 = e\hbar/2m_e$ – as we have to do for electrons. Hence for this (practically, most important) case, we may write

$$\chi_m\Big|_{\text{orbital}} = -\frac{1}{3}\chi_m\Big|_{\text{spin}},$$

i.e. for a free degenerate electron gas, the Landau diamagnetism is exactly three times weaker than the Pauli paramagnetism.[146] Note, however, that this ratio is sensitive to several effects common to real metals; for example, it is affected by the difference between the effective mass of electrons[147] and m_e. Note also that for dilute (non-degenerate) gases of atoms with uncompensated spins, the spin paramagnetism is *much* stronger than the orbital diamagnetism – see, e.g., EM Problem 5.18 and QM Problem 6.15.

Problem 3.12.* Explore the *Thomas-Fermi model* of a heavy atom, with nuclear charge $Q = Ze >> e$, in which the electrons are treated as a degenerate Fermi gas, interacting with each other only via their contribution to the common electrostatic potential $\phi(\mathbf{r})$. In particular, derive the ordinary differential equation obeyed by the radial distribution of the potential, and use it to estimate the effective radius of the atom.[148]

Solution: Due to the condition $Z >> 1$, we may expect the characteristic radius $r_{TF}(Z)$ of the neutral atom (i.e. of the electron cloud surrounding the point-like nucleus) to be much larger than the linear scale r_0 of the single electron's motion in the Coulomb field of the bare nucleus of charge $Q = Ze$. Indeed, quantum mechanics tells us[149] that r_0 is defined by the equality of the scales of the quantum-kinetic and potential energies of the electron in such a hydrogen-like "atom" – actually, of the ion with the net charge $(Z-1)e >> e$:

$$\frac{\hbar^2}{m_e r_0^2} = \frac{Ze^2}{4\pi\varepsilon_0 r_0}, \qquad \text{giving } r_0 = \frac{\hbar^2}{m_e}\bigg/\frac{Ze^2}{4\pi\varepsilon_0} \equiv \frac{r_B}{Z},$$

where r_B is the Bohr radius. (This assumption, $r_{TF} >> r_0$, will be confirmed by our solution.) Due to this relation, which means that the electron's electrostatic potential energy $U(\mathbf{r}) = -e\phi(\mathbf{r})$ changes in space slowly on the r_0-scale, we may calculate the electron density $n(\mathbf{r}) \equiv dN/d^3r$ in a small local volume (with $r_0 << dr << r_{TF}$) by neglecting the gradient of $U(\mathbf{r})$, i.e. considering the electrons as free particles with the full energy[150]

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[146] Note that by modifying Eq. (*) to include the contribution of the particle's spin (as is done, e.g., in the solution of QM Problem 5.50), it is possible to calculate the net magnetic response arising from both the Pauli paramagnetism and the Landau diamagnetism, in one shot.

[147] See, e.g., QM Sec. 2.8.

[148] Since this problem and the next one are important for atomic physics and, at their solution, thermal effects may be ignored, they were given in Chapter 8 of the QM part of this series as well, for the benefit of the readers who would not take this SM course. Note, however, that the argumentation in their solutions may be streamlined by using the notion of the chemical potential μ, which was introduced only in this course.

[149] See, e.g., QM Eq. (1.13).

[150] Let me hope that the difference between the electron's energy ε and the electrostatic constant ε_0 is absolutely clear from the context.

$$\varepsilon = \frac{p^2}{2m_e} + q\phi(\mathbf{r}) = \frac{p^2}{2m_e} - e\phi(\mathbf{r}), \tag{*}$$

where the second term is treated as a local constant. As a result, we may apply to this small local volume of this degenerate gas the analysis carried out at the beginning of Sec. 3.3 of the lecture notes, in particular, Eq. (3.54) with $N/V = n(\mathbf{r})$ and the spin degeneracy $g = 2$ pertinent to electrons, to write

$$n(\mathbf{r}) = \frac{p_F^3(\mathbf{r})}{3\pi^2\hbar^3}. \tag{**}$$

Next, if we accept the free electron energy at $r \to \infty$ as the reference, the chemical potential μ of the atom's electrons in this model has to be zero because they have to be in the chemical equilibrium with free electrons in the environment.[151] (One may say that the ionization energy of the Thomas-Fermi atom equals zero; in reality, the ionization energy of heavy atoms is different from zero but is much lower than E_H.) Hence, for negligible temperatures,[152] the largest value of the total energy ε has to equal zero for any r, so, according to Eq. (*), the maximum value $p_F^2/2m_e$ of the local kinetic energy $p^2/2m_e$ has to be equal to $-q\phi(\mathbf{r}) \equiv e\phi(\mathbf{r})$. Together with Eq. (**), this equality yields

$$n(\mathbf{r}) = \frac{1}{3\pi^2}\left[\frac{2m_e e\phi(\mathbf{r})}{\hbar^2}\right]^{3/2}. \tag{***}$$

The second relation between the functions $n(\mathbf{r})$ and $\phi(\mathbf{r})$ is given by the Poisson equation of electrostatics,[153]

$$\nabla^2\phi(\mathbf{r}) = -\frac{\rho(\mathbf{r})}{\varepsilon_0} \equiv -\frac{e[Z\delta(\mathbf{r}) - n(\mathbf{r})]}{\varepsilon_0},$$

where the spelled-up two parts of the electric charge density $\rho(\mathbf{r})$ represent, respectively, the point-like positive charge $Q = Ze$ of the nucleus at the origin and the space-distributed negative charge of the electron cloud, with the density $-en(\mathbf{r})$. Plugging $n(\mathbf{r})$ from Eq. (***), and spelling out the Laplace operator for our spherically-symmetric problem,[154] we get the following *Thomas-Fermi equation* for the radial distribution of the electrostatic potential ϕ:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\phi}{dr}\right) = \frac{e}{3\pi^2\varepsilon_0}\left(\frac{2m_e e\phi}{\hbar^2}\right)^{3/2}, \qquad \text{for } r > 0.$$

This ordinary differential equation has to be solved with the following boundary conditions. As the above Poisson equation shows, at $r \to 0$, the potential has to approach that of the atomic nucleus:

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[151] The reader who has already run into the solution of this problem in the QM part of this series might notice that in that course I had to use somewhat awkward reasoning to make this point without using the notion of the chemical potential.

[152] The apparent scale of temperatures at which this assumption becomes invalid is given by the Hartree energy $E_H = (m_e/\hbar^2)(e^2/4\pi\varepsilon_0)^2 \approx 27.2$ eV (see, e.g., QM Eq. (1.9) and its discussion), corresponding to $T_K = E_H/k_B \sim 3\times10^5$ K – about thousand times higher than the standard room temperature of 300 K. Actually, the solution of the next problem will show that the real validity threshold for T is even $\sim Z^{4/3} >> 1$ times higher than this estimate.

[153] See, e.g., EM Eq. (1.41).

[154] See, e.g., MA Eq. (10.9) with $\partial/\partial\theta = \partial/\partial\varphi = 0$.

$$\phi(r) \to \frac{Q}{4\pi\varepsilon_0 r} \equiv \frac{Ze}{4\pi\varepsilon_0 r}, \qquad \text{at } r \to 0\,.$$

On the other hand, due to the atom's neutrality, at large distances, its electrostatic potential should not only tend to zero but also do this faster than that of any nonvanishing net charge:[155]

$$r\phi(r) \to 0, \qquad \text{at } r \to \infty\,.$$

It is convenient to recast this boundary problem by introducing a dimensionless distance ξ from the origin, defined as

$$\xi \equiv \frac{r}{r_{\text{TF}}(Z)}, \qquad \text{with } r_{\text{TF}}(Z) \equiv b\frac{r_{\text{B}}}{Z^{1/3}} \equiv br_0 Z^{2/3} >> r_0, \quad \text{and } b \equiv \frac{1}{2}\left(\frac{3\pi}{4}\right)^{2/3} \approx 0.8853, \qquad (****)$$

and also a dimensionless function $\chi(\xi)$ defined by the following equality:

$$\phi(r) \equiv \frac{Ze}{4\pi\varepsilon_0 r}\chi(\xi).$$

With these replacements, the Thomas-Fermi boundary problem becomes free of any parameters, in particular, independent of the atomic number Z:

$$\frac{d^2\chi}{d^2\xi} = \frac{\chi^{3/2}}{\xi^{1/2}}, \qquad \text{with } \chi(\xi) \to \begin{cases} 1, & \text{at } \xi \to 0, \\ 0, & \text{at } \xi \to \infty. \end{cases}$$

Unfortunately, this nonlinear differential equation may be solved only numerically, but this is not a big loss: the solution shows that as the argument ξ is increased, the function $\chi(\xi)$ goes down from unity at $\xi = 0$ to zero at $\xi \to \infty$ monotonically (and very uneventfully), at distances $\xi \sim 1$. (For example, $\chi(1) \approx 0.4$.) This is why, even without the exact solution, we may conclude that Eq. (****) gives a fair scale of the effective atom's size. This relation shows that the effective radius $r_{\text{TF}}(Z)$ decreases with the atomic number Z very slowly, as $r_{\text{B}}/Z^{1/3}$, and hence, at $Z >> 1$, is much larger than $r_0 \equiv r_{\text{B}}/Z$, thus confirming our initial assumption. For atoms with $Z >> 1$, this result is in good agreement with those given by more accurate models – in particular those describing their quantized energy spectra.

Problem 3.13.* Use the Thomas-Fermi model that was explored in the previous problem to calculate the total binding energy of a heavy atom. Compare the result with that of the simpler model, in that the Coulomb electron-electron interaction is completely ignored.

Solution: The binding energy of the atom may be found, for example, as

$$E_{\text{b}} = \sum_{Z'=Z}^{0} \mathscr{W}(Z'), \qquad (*)$$

---

[155] A useful sanity check of the self-consistency of the Thomas-Fermi model may be done by using the above relations to prove that in this model, the total number of electrons, calculated as

$$N = \int n(\mathbf{r})d^3r \equiv 4\pi\int_0^\infty n(r)r^2dr,$$

equals exactly Z – a simple exercise, highly recommended to the reader.

where $\mathscr{W}(Z')$ is the work necessary to decrease the atomic number by one, from Z' to $(Z' - 1)$. To calculate $\mathscr{W}(Z')$, let us note that the process of decreasing the atomic number by one may be decomposed into two steps: first taking one electron out of the electron cloud, and then taking one proton, of charge $+e$, out of the nucleus. Since the chemical potential of the electrons in the Thomas-Fermi model is zero, the first step of this process requires no work, while the second step requires work $\mathscr{W}(Z') = -e\phi_e(0)$, where $\phi_e(r)$ is the part of the potential $\phi(r)$, which is due to electrons only.[156] Using the above relations, with the notation replacement $Z \to Z'$, we get

$$\phi_e(r) = \phi(r) - \frac{Z'e}{4\pi\varepsilon_0 r} \equiv \frac{Z'e}{4\pi\varepsilon_0 r}\chi(\xi) - \frac{Z'e}{4\pi\varepsilon_0 r} \equiv \frac{Z'e}{4\pi\varepsilon_0}\frac{\chi(\xi)-1}{r}.$$

Since $\chi(0) - 1 = 0$ by construction, at $r \to 0$, the last fraction tends to $(d\chi/dr)_{r=0}$, and we get

$$\mathscr{W}(Z') = -e\phi_e(0) = -\frac{Z'e^2}{4\pi\varepsilon_0}\left(\frac{d\chi}{dr}\right)_{r=0} \equiv \frac{Z'e^2}{4\pi\varepsilon_0 r_{\rm TF}(Z')}\left(-\frac{d\chi}{d\xi}\right)_{\xi=0}.$$

Due to the properties of the universal function $\chi(\xi)$, which were discussed in the model solution of the previous problem, we may expect the derivative $d\chi/d\xi$ to be negative, with its modulus of the order of 1 at $\xi = 0$. Indeed, the numerical solution of the boundary problem for this function yields

$$a \equiv \left(-\frac{d\chi}{d\xi}\right)_{\xi=0} \approx 1.5881,$$

so $\mathscr{W}(Z') > 0$ for any Z'. As a result, the total binding energy E_b given by Eq. (*) is positive as well. (This means that the atom's components, after they have been brought far apart, have higher total energy than the initial atom). Due to the condition $Z >> 1$, the sum (*) may be calculated as an integral:

$$E_b = \int_0^Z \mathscr{W}(Z')dZ' = a\int_0^Z \frac{Z'e^2}{4\pi\varepsilon_0 r_{\rm TF}(Z')}dZ' \equiv \frac{a}{b}\frac{e^2}{4\pi\varepsilon_0 r_{\rm B}}\int_0^Z Z'^{4/3}dZ' = \frac{3a}{7b}Z^{7/3}\frac{e^2}{4\pi\varepsilon_0 r_{\rm B}}.$$

But the last fraction is just the Hartree energy E_H,[157] so we finally get

$$E_b = \frac{3a}{7b}Z^{7/3}E_H \approx 0.7688\, Z^{7/3}E_H >> E_H, \qquad \text{for } Z >> 1.$$

Note the very non-trivial scaling of the energy with the atomic number Z.

Now let us consider a simpler model,[158] in which the direct electron-electron interaction is completely ignored, so $\phi(\mathbf{r})$ is just the unscreened electrostatic potential of the nucleus:

---

[156] Of course, in reality, each proton also interacts (and very strongly) with other protons of the nucleus. However, our goal is to calculate the *electron binding* energy, i.e. difference between the sum of energies of the "assembled" nucleus and individual electrons, far apart from it and each other, and that of the whole "assembled" atom. In the calculation of this difference, the change of the intrinsic energy of the nucleus has to be ignored.

[157] See, e.g., a footnote in the model solution of the previous problem.

[158] Very unfortunately, this model is sometimes called "statistical" – as if its counterpart, the Thomas-Fermi model, is not statistical.

$$\phi(\mathbf{r}) = \frac{Ze}{4\pi\varepsilon_0 r},$$

for all r. Here we still may use Eqs. (**) of the model solution of the previous problem,[159]

$$n(\mathbf{r}) = \frac{p_F^3(\mathbf{r})}{3\pi^2\hbar^3}, \tag{**}$$

but since in this model, the chemical potential μ is not known in advance, the local value of the maximum momentum, $p_F(\mathbf{r})$, should be found from Eq. (*) of the previous problem, with $\varepsilon = \mu$:

$$\frac{p_F^2}{2m_e} = \mu + e\phi(\mathbf{r}) \equiv \mu + \frac{Ze^2}{4\pi\varepsilon_0 r}. \tag{***}$$

In order to have the electrons localized near the nucleus, μ cannot be positive (relative to the electron energy at $r \to \infty$), so p_F, and hence the electron density as well, have to turn to zero at some finite radius r_{ef} defined as

$$\frac{Ze^2}{4\pi\varepsilon_0 r_{ef}} \equiv -\mu \geq 0,$$

in this model, playing the role of the atom's radius. With this notation, Eqs. (**) and (***) yield

$$n(\mathbf{r}) = \frac{1}{3\pi^2}\left[\frac{m_e e^2 Z}{2\pi\varepsilon_0\hbar^2}\left(\frac{1}{r} - \frac{1}{r_{ef}}\right)\right]^{3/2}.$$

Now we may calculate r_{ef} (and hence the chemical potential) by requiring the atom to be neutral, i.e. the number of electrons to be equal to Z:[160]

$$\int_{r \leq R} n(\mathbf{r})d^3r = Z.$$

Carrying out the integration, we get

$$\int_{r\leq R} n(\mathbf{r})d^3r = 4\pi\int_0^R r^2 dr\, n(\mathbf{r}) = \frac{4}{3\pi}\left(\frac{m_e e^2 Z}{2\pi\varepsilon_0\hbar^2}\right)^{3/2}\int_0^R\left(\frac{1}{r} - \frac{1}{r_{ef}}\right)^{3/2} r^2 dr$$
$$= \frac{4}{3\pi}\left(\frac{m_e e^2 Z r_{ef}}{2\pi\varepsilon_0\hbar^2}\right)^{3/2}\int_0^1 (1-\xi)^{3/2}\xi^{1/2}d\xi.$$

The last (dimensionless) integral may be recast into a sum of elementary integrals using the substitution $\xi \equiv \sin^2\alpha$ and then worked out using MA Eqs. (3.3d) and (3.4). The result is $\pi/16$, so the electron number balance becomes

$$\frac{4}{3\pi}\left(\frac{m_e e^2 Z r_{ef}}{2\pi\varepsilon_0\hbar^2}\right)^{3/2}\frac{\pi}{16} = Z, \tag{****}$$

---

[159] Just as in that problem, we assume the electron gas to be degenerate, with $T \ll \mu$.

[160] Evidently, in contrast to the Thomas-Fermi model, this rudimentary model is not self-consistent, because it implies that $\phi(r_{ef}) = Ze/4\pi\varepsilon_0 r_{ef} \neq 0$, while the exact electrostatic potential of a neutral, spherically-symmetrical system of charges should vanish at its effective surface.

giving

$$r_{\text{ef}} = (18)^{1/3}\frac{4\pi\varepsilon_0\hbar^2}{e^2 m_{\text{e}}}\frac{1}{Z^{1/3}} \equiv (18)^{1/3}\frac{r_{\text{B}}}{Z^{1/3}} \approx 2.620\frac{r_{\text{B}}}{Z^{1/3}}.$$

So, this rudimentary model gives the same order of magnitude of r_{TF} as the Thomas-Fermi model, though with a significantly larger numerical coefficient.[161]

Now let us calculate the binding energy (*) within this simple model. To avoid the calculation of the electron potential $\phi_{\text{e}}(0)$ felt by the nuclear charges, the partial work $\mathscr{W}(Z')$ may be found differently than for the Thomas-Fermi model. Namely, let us calculate the radius $r_{\text{ef}}(Z')$ and the chemical potential $\mu(Z')$ of an ion with Z' electrons but with the nuclear charge Q still equal to Ze. Reviewing the above calculations, we see that this may be done merely by replacing Z on the right-hand side of Eq. (****) with Z':

$$\frac{4}{3\pi}\left[\frac{m_{\text{e}}e^2 Z\, r_{\text{ef}}(Z')}{2\pi\varepsilon_0\hbar^2}\right]^{3/2}\frac{\pi}{16} = Z', \qquad \text{giving } r_{\text{ef}}(Z') = (18)^{1/3}\frac{Z'^{2/3}}{Z}r_{\text{B}}.$$

Now we may calculate the chemical potential as

$$-\mu(Z') = \frac{Ze^2}{4\pi\varepsilon_0 r_{\text{ef}}(Z')} = \frac{1}{(18)^{1/3}}\frac{Ze^2}{4\pi\varepsilon_0 r_{\text{B}}}\frac{Z}{Z'^{2/3}} \equiv \frac{E_{\text{H}}}{(18)^{1/3}}\frac{Z^2}{Z'^{2/3}}.$$

The work $\mathscr{W}(Z')$ necessary for the removal of an additional electron from the ion to infinity is $-\mu(Z')$, so, replacing the sum (*) with the corresponding integral, we get

$$E_{\text{b}} = -\int_0^Z \mu(Z')dZ' = \frac{E_{\text{H}}}{(18)^{1/3}}Z^2\int_0^Z\frac{dZ'}{Z'^{2/3}} = \frac{3}{(18)^{1/3}}Z^{7/3}E_{\text{H}} \approx 1.145\,Z^{7/3}E_{\text{H}}.$$

Very naturally, this value is higher than that calculated in the Thomas-Fermi model because in the simple model, each electron is attracted to the nucleus by the Coulomb field unscreened by other electrons, making their interaction stronger. Note, however, that the difference is not too large – just about 50%. This relative insignificance of the Coulomb interaction of electrons in atoms echoes that in the degenerate electron gas in metals – see Table 3.1 and its discussion in section 3.3 of the lecture notes.

Problem 3.14. Calculate the characteristic *Thomas-Fermi length* λ_{TF} of weak electric field's screening by conduction electrons in a metal, by modeling their ensemble as an isotropic degenerate Fermi gas, with the electrons' interaction limited (as in the two previous problems) by their contribution to the common electrostatic potential.

Hint: Assume that λ_{TF} is much larger than the Bohr radius r_{B}.

---

[161] To be fair, the r_{ef} is the *largest* electron distance from the nuclei, while the *average* distance, defined as

$$\langle r\rangle \equiv \frac{1}{Z}\int r\, n(\mathbf{r})d^3r,$$

is closer to r_{TF}. (A good additional exercise for the reader: calculate this distance.)

Solution: As was argued in the model solution of Problem 12, the relation $\lambda_{\text{TF}} >> r_{\text{B}}$ allows us to consider, in the electron's energy

$$\varepsilon = \frac{p^2}{2m_{\text{e}}} + U(\mathbf{r}) \equiv \frac{p^2}{2m_{\text{e}}} - e\phi(\mathbf{r}),$$

the potential-energy term as a (local) constant. As a result, the conduction electrons (fermions with $\varepsilon_{\text{F}} >> T$) fill, at point $\mathbf{r}$, all states with the kinetic energies $p^2/2m_{\text{e}}$ satisfying the condition $p < p_{\text{F}}(\mathbf{r})$, where

$$\frac{p_{\text{F}}^2(\mathbf{r})}{2m_{\text{e}}} - e\phi(\mathbf{r}) = \mu .$$

Since, as our solution will show, the screened field does not reach far into the conductor's bulk, the chemical potential μ has to be equal to its field-unperturbed value ε_{F}.[162] As a result, the local value $p_{\text{F}}(\mathbf{r})$ of the Fermi momentum, and hence the local electron density $n(\mathbf{r})$ (see Eq. (3.54) of the lecture notes, with $N/V \equiv n$) become functions of the local value of the electrostatic potential:

$$\frac{p_{\text{F}}^2(\mathbf{r})}{2m} = \varepsilon_{\text{F}} + e\phi(\mathbf{r}). \qquad (*)$$

The second relation between the functions $n(\mathbf{r})$ and $\phi(\mathbf{r})$ is given by the Poisson equation,[163]

$$\nabla^2\phi(\mathbf{r}) = \frac{e[n(\mathbf{r}) - n_0]}{\kappa\varepsilon_0},$$

where κ is the dielectric constant of the conductor's ion lattice, and n_0 is the equilibrium density of the electrons in the absence of the field, i.e., in an electrically neutral conductor. Let us consider the simplest geometry when the applied electric field $\mathscr{E}_0$ is normal to the plane surface of the conductor.[164] Then both n and ϕ are functions of just one Cartesian coordinate (say, x) normal to the surface, and the Poisson equation is reduced to

$$\frac{d^2\phi(x)}{dx^2} = \frac{e[n(x) - n_0]}{\kappa\varepsilon_0}. \qquad (**)$$

Since the left-hand side of Eq. (*) is a nonlinear function of n, the system of differential equations (*) and (**) generally cannot be solved analytically. However, if the external field is relatively weak,

$$\mathscr{E}_0 << \frac{\varepsilon_{\text{F}}}{e\lambda_{\text{TF}}},$$

then even the largest change of ϕ it causes (at the conductor's surface) is still much smaller than ε_{F}/e. In this case, we may linearize Eq. (*) with respect to small density variation

$$\tilde{n}(x) \equiv n(x) - n_0 \equiv n(x) - n(\infty),$$

---

[162] This value is lower than the energy of electrons in free space by a material-dependent constant called the *workfunction* ψ, for most metals between 4 and 5 eV – see, e.g., Sec. 6.3 of this course, and also EM Sec. 2.6 and QM Sec. 1.1. Note, however, that the value of ψ does not participate directly in the solution of this problem.

[163] See, e.g., EM Eq. (1.41) and Sec. 3.4.

[164] Indeed, in genuine electrostatics, i.e. at no current flowing in the conductor, the electric field at the surface has to be normal to it – see, e.g., EM Sec. 2.1.

where $x \to \infty$ corresponds to the conductor's bulk. The linearization yields

$$\frac{d}{dn}\left(\frac{p_{\rm F}^2}{2m}\right)\Big|_{\phi=0}\tilde{n}(x) = e\phi(x), \quad \text{i.e. } \tilde{n}(x) = g_3(\varepsilon_{\rm F})e\phi(x),$$

where $g_3(\varepsilon_{\rm F})$ is the volume-normalized density of states, $dn/d\varepsilon$, at the Femi surface of a free Fermi gas – see Eq. (3.55b) of the lecture notes:

$$g_3(\varepsilon_{\rm F}) \equiv \frac{dn}{d\varepsilon}\Big|_{\varepsilon=\varepsilon_{\rm F}} = \frac{3}{2}\frac{n_0}{\varepsilon_{\rm F}}.$$

Plugging this expression into the right-hand side of Eq. (**), we may rewrite the resulting equation as

$$\frac{d^2\phi(x)}{dx^2} = \frac{\phi(x)}{\lambda_{\rm TF}^2}, \qquad \text{where } \lambda_{\rm TF} \equiv \left[\frac{\kappa\varepsilon_0}{e^2 g_3(\varepsilon_{\rm F})}\right]^{1/2} \equiv \left[\frac{2\kappa\varepsilon_0\varepsilon_{\rm F}}{3e^2 n_0}\right]^{1/2} \propto \frac{1}{n_0^{1/6}}. \qquad (***)$$

This linear differential equation, solved with the boundary conditions

$$\frac{d\phi(x)}{dx}\Big|_{x=0} = -\mathscr{E}_0, \qquad \phi(\infty) = 0,$$

where $x = 0$ at the conductor's surface, describes the *Thomas-Fermi screening* – an exponential decrease of the electrostatic potential and of the electric field, both being proportional to $\exp\{-x/\lambda_{\rm TF}\}$. Hence, the above expression for $\lambda_{\rm TF}$ gives the solution of the posed problem.[165]

In good metals, the density of states on the Fermi surface is of the order of 10^{22} eV^{-1}cm^{-3} ≡ 10^{28} eV^{-1}m^{-3}, and the dielectric constant κ ranges approximately from 3 to 10. as a result, $\lambda_{\rm TF}$ is of the order of a few tenths of a nanometer, i.e. is only marginally larger than $r_{\rm B} \approx 0.05$ nm, making the Thomas-Fermi theory of screening applicable only semi-quantitatively. However, the theory is quantitatively valid for many degenerate semiconductors, with a smaller n_0 and hence larger $\lambda_{\rm TF}$, but still with $\varepsilon_{\rm F} >> T$.

Problem 3.15. For a degenerate ideal 3D Fermi gas of N particles confined in a rigid-wall box of volume V, calculate the temperature effects on its pressure P and the heat capacity difference ($C_P - C_V$), in the leading approximation in $T << \varepsilon_{\rm F}$. Compare the results with those for the ideal classical gas.

Hint: You may like to use the solution of Problem 1.9.

Solution: According to the universal (statistics-independent) relation for any non-relativistic ideal gas, given by Eq. (3.48) of the lecture notes,

$$PV = \frac{2}{3}E,$$

we may use the temperature dependence of E given by Eq. (3.68), and then Eq. (3.55b) for the 3D density of states, to write

$$P(T) = \frac{2}{3V}\left[E(0) + \frac{\pi^2}{6}g_3(\varepsilon_{\rm F})T^2\right] = P(0) + \frac{\pi^2}{6}\frac{N}{V}\frac{T^2}{\varepsilon_{\rm F}}, \qquad \text{for } T << \varepsilon_{\rm F}. \qquad (*)$$

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[165] Actually, the problem was solved, if only semi-quantitatively, in EM Sec. 2.1.

A comparison of this result with Eq. (1.44), $P = NT/V$, shows that the pressure (*) grows with temperature much slower than that of the classical gas of the same density N/V. This is very natural because, at low temperatures, only a minor fraction $\sim T/\varepsilon_\text{F}$ of the occupied particle states are in such close vicinity to the Fermi surface that they may be thermally excited – see Fig. 3.2 of the lecture notes.

Proceeding to the difference $(C_P - C_V)$, perhaps the easiest way to calculate it is to use Eq. (****) of the model solution of Problem 1.9:

$$C_P - C_V = -T\frac{(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T} \equiv \frac{VT}{K}\left(\frac{\partial P}{\partial T}\right)_V^2, \qquad (**)$$

where $K \equiv -V(\partial P/\partial V)_T$ is the bulk modulus (reciprocal compressibility) of the gas. Using Eq. (*) to calculate the involved derivative,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\pi^2}{3}\frac{N}{V}\frac{T}{\varepsilon_\text{F}},$$

we see that at $T/\varepsilon_\text{F} << 1$, Eq. (**) gives us the leading term ($\propto T^3$) of the temperature dependence of the difference $(C_P - C_V)$ even if we ignore the (weak) temperature dependence of the bulk modulus. Hence we may use its zero-temperature value given by Eq. (3.58) of the lecture notes:

$$K = \frac{2}{3}\frac{N}{V}\varepsilon_\text{F},$$

to get

$$C_P - C_V \approx VT\left(\frac{\pi^2}{3}\frac{N}{V}\frac{T}{\varepsilon_\text{F}}\right)^2 \Big/ \left(\frac{2}{3}\frac{N}{V}\varepsilon_\text{F}\right) \equiv \frac{\pi^4}{6}\left(\frac{T}{\varepsilon_\text{F}}\right)^3 N, \qquad \text{for } T << \varepsilon_\text{F}.$$

Thus the difference between the two heat capacities of a degenerate Fermi gas is much smaller than the capacities as such (see Eq. (3.70) of the lecture notes): $C_V, C_P \sim (T/\varepsilon_\text{F})N$, and also than the difference $C_P - C_V = N$ of the ideal classical gas.

Problem 3.16. How would the Fermi statistics of an ideal gas affect the barometric formula (3.28)?

Solution: Let us start with calculating the particle density $n(\mathbf{r})$, i.e. the number of all particles in a unit volume at a certain point **r**, regardless of their kinetic energy. This may be done, for example, by using Eq. (3.39) of the lecture notes (with the upper sign that corresponds to the Fermi-Dirac statistics), for a small volume d^3r at point **r**, by including the potential energy $U(\mathbf{r})$ of a particle into its energy ε:

$$n(\mathbf{r}) \equiv \frac{dN(\mathbf{r})}{d^3r} = \frac{g}{(2\pi\hbar)^3}\int \frac{1}{\exp\{(p^2/2m + U(\mathbf{r}) - \mu)/T\} + 1} d^3p. \qquad (*)$$

For high temperatures, when μ is strongly negative (see Fig. 3.1 of the lecture notes), we may ignore the last term in the denominator of the fraction, to get

$$n(\mathbf{r}) = \frac{g}{(2\pi\hbar)^3}\int \exp\left\{-\left(\frac{p^2}{2m} + U(\mathbf{r}) - \mu\right)/T\right\} d^3p \equiv e^{-U(\mathbf{r})/T} e^{\mu/T} \frac{g}{(2\pi\hbar)^3}\int \exp\left\{-\frac{p^2}{2mT}\right\} d^3p.$$

This integral may be readily worked out in Cartesian coordinates (see Sec. 3.1), but even regardless of it: if the temperature throughout the gas is constant, the integral does not depend on **r**, so the above expression already gives the explicit dependence $n(\mathbf{r})$,

$$n(\mathbf{r}) = n(0)\exp\left\{-\frac{U(\mathbf{r})}{T}\right\},$$

where $\mathbf{r} = 0$ is the point accepted for the potential energy reference: $U(0) = 0$. Now using the equation of state of the ideal classical gas in its local form $P(\mathbf{r}) = n(\mathbf{r})T$, for an isothermal atmosphere with $U(\mathbf{r}) = mgh$, we get the classical barometric formula (3.28):

$$P(h) = P(0)\exp\left\{-\frac{h}{h_0}\right\}, \qquad \text{with } h_0 \equiv \frac{T}{mg}.$$

These results were already obtained in Sec. 3.1 of the lecture notes from the Maxwell distribution; the advantage of our current approach is that it may be readily generalized to describe non-classical statistical effects as well. In particular, for a degenerate Fermi gas ($T << \mu$), the fraction in Eq. (*) is a step function equal to 1 if $p^2/2m + U(\mathbf{r}) < \mu$ and zero otherwise, so this relation yields

$$n(\mathbf{r}) = \frac{g}{(2\pi\hbar)^3}\int_{p^2/2m<\mu-U(\mathbf{r})} d^3p = \frac{g}{(2\pi\hbar)^3}\frac{4\pi}{3}p_F^3(\mathbf{r}), \qquad \text{where } \frac{p_F^2(\mathbf{r})}{2m} \equiv \varepsilon_F(\mathbf{r}) \equiv \mu - U(\mathbf{r}).$$

The first expression coincides with Eq. (3.54) of the lecture notes, which was derived for $U = 0$, so the "only" role of the external potential $U(\mathbf{r})$ is to offset the local Fermi energy $\varepsilon_F(\mathbf{r})$.[166] This is why we may use the second form of Eq. (3.57) to express the gas pressure via $\varepsilon_F(\mathbf{r})$ and $n(\mathbf{r})$ and then via $U(\mathbf{r})$:

$$P(\mathbf{r}) = \frac{2}{5}\varepsilon_F(\mathbf{r})n(\mathbf{r}) = \frac{2}{5}\varepsilon_F(\mathbf{r})\frac{g}{(2\pi\hbar)^3}\frac{4\pi}{3}[2m\varepsilon_F(\mathbf{r})]^{3/2} = \frac{2}{5}\frac{g}{(2\pi\hbar)^3}\frac{4\pi}{3}(2m)^{3/2}[\mu - U(\mathbf{r})]^{5/2}.$$

For $U(\mathbf{r}) = mgh$, this expression gives a barometric formula very much different from the classical one:

$$P(h) = P(0)\left(1 - \frac{mgh}{\mu}\right)^{5/2}, \qquad \text{for } h < \frac{\mu}{mg}.$$

The formula shows that at $T = 0$, the pressure of the gas sharply vanishes at $h = h_{\max} = \mu/mg$ because the quantum states with energies above μ are completely unpopulated, so at $h > h_{\max}$, there are no particles at all. The value of μ may be readily calculated, for example, if the number of particles per area A of the gas layer,

$$\frac{N}{A} = \int_0^\infty n(h)dh,$$

is known.

A nonvanishing but low ($T << \mu$) temperature smears this sharp threshold, creating a smooth transitional layer of thickness $\delta h \sim h_0 \equiv T/mg << h_{\max}$.

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[166] Actually, a particular form of this relation was already used for the analysis of the Thomas-Fermi model of heavy atoms in the model solutions of Problems 3.12-3.13.

Problem 3.17. Derive general expressions for the energy E and the chemical potential μ of a uniform Fermi gas of $N >> 1$ non-interacting, indistinguishable, ultra-relativistic particles.[167] Calculate E and also the gas pressure P explicitly in the degenerate gas limit $T \to 0$. In particular, is Eq. (3.48) of the lecture notes, $PV = (2/3)E$, valid in this case?

Solution: The energy ε of an ultra-relativistic free particle (with $\varepsilon >> mc^2$, where m is its rest mass) is related to its momentum p as $\varepsilon(p) = cp$.[168] In this case, Eq. (3.39) of the lecture notes (with the upper sign, which corresponds to the Fermi-Dirac statistics) yields

$$N = \frac{gV}{(2\pi\hbar)^3} \int_0^\infty \frac{4\pi p^2 dp}{e^{(cp-\mu)/T} + 1},$$

while Eq. (3.52), also with the upper sign, becomes

$$E = \frac{gV}{(2\pi\hbar)^3} \int_0^\infty cp \frac{4\pi p^2 dp}{e^{(cp-\mu)/T} + 1}.$$

As was repeatedly discussed in the lecture notes, in the limit $N >> 1$, these two relations, which are strictly valid for a grand canonical ensemble with given μ, may be also used as two equations for the calculation of μ and E in a canonical ensemble with given N.

The calculations are much simplified in the degenerate limit $T \to 0$ when the Fermi-Dirac distribution tends to a step function (see Fig. 3.2 and its discussion), so the integrals in the above relations may be easily worked out:

$$N \to \frac{gV}{(2\pi\hbar)^3} \int_0^{p_F} 4\pi p^2 dp = \frac{gV}{(2\pi\hbar)^3} 4\pi \frac{p_F^3}{3}, \qquad E \to \frac{gV}{(2\pi\hbar)^3} \int_0^{p_F} cp\, 4\pi p^2 dp = \frac{gV}{(2\pi\hbar)^3} 4\pi c \frac{p_F^4}{4} = \frac{3}{4} Ncp_F,$$

where p_F is the Fermi momentum defined by the equality $\varepsilon(p_F) \equiv cp_F = \mu$. The first of these relations, identical to Eq. (3.54) for a non-relativistic gas, yields

$$p_F = \left(\frac{6\pi^2}{4g}\right)^{1/3} \hbar \frac{N^{1/3}}{V^{1/3}}, \qquad \text{so } \mu = cp_F = \left(\frac{6\pi^2}{4g}\right)^{1/3} c\hbar \frac{N^{1/3}}{V^{1/3}}.$$

Plugging the last equality into the last expression for E, we get

$$E = \frac{3}{4}\left(\frac{6\pi^2}{g}\right)^{1/3} c\hbar \frac{N^{4/3}}{V^{1/3}}.$$

Now, by using the fact that according to the basic Eq. (1.33), $F \to E$ at $T \to 0$, we may calculate the gas pressure from Eq. (1.35) (with the implied condition $N = \text{const}$) as

$$P = -\left(\frac{\partial F}{\partial V}\right)_N \Big|_{T=0} = -\left(\frac{\partial E}{\partial V}\right)_N = \frac{1}{4}\left(\frac{6\pi^2}{g}\right)^{1/3} c\hbar \left(\frac{N}{V}\right)^{4/3}.$$

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[167] This is, for example, an approximate but reasonable model for electrons in a white dwarf star. (Their Coulomb interaction is mostly compensated by the electric charges of nuclei of fully ionized helium atoms.)

[168] See, e.g., EM Eq. (9.79).

Comparing the last expressions for P and E, we see that

$$P = \frac{1}{3}\frac{E}{V}.$$

This formula coincides with Eq. (2.92b) of the lecture notes for the electromagnetic field (which may be considered as a gas of ultra-relativistic Bose particles – photons) but differs by a factor of 2 from Eq. (3.48) for non-relativistic particles. As we will be shown in the solution of the next problem, this relation is valid for any temperature.

Problem 3.18. Use Eq. (3.49) of the lecture notes to calculate the pressure of an ideal gas of ultra-relativistic, indistinguishable quantum particles, for an arbitrary temperature, as a function of the total energy E of the gas and its volume V. Compare the result with the corresponding relations for the electromagnetic blackbody radiation and for an ideal gas of non-relativistic particles.

Solution: According to Eq. (3.49), the grand thermodynamic potential of a single-particle state with energy ε is

$$\Omega(\varepsilon) = \mp T \ln\left(1 \pm \exp\frac{\mu - \varepsilon}{T}\right),$$

where the upper sign corresponds to fermions, and the lower one, to bosons. The potential of the whole gas may be calculated as

$$\Omega = \int_0^\infty g(\varepsilon)\Omega(\varepsilon)d\varepsilon,$$

where $g(\varepsilon)$ is the density of quantum states: $g(\varepsilon) \equiv dN(\varepsilon)/d\varepsilon$, with $N(\varepsilon)$ being the number of states with energies below ε. For an isotropic 3D gas, the general rule (3.4) of quantum state counting,[169] with the account of the particle's spin degeneracy g, yields

$$N(\varepsilon) = \frac{gV}{(2\pi\hbar)^3}\int_{p' \leq p} d^3p' = \frac{gV}{(2\pi\hbar)^3}\frac{4\pi}{3}p^3, \qquad (*)$$

where p is the magnitude of the particle's momentum corresponding to the energy ε. As was shown in Sec. 3.2 of the lecture notes, for non-relativistic particles, with $\varepsilon = p^2/2m$, these expressions immediately lead to Eq. (3.48),

$$P = \frac{2E}{3V}. \qquad (**)$$

Now, according to the relativity theory,[170] for ultra-relativistic particles, we may take $\varepsilon = pc$, so $p = \varepsilon/c$, and Eq. (*) yields

$$N(\varepsilon) = \frac{gV}{(2\pi\hbar)^3}\frac{4\pi}{3}\frac{\varepsilon^3}{c^3}, \qquad \text{so } g(\varepsilon) \equiv \frac{dN(\varepsilon)}{d\varepsilon} = \frac{gV}{(2\pi\hbar)^3}\frac{4\pi}{3}\frac{3\varepsilon^2}{c^3} \equiv \frac{gV}{2\pi^2}\frac{\varepsilon^2}{(\hbar c)^3}.$$

As a result, for these particles,

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[169] See, e.g., QM Eq. (1.90).

[170] See, e.g., either the solution of the previous problem or EM Eq. (9.79).

$$\Omega = \mp \frac{TgV}{2\pi^2(\hbar c)^3}\int_0^\infty \varepsilon^2 \ln\left(1 \pm \exp\frac{\mu-\varepsilon}{T}\right)d\varepsilon .$$

This integral is similar to the one in Eq. (2.90), and its integration by parts gives a similar result:

$$\Omega = -\frac{gV}{6\pi^2(\hbar c)^3}\int_0^\infty \frac{\varepsilon^3}{\exp\{(\varepsilon-\mu)/k_B T\}\pm 1}d\varepsilon \equiv -\frac{gV}{6\pi^2(\hbar c)^3}\int_0^\infty \varepsilon^3 f(\varepsilon)d\varepsilon ,$$

where $f(\varepsilon)$ is either the Fermi-Dirac or the Bose-Einstein distribution:

$$f(\varepsilon) \equiv \frac{1}{\exp\{(\varepsilon-\mu)/k_B T\}\pm 1}.$$

But the last expression for Ω is just (–1/3) of the gas' energy

$$E = \int_0^\infty g(\varepsilon)\varepsilon f(\varepsilon)d\varepsilon = \frac{gV}{2\pi^2(\hbar c)^3}\int_0^\infty \varepsilon^3 f(\varepsilon)d\varepsilon ,$$

so $\Omega = -E/3$. Since, according to Eq. (1.60), for an arbitrary system, $\Omega = -PV$, we immediately get

$$P = \frac{E}{3V}. \qquad (***)$$

(In the previous problem this result was proved, by simpler means, for the particular case of fermions at $T \to 0$; see also the solution of Problem 2.23.)

The result (***) coincides with Eq. (2.92) for the electromagnetic blackbody radiation (which may be also considered as a gas of ultra-relativistic particles – photons), but differs, by a factor of ½, from Eq. (**) for an ideal gas of non-relativistic particles. (Strictly speaking, E in Eq. (**) does not include the rest-energy contribution, Nmc^2, while E in Eq. (***) does, but in our ultra-relativistic case, this contribution is negligibly small in comparison with the total energy of the gas.)

Problem 3.19.* Calculate the speed of sound in an ideal gas of ultra-relativistic fermions of density n, at negligible temperature.

Solution: As we know from classical mechanics,[171] the sound propagation velocity may be calculated as

$$v_s = \left(\frac{K}{\rho}\right)^{1/2}, \qquad \text{with } K \equiv -V\left(\frac{\partial P}{\partial V}\right)_N . \qquad (*)$$

Using the solution of Problem 17, in the form

$$E = \pi\frac{gV}{(2\pi\hbar)^3}cp_F^4, \qquad P = \frac{E}{3V} = \frac{\pi}{3}\frac{g}{(2\pi\hbar)^3}cp_F^4 \equiv \frac{1}{4}cp_F n \propto \frac{1}{V^{4/3}},$$

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[171] See, e.g., CM Eq. (7.114). As was discussed in the model solution of Problem 1.6, generally we have to distinguish the isothermal (T = const) and adiabatic (S = const) compressibility, with the former one relevant only at extremely low frequencies. However, at $T \to 0$, the entropy of an ideal gas is constant, so these notions coincide.

where

$$n \equiv \frac{N}{V} = \frac{4\pi}{3}\frac{g}{(2\pi\hbar)^3}p_F^3 \tag{*}$$

is the particle density of the gas, and $p_F \propto 1/V^{1/3}$ is its Fermi momentum, we readily get

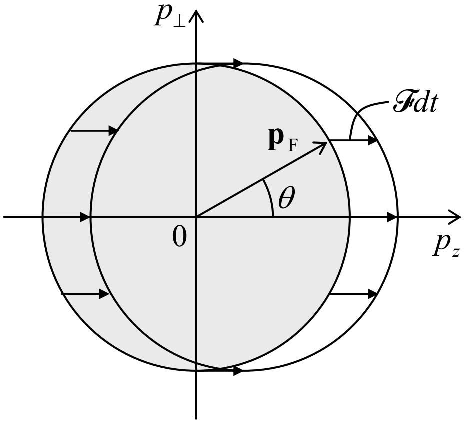
$$K = \frac{4}{3}P = \frac{1}{3}cp_F n .$$

The calculation of the mass density ρ of the gas is a bit more tricky. Indeed, it would be wrong to take it equal to nm, where m is the rest mass of the particle because for ultra-relativistic particles, with $p >> mc$, this mass does not affect any property of the gas. Rather, ρ has to be calculated as nm_{ef}, where m_{ef} is a measure of the gas' inertia at the application of a small external force $\mathscr{F}$ to each of its particles. In non-relativistic mechanics, we may take

$$m_{ef} \equiv \mathscr{F} \Big/ \left\langle \frac{d\mathbf{v}}{dt} \right\rangle$$

– exactly the definition used at the derivation of Eq. (*). However, in relativistic mechanics, the 2nd Newton law is only valid in the form[172]

$$\frac{d\mathbf{p}}{dt} = \mathscr{F} ,$$



where $\mathbf{p}$ is the relativistic momentum. For the degenerate Fermi gas, which, in the absence of the force, occupies all states inside the Fermi sphere $p \leq p_F$, this means that under the effect of the force during a short time interval dt, the whole sphere shifts by a small interval $\mathscr{F}dt$ in the direction of the force – in the figure on the right, along the z-axis. As a result, even though each particle still moves with the same speed $|\mathbf{v}| = c$ as before the force application, the number of particles at the Fermi surface, with the z-component of $\mathbf{v}$ in the direction of the force, increases, while that of the particles moving in the opposite direction, decreases. (The effects of other Cartesian components of $\mathbf{v}$ are averaged out at the summation over the particles.) This change may be evaluated as

$$dN = \frac{gV}{(2\pi\hbar)^3}\mathscr{F}dt \cos\theta \; p_F^2 d\Omega_p ,$$

where the first fraction is the density dN/d^3p of states in the momentum space, θ is the angle between the vectors $\mathbf{p}_F$ and $\mathscr{F}$ (see the figure above), and $d\Omega_p$ is an elementary solid angle in the momentum space. The z-component of the particle's velocity $\mathbf{v}$ in each state is $c\cos\theta$, so the average velocity change under the effect of the impulse $\mathscr{F}dt$ is

$$\langle dv \rangle = \frac{1}{N}\oint_{4\pi} c\cos\theta dN = \frac{1}{N}\frac{gVp_F^2}{(2\pi\hbar)^3}\mathscr{F}dt\, c \oint_{4\pi}\cos^2\theta d\Omega_p .$$

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[172] See, e.g., EM Sec. 9.6, in particular, Eq. (9.144).

After an easy integration,

$$\oint_{4\pi} \cos^2 \theta d\Omega_p = 2\pi \int_0^{\pi} \cos^2 \theta \sin \theta d\theta = 2\pi \int_{-1}^{+1} \cos^2 \theta d(\cos\theta) = 2\pi \frac{2}{3} \equiv \frac{4\pi}{3},$$

and the expression of $N = nV$ from Eq. (*), we get a very simple result:

$$\langle dv \rangle = \frac{c}{p_\mathrm{F}} \mathscr{F} dt, \qquad \text{so } m_\mathrm{ef} = \frac{p_\mathrm{F}}{c}, \quad \text{i.e. } \rho \equiv n m_\mathrm{ef} = n \frac{p_\mathrm{F}}{c}.$$

(As a sanity check, a similar calculation for the non-relativistic Fermi gas, with the replacement $c \to v_\mathrm{F} \equiv p_\mathrm{F}/m$, immediately yields $m_\mathrm{ef} = m$ and $\rho = nm$.)

With these K and ρ, Eq. (*) yields the sound velocity

$$v_\mathrm{s} = \left(\frac{K}{\rho}\right)^{1/2} = \left(\frac{1}{3} c p_\mathrm{F} n \Big/ n \frac{p_\mathrm{F}}{c}\right)^{1/2} = \frac{c}{\sqrt{3}} \approx 0.577\, c\,.$$

Remarkably, this result does not depend on the density n (and also the spin degeneracy g) of the particles. (Actually, this is true for the ideal classical gas as well – see the solution of Problem 1.6.)

Problem 3.20. Calculate basic thermodynamic characteristics, including all relevant thermodynamic potentials, specific heat, and the surface tension of a non-relativistic 2D electron gas with a constant areal density $n \equiv N/A$:

(i) at $T = 0$, and
(ii) at low temperatures (in the lowest nonvanishing order in $T/\varepsilon_\mathrm{F} << 1$),

neglecting the Coulomb interaction effects.[173]

Solution: At the stated conditions, the electrons may be treated as an ideal Fermi gas, so the average value of any thermodynamic variable $f(\varepsilon)$ is the sum of its values in all quantum states, weighed with the Fermi distribution. In the 2D case,

$$\langle f \rangle = \sum_k f_k \langle N_k \rangle = \frac{2A}{(2\pi\hbar)^2} \int_0^\infty f(\varepsilon) \langle N(\varepsilon) \rangle 2\pi p dp = \int_0^\infty f(\varepsilon) \langle N(\varepsilon) \rangle g_2(\varepsilon) d\varepsilon, \qquad (*)$$

where $\varepsilon = p^2/2m$ is the kinetic energy of a single particle (so $d\varepsilon = pdp/m$), the factor $g = 2$ describes the double spin degeneracy of each orbital state, $\langle N(\varepsilon) \rangle$ is the Fermi-Dirac distribution,

$$\langle N(\varepsilon) \rangle = \frac{1}{\exp\{(\varepsilon - \mu)/T\} + 1},$$

and $g_2(\varepsilon)$ is the 2D density of states. As was discussed in the model solution of Problem 8, this density turns out to be energy-independent:

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[173] This condition may be approached reasonably well, for example, in 2D electron gases formed in semiconductor heterostructures (see, e.g., the discussion in QM Sec. 1.8, and the solution of Problem 3.2 of that course), due to not only the electron field's compensation by background ionized atoms, but also by its screening by the highly doped semiconductor's bulk.

$$g_2(\varepsilon) = \frac{mA}{\pi\hbar^2}.$$

Let us apply Eq. (*) to the key variables. As usual, the chemical potential μ participating in the Fermi distribution may be found from the formal calculation of the average number of particles $N >> 1$ – which is, actually, given. Taking $f(\varepsilon) = 1$ (as appropriate for particle counting), we get

$$N = \int_0^\infty \langle N(\varepsilon)\rangle g_2(\varepsilon)d\varepsilon = \frac{mA}{\pi\hbar^2}\int_0^\infty \frac{d\varepsilon}{\exp\{(\varepsilon-\mu)/T\}+1} \equiv \frac{mA}{\pi\hbar^2}T\int_{-\mu/T}^\infty \frac{d\xi}{e^\xi+1},$$

where $\xi \equiv (\varepsilon - \mu)/T$. This is a table integral,[174] giving

$$N = \frac{mA}{\pi\hbar^2}T\ln\left(1+\exp\left\{\frac{\mu}{T}\right\}\right) \equiv \frac{mA\mu}{\pi\hbar^2} + \frac{mAT}{\pi\hbar^2}\ln\left(\exp\left\{-\frac{\mu}{T}\right\}+1\right). \qquad (**)$$

However, for some other variables, for example, the total energy

$$E(T) = \int_0^\infty \varepsilon\,\langle N(\varepsilon)\rangle g_2(\varepsilon)d\varepsilon = \frac{mA}{\pi\hbar^2}\int_0^\infty \frac{\varepsilon d\varepsilon}{\exp\{(\varepsilon-\mu)/T\}+1}, \qquad (***)$$

integrals (*) cannot be worked out analytically (more exactly, expressed via the elementary and special functions discussed in this series) for arbitrary temperatures. This is why let us proceed to the limiting cases specified in the assignment.

(i) $T = 0$. In this case, the second term in the last form of Eq. (**) vanishes, and it yields $N = (mA/\pi\hbar^2)\mu$, so

$$\mu(T=0) \equiv \varepsilon_F = \frac{\pi\hbar^2}{m}\frac{N}{A}.$$

Next, since at $T = 0$, $\langle N(\varepsilon)\rangle$ is a step function (see Eq. (3.53) and Fig. 3.2a in the lecture notes), Eq. (***) gives

$$E(0) = \frac{mA}{\pi\hbar^2}\int_0^{\varepsilon_F}\varepsilon d\varepsilon = \frac{mA}{\pi\hbar^2}\frac{\varepsilon_F^2}{2} = \frac{mA}{\pi\hbar^2}\frac{1}{2}\left(\frac{\pi\hbar^2}{m}\frac{N}{A}\right)^2 = \frac{1}{2}\frac{\pi\hbar^2}{m}\frac{N^2}{A},$$

so the average energy per particle[175]

$$\langle\varepsilon\rangle \equiv \frac{E(0)}{N} = \frac{\varepsilon_F}{2}.$$

Concerning other thermodynamic potentials, by definition, $F(0) = E(0)$, while $H(0) = G(0)$. The last potential may be found using Eq. (1.56):

$$G(0) = \mu(T=0)N = \varepsilon_F N = 2E(0),$$

so the grand potential, defined by the first of Eqs. (1.60), is $\Omega(0) \equiv F(0) - G(0) = -E(0)$.[176] In the 3D case, Ω is equal to $-PV$ – see Eq. (1.60) again. As was repeatedly discussed above, in the 2D case, the

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[174] See, e.g., MA Eq. (6.4a).

[175] The resulting expression $E = (1/2)\varepsilon_F N$ may be compared with the 3D formula (3.56): $E = (3/5)\,\varepsilon_F N$.

[176] As a reminder, in the 3D case, the coefficient in such relation is different, $\Omega = -(2/3)E$ – see Eq. (3.52).

volume's analog is the area A, so the analog of the pressure $P \equiv -(\partial F/\partial V)_{T,N}$ is the surface "anti-tension"[177] $\sigma \equiv -(\partial F/\partial A)_{T,N}$, i.e. $\Omega = -\sigma A$. For $T = 0$, we get

$$\sigma(0) = -\frac{\Omega(0)}{A} = \frac{E(0)}{A} = \frac{1}{2}\frac{\pi\hbar^2}{m}\frac{N^2}{A^2}.$$

Finally, to calculate the specific heat, we need to consider the case of finite temperatures.

(ii) $T << \varepsilon_F$, i.e. $T << \mu$. In this limit, the second term in Eq. (**) gives only an exponentially small correction to μ. For such a non-analytical function of T, the second term in the Sommerfeld expansion (3.59) vanishes, so we may still use for μ the same relation as at $T = 0$:

$$\mu(T << \varepsilon_F) \approx \varepsilon_F = \frac{\pi\hbar^2}{m}\frac{N}{A} = \text{const}.$$

From here

$$G(T) \approx \varepsilon_F N = G(0) = 2E(0).$$

For the energy, we may use the Sommerfeld expansion (3.59), which does not depend on the system's dimensionality:

$$I(T) \equiv \int_0^\infty \varphi(\varepsilon)\langle N(\varepsilon)\rangle d\varepsilon \approx \int_0^\mu \varphi(\varepsilon)d\varepsilon + \frac{\pi^2}{6}T^2\frac{d\varphi(\mu)}{d\mu},$$

Taking $\varphi(\varepsilon) = g_2\varepsilon = (mA/\pi\hbar^2)\varepsilon$ (so $d\varphi(\mu)/d\mu = mA/\pi\hbar^2 = \text{const}$), we get the following temperature dependence:

$$E(T) \approx E(0) + \frac{\pi^2}{6}T^2\frac{mA}{\pi\hbar^2} = E(0)\left[1 + \frac{\pi^2}{3}\left(\frac{T}{\varepsilon_F}\right)^2\right],$$

so the specific heat c_A (the heat capacity per particle at a fixed area) is small in comparison with that of the classical gas, and linear in temperature:

$$c_A = \frac{1}{N}\left(\frac{\partial E}{\partial T}\right)_{A,N} = \frac{\pi^2}{3}T\frac{mA}{\pi\hbar^2} = \frac{\pi^2}{3}\frac{T}{\varepsilon_F} << 1.$$

Just as in the 3D case discussed in the model solution of Problem 15, the difference between the low-temperature values of the specific heats at constant area (c_A) and at constant tension (c_σ) is proportional to $(T/\varepsilon_F)^3$ and is much smaller than the (virtually equal) c_A and c_σ, which scale as T/ε_F.

Now let us calculate the effect of temperature on the grand potential Ω:

$$\Omega(T) = -T\sum_k \ln\left(1 + \exp\left\{\frac{\mu - \varepsilon_k}{T}\right\}\right) = -T\frac{mA}{\pi\hbar^2}\int_0^\infty \ln\left(1 + \exp\left\{\frac{\mu - \varepsilon}{T}\right\}\right)d\varepsilon.$$

Integrating by parts, we get

$$\Omega(T) = -\frac{mA}{\pi\hbar^2}\int_0^\infty \langle N(\varepsilon)\rangle \varepsilon d\varepsilon = -E(T) = \Omega(0)\left[1 + \frac{\pi^2}{3}\left(\frac{T}{\varepsilon_F}\right)^2\right].$$

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[177] A discussion of the mechanical effects of the surface tension in liquids may be found in CM Sec. 8.2.

This result enables a ready completion of our calculations:

$$\sigma(T) = -\frac{\Omega(T)}{A} = \sigma(0)\left[1 + \frac{\pi^2}{3}\left(\frac{T}{\varepsilon_F}\right)^2\right], \qquad F(T) = G(T) + \Omega(T) = F(0)\left[1 - \frac{\pi^2}{3}\left(\frac{T}{\varepsilon_F}\right)^2\right],$$

$$S(T) = \frac{E(T) - F(T)}{T} = \frac{\pi^2}{3}\frac{mA}{\pi\hbar^2}T, \qquad H(T) = E(T) + \sigma(T)A = H(0)\left[1 + \frac{\pi^2}{3}\left(\frac{T}{\varepsilon_F}\right)^2\right].$$

Problem 3.21. Calculate the differential latent heat $\Lambda \equiv -N(\partial Q/\partial N_0)_{N,V}$ of evaporation of a spatially uniform Bose-Einstein condensate as a function of temperature T. Here Q is the heat absorbed by the (condensate + gas) system of $N >> 1$ particles as a whole, while N_0 is the number of particles in the condensate alone.

Solution: For a slow process, we can use the fundamental Eq. (1.17) of the lecture notes, in the form $dE = dQ - PdV$, to represent the differential latent heat as

$$\Lambda = -N\left(\frac{\partial E}{\partial N_0}\right)_{N,V}.$$

For the number N_0 of condensed particles in a spatially uniform system, we had Eq. (3.74a):

$$N_0 = N\left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right],$$

where T_c is the critical temperature. Solving this equation for T, we get

$$\frac{T}{T_c} = \left(1 - \frac{N_0}{N}\right)^{2/3}. \qquad (*)$$

On the other hand, for the system's energy below T_c, we had (3.78):

$$E(T) = E(T_c)\left(\frac{T}{T_c}\right)^{5/2},$$

where $E(T_c)$ may be expressed via N and T_c by comparing Eqs. (3.73) and Eq. (3.75),[178]

$$E(T_c) = \frac{\Gamma(5/2)\zeta(5/2)}{\Gamma(3/2)\zeta(3/2)}NT_c = \frac{3}{2}\frac{\zeta(5/2)}{\zeta(3/2)}NT_c.$$

Combining the last three formulas, we get a convenient relation between E and N_0,

$$E = \frac{3}{2}\frac{\zeta(5/2)}{\zeta(3/2)}NT_c\left(1 - \frac{N_0}{N}\right)^{5/3},$$

whose differentiation yields

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[178] The second step uses MA Eq. (6.7b) with $s = 3/2$.

$$\Lambda = -N\left(\frac{\partial E}{\partial N_0}\right)_{N,V} = \frac{5}{2}\frac{\zeta(5/2)}{\zeta(3/2)} NT_{\mathrm{c}}\left(1-\frac{N_0}{N}\right)^{2/3}.$$

Now we can use Eq. (*) again to rewrite this expression as

$$\Lambda = \frac{5}{2}\frac{\zeta(5/2)}{\zeta(3/2)} NT \approx 1.284\ NT.$$

This is a pretty curious result, showing that the effective latent heat of the system does not depend on T_{c}, and hence on the system's volume. On the other hand, it is completely natural that $\Lambda \to 0$ at $T \to 0$: in this limit, the average energy of particles in the gaseous phase tends to zero, so less and less heat is needed to evaporate the condensed particles with their $\mu = 0$.

Problem 3.22.* For a spatially uniform ideal Bose gas, calculate the law of the chemical potential's disappearance at $T \to T_{\mathrm{c}}$ and use the result to prove that at the critical point $T = T_{\mathrm{c}}$, the heat capacity C_V is a continuous function of temperature.

Solution: Let us consider a small increase $dT = T - T_{\mathrm{c}} << T_{\mathrm{c}}$ of temperature above its critical value. If, at this increase, the number N of particles is kept constant, the direct effect of dT on the pre-integral factor in Eq. (3.44) of the lecture notes has to be compensated by the change of the integral, due to the appearance of a small positive parameter $a^2 \equiv -\mu/T << 1$:

$$dN = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\left\{\frac{3}{2}T_{\mathrm{c}}^{1/2} dT\, I(0) + T_{\mathrm{c}}^{3/2}\left[I(a) - I(0)\right]\right\} = 0, \qquad (*)$$

where

$$I(a) \equiv \int_0^\infty \frac{\xi^{1/2} d\xi}{\exp\{\xi + a^2\} - 1} = 2\int_0^\infty \frac{\chi^2 d\chi}{\exp\{\chi^2 + a^2\} - 1}, \quad \text{where } \chi \equiv \xi^{1/2},$$

so the (small) difference between the integrals participating in Eq. (*), is

$$I(a) - I(0) = 2\int_0^\infty \chi^2 d\chi \left[\frac{1}{\exp\{\chi^2 + a^2\} - 1} - \frac{1}{\exp\{\chi^2\} - 1}\right].$$

Since at $a \to 0$, the main contribution to this expression comes from the region of small χ, we may expand the denominators of both fractions in the Taylor series in both a^2 and χ^2, getting

$$I(a) - I(0) \approx 2\int_0^\infty \chi^2 d\chi \left[\frac{1}{\chi^2 + a^2} - \frac{1}{\chi^2}\right] \equiv -2a^2\int_0^\infty \frac{d\chi}{\chi^2 + a^2}.$$

This is a table integral equal to $\pi/2a$,[179] so $I(a) - I(0) = -\pi a$, and with the value $I(0) = \Gamma(3/2)\zeta(3/2)$ (see Eq. (3.71) of the lecture notes), Eq. (*) yields

$$-\frac{\mu}{T} \equiv a^2 = \left(\frac{3I(0)}{2\pi}\frac{dT}{T_{\mathrm{c}}}\right)^2 = \left(\frac{3\Gamma(3/2)\zeta(3/2)}{2\pi}\frac{dT}{T_{\mathrm{c}}}\right)^2 \approx 1.222\left(\frac{dT}{T_{\mathrm{c}}}\right)^2 << 1. \qquad (**)$$

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[179] See, e.g., MA Eq. (6.5a).

So, the small negative chemical potential arising above T_c is proportional to the temperature increase squared. This is fully consistent with the plot shown with the blue line in Fig. 3.1 of the lecture notes. (On the log-log plot of Fig. 3.3a, this relation is less obvious.)

For the heat capacity calculation, it is convenient to use Eq. (3.52), with the appropriate negative sign, to define the notion of the energy $E_0(T)$ that the gas *would have* at $T \geq T_c$ if the chemical potential retained the value $\mu = 0$:

$$E_0 \equiv \frac{gVm^{3/2}T^{5/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty \frac{\xi^{3/2}}{e^\xi - 1}d\xi = E(T_c)\left(\frac{T}{T_c}\right)^{5/2}.$$

By this definition, the difference between the actual energy E and E_0 at the same temperature $T > T_c$ is only due to the change of the chemical potential, so at $dT << T_c$, we may write

$$E - E_0 = \left(\frac{\partial E}{\partial \mu}\right)_T \mu .$$

Now we may use Eq. (3.48), then Eq. (1.60), and then the last of Eqs. (1.62) to write

$$\left(\frac{\partial E}{\partial \mu}\right)_T = \frac{3}{2}\left[\frac{\partial (PV)}{\partial \mu}\right]_T = -\frac{3}{2}\left(\frac{\partial \Omega}{\partial \mu}\right)_T = -\frac{3}{2}N ,$$

where the constancy of volume is also implied. Combined with Eq. (**) for μ, these formulas yield

$$E - E_0 = -\frac{3}{2}NT\left(\frac{3\Gamma(3/2)\zeta(3/2)}{2\pi}\frac{dT}{T_c}\right)^2, \quad \text{for } 0 \leq dT << T_c .$$

Now notice that since the above definition of E_0 coincides with Eq. (3.78), which is valid for the actual energy at $T \leq T_c$, the temperature derivative of the difference $E - E_0$ (at constant volume), taken at $T = T_c$, gives the difference of the limiting values of the heat capacity:

$$C_V\Big|_{T=T_c+0} - C_V\Big|_{T=T_c-0} = \lim_{T\to T_c}\frac{d}{dT}\left(E - E_0\right) = \lim_{T\to T_c}\left[-3\left(\frac{3\Gamma(3/2)\zeta(3/2)}{2\pi}\right)^2\frac{N}{T_c}dT\right] \to 0 .$$

Hence, the heat capacity is indeed a continuous function of temperature. However, its temperature derivative is not:

$$\frac{dC_V}{dT}\Big|_{T=T_c+0} - \frac{dC_V}{dT}\Big|_{T=T_c-0} = -3\left(\frac{3\Gamma(3/2)\zeta(3/2)}{2\pi}\right)^2\frac{N}{T_c} \approx -3.665\frac{N}{T_c} .$$

This "cusp" is clearly visible in the (numerically calculated) plot shown in Fig. 3.5 of the lecture notes.

Problem 3.23. In Chapter 1 of the lecture notes, several thermodynamic relations involving entropy have been discussed, including the first of Eqs. (1.39):

$$S = -\left(\frac{\partial G}{\partial T}\right)_P .$$

If we combine this expression with the fundamental relation (1.56), $G = \mu N$, it looks like that, for the Bose-Einstein condensate, the entropy should vanish because its chemical potential μ equals zero for all temperatures below the critical point T_c. On the other hand, by dividing both parts of Eq. (1.19) by dT, and assuming that at this temperature change the volume is kept constant, we get

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V .$$

(This equality was also mentioned in Chapter 1.) If the C_V is known as a function of temperature, the last relation may be integrated over T to calculate S:

$$S = \int_{V=\text{const}} \frac{C_V(T)}{T} dT + \text{const.}$$

According to Eq. (3.80), the specific heat for the Bose-Einstein condensate is proportional to $T^{3/2}$, so the integration gives a nonvanishing entropy $S \propto T^{3/2}$. Resolve this apparent contradiction, and calculate the value of the genuine entropy at $T = T_c$.

Solution: Eqs. (1.39) of the lecture notes have been derived for uniform systems with a fixed number of particles and (as Eq. (1.53c) shows), in the general case, it should be rewritten as

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} .$$

We know, however, that below T_c, the Bose-Einstein condensate is essentially a two-phase system, in which the disordered gas coexists with the completely ordered (and hence entropy-free) condensate and the change of temperature results in the change of the number of the gaseous-phase particles,

$$N' \equiv N - N_0 = N\left(\frac{T}{T_c}\right)^{3/2},$$

even if the total number N of particles in the system does not change. Moreover, any temperature variation leads to a variation of pressure $P(T)$ as well – see Eq. (3.79), so it cannot be kept constant. As a result, the arguments based on Eq. (1.39) are not valid for this system, and we may indeed calculate the entropy (at $0 \leq T \leq T_c$) by using Eq. (3.80):

$$S(T) - S(0) = \int_0^T \frac{C_V(T)}{T} dT \Big|_{V=\text{const}} = \frac{5}{2}\frac{E(T_c)}{T_c^{5/2}}\int_0^T \frac{T^{3/2}}{T} dT = \frac{5}{3}\frac{E(T_c)}{T_c^{5/2}} T^{3/2} .$$

Hence, the entropy of the system[180] is indeed proportional to $T^{3/2}$ and (if we reasonably, though not compulsory, take $S(0) = 0$), then at $T \to T_c$, it reaches the value

$$S(T_c) = \frac{5}{3}\frac{E(T_c)}{T_c} \approx 1.284N.$$

It is straightforward (and highly recommended to the reader as an additional exercise) to check that the entropy of the gas reaches the same value at an approach to T_c from the higher temperature side where $\mu \neq 0$ and all N bosons are in the gas phase. Here, S may be indeed calculated by differentiation – either from the first of Eqs. (1.39) with $G = \mu N$, or even simpler, from the first of Eqs. (1.62),

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[180] Essentially, of its uncondensed fraction of N' particles.

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu},$$

with the potential Ω given by the first form of Eq. (3.51), with the appropriate (lower) sign.

Problem 3.24. The standard analysis of the Bose-Einstein condensation, outlined in Sec. 3.4 of the lecture notes, may seem to ignore the energy quantization of the particles confined in volume V. Use the particular case of a cubic confining volume $V = a\times a\times a$ with rigid walls to analyze whether the main conclusions of the standard theory, in particular Eq. (3.71) for the critical temperature of the system of $N >> 1$ particles, are affected by such quantization.

Solution: An elementary quantum-mechanical analysis of a single particle placed in such a box[181] yields the following energy spectrum:

$$\varepsilon_{n_x,n_y,n_z} = \varepsilon_0\left(n_x^2 + n_y^2 + n_z^2\right), \qquad \text{where } \varepsilon_0 \equiv \frac{\pi^2\hbar^2}{2ma^2} = \frac{\pi^2\hbar^2}{2mV^{2/3}}, \qquad (*)$$

where the quantum numbers n_x, n_y, and n_z may take independent positive integer values starting from 1. Let us use the Bose-Einstein distribution (2.118) to calculate the average number of independent particles in the case when the box is in full thermodynamic equilibrium with an environment with temperature T and chemical potential μ:

$$\langle N\rangle = g\sum_{n_x,n_y,n_z=1}^{\infty}\left\langle N_{n_x,n_y,n_z}\right\rangle = g\sum_{n_x,n_y,n_z=1}^{\infty}\left[\exp\left\{\frac{\varepsilon_{n_x,n_y,n_z}-\mu}{T}\right\}-1\right]^{-1}$$

$$\equiv g\sum_{n_x,n_y,n_z=1}^{\infty}\left[\exp\left\{\frac{\varepsilon_0\left(n_x^2+n_y^2+n_z^2\right)-\mu}{T}\right\}-1\right]^{-1},$$

where $g = 2s + 1$ is the spin degeneracy. Generally, as we know from Sec. 2.8 of the lecture notes, this expression is only valid for the grand canonical ensemble, in which the number N of particles in the box is not exactly fixed. However, as was repeatedly discussed in the lecture notes and earlier problem solutions, in the canonical ensemble of systems with the number N of particles in the box fixed but very large, we may use it, with the replacement $\langle N\rangle \to N$, for the calculation of the relation between the average values of N and μ, neglecting their small fluctuations whose relative r.m.s. values scale as $1/N^{1/2} << 1$. In particular, in accordance with the discussion in Sec. 3.4, in order to calculate T_c, we have to take μ equal to the lowest value of the single-particle energy ε (in this case, the ground state energy is $3\varepsilon_0$ – not exactly zero!), i.e. solve the following equation:

$$N = g\sum_{n_x,n_y,n_z=1}^{\infty}\left[\exp\left\{\frac{\varepsilon_0}{T_c}\left(n_x^2+n_y^2+n_z^2-3\right)\right\}-1\right]^{-1}. \qquad (**)$$

This sum converges as soon as the magnitude of the argument under the exponent becomes much larger than 1, i.e. at $n \equiv (n_x^2 + n_y^2 + n_z^2)^{1/2} \sim n_{\max} \equiv (T_c/\varepsilon_0)^{1/2}$. Since the first, most significant terms of the sum are of the order of 1, the sum itself may be estimated as $n^3_{\max}$, so, by the order of magnitude, Eq. (**) gives

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[181] If needed, see, e.g., QM Sec. 1.7, in particular Eq. (1.86).

$$N \sim g n_{\max}^3 \equiv \left(\frac{T_c}{\varepsilon_0}\right)^{3/2}, \qquad \text{i.e. } T_c \sim \varepsilon_0 \left(\frac{N}{g}\right)^{2/3}.$$

But since $N >> 1$, while $g \sim 1$, this means that T_c is much larger than ε_0, which is the scale of the distance between the adjacent energy levels (which differ by a unit change of one of the quantum numbers). Hence at $T \sim T_c$, many lower levels are populated, so in the sum in Eq. (**), the term (–3) may be neglected, and the sum as a whole may be approximated by an integral. As a result, the equation for T_c takes the form

$$N = g\int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \left[\exp\left\{\frac{\varepsilon_0}{T_c}\left(n_x^2 + n_y^2 + n_z^2\right)\right\} - 1\right]^{-1} \equiv \frac{g}{8}\int \left[\exp\left\{\frac{\varepsilon_0}{T_c} n^2\right\} - 1\right]^{-1} d^3n.$$

where $\mathbf{n} \equiv \{n_x, n_y, n_z\}$, so $n^2 = n_x^2 + n_y^2 + n_z^2$, and the factor (1/8) before the last integral compensates for the dropped condition $n_x, n_y, n_z > 0$. Now using the spherical coordinates in the space of vectors $\mathbf{n}$, we get

$$N = \frac{g}{8} 4\pi \int_0^\infty \left[\exp\left\{\frac{\varepsilon_0}{T_c} n^2\right\} - 1\right]^{-1} n^2 dn \equiv \frac{\pi g}{2} \int_0^\infty \frac{n^2 dn}{\exp\{\varepsilon_0 n^2 / T_c\} - 1}.$$

But this equation, with the integration variable replacement $\xi \equiv \varepsilon_0 n^2/T_c$ and with the account of Eq. (*) for ε_0, exactly coincides with Eq. (3.73) for T_c and hence yields the same result (3.71).

In hindsight, this is not surprising, because the arguments used in this solution essentially reproduce, for a particular system, the reasoning that has led us to the general quantum state counting rule (3.13) and eventually to Eq. (3.71). Nevertheless, the solution was not a vain exercise: it shows very clearly that the theory outlined in Sec. 3.4 of the lecture notes (and in Problems 21-23 above) is only valid for spatially uniform systems, in particular, only if the particle confinement is stiff – in the sense that the wall volume into which the wavefunctions of the particles partly penetrate is much smaller than the volume V of their free motion. In the opposite case of soft confinement, for example at the bottom of a quadratic-parabolic potential well, the value of T_c is rather different – see Eq. (3.74b) and its discussion in the lecture notes, and the next problem – to which this solution gives a good preparation.

Problem 3.25.* $N >> 1$ non-interacting bosons are confined in a spherically symmetric potential well $U(\mathbf{r}) = m\omega^2 r^2/2$. Develop the theory of the Bose-Einstein condensation in this system; in particular, prove Eq. (3.74b) of the lecture notes and calculate the critical temperature T_c^*. Looking at the solution, what is the most straightforward way to detect the condensation in experiment?

Solution: A well-known quantum-mechanical analysis[182] of single particle's motion in such a potential well (frequently called the *3D harmonic oscillator*) has the following energy spectrum:

$$\varepsilon_{n_x,n_y,n_z} = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right),$$

where the quantum numbers n_x, n_y, and n_z may take independent non-negative integer values starting from 0. Just as it was done in the solution of the previous problem, we may use the Bose-Einstein

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[182] See, e.g., QM Sec. 3.5, in particular Eq. (3.124) with $d = 3$.

distribution (2.118), with this spectrum, to calculate the average number of particles in the case when the gas is in equilibrium with an environment with temperature T and chemical potential μ:

$$\langle N\rangle = g\sum_{n_x,n_y,n_z=0}^{\infty}\left[\exp\left\{\frac{\varepsilon_{n_x,n_y,n_z}-\mu}{T}\right\}-1\right]^{-1} \equiv g\sum_{n_x,n_y,n_z=0}^{\infty}\left[\exp\left\{\frac{\hbar\omega\left(n_x+n_y+n_z+3/2\right)-\mu}{T}\right\}-1\right]^{-1},$$

where g is the spin degeneracy of each "orbital" state. Using the standard arguments for the transfer from the grand canonical to the canonical ensemble, quantitatively correct in the limit $N \gg 1$, and taking the chemical potential μ equal to the ground-state single-particle energy ε_g (in our current case, equal to $\varepsilon_{0,0,0} = (3/2)\hbar\omega$), we get the following equation for the critical temperature T_c^*:

$$N = g\sum_{n_x,n_y,n_z=0}^{\infty}\left[\exp\left\{\frac{\hbar\omega}{T_c^*}\left(n_x+n_y+n_z\right)\right\}-1\right]^{-1}. \qquad (*)$$

This sum converges as soon as the magnitude of the argument under the exponent becomes much larger than 1, i.e. at $n \equiv n_x + n_y + n_z \sim n_{\max} \equiv T_c^*/\hbar\omega$. Since the first, most significant terms of the sum are of the order of 1, the sum as a whole may be estimated as $n^3_{\max}$, so Eq. (*) gives the following estimate:

$$N \sim g n^3_{\max} \equiv \left(\frac{T_c^*}{\hbar\omega}\right)^3, \qquad \text{i.e. } T_c^* \sim \hbar\omega\left(\frac{N}{g}\right)^{1/3}. \qquad (**)$$

But since $N \gg 1$ and $g \sim 1$, $(N/g)^{1/3}$ is much larger than 1 as well. This means that T_c^* is much larger than $\hbar\omega$, i.e. the distance between the adjacent energy levels (which differ by a unit change of one of the quantum numbers). Hence at $T \sim T_c^*$, many lower levels are populated, so the sum (*) may be well approximated by an integral.

As a result of this approximation, the equation for the critical temperature takes the form

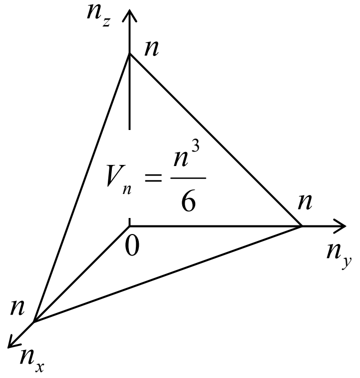
$$N = g\int_0^{\infty} dn_x \int_0^{\infty} dn_y \int_0^{\infty} dn_z \left[\exp\left\{\frac{\hbar\omega}{T_c^*}\left(n_x+n_y+n_z\right)\right\}-1\right]^{-1} = g\int_{n_x,n_y,n_z\geq 0}\left[\exp\left\{\frac{\hbar\omega}{T_c^*}\left(n_x+n_y+n_z\right)\right\}-1\right]^{-1} d^3n,$$

where $d^3n \equiv dn_x dn_y dn_z$ is an elementary volume of the state number space $\{n_x, n_y, n_z\}$. Since the function under the integral depends only on one linear combination, $n \equiv n_x + n_y + n_z$, of the Cartesian coordinates of this space, it is convenient to select the differential d^3n in the form[183]

$$d^3n = dV_n = d\left(\frac{n^3}{6}\right) \equiv \frac{n^2}{2}dn$$

(see the figure on the right), so our 3D integral reduces to a 1D one:

$$N = g\int_0^{\infty}\left[\exp\left\{\frac{\hbar\omega}{T_c^*}n\right\}-1\right]^{-1}\frac{n^2 dn}{2}.$$



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[183] This calculation is similar to the one in Sec. 2.2 of the lecture notes – see Fig. 2.3c and also Eq. (2.40) with N = 3.

With the integration variable replacement $\xi \equiv (\hbar\omega/T_c^*)n$, this equation takes the form

$$N = \frac{g}{2}\left(\frac{T_c^*}{\hbar\omega}\right)^3 \int_0^\infty \frac{\xi^2 d\xi}{e^\xi - 1}. \qquad (***)$$

This table integral[184] equals $\Gamma(3)\zeta(3) \equiv 2\zeta(3) \approx 2.404$, so, finally, we get

$$N = \zeta(3) g \left(\frac{T_c^*}{\hbar\omega}\right)^3, \qquad \text{i.e. } T_c^* = \hbar\omega\left(\frac{N}{g\zeta(3)}\right)^{1/3} \approx 0.9405\ \hbar\omega\left(\frac{N}{g}\right)^{1/3},$$

in agreement with our initial estimate (**).

A comparison of this expression with Eqs. (3.35) and (3.71) of the lecture notes (which are valid for the hard-confinement case) shows that the dependence of the critical temperature on the number of particles at the soft confinement is substantially weaker: $T_c^* \propto N^{1/3}$ vs. $T_c \propto N^{2/3}$. This is natural because the effective radius R of the confined gas cloud, which may be estimated from the relation

$$U \sim \frac{m\omega^2 R^2}{2} \sim \frac{T}{2}, \qquad (****)$$

and hence its effective volume $V_{ef} \sim R^3$, now grows with temperature, and hence (at $T \sim T_c^*$) with N.

The difference between the two confinement types also manifests itself in a different dependence of the condensed particle number N_0 on the temperature at $T \leq T_c^*$. Indeed, using the same argumentation as was used for the spatially uniform system (i.e. for the ultimately rigid particle confinement) in Sec. 3.4 of the lecture notes,[185] we may get this dependence from Eq. (***) by the replacements $N \to (N - N_0)$ and $T_c^* \to T$:

$$N - N_0 = \frac{g}{2}\left(\frac{T}{\hbar\omega}\right)^3 \int_0^\infty \frac{\xi^2 d\xi}{e^\xi - 1}, \qquad \text{at } T \leq T_c^*.$$

Now combining this expression with Eq. (***), we get Eq. (3.74b) of the lecture notes (which was presented there without proof):

$$N_0 = N\left[1 - \left(\frac{T}{T_c^*}\right)^3\right], \quad \text{for } T \leq T_c^*.$$

The reader is encouraged to explore other differences between BEC features at the soft and rigid confinement, but I will limit this solution to answering the last question of the assignment. According to the estimate (****), the optically visible area of all the gas cloud above but close to T_c^*, and hence of its uncondensed fraction just below the critical temperature, is of the order of

$$A \sim R^2 \sim \frac{T}{m\omega^2} \sim \frac{T_c^*}{m\omega^2} \sim \frac{\hbar}{m\omega}\left(\frac{N}{g}\right)^{1/3}.$$

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[184] See, e.g., MA Eq. (6.8b) with $s = 3$, and then Eqs. (2.7b) and (6.7c).

[185] In particular, see Eqs. (3.72) and (3.73).

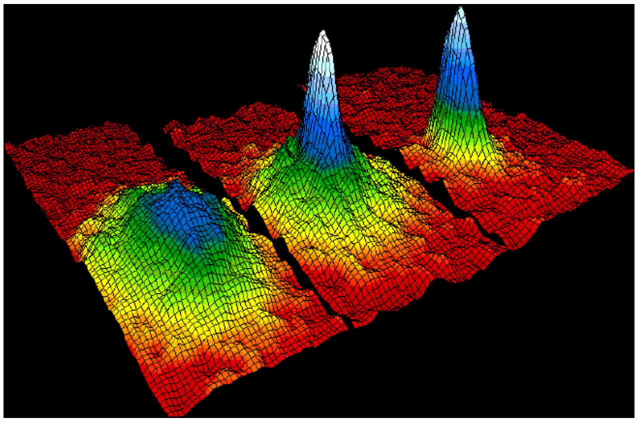
However, all particles of the condensed fraction of the gas, at $T < T_c^*$, are in their ground state, with energy $\varepsilon_g \equiv \varepsilon_{0,0,0} = (3/2)\hbar\omega$, so the radius R_c of their cloud should be estimated not from Eq. (****), but from the relation

$$U_c \sim \frac{m\omega^2 R_c^2}{2} \sim \varepsilon_g = \frac{3\hbar\omega}{2},$$

giving the visible area

$$A_c \sim R_c^2 \sim \frac{3\hbar}{m\omega} \sim \frac{3A}{(N/g)^{1/3}} << A, \qquad \text{for } N >> 1.$$

As a result, the most direct manifestation of the Bose-Einstein condensation, at soft confinement, is the appearance, at $T < T_c^*$, of a small, dense "blob" on the optical image of the gas, on the background of a larger cloud of the still uncondensed gas – see, e.g., the figure on the right, taken from the pioneering paper by M. Anderson *et al.*, *Science*, **269**, 198 (1995).[186]



Problem 3.26. Calculate the chemical potential of a uniform ideal 2D gas of spin-0 Bose particles as a function of its areal density n (the number of particles per unit area), and find out whether such gas can condense at low temperatures. Review your result for the case of a large ($N >> 1$) but finite number of particles.

Solution: As was already discussed in the solutions of Problems 8 and 20, the density $g_2(\varepsilon)$ of 2D quantum states is independent of the particle energy ε:

$$g_2(\varepsilon) = \frac{dN_{\text{states}}}{dE} = \frac{gA}{(2\pi\hbar)^2}\frac{d^2p}{d(p^2/2m)} = \frac{gA}{(2\pi\hbar)^2}\frac{2\pi p dp}{p dp/m} = \frac{gmA}{2\pi\hbar^2},$$

where $g = 2s + 1$ is the spin degeneracy factor, which is equal to 1 in our current case of spin-0 particles. Hence the number of particles inside area A may be calculated as

$$N = \frac{mA}{2\pi\hbar^2}\int_0^\infty \frac{d\varepsilon}{e^{(\varepsilon-\mu)/T}-1} = \frac{mA}{2\pi\hbar^2}T\int_{-\mu/T}^{\infty}\frac{d\xi}{e^{\xi}-1}, \qquad (*)$$

where $\xi \equiv (\varepsilon - \mu)/T$. This is a table integral,[187] giving

$$N = \frac{mA}{2\pi\hbar^2}T\ln\frac{1}{1-\exp\{\mu/T\}},$$

so the chemical potential is

$$\mu = T\ln\left(1-\exp\left\{-\frac{2\pi\hbar^2 n}{mT}\right\}\right), \qquad \text{with } n \equiv \frac{N}{A}.$$

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[186] Adopted from https://en.wikipedia.org/wiki/Bose-Einstein_condensate as a public-domain material.

[187] See, e.g., MA Eq. (6.4b).

Since the exponential function in this expression is between 0 and 1 for any gas density n and temperature T, the argument of the logarithm is always below 1, so the logarithm is negative, and hence the chemical potential is negative for all $T > 0$. Hence the Bose-Einstein condensation (which requires $\mu = 0$) is impossible in a uniform 2D gas. This fact might be evident already from the very beginning because, at $\mu = 0$, the integral (*) diverges at its lower limit. (This argument does not hold in 3D where the different dependence of the density of states on the particle energy, $g_3(\varepsilon)$, provides an extra factor of $\varepsilon^{1/2}$ in the numerator of the function under the integral, preventing its divergence at $\mu = 0$, and hence making compatible with the 3D Bose-Einstein condensation.)

Note, however, that this conclusion ($T_c = 0$) is strictly valid only in the limit $N \to \infty$ (and hence $A \to \infty$) because the divergence of the integral (*) at the lower limit at $\mu = 0$ is very weak (logarithmic), and may be cut off by virtually any factor. In particular, a large but finite area A of the gas-confining box keeps the particle energy quantized on a fine scale $\varepsilon_{\min} \sim \pi^2\hbar^2/2mA$, corresponding to $\xi_{\min} \sim \pi^2\hbar^2/2mAT_c << 1$. With this modification, Eq. (*) gives for T_c the following transcendental equation

$$N \approx \frac{mAT_c}{2\pi\hbar^2}\ln\frac{2mAT_c}{\pi^2\hbar^2},$$

where the argument of the logarithm is approximate. (What approximation is used for it does not make much difference because the logarithm's argument is very large, and the log function of a large argument is extremely insensitive to its modest change.) An approximate (with the so-called *logarithmic accuracy*) solution of this equation is

$$T_c \approx \frac{2\pi\hbar^2 n}{m}\frac{1}{\ln N},$$

So, at a fixed density $n \equiv N/A$, T_c indeed tends to zero at $N \to \infty$ but extremely slowly.

In this context, note that the very notion of the Bose-Einstein condensation (and, more generally, of *any* phase transition) makes full sense only in the limit $N \to \infty$. Indeed, as the solutions of the last three problems indicate very clearly, if the number of particles in a system is finite, the reduction of temperature leads "merely" to their gradual accumulation in some low-entropy state – in the BEC case, on the lowest, ground-state energy level. The whole idea of a phase transition (more exactly, of a *continuous* phase transition – see Chapter 4 for discussion) is that at $N >> 1$, most of this accumulation happens within a very narrow temperature interval near some temperature called T_c. At any finite N, this interval is always nonvanishing and gradually broadens with the reduction of N.

Problem 3.27. Can the Bose-Einstein condensation be achieved in a 2D system of $N >> 1$ non-interacting bosons placed into the axially symmetric potential well $U(\rho) = m\omega^2\rho^2/2$, where ρ is the 2D radius vector in the particle confinement plane? If yes, calculate the critical temperature of the condensation.

Solution: With the natural change from 3D to 2D, Eq. (*) of the model solution of Problem 25 for the critical temperature T_c^* of the gas becomes

$$N = g\sum_{n_x,n_y=0}^{\infty}\left[\exp\left\{\frac{\hbar\omega}{T_c^*}\left(n_x + n_y\right)\right\} - 1\right]^{-1}, \qquad (*)$$

where g is the particle spin degeneracy. Such a sum converges as soon as the magnitude of the argument under the exponent becomes much larger than 1, i.e. at $n \equiv n_x + n_y \sim n_{\max} \equiv T_c^*/\hbar\omega$. Since the first, most significant terms of the sum are of the order of 1, the sum itself may be estimated as $n_{\max}^2$, so Eq. (*) gives the following estimate:

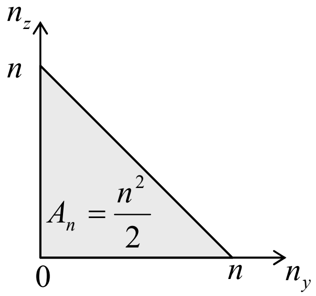
$$N \sim g n_{\max}^2 \equiv g\left(\frac{T_c^*}{\hbar\omega}\right)^2, \qquad \text{i.e. } T_c^* \sim \hbar\omega\left(\frac{N}{g}\right)^{1/2}. \qquad (**)$$

In order to calculate T_c* quantitatively, we may again use the strong inequality $N >> 1$ to justify the transition from the sum (*) to the integral

$$N = g\int_0^\infty dn_x \int_0^\infty dn_y \left[\exp\left\{\frac{\hbar\omega}{T_c^*}\left(n_x + n_y\right)\right\} - 1\right]^{-1} = g\int_{n_x, n_y \geq 0}\left[\exp\left\{\frac{\hbar\omega}{T_c^*}\left(n_x + n_y\right)\right\} - 1\right]^{-1} d^2n,$$

where $d^2n \equiv dn_x dn_y$ is an elementary area on the plane of quantum numbers $\{n_x, n_y\}$. Since the function under the integral depends only on one linear combination, $n \equiv n_x + n_y$, of the Cartesian coordinates of this space, we may select the differential d^2n in the form,[188]

$$d^2n = dA_n = d\left(\frac{n^2}{2}\right) \equiv ndn$$



(see the figure on the right), so our 2D integral reduces to a 1D one:

$$N = g\int_0^\infty \left[\exp\left\{\frac{\hbar\omega}{T_c^*}n\right\} - 1\right]^{-1} ndn .$$

With the integration variable replacement $\xi \equiv (\hbar\omega/T_c^*)\, n$, this equation takes the form

$$N = g\left(\frac{T_c^*}{\hbar\omega}\right)^2 \int_0^\infty \frac{\xi\, d\xi}{e^\xi - 1}.$$

This table integral[189] equals $\Gamma(2)\zeta(2) \equiv \pi^2/6$, so, finally, we get

$$N = g\frac{\pi^2}{6}\left(\frac{T_c^*}{\hbar\omega}\right)^2, \qquad \text{i.e. } T_c^* = \frac{\hbar\omega}{\pi}\left(\frac{6N}{g}\right)^{1/2},$$

in agreement with the estimate (**).

This expression shows that just as in a similar 3D system (see Problem 25), if the frequency ω of the effective 2D harmonic oscillator formed by each particle in the quadratic potential is nonvanishing, the critical temperature is different from zero as well. This fact does not contradict the solution of the previous problem, because the *free* (uniform) 2D gas analyzed there may be considered as the ultimate limit of the soft confinement with $\omega \to 0$ and hence with $T_c^* \to 0$.

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[188] This is essentially the same calculation that had been done in Sec. 2.2 of the lecture notes – see Fig. 2.3b, and also Eq. (2.40) with $N = 2$.

[189] See, e.g., MA Eq. (6.8b) with $s = 2$, and then Eq. (2.7b).

Problem 3.28. Use Eqs. (3.115) and (3.120) of the lecture notes to calculate the third virial coefficient $C(T)$ for the hardball model of particle interactions.

Solution: According to Eq. (3.120),

$$C(T) = \left(\frac{J_2^2}{J_1^2} - \frac{J_3}{3J_1} \right) V^2 ,$$

where, per Eq. (3.115),

$$J_1 = 1, \qquad J_2 = \frac{1}{V} \int \left(e^{-U(\mathbf{r})/T} - 1 \right) d^3 r \qquad J_3 = \frac{1}{V^2} \int \mathscr{F}(\mathbf{r}', \mathbf{r}'') d^3 r' d^3 r'',$$

$$\text{with } \mathscr{F}(\mathbf{r}', \mathbf{r}'') \equiv \exp\left\{ -\frac{U(\mathbf{r}', \mathbf{r}'')}{T} \right\} - \exp\left\{ -\frac{U(\mathbf{r}')}{T} \right\} - \exp\left\{ -\frac{U(\mathbf{r}'')}{T} \right\} - \exp\left\{ -\frac{U(\mathbf{r}''')}{T} \right\} + 2.$$

and the letters **r** denote the interparticle displacement vectors shown in Fig. 3.6b of the lecture notes – see also two figures below. (Note that $\mathbf{r}''' \equiv \mathbf{r}' - \mathbf{r}''$ is not an independent argument.)

For the hardball model, the integral J_2 is contributed only by the spatial region $r < 2r_0$, in which two spheres outlining the hardballs overlap, and essentially was calculated in the lecture notes – see the derivation of Eq. (3.96):

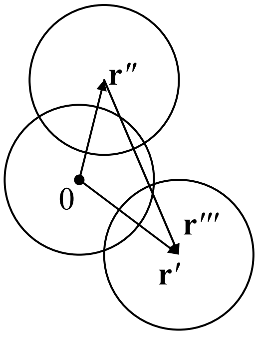
$$J_2 = -8 \frac{V_0}{V},$$

where $V_0 = (4\pi/3) r_0^3$ is the particle's volume. Similarly, the integral J_3 is contributed only by those regions of the 6D space $d^3\mathbf{r}' d^3\mathbf{r}''$ in that all three spheres overlap. (Indeed, if just two of them overlap, for example, if $r' < 2r_0$ but r'', $r''' > 2r_0$, then $U(\mathbf{r}', \mathbf{r}'') = U(\mathbf{r}') = \infty$, while $U(\mathbf{r}'') = U(\mathbf{r}''') = 0$, so $\mathscr{F} = 0 - 0 - 1 - 1 + 2 = 0$.) There are two options here:

(i) Two pairs of the three spheres overlap but the third pair does not, for example

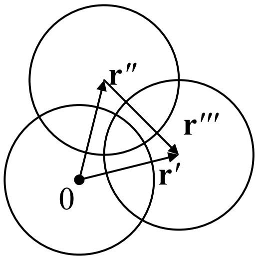
$$r', r'' < 2r_0, \quad r''' > 2r_0,$$

for example, as shown in the top figure on the right. In this region, whose 6D volume will be called W_i, $U(\mathbf{r}', \mathbf{r}'') = U(\mathbf{r}') = U(\mathbf{r}'') = \infty$, while $U(\mathbf{r}''') = 0$, so $\mathscr{F} = 0 + 0 + 0 - 1 + 2 = 1$, and the region's contribution to J_3 equals W_i/V^2. Since there are three similar regions like this (which differ by the choice of the pair of spheres that do not overlap), their total contribution to J_3 is $3W_\text{i}/V^2$.



(ii) All three spheres overlap, for example as shown in the bottom figure on the right:

$$r', r'', r''' < 2r_0 .$$

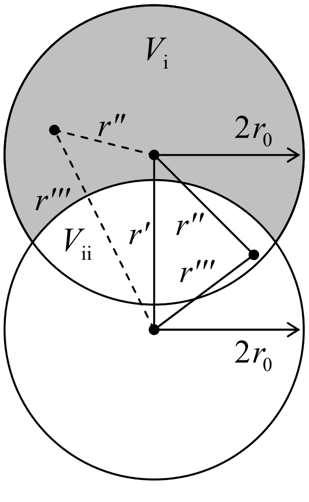


Here all potentials U are infinite, and $\mathscr{F} = 0 + 0 + 0 + 0 + 2 = 2$, so this 6D volume ($W_\text{ii}$) contributes to J_3 with the coefficient 2.

As a result, the total integral

$$J_3 = \frac{3W_\text{i} + 2W_\text{ii}}{V^2},$$

and we need only to calculate two 6D volumes: W_i and W_ii.

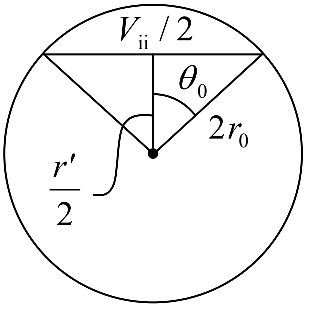


First of all, let us exploit the spherical symmetry of the problem with respect to the rotation of one of the displacement vectors (say, **r**'), provided that the second vector is rotated together with it:

$$W_{\text{i}} \equiv \int\limits_{\substack{r',r''<2r_0\\ r'''>2r_0}} d^3r'd^3r'' = 4\pi\int_0^{2r_0} r'^2dr'V_{\text{i}}(r'), \quad \text{with } V_{\text{i}}(r') \equiv \int\limits_{\substack{r''<2r_0\\ r'''>2r_0}} d^3r'',$$

$$W_{\text{ii}} \equiv \int\limits_{r',r'',r'''<2r_0} d^3r'd^3r'' = 4\pi\int_0^{2r_0} r'^2dr'V_{\text{ii}}(r'), \quad \text{with } V_{\text{ii}}(r') \equiv \int\limits_{r'',r'''<2r_0} d^3r'',$$

so the internal integrals V_{i} and V_{ii} may be worked out considering the direction of the vector **r**' fixed – say, vertical. The top figure on the right shows the geometrical sense of these integrals: V_{i} is just the volume shown in gray, while V_{ii} is its complement to the volume $8V_0$ of the sphere of radius $2r_0$: $V_{\text{i}} + V_{\text{ii}} = 8V_0$.



Thus the problem is reduced to a bit bulky but elementary 3D geometry: as shown in the bottom figure on the right, $V_{\text{ii}}/2$ is just the volume of a spherical sector with the polar angle $\theta_0 = \cos^{-1}(r'/4r_0)$, which may be calculated as the difference between the volumes of the spherical cone,

$$V_{\text{spherical cone}} = \frac{(2r_0)^3}{3}2\pi\int_0^{\theta_0}\sin\theta d\theta = \frac{(2r_0)^3}{3}2\pi\left(1-\frac{r'}{4r_0}\right) = 4V_0(1-\xi),$$

where $\xi \equiv r'/4r_0 = \cos\theta_0$, and the flat-base cone with the same polar angle and the height $h = r'/2$:

$$V_{\text{flat-base cone}} = \frac{1}{3}Ah = \frac{1}{3}\pi\left[(2r_0)^2 - \left(\frac{r'}{2}\right)^2\right]\frac{r'}{2} = 2V_0\left(1-\xi^2\right)\xi.$$

As a result, we get

$$V_{\text{ii}} = 2\left(V_{\text{spherical cone}} - V_{\text{flat-base cone}}\right) = 2\left[4V_0(1-\xi) - 2V_0\left(1-\xi^2\right)\xi\right] = 4V_0\left(2-3\xi+\xi^3\right),$$

$$V_{\text{i}} = 8V_0 - V_{\text{ii}} = 4V_0\left(3\xi-\xi^3\right), \qquad 3V_{\text{i}} + 2V_{\text{ii}} = 4V_0\left(4+3\xi-\xi^3\right).$$

Now we can complete the calculation of the 6D integral J_3,

$$J_3 = \frac{1}{V^2}\left(3W_{\text{i}} + 2W_{\text{ii}}\right) = \frac{1}{V^2}4\pi\int_0^{2r_0} r'^2dr'\left(3V_{\text{i}}+2V_{\text{ii}}\right) = \frac{1}{V^2}4\pi(4r_0)^3\int_0^{1/2}\xi^2d\xi\,\frac{16\pi}{3}r_0^3\left(4+3\xi-\xi^3\right)$$

$$= \frac{1}{V^2}\frac{2^{12}\pi^2}{3}r_0^6\left[4\cdot\frac{(1/2)^3}{3} + 3\cdot\frac{(1/2)^4}{4} - \frac{(1/2)^6}{6}\right] = \frac{1}{V^2}288\pi^2r_0^6 = 162\frac{V_0^2}{V^2},$$

and hence of the third virial coefficient:

$$C(T) = \left(\frac{J_2^2}{J_1^2} - \frac{J_3}{3J_1}\right)V^2 = (64-54)V_0^2 \equiv 10V_0^2.$$

In the hardball model, this coefficient is (quite naturally) temperature-independent.[190] Just for the reader's reference, the 4th virial coefficient (calculated analytically by L. Boltzmann) is approximately 18.36 V_0^3, the 5th one (calculated only numerically) is close to 28.2 V_0^4, etc., with the numerical factors before V_0^{k-1} growing rather slowly with the coefficient number k.

Problem 3.29. Assuming the hardball model, with volume V_0 per molecule, for the liquid phase, describe how the results of Problem 7 change if the liquid forms spherical drops of radius $R >> V_0^{1/3}$. Briefly discuss the implications of the result for water cloud formation in the atmosphere.

Hint: Surface effects in a macroscopic volume of a liquid may be well described by attributing an additional energy γ (equal to the surface tension) to the unit surface area.[191]

Solution: In the limit $R >> V_0^{1/3}$, when the number N of molecules in each drop is large, its radius may be calculated from the relation

$$N = \frac{4\pi}{3}\frac{R^3}{V_0}, \qquad \text{giving } R = \left(\frac{3V_0}{4\pi}\right)^{1/3} N^{1/3}. \qquad (*)$$

In the same limit, the drop surface area is

$$A = 4\pi R^2 = 4\pi \left(\frac{3V_0}{4\pi}\right)^{2/3} N^{2/3}.$$

Adding one molecule to the drop increases its area by

$$\Delta A \approx \frac{\partial A}{\partial N} = 4\pi \left(\frac{3V_0}{4\pi}\right)^{2/3} \frac{2}{3} N^{-1/3};$$

plugging into this expression the N from the first of Eqs. (*), we get $\Delta A = 2V_0/R$. Due to the surface increase, and the resulting increase of the surface energy γA, the total difference of molecular energy between the liquid and gaseous phases is now not just $-\Delta$ as was assumed in Problem 7 (and it is as at $R \to \infty$ in our current model), but rather

$$-\Delta' = -\Delta + \gamma\Delta A = -\Delta + \frac{2\gamma V_0}{R}. \qquad (**)$$

Now by repeating the arguments given in the model solution of Problem 7 but with this modification, we see that the saturated pressure $P(T)$ calculated there has to be multiplied by the additional factor

$$\kappa(R) = \exp\left\{\frac{2\gamma V_0}{RT}\right\}.$$

Though this result is quantitatively valid only for $R >> V_0^{1/3}$, qualitatively it works even for few-molecule droplets ("clusters"), enabling a semi-quantitative discussion of cloud formation dynamics. As an air mass with a certain concentration n of water molecules rises up in the atmosphere and as a result, is cooled down, the saturated pressure value $P(T)$ as calculated in Problem 7, which is a nearly exponential function of temperature, drops down to the actual partial pressure of the water vapor, still

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[190] As a reminder, so is the 2nd virial coefficient, $B(T) = -(J_2/2J_1)V = 4V_0$ – see Eq. (3.96) of the lecture notes.

[191] See, e.g., CM Sec. 8.2.

behaving almost as an ideal gas, $P \approx nT$. However, since the mass lacks the liquid phase, in the absence of other condensation centers, the water liquefaction cannot start. Only when the temperature is decreased to the level when the product $\kappa(R)P(T)$, of the order of $\kappa(V_0^{1/3})P(T)$, approaches nT, the first random droplets form. Since, according to Eq. (**), the energy gain Δ' at the condensation is largest for larger drops, they start to accumulate more molecules, thus growing in size and suppressing the average effective pressure $\kappa(R)P(T)$, so smaller droplets start to evaporate. In the absence of gravity, this competition would result in the formation of one gigantic liquid "drop" with negligible curvature. However, gravity forces larger drops, as soon as they have been formed, to go down. (This fall does not necessarily result in rain/snow because after reaching the lower, warmer atmosphere layers, the drops may evaporate again, leading to the formation of a dynamically equilibrium cloud.)

Problem 3.30. A 1D *Tonks' gas* is a set of N classical hard rods of length l, confined to a segment of length $L > Nl$ but otherwise free to move along it, in thermal equilibrium at temperature T.

(i) Calculate the system's average internal energy, entropy, both heat capacities, and the average force $\mathscr{F}$ exerted by the rods on the "walls" confining them to the segment L.

(ii) Expand the calculated equation of state $\mathscr{F}(L,T)$ into the Taylor series in the linear density N/L of the rods, find all virial coefficients, and compare the 2nd of them with the result following from the 1D version of Eq. (3.93) of the lecture notes.

Solutions:

(i) Just as was done in Eq. (3.88), we may factor the statistical sum of the system into a kinetic-energy multiplier (which is the same as for a free 1D ballistic motion of each rod[192])

$$\left(\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty}\exp\left\{-\frac{p^2}{2mT}\right\}dp\right)^N = \left(\frac{mT}{2\pi\hbar}\right)^{N/2}$$

and a potential-energy multiplier, in our current 1D case:

$$Z_N = \int_{x_k\subset L}\exp\left\{-\frac{U(x_1,...,x_k,...,x_N)}{T}\right\}dx_1...dx_k...dx_N .$$

Here x_k is the coordinate of a certain point of the k^{th} rod (for example, the distance of its left end from the left "wall" of the segment) and U is the hard rod interaction energy similar to that given by Eq. (3.97):

$$U(x_1,x_2,...,x_N) = \begin{cases} +\infty, & \text{if any } |x_k - x_{k-1}| < l, \\ 0, & \text{otherwise.}\end{cases}$$

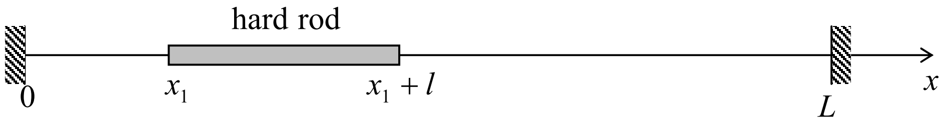
As a result, the expression for Z_N reduces to

$$Z_N = \int_{\substack{\text{all } x_k+l<x_{k+1};\\ 0<x_1;\ x_N<L-l}} dx_1...dx_k...dx_N .$$

---

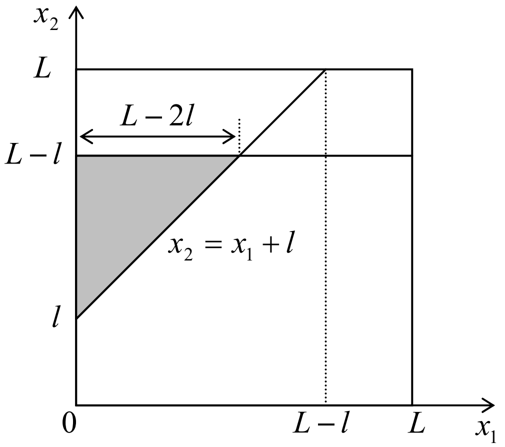
[192] This is just the 1D version of Eq. (3.15), with $g = 1$ and without the "correct Boltzmann counting" term $1/N!$ (In our 1D classical case, it is natural to assume that the rods keep their initial order, i.e. are distinguishable even if they are identical.)

In order to calculate the N-dimensional volume described by the last integral, let us start with the simplest case $N = 1$ – see the figure below.



The figure shows that in this case, the above conditions for x_k are reduced to $0 < x_1 < L - l$, so the 1D volume contributing to Z_1 equals $L - l$:

$$Z_1 = \int_0^{L-l} dx_1 = L - l.$$



Next, for $N = 2$, the conditions may be conveniently represented on the $[x_1, x_2]$-plane – see the figure on the right. The shaded region, where the above conditions (which are now reduced to $0 < x_1 < L - 2l$; $x_1 + l < x_2 < L - l$) are satisfied is a right triangle with both short sides equal to $(L - 2l)$, so its area is $(L - 2l)^2/2$. This result may be readily confirmed by an explicit integration:

$$Z_2 = \int_0^{L-2l} dx_1 \int_{x_1+l}^{L-l} dx_2 = \frac{1}{2}(L-2l)^2.$$

From these two particular results, Z_N may be already guessed, but to make the result even more clear, we may explicitly calculate

$$Z_3 = \int_0^{L-3l} dx_1 \int_{x_1+l}^{L-2l} dx_2 \int_{x_2+l}^{L-l} dx_3 = \frac{1}{6}(L-3l)^3.$$

From here, it should be obvious that

$$Z_N = \frac{1}{N!}(L-Nl)^N$$

– which is just the volume of an N-dimensional right pyramid with the side $(L - Nl)$.[193] By multiplying this result by the kinetic-energy factor, we get the full statistical sum of the system (or rather of its part related due to the rod motion and collisions):

$$Z = \frac{1}{N!}\left(\frac{mT}{2\pi\hbar}\right)^{N/2}(L-Nl)^N.$$

Now, the key formula (2.63) immediately gives the free energy of the system:

$$F = -T\ln Z = -T\left[\frac{N}{2}\ln\frac{mT}{2\pi\hbar} + N\ln(L-Nl) - \ln N!\right]. \qquad (*)$$

From here and the 1D version of the second of Eqs. (1.35), the average force exerted by the rods on the "walls" limiting the interval $[0, L]$ is[194]

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[193] Cf. the derivation of Eq. (2.40) in Sec. 2.2 of the lecture notes.

$$\mathscr{F} = -\left(\frac{\partial F}{\partial L}\right)_T = \frac{NT}{L - Nl}. \qquad (**)$$

Note that this equation of state is exact (within this model) and valid not only for any (not necessarily large!) integer number N of rods but also for an arbitrary value of the difference $L - Nl > 0$. In the limit $Nl \ll L$, when the rod interaction effects vanish, it reduces to the 1D version of Eq. (3.18) for an ideal classical gas:

$$\mathscr{F} = \frac{NT}{L}, \qquad \text{for } l \to 0.$$

Rewriting the general Eq. (**) in terms of the linear density N/L of the rods,

$$\mathscr{F} = \frac{NT}{L}\frac{1}{1 - l(N/L)},$$

and expanding it into the Taylor series in the dimensionless parameter $l(N/L)$, we get

$$\mathscr{F} = \frac{NT}{L}\left[1 + \left(l\frac{N}{L}\right) + \left(l\frac{N}{L}\right)^2 ...\right] \equiv T\left[\frac{N}{L} + l\left(\frac{N}{L}\right)^2 + l^2\left(\frac{N}{L}\right)^3 ...\right]. \qquad (***)$$

Comparing this expansion with the definition (3.100) of the virial coefficients, adjusted for the 1D case,

$$\mathscr{F} = T\left[\frac{N}{L} + B(T)\left(\frac{N}{L}\right)^2 + C(T)\left(\frac{N}{L}\right)^3 + ...\right],$$

we see that $B(T) = l$, and $C(T) = l^2$, etc.

Now reviewing the derivation of Eq. (3.93) in Sec. 3.5, we see that its 1D version is

$$B(T) = \frac{1}{2}\int\left(1 - e^{-U(x)/T}\right)dx, \qquad (****)$$

where x is the distance between the centers of the two adjacent rods, and $U(x)$ is the potential of their interaction. In the hard-rod model explored in our current problem,

$$U(x) = \begin{cases} +\infty, & \text{for } |x| < l, \\ 0, & \text{otherwise,} \end{cases} \qquad \text{i.e. } 1 - e^{-U(x)/T} = \begin{cases} 1, & \text{for } |x| < l, \\ 0, & \text{otherwise.} \end{cases}$$

With this substitution, Eq. (****) yields

$$B(T) = \frac{1}{2}\int_{-l}^{+l} dx = l,$$

in agreement with the general expansion (***).

In order to complete our assignments, we may use Eq. (*), together with the first of Eqs. (1.35), to calculate the system's entropy

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[194] Due to the absence of the acceleration of the system as a whole, this $\mathscr{F}$ is also the average force of repulsion of any two adjacent rods.

$$S = -\left(\frac{\partial F}{\partial T}\right)_L = \frac{N}{2}\left(\ln\frac{mT}{2\pi\hbar} + 1\right) + N\ln(L - Nl) - \ln N! \ .$$

From here, Eq. (1.33) gives a very simple result for the average internal energy of the system:

$$E = F + ST = \frac{NT}{2},$$

and hence for its heat capacity at constant L:

$$C_L \equiv \left(\frac{\partial E}{\partial T}\right)_L = \frac{N}{2}.$$

This means that (as we could expect from the discussion at the very end of Sec. 3.5 of the lecture notes) the hard-rod interactions do not contribute to the average energy, so it obeys the equipartition theorem for the kinetic energy alone.

Finally, to calculate the heat capacity at constant $\mathscr{F}$, we need to find the enthalpy and express it via the average force $\mathscr{F}$ and temperature T, by using Eq. (**) to eliminate L:

$$H \equiv E + \mathscr{F}L = \frac{NT}{2} + \mathscr{F}\left(\frac{NT}{\mathscr{F}} - Nl\right) \equiv \frac{3NT}{2} - \mathscr{F}Nl,$$

so

$$C_{\mathscr{F}} \equiv \left(\frac{\partial H}{\partial T}\right)_{\mathscr{F}} = \frac{3N}{2}.$$

Hence the difference $C_V - C_P = N$ is not affected by the reduced dimensionality of the system.

To summarize, the 1D version of the hard-core gas problem allows a simple and exact analytical solution – in contrast with its 3D sibling discussed in Sec. 3.5 of the lecture notes. As the solution shows, the reason is the relatively simple topology of the phase space of the rod system (more specifically, of its N-dimensional coordinate sub-space), which, in particular, does not allow the classical rods to exchange their positions.

Chapter 4. Phase Transitions

Problem 4.1. Calculate the entropy, the internal energy, and the specific heat c_V of the van der Waals gas, and discuss the results. For the gas with a temperature-independent c_V, find the relation between V and T during an adiabatic process.

Solution: Acting just as in Sec. 1.4 of the lecture notes for the ideal classical gas, we get the free energy

$$F = -\int PdV\Big|_{T=\text{const}} = -\int\left(\frac{NT}{V-Nb} - a\frac{N^2}{V^2}\right)dV\Big|_{T=\text{const}} = -NT\ln(V-Nb) - \frac{aN^2}{V} + Nf(T)\,. \qquad (*)$$

In order to simplify further calculations, let us recall that at $a = b = 0$, the van der Waals model describes the ideal gas, so by adding and subtracting the expression $NT\ln(V/N)$ to/from the right-hand side of Eq. (*), we may recast it into the following form:

$$F = NT\ln\frac{V}{N} + Nf(T) - NT\ln\frac{V-Nb}{V} - \frac{aN^2}{V} \equiv F_{\text{ideal}} - NT\ln\frac{V-Nb}{V} - \frac{aN^2}{V}\,.$$

Now, the remaining calculations are simple:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = S_{\text{ideal}} + N\ln\frac{V-Nb}{V}, \qquad E = F + TS = E_{\text{ideal}} - \frac{aN^2}{V},$$

where S_{ideal} and E_{ideal} are given by Eqs. (1.46)-(1.47) of the lecture notes.

Note that the coefficient b, describing the short-range repulsion of the particles, does not give any correction to the internal energy of the gas, at fixed N, V, and T. This could be expected: we know that the internal energy of an ideal gas does not depend on its volume, so losing some volume (Nb) to collisions does not affect it either.[1] Note that though in the van der Waals gas with $a \neq 0$, the energy acquires some dependence on V, this contribution to E does not affect the specific heat per unit particle:

$$c_V \equiv \frac{1}{N}\left(\frac{\partial E}{\partial T}\right)_V = c_{V\,\text{ideal}} = -T\frac{d^2 f(T)}{dT^2}, \quad \text{so} \quad \left(\frac{\partial c_V}{\partial V}\right)_T = 0.$$

Moreover, note that the long-range interaction constant a, while contributing to E, does not affect the entropy of the gas. This independence extends to the adiabatic process equation. Indeed, by rewriting our result for S as

$$S = S_{\text{ideal}} - N\ln V + N\ln(V - Nb),$$

we see that its only difference with the ideal-gas entropy is the replacement of V with ($V - Nb$). Now reviewing the derivation of the relation

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[1] For the hardball model of the classical gas, which is conceptually similar to the van der Waals gas with $a = 0$, the same conclusion was made at the very end of Sec. 3.5 of the lecture notes, while in the solution of Problem 3.30, the same fact was proved for a similar 1D model.

$$\frac{V}{N}T^{c_V} = \text{const}$$

for an adiabatic process (S = const) for an ideal gas with a temperature-independent c_V,[2] we see that this is the only replacement to be done here as well, so for the van der Waal gas, the requested relation is

$$\frac{V - Nb}{N}T^{c_V} = \text{const}, \qquad \text{for } c_V = \text{const}.$$

Note that all these results (as well as those of the next three solutions) are only valid for a uniform (single-phase) state of the van der Waals "gas", and need to be reviewed for its two-phase state.

Problem 4.2. Use two different approaches to calculate the coefficient $(\partial E/\partial V)_T$ for the van der Waals gas and the change of temperature of such a gas, with a temperature-independent C_V, at its very fast expansion.

Solution:

Approach 1 is to use one of the results of the previous problem's solution:

$$E = E_{\text{ideal}}(T) - \frac{aN^2}{V}. \qquad (*)$$

Since the ideal gas' energy depends on temperature only (see, e.g., Eq. (1.47) of the lecture notes), the partial derivative of E over V, at fixed T, is contributed by the second term alone:

$$\left(\frac{\partial E}{\partial V}\right)_T = a\frac{N^2}{V^2}. \qquad (**)$$

According to this result, this coefficient does not depend on the constant b, i.e. is not contributed by hard-core interaction between the particles, and is determined only by their long-range interaction characterized by the parameter a. (As was discussed in Sec. 3.5 of the lecture notes, for most neutral atomic and molecular gases, this coefficient is positive due to the long-range attraction of the particles.)

Now let us use Eq. (**) to analyze the rapid gas expansion into free space.[3] At such an expansion, the gas does not have time to exchange heat with the environment and is given no chance to perform any mechanical work, so its internal energy E has to stay constant. Applying this condition to Eq. (*) written for the initial (index 1) and the final (index 2) points of gas expansion, we get

$$E_{\text{ideal}}(T_1) - \frac{aN^2}{V_1} = E_{\text{ideal}}(T_2) - \frac{aN^2}{V_2}.$$

If C_V is temperature-independent, then $E_{\text{ideal}}(T_2) - E_{\text{ideal}}(T_1) = C_V\Delta T$, where $\Delta T \equiv T_2 - T_1$ is the temperature change, and we get

$$\Delta T = -\frac{aN^2}{C_V}\left(\frac{1}{V_1} - \frac{1}{V_2}\right).$$

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[2] See, e.g., the solution of Problem 1.5.

[3] Note that this process is different from the relatively slow throttling that was the subject of Problem 1.11, though both processes (and their close siblings) are used for gas cooling and liquefaction.

Since for expansion ($V_2 > V_1$), the expression in the parentheses is positive, for a typical gas with positive a, the change of temperature is negative.

Approach 2. Let us start with the thermodynamic relation whose proof was the last task of Problem 1.8:

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \qquad (***)$$

For the van der Waal equation of state,

$$P = \frac{NT}{V - Nb} - a\frac{N^2}{V^2},$$

it immediately gives Eq. (**) again.

Our second task may be also performed differently. Since the internal energy of any gas, with a fixed number N of particles, is uniquely determined by its temperature and volume, it may be described by a certain function $E(V, T)$. The general differential of this function of two independent arguments is

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV.$$

By definition, the first of these derivatives is just C_V, so

$$dE = C_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV.$$

Per the above discussion of the fast expansion, for this process, we may take $dE = 0$, so, for a gas with constant C_V, the last differential relation gives

$$dT = -\frac{1}{C_V}\left(\frac{\partial E}{\partial V}\right)_T dV,$$

and its integral is

$$\Delta T \equiv T_2 - T_1 = -\frac{1}{C_V}\int_{V_1}^{V_2}\left(\frac{\partial E}{\partial V}\right)_T dV.$$

Now using Eq. (**), and carrying out an easy integration, we get

$$\Delta T = -\frac{aN^2}{C_V}\left(\frac{1}{V_1} - \frac{1}{V_2}\right),$$

i.e. the same result as in the first approach.

Problem 4.3. For real gases, the Joule-Thomson coefficient $(\partial T/\partial P)_H$ (and hence the gas temperature change at its throttling, see Problem 1.11) inverts its sign at crossing the so-called *inversion curve* $T_{\text{inv}}(P)$. Calculate this curve for the van der Waals gas.

Solution: Per the solution of Problem 1.11, the Joule-Thomson coefficient may be expressed as

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right].$$

Since in all stable systems, the heat capacity C_P is positive, the coefficient inverts its sign at

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T}, \qquad \text{i.e.} \left(\frac{\partial T}{\partial V}\right)_P = \frac{T}{V}, \qquad \text{at } T = T_{\text{inv}}. \tag{*}$$

Solving the van der Waals equation (4.2) for temperature:

$$T = \frac{V - Nb}{N}\left(P + a\frac{N^2}{V^2}\right),$$

we may plug this relation into the right-hand side of Eq. (*), while its derivative over V at constant P, into its left-hand side, and in the result, use the van der Waals equation again to eliminate the combination $(P + N^2/V^2)$. The final result is

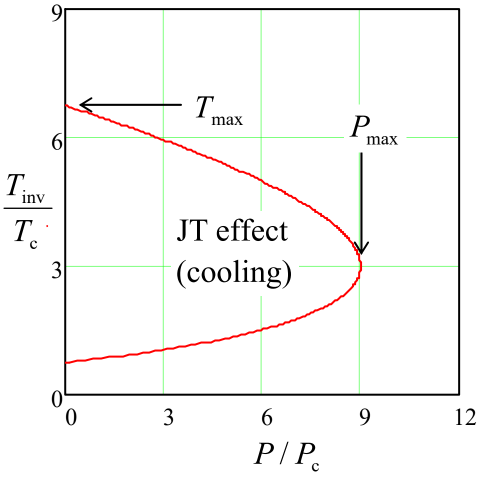
$$T_{\text{inv}} = \frac{2a}{b}\left(\frac{V - Nb}{V}\right)^2. \tag{**}$$

It is more common to express the inversion temperature via pressure rather than volume. By solving Eq. (**) for V and then plugging the result into the van der Waals equation, we get the following relation between P and T_{inv}:

$$P = \left(\frac{8aT_{\text{inv}}}{b^3}\right)^{1/2} - \frac{3T_{\text{inv}}}{2b} - \frac{a}{b^2},$$

which may be more conveniently represented in the normalized variables $p \equiv P/P_c$ and $t \equiv T/T_c$, where P_c and T_c are the critical values of pressure and temperature – see Eq. (4.3) of the lecture notes:

$$p = 24\sqrt{3}\, t_{\text{inv}}^{1/2} - 12t_{\text{inv}} - 27. \tag{***}$$



This relation is a readily solvable quadratic equation for $t_{\text{inv}}^{1/2}$, but it is even simpler to plot and discuss it in its current form – see the figure on the right. The Joule-Thomson coefficient is *positive* (and hence the pressure *reduction* at throttling leads to the gas cooling, i.e. to the Joule-Thomson effect) only in the region enveloped by the inversion curve. As the plot shows, the corresponding temperature range exists if the gas pressure is lower than the rightmost point of the curve: $P_{\max} = 9P_c \equiv a/3b^2$, which is reached at temperature $T = 3T_c \equiv (8/9)\, a/b$. At higher pressures (i.e. on the right of the inversion curve) the coefficient is negative, and hence the gas' expansion results in its heating. Hence, in order to use the throttling for refrigeration, the gas has to be pre-cooled at least below $T_{\max} \equiv T_{\text{inv}}(P = 0)$. Per Eq. (***), $T_{\max} = (27/4)\, T_c \equiv 6.75\, T_c$. (Note that the fast expansion to vacuum, which was analyzed in the previous problem, does not have this handicap, but is less convenient in practice.)

As with nearly all predictions of the van der Waals model, this inversion curve describes experimental results for most gases reasonably well. For example, for N_2, i.e. the main component of our air, $P_{\max}$ is close to 400 bar and is reached at the temperature 289 K (which is close to the room one), while $T_{\max}$ is close to 621 K,[4] so the ratio of these two temperatures is close to 2.15, instead of the value $9/4 \equiv 2.25$ following from Eq. (***).

Problem 4.4. Calculate the difference $C_P - C_V$ for the van der Waals gas, and compare the result with that for an ideal classical gas.

Solution: If the gas is uniform, with $N =$ const, we may use the thermodynamic relation

$$C_P - C_V = -T\frac{(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T}, \qquad (*)$$

whose derivation was the task of Problem 1.9. By calculating the involved partial derivatives from the equation of state of the van der Waals gas:

$$P = -a\frac{N^2}{V^2} + \frac{NT}{V - Nb},$$

we get

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{N}{V - Nb}, \qquad \left(\frac{\partial P}{\partial V}\right)_T = 2a\frac{N^2}{V^3} - \frac{NT}{(V - Nb)^2},$$

so, finally,

$$C_P - C_V = -T\left(\frac{N}{V - Nb}\right)^2 \Bigg/ \left[2a\frac{N^2}{V^3} - \frac{NT}{(V - Nb)^2}\right] \equiv \frac{N}{1 - 2aN(V - Nb)^2/V^3T}. \qquad (**)$$

Since this model can give physically meaningful values of P only for $a \geq 0$ and $V > Nb$ (see, e.g., Fig. 4.1 of the lecture notes), the last term in the denominator of Eq. (**) cannot be negative. Hence $C_P - C_V \geq N$, with the equality reached only either at a negligibly small long-range attraction between the particles ($a \to 0$) or in the ideal-gas limit (say, at $T \to \infty$ with fixed N and V).

Moreover, the denominator tends to zero (and hence C_P diverges) at an approach not only to the critical point $V_c = 3Nb$, $T_c = 8a/27b$ (see Eq. (4.3) of the lecture notes), but to any point at the border of the single-phase instability region (shaded in Fig. 4.1). This is natural because at the border, the system's isotherms become horizontal, i.e. the derivative $(\partial P/\partial V)_T$ in the denominator of Eq. (*) diverges. As was discussed in Sec. 4.1, inside this region, the system may be in stable equilibrium only if it has two distinct phases (see the horizontal line 1-2 in Fig. 4.2). In this case, Eq. (**) is invalid – formally because the number of particles in each phase is not fixed, as was assumed at its derivation. The calculation of the specific heat of the two-phase system, which is possible to perform analytically in the limits $T/T_c \to 1$ and $T/T_c \to 0$, is a good additional exercise, highly recommended to the reader.

Problem 4.5. For the van der Waals model, calculate the temperature dependence of the phase-equilibrium pressure $P_0(T)$ and the latent heat $\Lambda(T)$, in the low-temperature limit $T \ll T_c$.

Solution: Plugging the van der Waals expression for P,

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[4] Another example, which is important for low-temperature experiment, is helium with $T_{\max} \approx 34$ K, so before throttling, it is usually pre-cooled with liquid hydrogen.

$$P = \frac{NT}{V - Nb} - a\frac{N^2}{V^2}, \qquad (*)$$

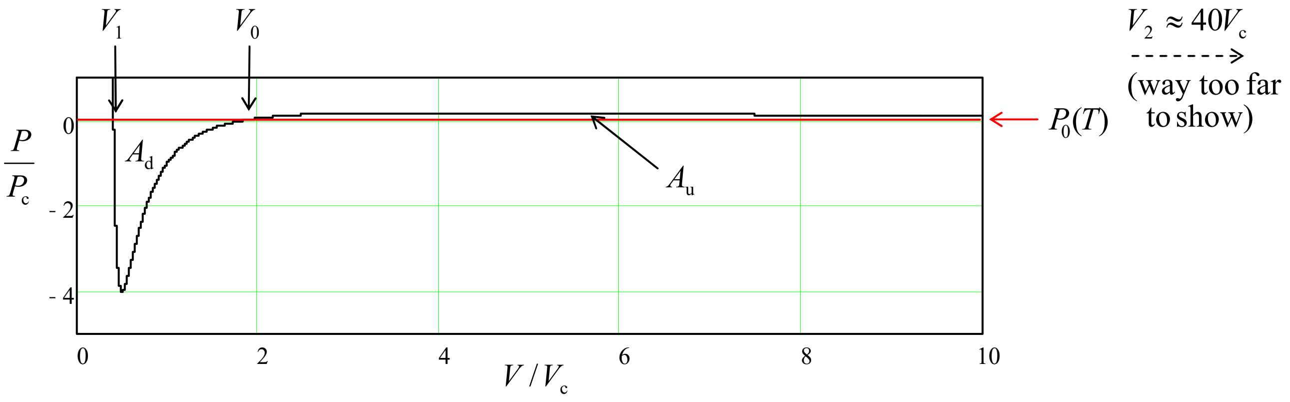
into the Maxwell rule given by Eq. (4.11) of the lecture notes, performing the integration, and dividing the result by $(V_2 - V_1)$, we get the following relation:

$$P_0(T) = \frac{NT}{V_2 - V_1}\ln\frac{V_2 - Nb}{V_1 - Nb} - \frac{aN^2}{V_1 V_2}. \qquad (**)$$

Since $P_0(T)$ has to satisfy the single-phase equation of state (*) at points 1 and 2 (see Fig. 4.2 of the lecture notes), Eqs. (*) and (**) give us the following system of two equations for finding V_1 and V_2:

$$\frac{NT}{V_{1,2} - Nb} - \frac{aN^2}{V_{1,2}^2} = \frac{NT}{V_2 - V_1}\ln\frac{V_2 - Nb}{V_1 - Nb} - \frac{aN^2}{V_1 V_2}.$$

For arbitrary temperatures, this system of transcendental equations does not have an analytical solution, so let us proceed to the limit $T \to 0$ specified in the assignment. In this limit, in order to satisfy the Maxwell rule $A_u = A_d$ (see Fig. 4.2 again), $P_0(T)$ should tend to zero very fast – see, e.g., the numerical plot of the equation of state for $T/T_c = 0.5$ below. (For really low values of T/T_c, the trend is too strong to show it on such a linear scale.)



As a result, the gas-phase volume V_2 is much larger than not only the liquid-phase volume $V_1 \sim Nb$ but also the unstable-equilibrium volume $V_0 \sim aN/T \sim (T_c/T)V_c > V_c$.[5] Hence for finding V_2, we may drop both corrections to the ideal gas law and take

$$V_2 \approx \frac{NT}{P_0(T)}.$$

Also, the volume V_1 is close to the divergence point Nb of the right-hand side of Eq. (*), so we can take $V_1 = Nb$ in all expressions besides the difference $V_1 - Nb$. This difference may be evaluated from the van der Waals equation with $P = 0$ and with $V_1 = Nb$ in the a-term:

$$0 \approx \frac{NT}{V_1 - Nb} - a\frac{N^2}{(Nb)^2}, \qquad \text{giving } V_1 - Nb \approx \frac{NTb^2}{a}.$$

---

[5] This crude estimate for V_0 may be obtained by requiring that at $V = V_0$, both contributions to P in Eq. (*) are comparable; the numerical plot above confirms this estimate for the particular value $T_c/T = 2$.

Plugging these approximations for $V_{1,2}$ into Eq. (**), and canceling common factors, we get a simple equation for $P_0(T)$:

$$1 = \ln\frac{a}{P_0 b^2} - \frac{a}{bT},$$

which yields Eq. (4.12) of the lecture notes (there, given without proof):

$$P_0(T) = \frac{a}{b^2}\exp\left\{-\frac{a}{bT} - 1\right\} \equiv 27P_c \exp\left\{-\frac{27}{8}\frac{T_c}{T} - 1\right\} \equiv 27e^{-1}P_c \exp\left\{-\frac{27}{8}\frac{T_c}{T}\right\} << P_c.$$

(As a sanity check, this result gives

$$V_2 \approx \frac{NT}{P_0(T)} \sim \frac{T}{T_c}V_c \exp\left\{\frac{27}{8}\frac{T_c}{T}\right\} >> V_0, V_1,$$

thus confirming the above assumptions.)

Note that this temperature dependence of $P_0(T)$ is just the Arrhenius exponent,[6] with the activation energy $\Delta = a/b \equiv (27/8)T_c$ per molecule, in accordance with the physical picture of evaporation as the thermal activation of the molecules from the condensed phase. However, its comparison with Eq. (*) of the model solution of Problem 3.7 shows that the (phenomenological) van der Waals model falls short of describing the pre-exponential factor $\propto T^{5/2}$ given by the microscopic model of vapor/liquid equilibrium; at $T << T_c$, this deficiency is not important for most applications.

Now, using the Clapeyron-Clausius law (4.17), for the latent heat of evaporation, we get a temperature-independent value:

$$\Lambda(T) = T(V_2 - V_1)\frac{dP_0}{dT} \approx T\frac{NTb^2}{a}\frac{27}{8}\frac{T_c}{T^2} \equiv \frac{27}{8}NT_c \equiv N\Delta, \qquad \text{for } T/T_c \to 0.$$

This independence is completely consistent with the thermal-activation picture of evaporation. Note that this approximation is only valid if $T << \Delta$, i.e. if $\Lambda >> NT$.

Problem 4.6. Perform the same tasks as in the previous problem, in the opposite limit: in close vicinity of the critical point T_c.

Solution: At $T \approx T_c$ (and $T \leq T_c$), the phase equilibrium region is small and located near critical point $\{P_c, V_c, T_c\}$ – see Eq. (4.3) of the lecture notes. Let us introduce normalized deviations from the point as follows:

$$\tilde{p} \equiv p - 1 \equiv \frac{P}{P_c} - 1, \qquad \tilde{v} \equiv v - 1 \equiv \frac{V}{V_c} - 1, \qquad \tilde{t} \equiv t - 1 \equiv \frac{T}{T_c} - 1 \leq 0\,.$$

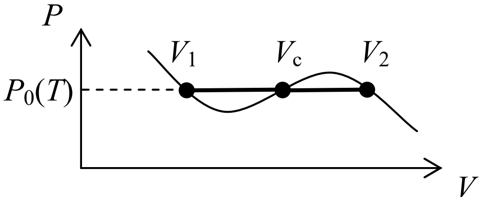
Plugging these relations into the normalized van der Waals equation (4.4), in the limit $\tilde{p}, \tilde{v}, \tilde{t} \to 0$, we get

$$\tilde{p} = 4\tilde{t} - 6\tilde{t}\tilde{v} - \frac{3}{2}\tilde{v}^3. \qquad (*)$$

---

[6] Again, it is amazing how well is this exponential law hidden inside the van der Waals equation of state!

Note that in this expression, only the terms linear in $\tilde{p}$ and $\tilde{t}$ are kept, but both the linear and cubic terms in $\tilde{v}$ are retained because this is necessary to describe the non-monotonic shape of the system's isotherm, and hence the coexistence of its condensed and gaseous phases at $T < T_c$ – see the figure on the right.



Formula (*) shows that in this limit, the difference $\tilde{p} - 4\tilde{t}$ is an antisymmetric function of $\tilde{v}$:

$$\tilde{p}(-\tilde{v}) - 4\tilde{t} = -\tilde{p}(\tilde{v}) - 4\tilde{t}\ .$$

According to the Maxwell rule (4.11), this means that the phase equilibrium line $P = P_0(T)$ passes through the point $\tilde{v} = 0$ (i.e. $V = V_c$), so

$$\tilde{p}_0 = 4\tilde{t} \le 0, \qquad \text{i.e.}\quad P_0(T) = P_c - 4P_c\left(1 - \frac{T}{T_c}\right) \le P_c .$$

Because of the same asymmetry, the endpoints $V_{1,2}$ of the segment are at an equal distance from V_c:

$$V_2 - V_c = V_c - V_1 \equiv V_c\tilde{v}_0 \ne 0,$$

where, per Eq. (*),

$$-6\tilde{t}\tilde{v}_0 - \frac{3}{2}\tilde{v}_0^3 = 0, \qquad \text{i.e.}\ -6\tilde{t}_0 - \frac{3}{2}\tilde{v}_0^2 = 0,$$

and hence

$$\tilde{v}_0 = 2\left(-\tilde{t}\right)^{1/2}, \qquad \text{i.e.}\ V_2 - V_1 = 2V_c\tilde{v}_0 \equiv 4V_c\left(1 - \frac{T}{T_c}\right)^{1/2} << V_c .$$

Now from the Clapeyron-Clausius formula (4.17), for the latent heat we get

$$\Lambda(T) = T(V_2 - V_1)\frac{dP_0}{dT} \approx T_c 4V_c\left(\frac{T_c - T}{T_c}\right)^{1/2}\frac{4P_c}{T_c} \equiv 16P_cV_c\left(1 - \frac{T}{T_c}\right)^{1/2} .$$

This expression may be simplified by noting that according to Eqs. (4.3), $P_cV_c = (1/9)aN/b = (3/8)NT_c$, so

$$\Lambda(T) = 6NT_c\left(1 - \frac{T}{T_c}\right)^{1/2} .$$

(This approximation is only valid if $0 \le T_c - T << T$, i.e. if $\Lambda << NT$.)

As could be expected, the latent heat turns into zero at $T = T_c$, because above this temperature, the system may be only in one (gaseous) phase.

Problem 4.7. Calculate C_V and C_P for the stable gas-liquid system described by the van der Waals equation, for $V = V_c$ and $0 < T_c - T << T_c$.

Solution: As was shown in the solution of the previous problem, at a temperature just below the critical value $T_c = (8/27)a/b$, the stable solutions of the Waals equation of state, which correspond to the condensed ("liquid") and gaseous states of the system, are

$$\begin{aligned} V_{1,2} &\approx V_c\left(1 \mp \tilde{v}_0\right), \quad \text{with } \tilde{v}_0^2 = -4\tilde{t}, \\ P_{1,2} &= P_0(T) \approx P_c\left(1 + 4\tilde{t}\right) \le P_c, \end{aligned} \qquad \text{for } \tilde{t} \le 0;\ \left|\tilde{t}\right| << 1, \qquad (*)$$

where $\tilde{v}$ and $\tilde{t}$ are normalized deviations from, respectively, V_c and T_c:

$$\tilde{v} \equiv \frac{V}{V_c} - 1, \qquad \tilde{t} \equiv \frac{T}{T_c} - 1.$$

At each of these stable points, the system is uniform (single-phase), so for them, we may use the expressions derived in the solutions of Problems 2 and 5:

$$\frac{E}{N} = \frac{E_{\text{ideal}}}{N} - \frac{aN}{V} \equiv \frac{E_{\text{ideal}}}{N} - \frac{aN}{V_c\left(1 + \tilde{v}\right)}, \qquad (**)$$

$$\frac{C_P - C_V}{N} = \frac{1}{1 - 2aN(V - Nb)^2 / V^3 T} \to \frac{1}{\tilde{t} + 3\tilde{v}^2/4}, \quad \text{for } \tilde{t}, \tilde{v} \to 0. \qquad (***)$$

Since, as Eq. (*) shows, the deviations of $V_{1,2}$ from V_c are equal and opposite, the concentrations of these two phases in the stable state at $V = V_c$ are equal,[7] and we may use Eq. (**) to calculate the internal energy of this system as

$$\frac{E}{N} = \frac{E_1 + E_2}{2N} \approx \frac{E_{\text{ideal}}}{N} - \frac{aN}{2V_c}\left(\frac{1}{1 - \tilde{v}_0} + \frac{1}{1 + \tilde{v}_0}\right) \approx \frac{E_{\text{ideal}}}{N} - \frac{aN}{2V_c}\left(2 + 2\tilde{v}_0^2\right) = \frac{E_{\text{ideal}}}{N} - \frac{aN}{V_c}\left(1 - 4\tilde{t}\right),$$

so[8]

$$\frac{C_V}{N} \equiv \left(\frac{\partial E/N}{\partial T}\right)_V = \frac{1}{T_c}\left(\frac{\partial E/N}{\partial \tilde{t}}\right)_V \approx \left(\frac{C_V}{N}\right)_{\text{ideal}} + 4\frac{aN}{T_c V_c}.$$

Since, per the same Eq. (**), $C_V = C_{V\text{ideal}}$ at $T > T_c$, this result means that at the critical point $T = T_c$, the heat capacity performs a finite jump

$$\frac{\Delta C_V}{N} \equiv \frac{C_V(T + 0) - C_V(T - 0)}{N} = -4\frac{aN}{T_c V_c} \equiv -\frac{9}{2}.$$

This discontinuity reminds the one for C_h, given by Eq. (4.49) that was derived for the continuous phase transition described by Landau's mean-field theory. However, this analogy is false because according to the discussion in Sec. 1.1 of the lecture notes, the genuine analog of C_h in mechanical systems is C_P rather than C_V,[9] and as Eq. (***) shows, the former heat capacity diverges as

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[7] As a reminder, there is also a *single-phase* state corresponding to this point, but it is mechanically unstable – see, e.g., either Fig. 4.2 in the lecture notes or the figure in the previous problem's solution.

[8] Note that the change of the sub-volumes $V_{1,2}$ with temperature is compatible with the requirement V = const imposed on this partial differentiation, because this requirement applies only to the total volume $V = (V_1 + V_2)/2 = V_c$ = const. A more complete expansion of the van der Waals equation near T_c, describing a small asymmetry of V_1 and V_2 with respect to V_c, leads to a small correction (proportional to $\tilde{t} \to 0$) to the above result for C_V.

[9] This point will be further discussed in the model solution of Problem 12.

the temperature approaches T_c from either side. Indeed, since that formula, derived for single-phase states of the van der Waals system, gives the same results for the sub-volumes V_1 and V_2, it is applicable to the 50/50 mix of the liquid and gaseous components of the two-phase system with volume $V = V_\text{c}$ as well:

$$\frac{C_P - C_V}{N} = \frac{1}{\tilde{t} + 3\tilde{v}_0^2/4} = \frac{1}{-2\tilde{t}} \equiv \frac{1}{2(T_c - T)}, \quad \text{at } 0 < T_\text{c} - T << T_\text{c}.$$

Since we have already seen that the function $C_V(T)$ is not singular at $T = T_\text{c}$, all this singularity may be attributed to C_P, so since Eq. (***) is valid at $T > T_\text{c}$ with $\tilde{v}^2 = 0$, we may write

$$\left.\frac{C_P}{N}\right|_{\substack{V=V_c\\ T\to T_c}} \to \begin{cases} 1/2(T_\text{c} - T), & \text{for } T < T_\text{c}, \\ 1/(T - T_\text{c}), & \text{for } T > T_\text{c}, \end{cases}$$

with $C_P > 0$ in both cases.

<u>Problem 4.8</u>. Calculate the critical values P_c, V_c, and T_c for the so-called *Redlich-Kwong model* of the real gas, with the following equation of state:[10]

$$P + \frac{a}{V(V + Nb)T^{1/2}} = \frac{NT}{V - Nb},$$

with constant parameters a and b.

Hint: Be prepared to solve a cubic equation with particular (numerical) coefficients.

Solution: Just as the van der Waals model, the Redlich-Kwong equation of state gives an explicit expression of pressure as a function of volume and temperature:

$$P = \frac{NT}{V - Nb} - \frac{a}{V(V + Nb)T^{1/2}} \equiv \frac{T}{b}\frac{1}{\xi - 1} - \frac{a}{N^2 b^2 T^{1/2}}\frac{1}{\xi(1 + \xi)} \tag{*}$$

(where the last form uses the dimensionless parameter $\xi \equiv V/Nb$), making the calculations rather straightforward. Indeed, by using Eq. (*), the critical point conditions,

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0, \qquad \text{at } V = V_\text{c} \text{ and } T = T_\text{c},$$

may be readily spelled out:

$$\frac{N^2 b T_\text{c}^{3/2}}{a}\frac{1}{(\xi - 1)^2} - \frac{2\xi + 1}{\xi^2(1 + \xi)^2} = 0, \qquad \frac{N^2 b T_\text{c}^{3/2}}{a}\frac{1}{(\xi - 1)^3} - \frac{3\xi^2 + 3\xi + 1}{\xi^3(1 + \xi)^3} = 0. \tag{**}$$

Eliminating the leftmost fraction from the system of these two equations, we get a simple cubic equation for the dimensionless critical volume:

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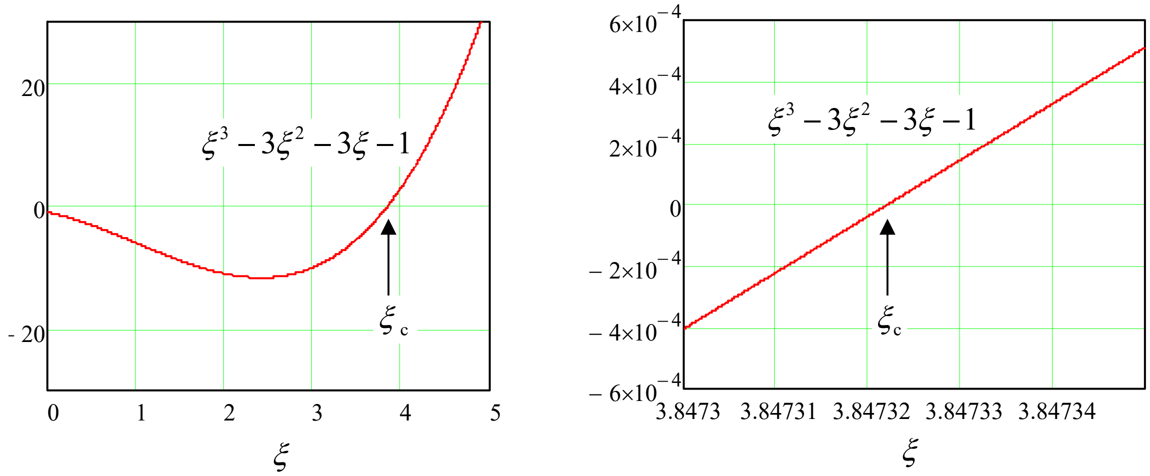
[10] This equation of state, suggested in 1949, describes most real gases better than not only the older van der Waals model but also other two-parameter alternatives, such as the *Berthelot*, *modified-Berthelot*, and *Dieterici* models, though some approximations with more fitting parameters (such as the *Soave-Redlich-Kwong model*) work even better.

$$\xi^3 - 3\xi^2 - 3\xi - 1 = 0 .$$

As the figure below (whose two panels differ just by the ranges of the argument's variation) shows, this equation has just one positive (i.e. physically sensible) root:[11]

$$\xi_c \approx 3.84732, \qquad \text{so that } V_c \equiv \xi_c Nb \approx 3.84732\; Nb$$

(cf. $V_c = 3Nb$ for the van der Waals model – see Eq. (4.3) of the lecture notes).



Now plugging this value into any of Eqs. (**), we may calculate the critical temperature:

$$T_c = \tau \left(\frac{a}{bN^2} \right)^{2/3}, \qquad \text{where } \tau \equiv \left[\frac{(\xi_c - 1)^2 (2\xi_c + 1)}{\xi_c^2 (\xi_c + 1)^2} \right]^{2/3} \approx 0.34504 ,$$

while Eq. (*) yields the following result for critical pressure:

$$P_c = \zeta \left(\frac{a^2}{b^5 N^4} \right)^{1/3}, \qquad \text{where } \zeta \equiv \frac{\tau}{\xi_c - 1} - \frac{1}{\xi_c (\xi_c + 1) \tau^{1/2}} \approx 0.029894 .$$

(The results for P_c and T_c are functionally different from Eqs. (4.3) for the van der Waals gas, because of a different definition of the coefficient *a*.)

Note that in literature, these results are frequently represented backward, as expressions for the coefficients *a* and *b* via the critical values of temperature and pressure:[12]

$$a = \frac{\zeta}{\tau^{5/2}} \frac{N^2 T_c^{5/2}}{P_c} \approx 0.42748 \frac{N^2 T_c^{5/2}}{P_c}, \qquad b = \frac{\zeta}{\tau} \frac{T_c}{P_c} \approx 0.086640 \frac{T_c}{P_c} .$$

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[11] Actually, using the bulky ("quasi-analytical") Tartaglia-Cardano formulas, it is possible to show that this value is just $(2^{2/3} + 2^{1/3} + 1)$. However, for the solution of parameter-free algebraic equations, the numerical method demonstrated here is faster, more general, and perfectly suitable for most applications.

[12] From the "analytical" value of ξ_c, mentioned in the previous footnote, it is straightforward to show that the numerical coefficients in these two relations are $\zeta/\tau^{5/2} = 1/9(2^{1/3} - 1)$ and $\zeta/\tau = (2^{1/3} - 1)/3$.

Problem 4.9. Calculate the critical values P_c, V_c, and T_c for the phenomenological *Dieterici model*, with the following equation of state:[13]

$$P = \frac{NT}{V-b}\exp\left\{-\frac{a}{NTV}\right\},$$

with constant parameters a and b. Compare the value of the dimensionless factor P_cV_c/NT_c with those given by the van der Waals and Redlich-Kwong models.

Solution: According to the discussion in Sec. 4.1 of the lecture notes (see, e.g., Fig. 4.1), in the critical point, the following two conditions should be fulfilled:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0, \qquad \text{at } V = V_c \text{ and } T = T_c.$$

Let us calculate these two derivatives, so far for arbitrary V and T:

$$\frac{1}{NT}\left(\frac{\partial P}{\partial V}\right)_T = \left[\frac{1}{(V-b)}\frac{a}{NTV^2} - \frac{1}{(V-b)^2}\right]\exp\left\{-\frac{a}{NTV}\right\}, \tag{*}$$

$$\frac{1}{NT}\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \left\{\begin{aligned}&\left[\frac{1}{(V-b)}\frac{a}{NTV^2} - \frac{1}{(V-b)^2}\right]\frac{a}{NTV^2}\\ &+\left[-\frac{a}{NT}\frac{(3V-2b)}{(V-b)^2V^3} + \frac{2}{(V-b)^3}\right]\end{aligned}\right\}\times\exp\left\{-\frac{a}{NTV}\right\}. \tag{**}$$

The second expression looks bulky, but we need to evaluate it only at the critical point $\{V_c, T_c\}$, where the first derivative of P, and hence the expression in the square brackets in Eq. (*), equal zero:

$$\left[\frac{1}{(V_c-b)}\frac{a}{NT_cV^2} - \frac{1}{(V_c-b)^2}\right] = 0, \qquad \text{giving } NT_c = \frac{a(V_c-b)}{V_c^2}. \tag{***}$$

Hence the similar expression in the first square brackets in Eq. (**) has to equal zero as well, so the requirement of having the second derivative equal to zero is reduced to the condition that the second square bracket in that expression also vanishes:

$$\left[-\frac{a}{NT_c}\frac{(3V_c-2b)}{(V_c-b)^2V_c^3} + \frac{2}{(V_c-b)^3}\right] = 0, \qquad \text{giving } NT_c = \frac{a(3V_c-2b)(V_c-b)}{2V_c^3}.$$

Requiring the two obtained expressions for NT_c to coincide and canceling the common factor $a(V_c - b)/V_c^2$, we get an elementary equation for V_c:

$$1 = \frac{3V_c - 2b}{2V_c}, \qquad \text{giving } V_c = 2b.$$

From this result and the last of Eqs. (***), we may readily calculate the critical temperature,

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[13] For practical applications, this approximation is currently less popular than the Redlich-Kwong model (also with two fitting parameters), whose analysis was the task of the previous problem.

$$NT_c = \frac{a(V_c - b)}{V_c^2} = \frac{a}{4b},$$

and now the pressure at the critical point may be calculated from the equation of state:

$$P_c = \frac{NT_c}{V_c - b}\exp\left\{-\frac{a}{NT_cV_c}\right\} = \frac{a}{4b^2}e^{-2} \approx 0.0338\frac{a}{b^2}.$$

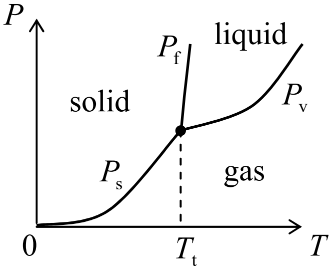
Note that according to these results, the dimensionless combination P_cV_c/NT_c, which may be conveniently used to characterize the deviation from the ideal classical gas (for which $PV/NT = 1$ at any point), does not depend on the fitting parameters a and b, and is just a fixed number:

$$\frac{P_cV_c}{NT_c}\Big|_{\text{Dieterici}} = 2e^{-2} \approx 0.2707.$$

The same is true for the van der Waals model (see Eqs. (4.3) of the lecture notes), and the Redlich-Kwong model (see the previous problem), but for them, the numbers are somewhat different:

$$\frac{P_cV_c}{NT_c}\Big|_{\text{van der Waals}} = \frac{3}{8} = 0.375, \qquad \frac{P_cV_c}{NT_c}\Big|_{\text{Redlich-Kwong}} = \frac{\xi_c\zeta}{\tau} \approx 0.333.$$

For comparison, the experimental value of this parameter for water is close to 0.23, while for the diethyl ether (see its discussion in Sec. 4.1 of the lecture notes) it is close to 0.27. This difference shows that it is impossible to design a two-parameter model (with a parameter-independent ratio P_cV_c/NT_c) that would fit all real substances very closely.



Problem 4.10. In the crude sketch shown in Fig. 4.3b of the lecture notes (partly reproduced on the right), the derivatives dP/dT of the phase transitions liquid-gas ("vaporization") and solid-gas ("sublimation"), at the triple point, are different, with

$$\left(\frac{dP_v}{dT}\right)_{T=T_t} < \left(\frac{dP_s}{dT}\right)_{T=T_t}.$$

Is this occasional? What relation between these derivatives can be obtained from thermodynamics?

Solution: The by-product (4.16) of the Clapeyron-Clausius relation's derivation (in Sec. 4.1 of the lecture notes) may be rewritten as

$$\frac{dP_0}{dT} = \frac{S_1 - S_2}{V_1 - V_2}, \qquad (*)$$

where the indices 1 and 2 number the phases separated, on the phase diagram, by the critical line $P_0(T)$. For most materials, the gaseous phase volume (of a fixed number of particles) is much larger than those in the liquid and solid phases, at the same pressure, so Eq. (*), applied to the vaporization and sublimation transitions, may be well approximated as

$$\frac{dP_v}{dT} \approx \frac{S_{\text{gas}} - S_{\text{liquid}}}{V_{\text{gas}}}, \qquad \frac{dP_s}{dT} \approx \frac{S_{\text{gas}} - S_{\text{solid}}}{V_{\text{gas}}}.$$

But the solid phase is more ordered than the liquid phase, so its entropy is lower, i.e. the difference ($S_{\text{gas}} - S_{\text{solid}}$) has to be larger than the difference ($S_{\text{gas}} - S_{\text{liquid}}$), at the same temperature. Since the only temperature where both these transitions take place is T_t, the relation given in the assignment is indeed valid for all usual materials with $V_{\text{gas}} >> V_{\text{liquid}}, V_{\text{solid}}$.

However, for some materials, notably including the usual water H_2O, the difference between these derivatives is very small, implying in particular that the water ice is not much more ordered than the liquid water. This is indeed the case: near the triple point (273.16 K, i.e. 0.01°C), the ice is a mixture of 16 different "packing geometries" – essentially, different phases, though one of them (called I_h) is prevalent.

A related peculiar feature of water at $T \approx T_t$ is that the ice is slightly less dense than the liquid water ($V_{\text{liquid}} < V_{\text{solid}}$),[14] so the same Eq. (*), applied to the "fusion" (or "melting") transition water-ice, yields

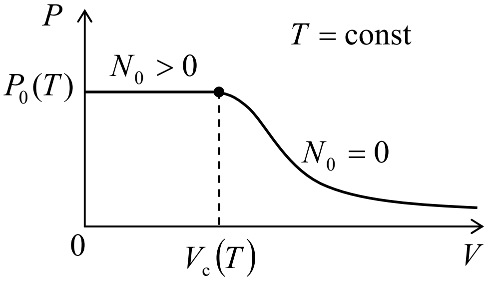
$$\frac{dP_f}{dT} = \frac{S_{\text{liquid}} - S_{\text{solid}}}{V_{\text{liquid}} - V_{\text{solid}}} < 0 .$$

This means that the slope of the curve $P_f(T)$ for water is negative at this point, i.e. opposite to that shown in the figure above – which is typical for most common materials.

Problem 4.11. Use the Clapeyron-Clausius formula (4.17) to calculate the latent heat Λ of the Bose-Einstein condensation, and compare the result with that obtained in the solution of Problem 3.21.

Solution: Per the discussion in Sec. 3.4 of the lecture notes, an isotherm of an ideal, uniform Bose-Einstein gas looks as sketched in the figure on the right, where the critical volume V_c may be found from the critical transition condition (3.73), taking into account the involved integral's value $\Gamma(3/2)\zeta(3/2)$:

$$V_c(T) = \frac{\sqrt{2}\pi^2}{\Gamma(3/2)\zeta(3/2)} \frac{N}{g} \left(\frac{\hbar^2}{mT} \right)^{3/2} . \qquad (*)$$



This plot, when compared with Fig. 4.2, shows that for this particular phase transition, the volume V_1 corresponding to the pure "liquid" (condensed) phase is formally equal to zero, while $V_2 = V_c(T)$, so the Clapeyron-Clausius formula is reduced to

$$\Lambda = TV_c(T)\frac{dP_0}{dT} .$$

The equilibrium pressure $P_0(T)$, which corresponds to $V \leq V_c(T)$, i.e. to the Bose-Einstein condensation region, may be calculated from Eqs. (3.76) and (3.79):

$$P_0(T) = \frac{\zeta(5/2)}{\zeta(3/2)} \frac{N}{VT_c^{3/2}} T^{5/2}, \qquad \text{so} \quad \frac{dP_0}{dT} = \frac{5}{2} \frac{\zeta(5/2)}{\zeta(3/2)} \frac{N}{VT_c^{3/2}} T^{3/2} , \qquad (**)$$

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[14] This is of course very fortunate: if the ice was denser than the water, then most lakes, rivers, and even some seas would freeze to the bottom in winter, and life on the Earth might be possible only in the tropics.

where T_c should now be understood as a function of V. (It may be obtained from the same critical condition (*) by moving the subscript "c" from V to T.[15]) These relations may also be used in the ultimate, critical point $V = V_c$, where $T_c = T$, so we finally get

$$\Lambda = TV_c(T)\frac{5}{2}\frac{\zeta(5/2)}{\zeta(3/2)}\frac{N}{V_c(T)T^{3/2}}T^{3/2} \equiv \frac{5}{2}\frac{\zeta(5/2)}{\zeta(3/2)}NT \approx 1.284NT.$$

This is the same result as was obtained in the solution of Problem 3.21 by using a completely different approach.

Problem 4.12. As was discussed in Sec. 4.1 of the lecture notes, properties of systems with *first-order* phase transitions (such as the van der Waals gas) change qualitatively at the critical temperature: at $T < T_c$, the system may include two different phases of the same substance. However, since the difference in the density of these phases, in equilibrium, is a continuous function of the difference $T_c - T$, this change itself is sometimes considered a *continuous* phase transition between the purely gaseous phase and the mixed gas-liquid "phase". From this viewpoint, what are the most reasonable analogs of the critical exponents β, γ, and δ, which were defined in Sec. 4.2, for such a continuous transition? Evaluate these exponents for the van der Waals model.

Solution: The critical exponents in question are usually defined, by Eqs. (4.26), (4.29), and (4.32) of the lecture notes, for a ferromagnetic phase transition, and thus have to be re-defined for "mechanical" (gas-liquid) systems. As was repeatedly discussed earlier in this course, starting for Sec. 1.1, for such systems, the most adequate thermodynamic analog of such generalized force as the external magnetic field is pressure P, and that of the magnetization (which, in magnetic systems, is taken for the order parameter η) is volume V. However, since the "continuous phase transition" we are discussing takes place at the critical point $\{P_c, V_c, T_c\}$ of the background (first-order) phase transition, more adequate generalized force and coordinate are not P and V as such, but their deviations from, respectively, P_c and V_c. Hence, the critical exponents in question may be defined as follows:

$$V - V_c \propto (-\tilde{t})^{\beta} \equiv |\tilde{t}|^{\beta}, \qquad \text{for } \tilde{t} < 0,$$

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T\Big|_{P=P_c} \propto |\tilde{t}|^{-\gamma},$$

$$V - V_c \propto (P - P_c)^{1/\delta}, \qquad \text{for } \tilde{t} = 0.$$

where $\tilde{t}$ is defined by Eq. (4.27):

$$\tilde{t} \equiv t - 1 \equiv \frac{T}{T_c} - 1, \quad \text{with } |\tilde{t}| << 1.$$

In the solution of Problem 6, the van der Waals equation was reduced to the following form:

$$\tilde{p} = 4\tilde{t} - 6\tilde{t}\tilde{v} - \frac{3}{2}\tilde{v}^3, \qquad (*)$$

valid in a close vicinity of the critical point, i.e. if the moduli of the normalized deviations from it,

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[15] Since, according to that formula, $T_c^{3/2} \propto 1/V$, the function $P_0(T)$ given by the first of Eqs. (**) does not depend on V, just as it should be – see the figure above.

$$\tilde{p} \equiv \frac{P}{P_c} - 1, \qquad \tilde{v} \equiv \frac{V}{V_c} - 1,$$

are much smaller than 1. For the equilibrium volumes $V_{1,2}$ of the two phases at $\tilde{t} < 0$, i.e. $T < T_c$ (see Fig. 4.2), Eq. (*) yields

$$\left|\tilde{v}_{1,2}\right| = 2\left(-\tilde{t}\right)^{1/2},$$

so the comparison with the above definition yields $\beta = ½$. Next, according to the same equation,

$$\left(\frac{\partial \tilde{p}}{\partial \tilde{v}}\right)_{\tilde{t}} = -6\tilde{t} - \frac{9}{2}\tilde{v}^2 = \begin{cases} -6\tilde{t}, & \text{for } \tilde{t} > 0, \\ 12\tilde{t}, & \text{for } \tilde{t} < 0, \end{cases} \qquad \text{i.e.} \left(\frac{\partial \tilde{v}}{\partial \tilde{p}}\right)_{\tilde{t}} \propto \frac{1}{\left|\tilde{t}\right|},$$

so $\gamma = 1$. Finally, at $\tilde{t} = 0$ (or at $\tilde{t} \neq 0$ but for a relatively strong "field" $\tilde{p}$), Eq. (*) yields

$$\tilde{p} = -\frac{3}{2}\tilde{v}^3, \qquad \text{i.e. } \tilde{v} \propto \tilde{p}^{1/3},$$

meaning that $\delta = 3$.

So, the critical exponents β, γ, and δ defined above have the same values as in Landau's theory – see Sec. 4.3 (in particular, Table 4.1) of the lecture notes. This is hardly a big surprise because as the above solution shows, these values result from a very natural Taylor expansion (*) of the equation of state near the critical point, and do not depend on the particular coefficients in this expansion. This is not in contradiction with the solution of Problem 7, which implies that one more major critical exponent, the α defined by Eq. (4.28) with $c_h \to c_P$, equals 1 and hence differs from the Landau-theory result $\alpha = 0$. Indeed, the "continuous phase transition" discussed in this solution takes place on the background of the primary first-order transition, and the result $\alpha = 0$ is valid for another ("differential") definition of dH and hence c_P – the task left for the reader's additional exercise.

Problem 4.13.

(i) Compose such an effective single-particle Hamiltonian that the corresponding stationary Schrödinger equation coincides with the Gross-Pitaevski equation (58).

(ii) Use this *Gross-Pitaevskii Hamiltonian*, with the particular confining potential $U(\mathbf{r}) = m\omega^2 r^2/2$, to calculate the ground-state energy E of $N >> 1$ confined particles, by assuming the natural trial solution $\psi \propto \exp\{-r^2/2r_0^2\}$.[16]

(iii) Explore the function $E(r_0)$ for positive and negative values of the constant b, and interpret the results.

(iv) For $b < 0$ with small $|b|$, estimate the largest number N of particles that may form a metastable Bose-Einstein condensate.

Solutions:

(i) The only difference between Eq. (4.58) and the usual (linear) stationary Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U(\mathbf{r})\psi = E\psi,$$

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[16] This task is essentially the first step of the variational method of quantum mechanics – see, e.g., QM Sec. 2.9.

is the term $b|\psi^2|$ added to $U(\mathbf{r})$, so the requested (Gross-Pitaevskii) Hamiltonian[17] is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + b|\psi|^2 + U(\mathbf{r}).$$

(ii) For the quadratic-parabolic potential specified in the assignment, the Hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{m\omega^2 r^2}{2} + b|\psi|^2,$$

i.e. is different from the usual Hamiltonian of an isotropic 3D harmonic oscillator only by the last term. To find the stationary energy E corresponding to the suggested trial wavefunction $\psi(\mathbf{r})$, we need to calculate the expectation value of the corresponding operator, i.e. of the Hamiltonian:

$$\begin{aligned} E = \langle H \rangle &= \int \psi^*(\mathbf{r})\hat{H}\psi(\mathbf{r})d^3r \\ &= -\frac{\hbar^2}{2m}\int \psi^*(\mathbf{r})\nabla^2\psi(\mathbf{r})d^3r + \frac{m\omega^2}{2}\int |\psi(\mathbf{r})|^2 r^2 d^3r + b\int |\psi(\mathbf{r})|^4 d^3r, \end{aligned}$$

with the normalization condition

$$N = \int \psi^*(\mathbf{r})\psi(\mathbf{r})d^3r \equiv \int |\psi(\mathbf{r})|^2 d^3r.$$

For our factorable trial function,

$$\psi(\mathbf{r}) = C\exp\left\{-\frac{r^2}{2r_0^2}\right\} \equiv C\exp\left\{-\frac{x^2}{2r_0^2}\right\}\exp\left\{-\frac{y^2}{2r_0^2}\right\}\exp\left\{-\frac{z^2}{2r_0^2}\right\}$$

(where the normalization constant C may be always taken real) and coordinate-separable operators

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \text{and} \quad r^2 = x^2 + y^2 + z^2,$$

the simplest way to work out all the involved integrals is to factor them into Cartesian coordinate components:

$$\begin{aligned} \int \psi^*(\mathbf{r})\nabla^2\psi(\mathbf{r})d^3r &= 3C^2\int_{-\infty}^{+\infty}\exp\left\{-\frac{x^2}{2r_0^2}\right\}\frac{\partial^2}{\partial x^2}\exp\left\{-\frac{x^2}{2r_0^2}\right\}dx\int_{-\infty}^{+\infty}\exp\left\{-\frac{y^2}{r_0^2}\right\}dy\int_{-\infty}^{+\infty}\exp\left\{-\frac{z^2}{r_0^2}\right\}dz \\ &\equiv 3C^2 r_0\left(\int_{-\infty}^{+\infty}\exp\left\{-\frac{\xi^2}{2}\right\}\frac{\partial^2}{\partial \xi^2}\exp\left\{-\frac{\xi^2}{2}\right\}d\xi\right)\left(\int_{-\infty}^{+\infty}\exp\left\{-\xi^2\right\}d\xi\right)^2 \\ &= 3C^2 r_0\left(\int_{-\infty}^{+\infty}\exp\left\{-\xi^2\right\}\left(\xi^2-1\right)d\xi\right)\left(\int_{-\infty}^{+\infty}\exp\left\{-\xi^2\right\}d\xi\right)^2 = -\frac{3C^2 r_0\pi^{3/2}}{2}, \end{aligned}$$

$$\int |\psi(\mathbf{r})|^2 r^2 d^3r = 3C^2\int_{-\infty}^{+\infty}\exp\left\{-\frac{x^2}{r_0^2}\right\}x^2dx\int_{-\infty}^{+\infty}\exp\left\{-\frac{y^2}{r_0^2}\right\}dy\int_{-\infty}^{+\infty}\exp\left\{-\frac{z^2}{r_0^2}\right\}dz$$

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[17] Note that the Gross-Pitaevskii Hamiltonian should be used with care because this phenomenological construct does not belong to the family of linear operators, for which the standard formalism of quantum mechanics is strictly valid.

$$\equiv 3C^2 r_0^5 \left(\int_{-\infty}^{+\infty} \exp\{-\xi^2\} \xi^2 d\xi \right) \left(\int_{-\infty}^{+\infty} \exp\{-\xi^2\} d\xi \right)^2 = \frac{3C^2 r_0^5 \pi^{3/2}}{2},$$

$$\int |\psi(\mathbf{r})|^4 d^3r = C^4 \int_{-\infty}^{+\infty} \exp\left\{-\frac{2x^2}{r_0^2}\right\} dx \int_{-\infty}^{+\infty} \exp\left\{-\frac{2y^2}{r_0^2}\right\} dy \int_{-\infty}^{+\infty} \exp\left\{-\frac{2z^2}{r_0^2}\right\} dz$$

$$\equiv C^4 r_0^3 \left(\int_{-\infty}^{+\infty} \exp\{-2\xi^2\} d\xi \right)^3 = \frac{C^4 r_0^3 \pi^{3/2}}{2^{3/2}},$$

$$\int |\psi(\mathbf{r})|^2 d^3r = C^2 \int_{-\infty}^{+\infty} \exp\left\{-\frac{x^2}{r_0^2}\right\} dx \int_{-\infty}^{+\infty} \exp\left\{-\frac{y^2}{r_0^2}\right\} dy \int_{-\infty}^{+\infty} \exp\left\{-\frac{z^2}{r_0^2}\right\} dz$$

$$\equiv C^2 r_0^3 \left(\int_{-\infty}^{+\infty} \exp\{-\xi^2\} d\xi \right)^3 = C^2 r_0^3 \pi^{3/2}.$$

where at the last steps of all four calculations, the well-known dimensionless Gaussian integrals[18] have been used. As a result, we get

$$N = C^2 r_0^3 \pi^{3/2}, \qquad \text{giving } C^2 = \frac{N}{\pi^{3/2} r_0^3},$$

$$E = -\frac{\hbar^2}{2m}\left(-\frac{3C^2 r_0 \pi^{3/2}}{2}\right) + \frac{m\omega^2}{2}\frac{3C^2 r_0^5 \pi^{3/2}}{2} + b\frac{C^4 r_0^3 \pi^{3/2}}{2^{3/2}} \equiv N\left[\frac{3\hbar^2}{4mr_0^2} + \frac{3m\omega^2 r_0^2}{4} + \frac{bN}{(2\pi)^{3/2} r_0^3}\right]. \quad (*)$$

(iii) If the product of the coefficient b (characterizing the interaction between the particles) by their number N is negligible, then the energy (*) is just a sum of N similar energies,

$$\varepsilon = \frac{3\hbar^2}{4mr_0^2} + \frac{3m\omega^2 r_0^2}{4},$$

of single particles placed into the quadratic-parabolic 3D potential well, i.e. of N 3D harmonic oscillators.[19] Following the variational method, the ground-state energy of such an oscillator may be found by minimizing ε (and hence $E = N\varepsilon$) over the fitting parameter r_0:

$$\frac{\partial \varepsilon}{\partial (r_0^2)} \equiv -\frac{3\hbar^2}{4mr_0^4} + \frac{3m\omega^2}{4} = 0, \qquad \text{at } r_0 = (r_0)_{\text{opt}},$$

giving

$$(r_0)_{\text{opt}} = \left(\frac{\hbar}{m\omega}\right)^{1/2}, \qquad \varepsilon = \varepsilon_{\text{g}} \equiv \frac{3}{2}\hbar\omega. \quad (**)$$

(Due to the "smart" choice of the trial function, in this limit, the variational method gives exact results for the ground-state energy and the wavefunction' spread scale r_0.)

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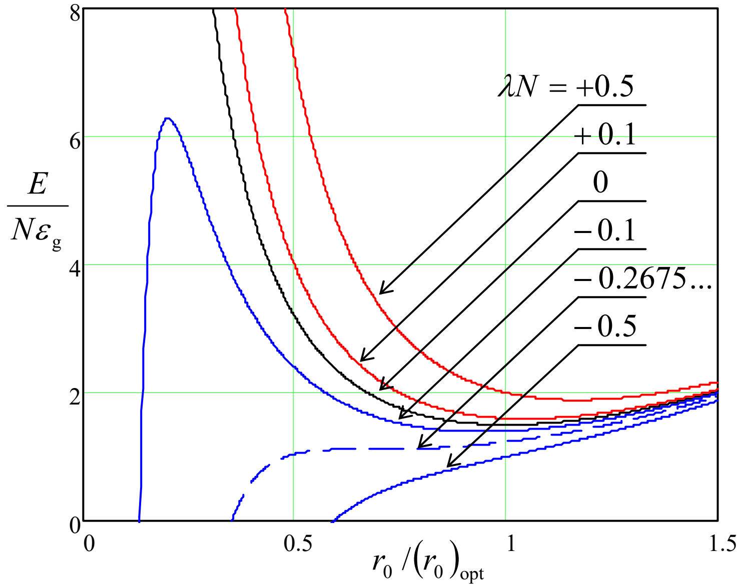
[18] See, e.g., MA Eqs. (6.9b) and (6.9c).

[19] See, e.g., QM Sec. 3.6.



Formula (*) shows that if the constant b is positive, describing a weak particle *repulsion*, and the product bN is small, it does not affect the function $E(r_0)$ given by Eq. (*), quantitatively – see the red lines in the figure on the right, where λ is the dimensionless interaction parameter

$$\lambda \equiv b\left(\frac{m\omega}{2\pi\hbar}\right)^{3/2}.$$

(At larger $b > 0$, the increase of the number N of particles leads to a faster growth of the critical temperature T_c* of the condensation than at $b = 0$ – see the solution of Problem 3.25. The reader is challenged to combine these two solutions to calculate T_c* as a function of N for $b > 0$.)

However, if the coefficient b is negative, describing a mutual *attraction* of the particles, then for any N >>1, the energy E becomes infinitely negative at $r_0 \to 0$ – see the blue lines in the same figure. This trend describes a possible freeze-out of the particles into an “ice blob” – the essentially classical effect, very much different from the Bose-Einstein condensation, and in practice, preventing its implementation for systems with a large number of particles. (The Gross-Pitaevskii equation with $b < 0$, which does not describe short-range repulsion of the particles, is insufficient to calculate the size of that “blob”.)

(iv) The largest number $N_{\max}$ of attracting particles, for that the Bose-Einstein condensation still may be implemented (at $T \to 0$) may be estimated by requiring the function $E(r_0)$ to retain a minimum corresponding to the condensation. This means that at $N = N_{\max}$, this function has a horizontal inflection point $(r_0)_{\text{inf}}$, where

$$\frac{\partial E}{\partial r_0} = 0 \quad \text{and} \quad \frac{\partial^2 E}{\partial r_0^2} = 0$$

– see the dashed blue curve in the figure above. With Eq. (*), these two conditions become

$$-\frac{3\hbar^2}{2mr_0^3} + \frac{3m\omega^2 r_0}{2} - \frac{3bN}{(2\pi)^{3/2} r_0^4} = 0, \qquad \frac{9\hbar^2}{2mr_0^4} + \frac{3m\omega^2}{2} + \frac{12bN}{(2\pi)^{3/2} r_0^5} = 0,$$

A bit counter-intuitively, this system of two nonlinear equations may be readily solved (say, by a brute-force elimination of the term proportional to bN), giving

$$(r_0)_{\text{inf}} = \frac{1}{5^{1/4}}(r_0)_{\text{opt}} \approx 0.6687(r_0)_{\text{opt}}, \qquad N_{\max} = \frac{2}{5^{5/4}}\frac{1}{|\lambda|} \approx 0.2675\frac{1}{|\lambda|}.$$

For typical parameters of experiments with weakly attracting atoms (a historic example is ^{7}Li), this result yields $N_{\max} \sim 10^3$, in a semi-quantitative agreement with experimental data. Note again that if $\lambda < 0$, then even at $N < N_{\max}$, the minimum of the function $E(r_0)$ at $r_0 \neq 0$, in which the Bose-Einstein condensate may form at sufficiently low temperatures, is local rather than global, so such condensate is always metastable, with a certain finite lifetime with respect to the "ice blob" formation.

Problem 4.14. Superconductivity may be suppressed by a sufficiently strong magnetic field. In the simplest case of a bulk, long cylindrical sample of a type-I superconductor placed into an external magnetic field $\mathscr{H}_{\text{ext}}$ parallel to its axis, this suppression takes a simple form of a simultaneous transition of the whole sample from the superconducting state to the "normal" (non-superconducting) state at a certain value $\mathscr{H}_c(T)$ of the field's magnitude. This *critical field* gradually decreases with temperature from its maximum value $\mathscr{H}_c(0)$ at $T \to 0$ to zero at the critical temperature T_c. Assuming that the function $\mathscr{H}_c(T)$ is known, calculate the latent heat of this phase transition as a function of temperature, and spell out its values at $T \to 0$ and $T = T_c$.

Hint: In this particular context, "bulk sample" means a sample much larger than the intrinsic length scales of the superconductor, such as the London penetration depth δ_L and the coherence length ξ.[20] For such bulk superconductors, magnetic properties of the superconducting phase may be well described as perfect diamagnetism, with $\mathscr{B} = 0$ inside it.

Solution: In this simple geometry (only!), the state of the sample cannot affect the magnetic field outside it, so at any external point, including those close to the sample surface, $\mathscr{H}_{\text{out}} = \mathscr{H}_{\text{ext}}$. This field is parallel to the sample surface, and according to the basic electrodynamics, should be continuous at the border.[21] So, inside the sample, $\mathscr{H}_{\text{int}} = \mathscr{H}_{\text{out}} = \mathscr{H}_{\text{ext}}$, i.e. the field does not depend on whether the sample is superconducting or not. On the other hand, in the ideal-diamagnetism (coarse-grain) approximation,

$$\mathscr{B}_{\text{int}} = \begin{cases} \mu_0 \mathscr{H}_{\text{int}} = \mu_0 \mathscr{H}_{\text{ext}}, & \text{in the normal state,} \\ 0, & \text{in the superconducting state.} \end{cases} \tag{*}$$

Since the field $\mathscr{H}$ is defined by the relation $\mathscr{H} = \mathscr{B}/\mu_0 - \mathscr{M}$, where $\mathscr{M}$ is the magnetization of the medium,[22] Eq. (*) may be rewritten as

$$\mathscr{M}_{\text{int}} = \begin{cases} 0, & \text{in the normal state,} \\ -\mathscr{H}_{\text{ext}}, & \text{in the superconducting state.} \end{cases} \tag{**}$$

As was discussed in Sec. 1.1 of the lecture notes, the effect of the external magnetic field on the energy of a magnetic material is similar to the external pressure. In particular, the comparison of Eqs. (1.1) and (1.3a) shows that we may describe the effect by replacing, in all formulas of the traditional thermodynamics, the usual mechanical pair $\{-P, V\}$ of the generalized force and coordinate with the set of magnetic pairs $\{\mu_0\mathscr{H}_j, \mathscr{M}_j\}$ for each Cartesian component $j = 1, 2, 3$ of the corresponding vectors. For our simple geometry, there is only one such component, parallel to the applied field (and hence to the

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[20] A discussion of these parameters, as well as of the difference between the type-I and type-II superconductivity, may be found in EM Secs. 6.4-6.5. However, those details are not needed for the solution of this problem.

[21] See, e.g., EM Eq. (5.117). Note that in superconductors, this condition is only valid within the so-called *coarse-grain model* that sidesteps an explicit description of the field-induced supercurrents flowing in a surface layer of thickness $\sim\delta_L$. However, the perfect diamagnetism mentioned in the *Hint* implies using exactly this model. (For more on that model, see EM Sec. 6.4.)

[22] If you need a reminder, you may have a look at EM Eq. (5.108) and its discussion.

sample's surface), so the necessary replacements are just $-P \to \mu_0\mathscr{H}$, and $V \to \mathscr{M}$. With these replacements, the Clapeyron-Clausius relation (4.17) for the latent heat per unit volume becomes

$$\lambda \equiv \frac{\Lambda}{V} = T\left(\mathscr{M}_\text{n} - \mathscr{M}_\text{s}\right)\frac{d\left(-\mu_0\mathscr{H}_\text{c}\right)}{dT},$$

where the indices "n" and "s" denote, respectively, the normal and superconducting phases. Now using Eq. (**), we get[23]

$$\lambda = -\mu_0 T\mathscr{H}_\text{c}\frac{d\mathscr{H}_\text{c}}{dT}. \tag{***}$$

Since the critical field drops with temperature, $d\mathscr{H}_\text{c}/dT < 0$, this expression yields positive latent heat, as it should. (A superconductor needs to be heated to make it normal.) In particular, Eq. (***) shows that the latent heat vanishes both at $T = 0$ and $T = T_\text{c}$ – in the latter case because $\mathscr{H}_\text{c}(T_\text{c}) = 0$. The last fact shows that in the absence of the external magnetic field, the thermally induced phase transition from the superconducting to the normal state at $T = T_\text{c}$ may be considered a continuous one – see Secs. 4.2-4.3 of the lecture notes.

Problem 4.15. In some textbooks, the discussion of thermodynamics of superconductivity is started by displaying, as self-evident, the following formula:

$$F_\text{n}(T) - F_\text{s}(T) = \frac{\mu_0\mathscr{H}_\text{c}^2(T)}{2}V,$$

where F_s and F_n are the free energy values in the superconducting and non-superconducting ("normal") phases, and $\mathscr{H}_\text{c}(T)$ is the critical value of the external magnetic field. Is this formula correct, and if not, what qualification is necessary to make it valid? Assume that all the conditions of a simultaneous field-induced phase transition in the whole sample, spelled out in the previous problem, are satisfied.

Solution: With the replacements $-P \to \mu_0\mathscr{H}$ and $V \to \mathscr{M}$, which were discussed in Sec. 1.1 of the lecture notes (and in the solution of the previous problem), the usual relation $G = F + PV$ between the free energy and the Gibbs energy (per unit volume) becomes[24]

$$\frac{G}{V} = \frac{F}{V} - \mu_0\boldsymbol{\mathscr{H}}_\text{int}\cdot\boldsymbol{\mathscr{M}}_\text{int}. \tag{*}$$

As was discussed in the solution of the previous problem, in the bulk cylindrical geometry, $\boldsymbol{\mathscr{H}}_\text{int} = \boldsymbol{\mathscr{H}}_\text{ext}$ in any phase, while

$$\boldsymbol{\mathscr{M}}_\text{int} = \begin{cases} 0, & \text{in the normal state,} \\ -\boldsymbol{\mathscr{H}}_\text{ext}, & \text{in the superconducting state.,} \end{cases}$$

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[23] Note that according to Eq. (4.14) of the lecture notes, the factor after T also gives the difference of entropies in the superconducting state and the normal state.

[24] Note again that (as was discussed in Sec. 1.4 of the lecture notes), this relation is only true if the effect of the field $\boldsymbol{\mathscr{H}}$ is not included in the energy of each particle of the medium, as it is done, for example, in the Ising-type problems – see, e.g., the last terms in Eqs. (4.21) and (4.23). In the latter case, there is no difference between the thermodynamic potentials G and F – unless the usual pressure P (or any other generalized force but $\boldsymbol{\mathscr{H}}$) interferes.

so Eq. (*) yields

$$G_{\text{n}}(T) - G_{\text{s}}(T) = F_{\text{n}}(T) - F_{\text{s}}(T) - \mu_0 \mathscr{H}_{\text{ext}}^2 V\ . \qquad (**)$$

Next, by using the same analogy $-P \leftrightarrow \mu_0\mathscr{H}$ and repeating the arguments of Sec. 1.4, we may conclude that the thermodynamic equilibrium of a magnetic system with fixed $\mathscr{H}_{\text{ext}}$ and T corresponds to the minimum of the Gibbs energy – see Eq. (1.43) and its discussion. Hence, as the magnetic field reaches the critical value $\mathscr{H}_{\text{c}}(T)$, the difference of G in the superconducting and normal phases has to vanish, and Eq. (**) yields the result

$$F_{\text{n}}(T) - F_{\text{s}}(T) = \mu_0 \mathscr{H}_{\text{c}}^2(T) V\ , \qquad (***)$$

which differs from the relation cited in the assignment by a factor of two.

However, let us consider the relationship between the free energies $F_{\text{n}}^{(0)}$ and $F_{\text{s}}^{(0)}$ of these phases at the same temperature T but *in the absence of magnetic field*. Due to the free energy's definition $F \equiv E - TS$, in the normal phase, it includes the same additional magnetic field energy $\mathscr{B}^2/2\mu_0$ as the internal energy E:[25]

$$F_{\text{n}}(T) = F_{\text{n}}^{(0)}(T) + \frac{\mathscr{B}^2}{2\mu_0}V = F_{\text{n}}^{(0)}(T) + \frac{\mu_0 \mathscr{H}_{\text{ext}}^2}{2}V\ ,$$

while in the superconducting phase, with $\mathscr{B} = 0$, there is no such additional contribution:

$$F_{\text{s}}(T) = F_{\text{s}}^{(0)}(T).$$

Plugging these relations, taken at the field $\mathscr{H}_{\text{ext}}(T) = \mathscr{H}_{\text{c}}(T)$, into Eq. (***), we see that one-half of its right-hand side cancels with the field energy term, and we get

$$F_{\text{n}}^{(0)}(T) - F_{\text{s}}^{(0)}(T) = \frac{\mu_0 \mathscr{H}_{\text{c}}^2(T)}{2}V\ .$$

Hence the relation cited in the problem's assignment is valid only for the field-free values of the free energy – while for its values in the field, Eq. (***) is valid. Fortunately, this qualification is made in more competent texts.

Problem 4.16. Consider a system of $N = 3$ Ising "spins" ($s_k = \pm 1$) with similar ferromagnetic coupling J of each pair of them, in thermal equilibrium.

(i) Calculate the order parameter η and the low-field susceptibility $\chi \equiv \partial\eta/\partial h|_{h=0}$.

(ii) Use the low-temperature limit of the result for χ to predict it for a similar "ring" with an arbitrary N, and verify your prediction by a direct calculation (in this limit).

(iii) Discuss the relation between the last result, in the limit $N \to \infty$, and Eq. (4.91) of the lecture notes.

Solutions:

(i) The energy of each state of the system may be expressed by Eq. (4.78) of the lecture notes, with $N = 3$:

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[25] I am sure the reader knows this formula – but if not, please see EM Sec. 5.3 and 6.2, in particular Eq. (5.57).

$$E_m = -J\left(s_1 s_2 + s_2 s_3 + s_3 s_1\right) - h\left(s_1 + s_2 + s_3\right).$$

In one of the $2^3 = 8$ possible states of the system, in which all spins are aligned with the field, the system's energy is the lowest and equal to $(-3J - 3h)$. In one more state, with all spins directed against the field, the energy is $(-3J + 3h)$. In the six remaining states, one of the spins has a direction opposite to the other two, so the net coupling energy is $-J + 2J \equiv +J$, while the energy of interaction with the field is $\pm h$, depending on the orientation of the two similar spins, with three states in each group. Hence system's statistical sum is

$$Z \equiv \sum_m \exp\left\{-\frac{E_m}{T}\right\} = \exp\left\{-\frac{-3J-3h}{T}\right\} + \exp\left\{-\frac{-3J+3h}{T}\right\} + 3\exp\left\{-\frac{J+h}{T}\right\} + 3\exp\left\{-\frac{J-h}{T}\right\}$$
$$\equiv 2e^{3J/T}\cosh\frac{3h}{T} + 6e^{-J/T}\cosh\frac{h}{T}.$$

From here and the basic Eq. (2.63), the free energy of the system is

$$F = -T\ln Z = -T\ln\left(2e^{3J/T}\cosh\frac{3h}{T} + 6e^{-J/T}\cosh\frac{h}{T}\right).$$

Now using Eq. (4.90) of the lecture notes, we get

$$\eta = -\frac{1}{3}\left(\frac{\partial F}{\partial h}\right)_T = \frac{T}{3}\frac{\partial}{\partial h}\ln\left(2e^{3J/T}\cosh\frac{3h}{T} + 6e^{-J/T}\cosh\frac{h}{T}\right) = \frac{e^{3J/T}\sinh(3h/T) + e^{-J/T}\sinh(h/T)}{e^{3J/T}\cosh(3h/T) + 3e^{-J/T}\cosh(h/T)}.$$

For low fields, $h/T \to 0$, both sinh functions in the last expression tend to the values of their arguments, while both cosh functions tend to 1, so

$$\eta \to \frac{e^{3J/T}(3h/T) + e^{-J/T}(h/T)}{e^{3J/T} + 3e^{-J/T}} \equiv \frac{h}{T}\frac{3 + e^{-4J/T}}{1 + 3e^{-4J/T}}, \qquad \text{i.e. } \chi = \frac{1}{T}\frac{3 + e^{-4J/T}}{1 + 3e^{-J/T}}. \qquad (*)$$

Note that for this system (and for any system with a finite N, for any reasonable physical model), all average variables are continuous functions of temperature, so we cannot speak about a definite phase transition temperature, and even about the phase transition as such – this is just a (very useful!) abstraction strictly valid only in the limit $N \to \infty$.

(ii) In the low-temperature limit ($T/J \to 0$), the exponent in the last displayed expression is negligible, and the result is reduced to

$$\chi = \frac{3}{T}, \qquad \text{for } T << J.$$

Comparing this result with Eq. (4.77) for a single spin, we may guess that for the Ising ring of N spins,

$$\chi = \frac{N}{T}, \qquad \text{for } T << J. \qquad (**)$$

Indeed, reviewing the above exact calculation for $N = 3$, we may see that the low-temperature limit corresponds to a negligible effect of the contribution from $\exp\{-4J/T\}$ in Eq. (*). But this exponent is just the Gibbs factor describing the effect of a single thermal excitation of the system, whose energy (in a negligibly low field) is the additional energy of flipping one spin, i.e. increasing the coupling energy of each of its two bonds with the neighbors by $2J$, so $\Delta E = 4J$.[26] Hence, Eq. (**) may be derived by ignoring such excitations, i.e. by taking into account only two states of the system (of all 2^N possible!): both with all spins aligned – either along the field or against it, with energies $E\uparrow = -N(J+h)$ and $E\downarrow = -N(J-h)$:

$$Z \approx \exp\left\{-\frac{-N(J+h)}{T}\right\} + \exp\left\{-\frac{-N(J-h)}{T}\right\} \equiv 2\exp\left\{\frac{NJ}{T}\right\}\cosh\frac{Nh}{T}, \qquad \text{at } T \ll J,$$

so

$$\ln Z \approx \frac{NJ}{T} + \ln\left(2\cosh\frac{Nh}{T}\right).$$

The field-dependent part of this expression is absolutely similar to that of a single "spin",[27] with the only difference that the field's effect is N times larger, so in the low-field limit,

$$Nh \ll T. \qquad (***)$$

it immediately yields Eq. (**). This result should not be surprising, because firmly aligned spins behave as a single one, just with the magnetic moment N times larger.

(iii) In the limit $N \to \infty$, Eq. (**) yields $\chi \to \infty$, i.e. a result different from the finite (if exponentially large) value (4.91), given by the exact theory described in Sec. 4.5 of the lecture notes. The reason for this discrepancy is that for such an infinite system, the limit (***) cannot be followed. This paradox emphasizes again that the notion of an "infinite system" should be taken with the same grain of salt as that of the "phase transition", especially in systems of low dimensionality – see also Eq. (4.93) and its discussion.

Problem 4.17. Calculate the average energy, entropy, and heat capacity of a uniform three-site ring of Ising-type "spins" ($s_k = \pm 1$), with *antiferromagnetic* coupling (of magnitude J) between the sites, in thermal equilibrium at temperature T, with no external magnetic field. Find the asymptotic behavior of its heat capacity for low and high temperatures, and give an interpretation of the results.

Solution: The internal energy of this system may be represented similarly to that in the previous problem (see also Eq. (4.78) of the lecture notes), but with the opposite sign of the coupling energy:

$$E_m = J(s_1 s_2 + s_2 s_3 + s_3 s_1), \quad \text{with } J > 0.$$

In two of the $2^3 = 8$ possible states of the system, all spins are aligned, and the system's energy equals $+3J$, while in all other 6 states, one of the spins has a direction opposite to its two counterparts, so the energy equals $J - 2J \equiv -J$. Hence the system's statistical sum is

$$Z = 2\exp\left\{-\frac{3J}{T}\right\} + 6\exp\left\{\frac{J}{T}\right\} \equiv 2\exp\{-3\beta J\} + 6\exp\{\beta J\}, \quad \text{where } \beta \equiv \frac{1}{\mathrm{T}}.$$

From here, we may readily calculate the free energy of the system,

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[26] Note that for an *open* Ising chain, the lowest excitation has twice lower energy – see Fig. 4.11 and its discussion in Sec. 4.5. However, this difference does not affect the validity of Eq. (**).

[27] See, e.g., Eq. (4.68) of the lecture notes, for the particular case $h_{\text{ef}} = h$.

$$F = -T\ln Z = -T\ln\left(2\exp\left\{-\frac{3J}{T}\right\} + 6\exp\left\{\frac{J}{T}\right\}\right),$$

its average energy,

$$E = -\frac{\partial(\ln Z)}{\partial\beta} = -J\,\frac{1-\exp\{-4\beta J\}}{1+(1/3)\exp\{-4\beta J\}} \equiv -J\,\frac{1-\exp\{-4J/T\}}{1+(1/3)\exp\{-4J/T\}},$$

the entropy,

$$S = \frac{E-F}{T} = \ln\left(2\exp\left\{-\frac{3J}{T}\right\} + 6\exp\left\{\frac{J}{T}\right\}\right) - \frac{J}{T}\,\frac{1-\exp\{-4J/T\}}{1+(1/3)\exp\{-4J/T\}},$$

and the heat capacity:

$$C \equiv \frac{\partial E}{\partial T} = \frac{16}{3}\left(\frac{J}{T}\right)^2 \frac{1}{\left[\exp\{+2J/T\} + (1/3)\exp\{-2J/T\}\right]^2}. \qquad (*)$$

At low temperatures, $T << J$, the second exponent in the denominator is negligible, so the heat capacity is exponentially low:

$$C \approx \frac{16}{3}\left(\frac{J}{T}\right)^2 \exp\left\{-\frac{4J}{T}\right\}, \qquad \text{at } T \to 0.$$

This result is very natural because the system stays mostly in one of its six lowest-energy, "almost-antiferromagnetic" states (with energy $E = -J$), separated from the two higher-energy states (with energy $E = +3J$) by the energy gap $\Delta = 4J$.

In the opposite limit $T \to \infty$, both factors $\exp\{\pm 2J/T\}$ in Eq. (*) approach 1, and

$$C \approx 3\left(\frac{J}{T}\right)^2 \to 0, \qquad \text{at } T >> J.$$

Such a gradual decrease of the heat capacity with temperature is also natural because at high temperatures, all eight states of the system are almost equally populated, and the remaining low heat capacity is due to the gradual decrease of the small remaining imbalance of these populations with temperature.

Problem 4.18. Using the results discussed in Sec. 4.5 of the lecture notes for the infinite 1D Ising model, calculate the average energy, free energy, entropy, and heat capacity (all per one "spin") as functions of temperature T and external field h. Sketch the temperature dependence of the heat capacity for various values of the h/J ratio and give a physical interpretation of the result.

Solution: From Eq. (4.88) of the lecture notes, rewritten as

$$Z = \lambda_+^N, \qquad \text{with } \lambda_+ = \left[\cosh\beta h + \left(\sinh^2\beta h + \exp\{-4\beta J\}\right)^{1/2}\right]\exp\{\beta J\},$$

where $\beta \equiv 1/T$, we can readily calculate the free energy:

$$\frac{F}{N} = -\frac{T}{N}\ln Z = -\frac{\ln\lambda_+}{\beta},$$

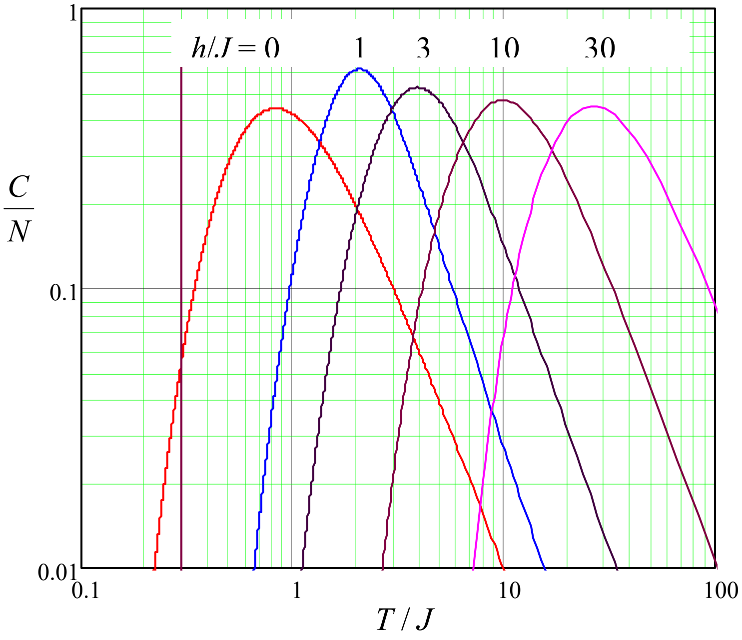
the average energy:

$$\frac{E}{N} = -\frac{1}{N}\frac{\partial(\ln Z)}{\partial\beta} = -\frac{\partial(\ln\lambda_+)}{\partial\beta},$$

and then use thermodynamic relations to calculate the entropy and the heat capacity (all per "spin"):

$$\frac{S}{N} = \frac{E-F}{NT} = \ln\lambda_+ - \beta\frac{\partial(\ln\lambda_+)}{\partial\beta}, \qquad \frac{C}{N} = \frac{1}{N}\frac{\partial E}{\partial T} = -\frac{\beta^2}{N}\frac{\partial E}{\partial\beta} = \beta^2\frac{\partial^2(\ln\lambda_+)}{\partial\beta^2}.$$

The figure on the right shows the log-log plots of this specific heat as a function of temperature, for several values of the ratio h/J.



At negligible magnetic field ($h << J$, T), the results simplify:

$$\lambda_+ = 2\cosh\frac{J}{T}, \qquad \frac{F}{N} = -T\ln\left(2\cosh\frac{J}{T}\right),$$

$$\frac{E}{N} = -J\tanh\frac{J}{T}, \qquad \frac{C}{N} = \left[\frac{J/T}{\cosh(J/T)}\right]^2.$$

This behavior of the heat capacity[28] is similar to that of the usual two-level system (formally corresponding to the 0D Ising model) – see, e.g., the model solution of Problem 2.2, with the substitution $\Delta = 2J$. This fact may be interpreted as the dominant effect, on the thermodynamics of the field-free system, of independent lowest-energy excitations, namely of the Bloch walls with the energy $E_W = 2J$ – see their discussion in Sec. 4.5 of the lecture notes.

In the opposite limit when the energy h of the spin interaction with the field is much higher than the energy J of the coupling between them but still may be comparable with the thermal energy scale T, the general formula for λ_+ reduces to

$$\lambda_+ \approx 2\cosh\frac{h}{T}, \qquad \text{for } J << h, T,$$

showing that all characteristics of the system become dependent only on the h/T ratio. (This trend is clearly visible in the figure above as a rigid horizontal shift of the plot along the axis of T/J as the ratio h/J is increased well above 1.) Moreover, this expression for λ_+, and hence those for all other thermodynamic variables including the heat capacity, are similar to those for the low-field limit, but with the replacement $J \rightarrow h$. So, the temperature dependence of C is again similar to that obtained in the solution of Problem 2.2, but now with the substitution $\Delta = 2h$. This behavior is readily explainable: at negligible coupling J, the system is just a set of N independent Ising "spins" (i.e. two-level systems), with the energy difference $\Delta = 2h$ between their possible orientations in the field.

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[28] The formulas for F/N and E/N are functionally different from those in the solution of Problem 2.2 only because of the shift of their reference level by $-J$. (This temperature-independent shift does not affect the heat capacity $C \equiv \partial E/\partial T$.)

As the figure above shows, in between these two limits, i.e. at $h \sim J$, the temperature dependence of the specific heat is quantitatively different but qualitatively similar: C vanishes both at $T \to 0$ and at $T \to \infty$, with a maximum $C_{\max} \sim N$ at $T \sim h$.

Problem 4.19. Calculate the specific heat (per "spin") for the d-dimensional Ising problem in the absence of the external field, in the molecular-field approximation. Sketch the temperature dependence of C and compare it with the corresponding plot in the previous problem's solution.

Solution: By performing the statistical averaging of both sides of Eq. (4.64) of the lecture notes, and then using Eq. (4.62), Eq. (4.66) with $h = 0$, and Eq. (4.72), we get the following expression for the average energy E:

$$\frac{E}{N} \equiv \frac{\langle E_m \rangle}{N} = Jd\eta^2 - h_{\text{ef}} \langle s_k \rangle \equiv Jd\eta^2 - (0 + 2Jd\eta)\eta \equiv -Jd\eta^2 \equiv -\frac{T_{\text{c}}}{2}\eta^2, \qquad (*)$$

where the order parameter $\eta \equiv \langle s_k \rangle$ is the solution of Eq. (4.71):

$$\eta = \tanh\left(\frac{2Jd}{T}\eta\right), \qquad \text{i.e. } \eta = \tanh\left(\frac{T_{\text{c}}}{T}\eta\right). \qquad (**)$$

In order to calculate the heat capacity, we may differentiate Eq. (*) over temperature:

$$\frac{C}{N} \equiv \frac{\partial}{\partial T}\frac{E}{N} = -T_{\text{c}}\eta\frac{\partial \eta}{\partial T},$$

and then calculate the needed derivative $\partial\eta/\partial T$ by differentiating both sides of Eq. (**):

$$\frac{\partial \eta}{\partial T} = \frac{1}{\cosh^2(T_{\text{c}}\eta/T)}\left(\frac{T_{\text{c}}}{T}\frac{\partial \eta}{\partial T} - \frac{T_{\text{c}}}{T^2}\eta\right),$$

and solving this simple (linear) equation:

$$\frac{\partial \eta}{\partial T} = -\frac{\eta}{T}\bigg/\left(\frac{T}{T_{\text{c}}}\cosh^2\frac{T_{\text{c}}\eta}{T} - 1\right),$$

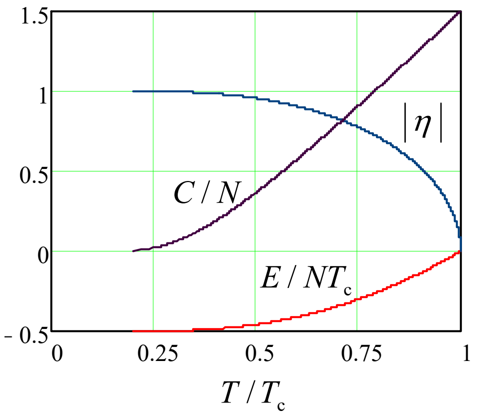
so, finally,

$$\frac{C}{N} = \frac{T_{\text{c}}}{T}\eta^2\bigg/\left(\frac{T}{T_{\text{c}}}\cosh^2\frac{T_{\text{c}}\eta}{T} - 1\right). \qquad (***)$$

All these results may be visualized without solving the transcendental equation (**) for η – simply by plotting E/N and C/N vs the normalized temperature T/T_{c}, using η as the parameter in Eqs. (*), (***), and in the relation resulting from solving Eq. (**) for the ratio T/T_{c}:

$$\frac{T}{T_{\text{c}}} = \frac{\eta}{\tanh^{-1}\eta}$$

– see the figure on the right. As the temperature is increased, the gradually growing thermal fluctuations suppress the order parameter from ±1 (full order) at $T = 0$ to zero (no order) at $T = T_{\text{c}}$. Correspondingly, the average interaction energy is increased from $(-T_{\text{c}}/2)$ to zero – see Eq. (*) again.



The heat capacity (***) requires a slightly more careful analysis. At $T \to 0$, $\eta \to \pm 1$, so $\cosh(T_c\eta/T) \to ½\exp\{T_c/T\} \to \infty$, the unity in the denominator of Eq. (***) is negligible, and we get

$$\frac{C}{N} \approx 4\left(\frac{T_c}{T}\right)^2 \exp\left\{-\frac{2T_c}{T}\right\} << 1, \qquad \text{for } T << T_c .$$

On the other hand, at $T \to T_c$, the order parameter η tends to zero, but to obtain a more exact asymptotic expression, we need to use the Taylor expansion $\tanh\xi \approx \xi(1 - \xi^2/3)$ at $\xi << 1$. Applying it to Eq. (**), we get[29]

$$\eta^2 \approx 3\left(1 - \frac{T}{T_c}\right), \qquad \text{for } 0 < 1 - \frac{T}{T_c} << 1 .$$

Plugging this expression into Eq. (***), and using the expansion $\cosh\xi \approx 1 + \xi^2/2$ at $\xi << 1$, we get

$$C \to \frac{3}{2}N, \qquad \text{for } T \to T_c .$$

This trend is clearly visible in the figure above.

Note that for all temperatures *above* T_c, the molecular-field approach gives $\eta = 0$, $E = 0$, and hence $C \equiv \partial E/\partial T = 0$, so a more "global" plot of the function $C(T)$ would have a sawtooth-like form with a vertical drop at $T = T_c \equiv 2Jd$. Comparing this result with the exact solution of the 1D Ising problem (see the leftmost plot, for $h/J = 0$, in the model solution of the previous problem), we see that the results are qualitatively similar: in both cases, the functions $C(T)$ tend to zero at $T \to 0$ and $T \to \infty$, having a peak with $C_{\max} \sim N$ at temperature $T \sim Jd$. The quantitative difference of these results should not be too surprising: as a reminder, for the systems with next-neighbor interactions, the molecular-field approximation works much better for higher dimensionalities – see, e.g., Table 4.2 in the lecture notes. Indeed, the exact and quasi-exact (numerical) solutions of the Ising problem for $d = 2$ and $d = 3$ show that for them, the functions $C(T)$ have singularities at $T = T_c$.

Problem 4.20. Prove that in the limit $T \to T_c$, the molecular-field approximation, applied to the Ising model with a spatially constant order parameter, gives results similar to those of Landau's mean-field theory with certain coefficients *a* and *b*. Calculate these coefficients and list the critical exponents defined by Eqs. (4.26), (4.28), (4.29), and (4.32), given by this approximation.

Solution: In the molecular-field approximation, the statistical sum of a *d*-dimensional Ising system is given by Eq. (4.68) of the lecture notes:

$$Z = 2\cosh\frac{h_{\text{ef}}}{T}, \qquad \text{where } h_{\text{ef}} \equiv h + 2Jd\eta.$$

Using it to construct the free energy, we have to include the background term $\Delta F = JdN\eta^2$, i.e. the first term in Eq. (4.64), as well because it also depends on the order parameter. From here, and the fundamental Eq. (2.63), the free energy per "spin" is

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[29] Note that according to Eq. (4.26), this relation means that the critical exponent β is equal to ½, as was already found (using a different approach) in the solution of Problem 14.

$$\frac{F}{N}=\frac{\Delta F}{N}-T\ln Z=Jd\eta^2-T\ln\left(2\cosh\frac{h_{\text{ef}}}{T}\right). \qquad (*)$$

As a sanity check, the equilibrium condition $\partial F/\partial\eta = 0$ yields the equation

$$\eta=\tanh\frac{h_{\text{ef}}}{T},$$

which coincides with Eq. (4.69) derived directly from statistics.

Landau's mean-field theory may be quantitatively correct only if the order parameter η tends to zero, and the external field h is also small, so $h_{\text{ef}} \to 0$. In this limit, we may expand Eq. (*) into the Taylor series in small η and h. By combining the series $\ln(1+\zeta)=\zeta-\zeta^2/2+\dots$ and $\cosh\xi = 1+\xi^2/2+\xi^4/24+\dots$, we get

$$\ln(\cosh\xi)=\left(\frac{\xi^2}{2}+\frac{\xi^4}{24}+\dots\right)-\frac{1}{2}\left(\frac{\xi^2}{2}+\frac{\xi^4}{24}+\dots\right)^2+\dots=\frac{\xi^2}{2}-\frac{\xi^4}{12}+\dots,$$

and displaying, per Eq. (4.46), only the leading terms up to $O(\eta^4)$ and $O(h)$, we get

$$\frac{F}{N}=Jd\eta^2-T\ln 2-\frac{T}{2}\left(\frac{2Jd\eta}{T}\right)^2+\frac{T}{12}\left(\frac{2Jd\eta}{T}\right)^4-\frac{T}{2}2h\frac{2Jd\eta}{T}+\dots.$$

Since according to Eq. (4.72), in the molecular-field approximation, the product $2Jd$ is just the critical temperature T_{c}, the last formula may be rewritten as

$$\frac{F}{N}=-T\ln 2-\frac{T_{\text{c}}}{2}\left(\frac{T_{\text{c}}}{T}-1\right)\eta^2+\frac{T}{12}\left(\frac{T_{\text{c}}}{T}\right)^4\eta^4-\frac{T_{\text{c}}}{T}h\eta+\dots.$$

Comparing this result with Landau's expansion (4.46) with $\nabla\eta = 0$,

$$\Delta f\equiv\frac{F(\eta)-F(0)}{V}=a\tilde{t}\,\eta^2+\frac{1}{2}b\eta^4-nh\eta+\dots,$$

where $0<-\tilde{t}\equiv(T_{\text{c}}-T)/T_{\text{c}}\ll 1$, we see that all their three leading terms coincide if

$$a=n\frac{T_{\text{c}}}{2},\qquad b=n\frac{T_{\text{c}}}{6},$$

where $n = N/V$ is the volumic density of the "spins".

So, in the molecular-field approximation, the free energy of the Ising model (and hence all its thermodynamic characteristics) is reduced, at $T \to T_{\text{c}}$, to that described by Landau's mean-field theory, at least for the spatially-independent order parameter.[30] As a result, the critical exponents of the latter theory, calculated in Sec. 4.3:

$$\alpha=0,\qquad\beta=½,\qquad\gamma=1,\qquad\delta=3,$$

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[30] An extension of this analysis to (relatively slow) variations of the order parameter in space requires the molecular-field approximation to be generalized – similarly in spirit to the van der Pol method in classical mechanics (see, e.g., CM Sec. 5.3) and the WKB approximation in quantum mechanics (see, e.g., QM Sec. 2.4). Such generalization is a very good additional exercise, highly recommended to advanced readers.

are valid for the former approximation as well.

This calculation illustrates again that Weiss' molecular-field approximation and Landau's theory belong to different levels of physical phenomenology, and shows how dangerous it is to label them both "mean-field theories". (Unfortunately, in physics this term is over-used, and often requires a qualification.)

Problem 4.21. Assuming that the statistical sum Z_N of a field-free, open-ended 1D Ising system of N "spins" with arbitrary coefficients J_k is known, calculate Z_{N+1}. Then use the result to obtain an explicit expression for Z_N and compare it with Eq. (4.88) of the lecture notes.

Solution: For a field-free, open-ended chain with arbitrary J_k, Eq. (4.23) of the lecture notes may be rewritten as

$$E_m = -\sum_{k=1}^{N-1} J_k s_k s_{k+1} .$$

The statistical sum of the chain is

$$Z_N = \sum_m \exp\left\{-\frac{E_m}{T}\right\} \equiv \sum_{\substack{s_k=\pm1,\text{ for}\\ k=1,2,\dots,N}} \exp\left\{\sum_{k=1}^{N-1}\frac{J_k}{T}s_k s_{k+1}\right\} \equiv \sum_{\substack{s_k=\pm1,\text{ for}\\ k=1,2,\dots,N}} \prod_{k=1}^{N-1}\exp\left\{\frac{J_k}{T}s_k s_{k+1}\right\}. \qquad (*)$$

Let us assume that we already know this sum (of 2^{N-1} terms), and use it to calculate the statistical sum Z_{N+1} (of 2^N terms) for a similar chain of Z_{N+1} spins. The energy of the new system differs from that of the old one only by the addition of the energy $\Delta = -J_N s_N s_{N+1}$ of the new coupling link. For any fixed set of "old" spins $\{s_1, s_2,\dots, s_N\}$, the additional energy may take only two values, $\pm J_N$, thus replacing each term of the sum (*) with two terms, with additional factors $\exp\{-\Delta/T\} = \exp\{\mp J_N/T\}$. As a result, we get

$$Z_{N+1} = \sum_{\substack{s_k=\pm1,\text{ for}\\ k=1,2,\dots,N}} \exp\left\{\sum_{k=1}^{N-1}\frac{J_k}{T}s_k s_{k+1}\right\}\left(\exp\left\{-\frac{J_N}{T}\right\}+\exp\left\{+\frac{J_N}{T}\right\}\right) \equiv Z_N \times 2\cosh\frac{J_N}{T}. \qquad (**)$$

Now we may apply this simple recurrence relation sequentially, starting from the (easy) case $N = 2$, i.e. for the system with just one link, whose statistical sum has only four terms, with two equal pairs:

$$Z_2 = \sum_{\substack{s_k=\pm1,\text{ for}\\ k=1,2}} \exp\left\{\frac{J_1}{T}s_1 s_2\right\} = 2\exp\left\{+\frac{J_1}{T}\right\} + 2\exp\left\{-\frac{J_1}{T}\right\} \equiv 2\times 2\cosh\frac{J_1}{T}.$$

Now we can use Eq. (**) sequentially to write the result for an arbitrary $N \geq 2$:

$$Z_N = 2\times 2\cosh\frac{J_1}{T}\times 2\cosh\frac{J_2}{T}\times\dots\times 2\cosh\frac{J_{N-1}}{T} \equiv 2\prod_{k=1}^{N-1}\left(2\cosh\frac{J_k}{T}\right).$$

For a uniform chain, with $J_1 = J_2 =\dots= J_{N-1} \equiv J$, this expression reduces to

$$Z_N = 2\left(2\cosh\frac{J}{T}\right)^{N-1}.$$

This formula differs from Eq. (4.88), for a ring of $(N - 1)$ sites and our current case $h = 0$, only by an inconsequential front factor of 2. So, as the reader can see, for the zero-field case, this solution of the 1D Ising problem is much easier than the transfer matrix approach described in Sec. 4.5 of the lecture notes.

Problem 4.22. Use the molecular-field approximation to calculate the critical temperature and the low-field susceptibility of a d-dimensional cubic lattice of spins, described by the so-called *classical Heisenberg model*:[31]

$$E_m = -J\sum_{\{k,k'\}} \mathbf{s}_k \cdot \mathbf{s}_{k'} - \sum_k \mathbf{h}\cdot\mathbf{s}_k \ .$$

Here, in contrast to the (otherwise, very similar) Ising model (4.23), the spin of each site is described as a classical 3D vector $\mathbf{s}_k = \{s_{xk}, s_{yk}, s_{zk}\}$ of unit length: $s_k^2 = 1$.

Solution: Let us align the z-axis with the direction of the external magnetic field $\mathbf{h}$, and use the shorthand $s_{zk} \equiv s_k$; then the energy of the m^{th} state may be rewritten as

$$E_m = -J\sum_{\{k,k'\}}\left(s_k s_{k'} + s_{xk}s_{xk'} + s_{yk}s_{yk'}\right) - h\sum_k s_k \ .$$

In the molecular-field approximation, each Cartesian component of the spin should be represented in a form similar to Eq. (4.62) of the lecture notes. However, due to the symmetry of the problem with respect to the reflections $x \to -x$ and $y \to -y$, the average $\langle s\rangle$ may be different from zero only for the z-component (for which it equals η). Hence the two last terms in the parentheses include only the squares of fluctuation terms:

$$E_m = -J\sum_{\{k,k'\}}(\eta+\tilde{s}_k)(\eta+\tilde{s}_{k'}) - J\sum_{\{k,,k'\}}\left(\tilde{s}_{xk}\tilde{s}_{xk'} + \tilde{s}_{yk}\tilde{s}_{yk'}\right) - h\sum_k s_k, \qquad \text{with } |\tilde{s}_k| << 1 .$$

Multiplying the parentheses under the first sum and neglecting all terms quadratic in small fluctuations (see the discussion of the transition from Eq. (4.63) to Eq. (4.64) of the lecture notes), we get an expression formally similar to Eq. (4.64) for the Ising model,

$$E_m \approx (NJd)\eta^2 - h_{\text{ef}}\sum_k s_k ,$$

describing a set of N independent classical "spins" s_k placed into the effective (external + "molecular") field (4.65):

$$h_{\text{ef}} \equiv h + (2Jd)\eta . \qquad (*)$$

However, in contrast with the Ising model, s_k may now take any real values from –1 to +1.

This situation was one of the subjects of Problem 2.4, and we can use its solution. In our current notation, the result for the order parameter reads

$$\eta \equiv \langle s\rangle = L\left(\frac{h_{ef}}{T}\right) \equiv \coth\frac{h_{\text{ef}}}{T} - \frac{T}{h_{\text{ef}}}. \qquad (**)$$

This *Langevin function* is qualitatively but not quantitatively similar to Eq. (4.69) for the Ising model; most substantially, it has a three-fold lower slope at the origin:

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[31] This classical model is formally similar to the generalization of the genuine (quantum) Heisenberg model (21) to an arbitrary spin s and serves as its infinite-spin limit.

$$\frac{\partial \eta}{\partial h_{\text{ef}}}\bigg|_{h_{\text{ef}}=0} = \frac{1}{3T}.$$

This difference affects the phase transition temperature T_c. Indeed, combining Eqs. (*) and (**), and linearizing the result in small h, h_{ef}, and η (exactly as was done in Sec. 4.4 of the lecture notes for the Ising model), for the low-field susceptibility, we get the same Curie-Weiss law (4.76),

$$\chi \equiv \frac{\partial \eta}{\partial h}\bigg|_{h=0} = \frac{1}{T - T_c},$$

but with a three times lower critical temperature:

$$T_c = \frac{2Jd}{3}.$$

This reduction is a natural result of the spin-to-field interaction weakening due to the availability of intermediate values, $-1 < s_k < +1$, of the field-aligned spin components. In turn, this availability is the immediate result of taking into account all three Cartesian components of the vector **s**.

Problem 4.23. Use the molecular-field approximation to calculate the coefficient a in Landau's expansion (4.46) for a 3D cubic lattice of spins described by the classical Heisenberg model (whose analysis was the subject of the previous problem).

Solution: As was discussed in the model solution of the previous problem, in the molecular-field approximation, the energy of such a system (for the case $d = 3$) is reduced to

$$E_m' \equiv E_m - 3NJ\eta^2 = -h_{\text{ef}} \sum_k s_k \equiv -h_{\text{ef}} \sum_k \cos\theta_k, \qquad \text{with } h_{\text{ef}} \equiv h + 6J\eta, \qquad \eta \equiv \langle \cos\theta \rangle,$$

where θ_k is the angle between the direction of the k^{th} spin vector (of the unit length) and the applied field. Besides the non-fluctuating offset

$$\Delta E \equiv E_m - E_m' = 3NJ\eta^2,$$

this is just the energy of a system of independent classical magnetic dipoles in the effective external field h_{ef}. Though an analysis of this system was one of the subjects of Problem 2.4, the statistical sum was not directly calculated in its model solution; let us do this now, by using the same transition from summation to integration over the full solid angle $d\Omega = \sin\theta d\theta d\varphi$:

$$Z = \sum_m \exp\left\{-\frac{E_m'/N}{NT}\right\} = 2\pi \int_0^{\pi} \exp\left\{-\frac{h_{\text{ef}}\cos\theta}{T}\right\} \sin\theta d\theta = \frac{2\pi T}{h_{\text{ef}}} \int_{-h_{\text{ef}}/T}^{+h_{\text{ef}}/T} e^{\xi} d\xi = \frac{4\pi T}{h_{\text{ef}}} \sinh\frac{h_{\text{ef}}}{T}.$$

At $h = 0$, i.e. $h_{\text{ef}} = 6J\eta$, this expression is reduced to

$$Z = \frac{2\pi T}{3J\eta} \sinh\frac{6J\eta}{T}.$$

Now, similarly to how this task was performed for the Ising model in the solution of Problem 20, we may calculate the free energy F/N per spin by using Eq. (2.63) of the lecture notes, but adding to it the non-fluctuating offset of the energy, $\Delta F/N = \Delta E/N = 3J\eta^2$:

$$\frac{F}{N} = -T\ln Z + \frac{\Delta F}{N} = -T\ln\left(\frac{2\pi T}{3J\eta}\sinh\frac{6J\eta}{T}\right) + 3J\eta^2.$$

Expanding this expression into the Taylor series in the small order parameter η, and, we get[32]

$$\frac{F}{N} \approx -T\ln\left\{\frac{2\pi T}{3J\eta}\left[\left(\frac{6J\eta}{T}\right) + \frac{1}{3!}\left(\frac{6J\eta}{T}\right)^3\right]\right\} + 3J\eta^2 \equiv -T\ln 4\pi - T\ln\left[1 + \frac{1}{6}\left(\frac{6J\eta}{T}\right)^2\right] + 3J\eta^2$$

$$\approx -T\ln 4\pi - T\frac{1}{6}\left(\frac{6J\eta}{T}\right)^2 + 3J\eta^2 \equiv -T\ln 4\pi - 3J\left(\frac{2J}{T} - 1\right)\eta^2.$$

We see that the coefficient at η^2 vanishes at $T = 2J$, i.e. at the critical temperature $T_c = 2J$ (already calculated in Problem 22 for an arbitrary dimensionality d), and is negative below T_c, as it should – see Eq. (4.44) of the lecture notes. Now comparing this result with the Landau's expansion of F at temperatures close to T_c,

$$\frac{F(T)}{V} = \frac{F(0)}{V} - a\left(\frac{T_c}{T} - 1\right)\eta^2 + ...,$$

where V is the volume of the system, we get

$$a = 3Jn = \frac{3}{2}nT_c,$$

where $n = N/V$ is the spin density. Note that this value of a, in terms of the critical temperature, is three times higher than that calculated in the solution of Problem 20 for the Ising model, at the same coupling constant J. This is the same three-fold change as was discussed, for the low-field susceptibility of single spins, in the solution of Problem 2.4, and for the molecular-field value of the critical temperature, in the solution of the previous problem.

Problem 4.24. Use the molecular-field approximation to calculate the critical temperature of the ferromagnetic transition for the d-dimensional cubic Heisenberg lattice of arbitrary (either integer or half-integer) quantum spins s.

Hint: This model is described by Eq. (4.21) of the lecture notes, with $\hat{\boldsymbol{\sigma}}$ now meaning the vector operator of spin s, in units of Planck's constant $\hbar$.

Solution: Let us start with rewriting the *classical* Ising model (4.23) in an equivalent form

$$E_m = \sum_k E_k, \qquad \text{with } E_k = -s_k\left(h + J\sum_{k'} s_{k'}\right),$$

where the sum over k' is limited to the sites adjacent to the site number k. As Eqs. (4.64)-(4.65) show, the molecular-field approximation is reduced to the replacement of the expression in the parentheses with its ensemble average (plus a constant irrelevant for the averaging procedure):

$$E_k \to E_k' = -s_k h_{\text{ef}} + \text{const}, \qquad \text{where } h_{\text{ef}} \equiv h + J\sum_{k'}\langle s_{k'}\rangle.$$

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[32] The second Landau coefficient, b, may be readily calculated by keeping the next term, proportional to η^5, in the Taylor expansion of the sinh function.

Inspired by this observation, let us rewrite Eq. (4.21) in a similar form:

$$\hat{H} = \sum_k \hat{H}_k, \qquad \text{with } \hat{H}_k = -\hat{\boldsymbol{\sigma}}_{k'} \cdot \left(\mathbf{h} + J \sum_{k'} \hat{\boldsymbol{\sigma}}_{k'} \right), \tag{*}$$

and pursue the mean-field approximation by averaging the expression in the parentheses, with the only difference that now this should be the average not only over an ensemble of many similar spins but also over the quantum states of each spin – i.e. its quantum-mechanical expectation value:[33]

$$\hat{H}_k \to \hat{H}_k' \equiv -\hat{\boldsymbol{\sigma}}_k \cdot \mathbf{h}_{\text{ef}} + \text{const}, \qquad \text{where } \mathbf{h}_{\text{ef}} \equiv \mathbf{h} + J \sum_{k'} \langle \boldsymbol{\sigma}_{k'} \rangle .$$

Since this averaging gives similar results for all spins of the lattice, including the $2d$ ones adjacent to any given site, this relation becomes

$$\mathbf{h}_{\text{ef}} \equiv \mathbf{h} + 2Jd \langle \boldsymbol{\sigma} \rangle .$$

The quantum properties of a system with the Hamiltonian, i.e. of a spin placed into a classical magnetic field, are well-known. In this series, besides a detailed discussion of these properties in QM Sec. 5.7, their summary sufficient for our current purposes was given in the *Hint* to Problem 2.7 of this course. Moreover, the statistical properties of this system were already calculated in the solution of that problem. In particular, it shows that the average spin is directed along the applied field, and in the low-field limit (in our current notation – see Eq. (4.22) of the lecture notes):

$$\langle \boldsymbol{\sigma} \rangle \to \frac{s(s+1)}{3T} \gamma \hbar \boldsymbol{\mathscr{B}} \equiv \frac{s(s+1)}{3T} \mathbf{h}, \qquad \text{for } \mathbf{h} \to 0. \tag{**}$$

With the replacement $\mathbf{h} \to \mathbf{h}_{\text{ef}}$, Eq. (**) turns into the self-consistency relation

$$\langle \boldsymbol{\sigma} \rangle = \frac{s(s+1)}{3T} \left(\mathbf{h} + 2Jd \langle \boldsymbol{\sigma} \rangle \right).$$

This relation is satisfied at $\mathbf{h} \to 0$ (i.e. the order parameter arises even without an external field) when $2Jds(s+1)/3T = 1$, giving us the following critical temperature of the ferromagnetic transition in the Heisenberg lattice:

$$T_{\text{c}} = \frac{2Jd\, s(s+1)}{3}. \tag{***}$$

This result may be compared with Eq. (4.72) of the lecture notes for the classical Ising system, and the solution of Problem 22. In particular, at $s \to \infty$, Eq. (***) tends to the critical temperature of the classical Heisenberg model, after the proper rescaling of the "spin" magnitude ($s^2 \to 1$).

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[33] See, e.g., QM Secs 1.2-1.3.

Chapter 5. Fluctuations

Problem 5.1. By treating the first 30 digits of number $\pi = 3.1415\ldots$ as a statistical ensemble of integers k (equal to 3, 1, 4, 1, 5,…), calculate the average $\langle k\rangle$ and the r.m.s. fluctuation δk. Compare the results with those for the ensemble of randomly selected decimal integers 0, 1, 2,…, 9.

Solution: A high-precision value of π may be either found on many Web sites, e.g., in *Wikipedia* (http://en.wikipedia.org/wiki/Pi), or generated by using any digital calculator (say, that on your smartphone) – for example, as $4\tan^{-1}(1)$. For our purposes, we need just $M = 30$ first digits:

$$\pi = 3.14159\ 26535\ 89793\ 23846\ 26433\ 8327\ldots$$

From here, the calculation can be done either with a computer, by writing and running a simple script, using the number rounding routine readily available in virtually all numerical libraries to reformat the number into the integer array $k_m = 3, 1, 4,\ldots$, or just by brute force, by using a calculator. For 30 digits, the required time is comparable (and insignificant :-). The results are:

$$\langle k\rangle \equiv \frac{1}{M}\sum_{m=1}^{M} k_m \approx 4.70\,;$$

$$\langle \tilde{k}^2\rangle \equiv \frac{1}{M}\sum_{m=1}^{M}\tilde{k}_m^2 \equiv \frac{1}{M}\sum_{m=1}^{M}\left(k_m - \langle k\rangle\right)^2 = \frac{1}{M}\sum_{m=1}^{M}k_m^2 - \langle k\rangle^2 \approx 6.08\,,$$

so

$$\delta k \equiv \langle \tilde{k}^2\rangle^{1/2} \approx 2.47, \qquad \frac{\delta k}{\langle k\rangle} \approx 0.52.$$

For an infinite set of random decimal integers (with equal probabilities $W_n = 1/N$ to take any of $N = 10$ possible values $k_n = n' \equiv n - 1 = 0, 1, 2,\ldots,9$), the corresponding expectation values are[34]

$$\langle k\rangle = \sum_{n=1}^{N} k_n W_n = \frac{1}{N}\sum_{n=1}^{N} k_n = \frac{1}{N}\sum_{n'=0}^{N-1} n' = \frac{1}{N}\frac{(N-1)N}{2} \equiv \frac{N-1}{2} = 4.5\,,$$

$$\langle \tilde{k}^2\rangle = \frac{1}{N}\sum_{n=1}^{N} k_n^2 - \langle k\rangle^2 = \frac{1}{N}\sum_{n'=0}^{N-1} n'^2 - \langle k\rangle^2 = \frac{1}{N}\frac{(N-1)N(2N-1)}{6} - \left(\frac{N-1}{2}\right)^2 \equiv \frac{N^2-1}{12} = 8.25\,,$$

so

$$\delta k \equiv \langle \tilde{k}^2\rangle^{1/2} = \left(\frac{N^2-1}{12}\right)^{1/2} \approx 2.87, \qquad \frac{\delta k}{\langle k\rangle} \approx 0.638\,,$$

i.e. close to the results as for the digits of the number π.

A good sanity check here is that the difference between the calculated averages of k in these two (very similar) statistical ensembles is much smaller than their absolute r.m.s. uncertainties. Note also that the *relative* statistical uncertainty of the random integer set would be nonvanishing (and substantial!) even if their number N was infinite:

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[34] For the sum calculation, the well-known MA Eqs. (2.5b) and (2.6a) may be used.

$$\frac{\delta k}{\langle k \rangle} = \left[\frac{N+1}{3(N-1)} \right]^{1/2} \rightarrow_{N\to\infty} = \frac{1}{\sqrt{3}} \approx 0.577\,.$$

Problem 5.2. An ideal classical gas of N similar particles fills a spherical cavity of radius R. Calculate the variance of fluctuations of the position $\mathbf{r}$ of its center of mass, in equilibrium.

Solution: According to the center of mass definition,[35] for a system of particles of the same mass, its radius vector $\mathbf{r}$ is expressed via those of the particles as

$$\mathbf{r} = \frac{1}{N} \sum_{k=1}^{N} \mathbf{r}_k \,, \tag{*}$$

where k are particle numbers. (The numbering order is arbitrary.) Due to the spherical symmetry of our problem, the average position of the center of mass has to be in the cavity's center, so by taking this point for the origin, we have $\langle \mathbf{r} \rangle = 0$. Due to the spherical symmetry of our system, the probabilities of the c.o.m.'s deviations from that point in any direction are equal, so let us start with the calculation of the scalar variance

$$\left\langle \tilde{r}^2 \right\rangle \equiv \left\langle \tilde{\mathbf{r}}^2 \right\rangle \equiv \left\langle (\mathbf{r} - \langle \mathbf{r} \rangle)^2 \right\rangle = \left\langle r^2 \right\rangle.$$

Since for an ideal gas, all $\mathbf{r}_k$ are uncorrelated, Eq. (*) is functionally similar to Eq. (5.7) of the lecture notes, so by reviewing the derivation of Eq. (5.11), we can readily get its analog:

$$\left\langle r^2 \right\rangle = \frac{1}{N} \left\langle r_k^2 \right\rangle.$$

Since all positions of a free particle inside the cavity have the same probability density $w = 1/V$, where $V = (4\pi/3)R^3$ is the sphere's volume, we may use Eq. (2.10) to write

$$\left\langle r_k^2 \right\rangle = \frac{1}{V} \int_V r_k^2 d^3 r_k = \frac{4\pi}{V} \int_0^R r_k^4 dr_k = \frac{4\pi}{V} \frac{R^5}{5} = \frac{3}{5} R^2,$$

so, finally,

$$\left\langle \tilde{r}^2 \right\rangle = \left\langle r^2 \right\rangle = \frac{3}{5N} R^2.$$

Also, due to the already mentioned fluctuation isotropy, the variances of all Cartesian coordinates of the center of mass of this system are equal; hence we may write

$$\tilde{x}^2 = \tilde{y}^2 = \tilde{z}^2 = \frac{1}{3} \left\langle \tilde{x}^2 + \tilde{y}^2 + \tilde{z}^2 \right\rangle \equiv \frac{1}{3} \left\langle \tilde{r}^2 \right\rangle = \frac{1}{5N} R^2.$$

Problem 5.3. Calculate the variance of fluctuations of a magnetic moment $\mathscr{m}$ placed into an external magnetic field $\mathscr{H}$, within the same two models as in Problem 2.4:[36]

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[35] See, e.g., CM Eq. (4.13).

[36] Note that these two cases may be considered as the non-interacting limits of, respectively, the Ising model (4.23) and the classical limit of the Heisenberg model (4.21), whose analysis within the Weiss approximation was the subject of Problems 4.22 and 4.23.

(i) a spin-½ with a gyromagnetic ratio γ, and

(ii) a classical magnetic moment $\boldsymbol{\mathscr{m}}$, of a fixed magnitude $\mathscr{m}_0$, but an arbitrary orientation,

both in thermal equilibrium at temperature T. Compare the results.

Hint: Mind all three Cartesian components of the vector $\boldsymbol{\mathscr{m}}$.

Solutions:

(i) As was discussed in the model solution of Problems 2.2-2.4, for a spin-½ in an external magnetic field, the stationary values of the magnetic moment's component in the field's direction are $\pm\mathscr{m}_0$, where $\mathscr{m}_0 \equiv \gamma\hbar/2$. The corresponding energies are

$$E_m = \pm \mathscr{m}_0 \mathscr{B} \equiv \pm h, ,$$

so their probabilities $W_\pm$ in the canonical ensemble are

$$W_\pm = \frac{1}{Z}\exp\left\{\mp\frac{h}{T}\right\} = \frac{\exp\{\mp h/T\}}{\exp\{+h/T\}+\exp\{-h/T\}}, \qquad \text{with } W_+ + W_- = 1,$$

so

$$\langle \mathscr{m}_z \rangle = (+\mathscr{m}_0)W_- + (-\mathscr{m}_0)W_- = \mathscr{m}_0 \frac{\exp\{+h/T\}-\exp\{+h/T\}}{\exp\{+h/T\}+\exp\{-h/T\}} \equiv \mathscr{m}_0 \tanh\frac{h}{T}.$$

The average square of $\mathscr{m}_z$ may be calculated similarly:

$$\langle \mathscr{m}_z^2 \rangle = (+\mathscr{m}_0)^2 W_+ + (-\mathscr{m}_0)^2 W_- \equiv \mathscr{m}_0^2 (W_+ + W_-) = \mathscr{m}_0^2 .$$

Now we can use the general Eq. (5.4b) to calculate the variance of the moment's fluctuations:

$$\langle \tilde{\mathscr{m}}_z^2 \rangle = \langle \mathscr{m}_z^2 \rangle - \langle \mathscr{m}_z \rangle^2 = \mathscr{m}_0^2 - \mathscr{m}_0^2 \tanh^2\frac{h}{T} \equiv \frac{\mathscr{m}_0^2}{\cosh^2(h/T)}. \qquad (*)$$

Note that this result may be also obtained differently – by using Eq. (5.37a) of the lecture notes and the analogy between two canonical pairs of variables: $\{-P, V\}$ for a system under mechanical pressure and $\{\mu_0\mathscr{H}, \mathscr{m}_z\}$ for a single magnetic moment, or rather its component in the direction of the field.[37] This analogy immediately yields Eq. (*) again:

$$\langle \tilde{\mathscr{m}}_z^2 \rangle = T\left(-\frac{\partial\langle \mathscr{m}_z\rangle}{\partial(-\mathscr{B})}\right)_T \equiv T\mathscr{m}_0^2\left(\frac{\partial}{\partial h}\tanh\frac{h}{T}\right)_T = \frac{\mathscr{m}_0^2}{\cosh^2(h/T)}.$$

In the limit of relatively high temperatures, i.e. of relatively low fields ($h << T$), the denominator of this expression tends to 1, so the moment's variance is the largest, approaching $\mathscr{m}_0^2$, while in the opposite, low-temperature (high-field) limit, the fluctuations are exponentially small:

$$\langle \tilde{\mathscr{m}}_z^2 \rangle \to 4\mathscr{m}_0^2 \exp\left\{-\frac{2h}{T}\right\} \to 0, \qquad \text{at } \frac{h}{T}\to\infty .$$

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[37] See, e.g., Secs. 1.1 and 4.5 of the lecture notes, in particular Eq. (1.3), and the discussion leading to Eq. (4.90).

This is a natural result for a system with the energy gap $\Delta = 2h$ separating the ground state of the system from its (only) excited state.

Now let us consider two other components of the magnetic moment. Their averages evidently equal zero due to the axial symmetry of the system:

$$\langle \mathscr{m}_x \rangle = \langle \mathscr{m}_y \rangle = 0 .$$

The same symmetry may be used to write $\langle \mathscr{m}_x^2 \rangle = \langle \mathscr{m}_y^2 \rangle$, so since $\langle \mathscr{m}^2 \rangle \equiv \langle \mathscr{m}_x^2 \rangle + \langle \mathscr{m}_y^2 \rangle + \langle \mathscr{m}_z^2 \rangle$, we have

$$\langle \mathscr{m}_x^2 \rangle = \langle \mathscr{m}_y^2 \rangle = \frac{1}{2}\left(\langle \mathscr{m}_x^2 \rangle + \langle \mathscr{m}_y^2 \rangle \right) = \frac{1}{2}\left(\langle \mathscr{m}^2 \rangle - \langle \mathscr{m}_z^2 \rangle \right) = \frac{1}{2}\left(\langle \mathscr{m}^2 \rangle - \mathscr{m}_0^2 \right).$$

Here we should avoid the error of taking $\langle \mathscr{m}^2 \rangle$ equal to $\mathscr{m}_0^2$. Indeed, in quantum mechanics, the expectation value of the spin's square is $\langle S^2 \rangle = \hbar^2 s(s+1)$, so for a spin-½, $\langle S^2 \rangle = (3/4)\hbar^2$. (Since this equality is valid for any quantum state of the spin, it is also valid for the average over any statistical ensemble.) Hence, for $\mathscr{m} \equiv \gamma \mathbf{S}$, we get

$$\langle \mathscr{m}^2 \rangle = \gamma^2 \langle S^2 \rangle = \frac{3}{4}\gamma^2 \hbar^2 \equiv 3\mathscr{m}_0^2 ,$$

so

$$\langle \tilde{\mathscr{m}}_x^2 \rangle = \langle \tilde{\mathscr{m}}_y^2 \rangle = \langle \mathscr{m}_x^2 \rangle = \langle \mathscr{m}_y^2 \rangle = \frac{1}{2}\left(3\mathscr{m}_0^2 - \mathscr{m}_0^2 \right) \equiv \mathscr{m}_0^2 .$$

This is the same result as we had for $\langle \tilde{\mathscr{m}}_z^2 \rangle$ in the absence of the field – a good sanity check.

So, the fluctuations of the lateral components of the magnetic moment are temperature-independent and physically caused just by their quantum uncertainty. (These fluctuations are ultimately large even at $T = 0$, and thermal agitation of the spin at $T > 0$ cannot increase them.)

(ii) As was discussed in the model solution of Problem 2.4, in this model, the probability distribution is continuous, with the angular density

$$w \equiv \frac{dW}{d\Omega} = \frac{1}{Z}\exp\left\{ -\frac{E}{T} \right\}, \qquad \text{with } E = -\mathbf{m} \cdot \mathscr{B} = -h\cos\theta$$

(with the same notation, $h \equiv \mathscr{m}\mathscr{B}$, for the normalized magnetic field), giving the following averages:

$$\begin{aligned}
\langle \mathscr{m}_x \rangle &= \oint_{4\pi} \mathscr{m}_0 \sin\theta \cos\varphi \exp\left\{ \frac{h\cos\theta}{T} \right\} d\Omega \Big/ \oint_{4\pi} \exp\left\{ \frac{h\cos\theta}{T} \right\} d\Omega = 0, \\
\langle \mathscr{m}_y \rangle &= \oint_{4\pi} \mathscr{m}_0 \sin\theta \sin\varphi \exp\left\{ \frac{h\cos\theta}{T} \right\} d\Omega \Big/ \oint_{4\pi} \exp\left\{ \frac{h\cos\theta}{T} \right\} d\Omega = 0, \qquad . \\
\langle \mathscr{m}_z \rangle &= \oint_{4\pi} \mathscr{m}_0 \cos\theta \exp\left\{ \frac{h\cos\theta}{T} \right\} d\Omega \Big/ \oint_{4\pi} \exp\left\{ \frac{h\cos\theta}{T} \right\} d\Omega = m_0 \left(\coth\frac{h}{T} - \frac{T}{h} \right).
\end{aligned}$$

We may now calculate the average squares of all Cartesian components of the vector $\mathscr{m}$ in the same way. However, since due to the axial symmetry of the problem, those of the x- and y-components have to be equal, it is convenient to calculate them both in one shot:

$$\langle \mathscr{m}_x^2 \rangle = \langle \mathscr{m}_y^2 \rangle = \frac{1}{2}\langle \mathscr{m}_x^2 + \mathscr{m}_y^2 \rangle = \frac{1}{2}\left\langle (\mathscr{m}_0 \sin\theta \cos\varphi)^2 + (\mathscr{m}_0 \sin\theta \sin\varphi)^2 \right\rangle \equiv \frac{\mathscr{m}_0^2}{2}\langle \sin^2\theta \rangle$$

$$= \frac{\mathscr{m}_0^2}{2}\int_0^\pi \sin^2\theta \exp\left\{\frac{h\cos\theta}{T}\right\}\sin\theta d\theta \Bigg/ \int_0^\pi \exp\left\{\frac{h\cos\theta}{T}\right\}\sin\theta d\theta .$$

These integrals may be worked out exactly as in the solution of Problem 2.4, by introducing the new variable $\xi \equiv (h/T)\cos\theta$, so $\cos\theta = (T/h)\xi$, $\sin\theta d\theta \equiv -d(\cos\theta) = -(T/h)d\xi$, and $\sin^2\theta = 1 - (T/h)^2\xi^2$:

$$\int_0^\pi \exp\left\{\frac{h\cos\theta}{T}\right\}\sin\theta d\theta = \frac{T}{h}\int_{-h/T}^{+h/T} e^{\xi} d\xi = \frac{T}{h}\left(e^{\xi}\right)_{\xi=-h/T}^{\xi=+h/T} = \frac{2T}{h}\sinh\frac{h}{T},$$

$$\int_0^\pi \sin^2\theta \exp\left\{\frac{h\cos\theta}{T}\right\}\sin\theta d\theta = \frac{T}{h}\int_{-h/T}^{+h/T}\left[1 - \left(\frac{T}{h}\right)^2 \xi^2\right] e^{\xi} d\xi \equiv \frac{T}{h}\int_{-h/T}^{+h/T} e^{\xi} d\xi - \left(\frac{T}{h}\right)^3 \int_{-h/T}^{+h/T} \xi^2 e^{\xi} d\xi .$$

The first of these two integrals is exactly the same as was (easily :-) worked out above, while the second one requires two sequential integrations by parts, giving

$$\int_{-h/T}^{+h/T} \xi^2 e^{\xi} d\xi = \left[\left(\xi^2 - 2\xi + 2\right)e^{\xi}\right]_{\xi-h/T}^{\xi=+h/T} = 2\left[\left(\frac{h}{T}\right)^2 + 2\right]\sinh\frac{h}{T} - 4\frac{h}{T}\cosh\frac{h}{T} .$$

As a result, we get

$$\langle \mathscr{m}_x^2 \rangle = \langle \mathscr{m}_y^2 \rangle = \mathscr{m}_0^2 \frac{T}{h}\left(\coth\frac{h}{T} - \frac{T}{h}\right). \qquad (**)$$

Finally, since the length $\mathscr{m}_0$ of the vector $\mathscr{m}$ is the same in all its possible states, we may write

$$\langle \mathscr{m}^2 \rangle \equiv \langle \mathscr{m}_x^2 \rangle + \langle \mathscr{m}_y^2 \rangle + \langle \mathscr{m}_z^2 \rangle = \mathscr{m}_0^2 ,$$

so the square of the remaining, field-aligned component of the magnetic moment may be calculated as

$$\langle \mathscr{m}_z^2 \rangle = \mathscr{m}_0^2 - \left(\langle \mathscr{m}_x^2 \rangle + \langle \mathscr{m}_y^2 \rangle\right) = \mathscr{m}_0^2\left[1 - 2\frac{T}{h}\left(\coth\frac{h}{T} - \frac{T}{h}\right)\right],$$

and the general relation (5.4b) yields

$$\langle \tilde{\mathscr{m}}_z^2 \rangle = \langle \mathscr{m}_z^2 \rangle - \langle \mathscr{m}_z \rangle^2 = \mathscr{m}_0^2\left[1 - 2\frac{T}{h}\left(\coth\frac{h}{T} - \frac{T}{h}\right) - \left(\coth\frac{h}{T} - \frac{T}{h}\right)^2\right]. \qquad (***)$$

As was already discussed in the model solution of Problem 2.4, in the high-temperature (low-field) limit $h << T$, the expression in the parentheses participating in Eqs. (**) and (***) approaches $h/3T << 1$, so our results are reduced to a very simple, field-independent expression

$$\langle \tilde{\mathscr{m}}_x^2 \rangle = \langle \tilde{\mathscr{m}}_y^2 \rangle = \langle \tilde{\mathscr{m}}_z^2 \rangle = \frac{1}{3}\mathscr{m}_0^2 .$$

This is very natural because in the absence of the field, the system is fully isotropic.

However, in the opposite, low-temperature/high-field limit, when the same expression in the parentheses tends to 1 – T/h, Eqs. (**) and (***) give very different results for the field-aligned and field-normal components:

$$\left\langle \tilde{m}_x^2 \right\rangle = \left\langle \tilde{m}_y^2 \right\rangle \approx m_0^2 \frac{T}{h}, \qquad \left\langle \tilde{m}_z^2 \right\rangle \approx m_0^2 \left(\frac{T}{h}\right)^2 << \left\langle \tilde{m}_{x,y}^2 \right\rangle, \qquad \text{for } T << h .$$

The physical reason for this difference is that small deviations of the moment vector from the field-aligned direction $\mathbf{n}_z$ give an energy contribution that is quadratic in m_x and m_y:

$$E(\theta) - E(0) = -h\cos\theta + h \approx h\frac{\theta^2}{2} = \frac{h}{2m_0^2}\left(m_x^2 + m_y^2\right) = \frac{h}{2m_0^2}\left(\tilde{m}_x^2 + \tilde{m}_y^2\right), \qquad \text{for } \tilde{m}_x^2, \tilde{m}_y^2 << m_0^2 ,$$

so their variances have to (and do!) satisfy the equipartition theorem (2.48):

$$\left\langle \frac{h\tilde{m}_x^2}{2m_0^2} \right\rangle = \left\langle \frac{h\tilde{m}_y^2}{2m_0^2} \right\rangle = \frac{T}{2}, \qquad \text{for } T << h .$$

On the other hand, the deviations of the z-component of the momentum from its value (m_0) corresponding to the exact alignment, in this limit, are much smaller:

$$\tilde{m}_z = m_z - m_0 = \left[m_0^2 - \left(\tilde{m}_x^2 + \tilde{m}_y^2\right)\right]^{1/2} - m_0 \approx -\frac{\tilde{m}_x^2 + \tilde{m}_y^2}{2m_0}, \qquad \text{for } \tilde{m}_x^2, \tilde{m}_y^2 << m_0^2 ;$$

as a result, their variance is of a higher order in the small parameter T/h.

Finally, comparing the results for the two models of a spin in a magnetic field, we see that they are rather different. Most significantly, in the low-temperature limit, the classical Heisenberg model (which agrees with quantum mechanics for large values of spin, $s >> 1$) does not exhibit the exponentially small fluctuations of m_z, which are typical for $s = ½$ (and any finite value of spin), because of the availability of intermediate states with $0 < \theta < \pi$, filling the gap between the two extreme values ($E = \pm h$) of the energy.

Problem 5.4. For a field-free two-site Ising system with energy values $E_m = -Js_1s_2$, in thermal equilibrium at temperature T, calculate the variance of energy fluctuations. Explore the low-temperature and high-temperature limits of the result.

Solution: This system has two doubly degenerate values of its energy E:

$$E_m = \begin{cases} -J, & \text{for } s_1 = s_2 = +1 \text{ and } s_1 = s_2 = -1, \\ +J, & \text{for } s_1 = -s_2 = +1 \text{ and } s_1 = -s_2 = -1. \end{cases}$$

Hence its statistical sum is

$$Z = 2\exp\left\{+\frac{J}{T}\right\} + 2\exp\left\{-\frac{J}{T}\right\} \equiv 4\cosh\frac{J}{T},$$

the average of the system's energy is

$$\langle E\rangle = \frac{1}{Z}\sum_m E_m \exp\left\{-\frac{E_m}{T}\right\} = \frac{1}{4\cosh(J/T)}\left[2J\exp\left\{-\frac{J}{T}\right\} - 2J\exp\left\{+\frac{J}{T}\right\}\right] \equiv -J\tanh\frac{J}{T},$$

and that of E^2 is

$$\langle E^2\rangle = \frac{1}{Z}\sum_m E_m^2 \exp\left\{-\frac{E_m}{T}\right\} = \frac{1}{4\cosh(J/T)}\left[2J^2\exp\left\{-\frac{J}{T}\right\} + 2J^2\exp\left\{+\frac{J}{T}\right\}\right] \equiv J^2,$$

so the energy fluctuation variance[38]

$$\langle \tilde{E}^2\rangle = \langle E^2\rangle - \langle E\rangle^2 = J^2\left(1-\tanh^2\frac{J}{T}\right) \equiv \frac{J^2}{\cosh^2(J/T)}.$$

At low temperatures, $T << J$, the function $\cosh(J/T)$ is very large, so the fluctuations are exponentially small, due to the gap $2J$ in the energy spectrum of the system. On the other hand, in the opposite limit of high temperatures, $\cosh(J/T) \to 1$, and the energy fluctuation variance approaches the temperature-independent value J^2.

Problem 5.5. In a system in thermodynamic equilibrium with fixed T and μ, both the number N of particles and the internal energy E may fluctuate. Express the mutual correlation factor of these fluctuations via the average of E. Spell out the result for an ideal classical gas of $N >> 1$ particles.

Solution: The mutual correlation factor of the fluctuations $\tilde{N} \equiv N - \langle N\rangle$ and $\tilde{E} \equiv E - \langle E\rangle$ may be readily expressed via the averages $\langle N\rangle$, $\langle E\rangle$, and $\langle NE\rangle$:[39]

$$\langle \tilde{N}\tilde{E}\rangle = \langle (N-\langle N\rangle)(E-\langle E\rangle)\rangle = \langle NE\rangle - \langle N\rangle\langle E\rangle. \qquad (*)$$

In the lecture notes, the average energy $\langle E\rangle$ was expressed via the statistical sum Z of the Gibbs (canonical) ensemble – see Eqs. (2.61b) and (5.16). However, our current system, with fixed T and μ, is a member of a *grand canonical* ensemble, so let us first express $\langle E\rangle$ via the *grand* statistical sum (2.107). According to Eq. (2.106),

$$\langle E\rangle = \frac{1}{Z_G}\sum_{m,N} E_{m,N}\exp\{\beta(\mu N - E_{m,N})\}, \qquad \text{where } Z_G = \sum_{m,N}\exp\{\beta(\mu N - E_{m,N})\}, \quad \beta \equiv \frac{1}{T}.$$

Now, taking clues from the calculations of the variances of N and E at the beginning of Sec. 5.2, let us rewrite the first of these expressions as

$$Z_G\langle E\rangle = \sum_{m,N} E_{m,N}\exp\{\beta(\mu N - E_{m,N})\},$$

and differentiate both sides over the chemical potential:

$$\frac{\partial}{\partial\mu}Z_G\langle E\rangle = \beta\sum_{m,N} NE_{m,N}\exp\{\beta(\mu N - E_{m,N})\} \equiv \beta Z_G\langle NE\rangle.$$

This means that we may write

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[38] Alternatively, the same result may be obtained as $\partial\langle E\rangle/\partial(-\beta)$ – see Eq. (5.19) of the lecture notes,

[39] Cf. Eq. (5.3) for the variance.

$$\langle NE\rangle = \frac{T}{Z_G}\frac{\partial}{\partial\mu}\left(\langle E\rangle Z_G\right) \equiv T\frac{\partial\langle E\rangle}{\partial\mu} + \langle E\rangle T\frac{1}{Z_G}\frac{\partial Z_G}{\partial\mu}.$$

But according to Eq. (5.22) of the lecture notes, the last term is just the product ⟨E⟩⟨N⟩, so comparing the resulting relation with Eq. (*), we get a very simple result:

$$\left\langle \tilde{N}\tilde{E}\right\rangle = T\frac{\partial\langle E\rangle}{\partial\mu}, \qquad (**)$$

which is structurally similar to Eqs. (5.19) and (5.24) for the variances of these two fluctuations.

In a classical gas of non-interacting particles, the total internal energy E is the sum of individual energies of all particles, whose average ε is a function of temperature alone, so for $\langle N\rangle >> 1$, $\langle E\rangle \approx \langle N\rangle\varepsilon(T)$, giving

$$\frac{\partial\langle E\rangle}{\partial\mu} = \varepsilon(T)\frac{\partial\langle N\rangle}{\partial\mu}.$$

But according to Eq. (5.26) of the lecture notes, the last derivative equals $\langle N\rangle/T$, so the general Eq. (**) is reduced to

$$\left\langle \tilde{N}\tilde{E}\right\rangle = T\varepsilon(T)\frac{\langle N\rangle}{T} = \langle E\rangle,$$

very much in the spirit of Eq. (5.27). The close similarity of these results is especially evident in their normalized form:

$$\frac{\left\langle \tilde{N}\tilde{E}\right\rangle}{\langle N\rangle\langle E\rangle} = \frac{\left\langle \tilde{N}^2\right\rangle}{\langle N\rangle^2} = \frac{1}{\langle N\rangle}.$$

<u>Problem 5.6</u>. As was mentioned in Sec. 5.2 of the lecture notes, the variance of energy fluctuations in a system with fixed T and μ (i.e. a member of a *grand canonical* ensemble) is generally different from that in a similar system in which T and N are fixed, i.e. a member of a *canonical* ensemble. Calculate and interpret the difference.

Solution: According to Eq. (2.106) of the lecture notes, for the grand canonical ensemble,

$$\langle E\rangle = \frac{1}{Z_G}\sum_{m,N} E_{m,N}\exp\{\beta(\mu N - E_{m,N})\}, \qquad \text{i.e. } Z_G\langle E\rangle = \sum_{m,N} E_{m,N}\exp\{\beta(\mu N - E_{m,N})\}, \qquad (*)$$

where

$$Z_G = \sum_{m,N}\exp\{\beta(\mu N - E_{m,N})\}, \quad \beta \equiv \frac{1}{T}. \qquad (**)$$

Taking clues from Eq. (5.19), let us differentiate both sides of the second of Eqs. (*) over $(-\beta)$:

$$\frac{\partial}{\partial(-\beta)}\left(Z_G\langle E\rangle\right) = \sum_{m,N} E_{m,N}\left(E_{m,N} - \mu N\right)\exp\{\beta(\mu N - E_{m,N})\} \equiv Z_G\left\langle E^2\right\rangle - \mu Z_G\langle NE\rangle.$$

From here:

$$\left\langle E^2\right\rangle = \frac{1}{Z_G}\frac{\partial}{\partial(-\beta)}\left(Z_G\langle E\rangle\right) + \mu\langle NE\rangle \equiv \frac{\partial\langle E\rangle}{\partial(-\beta)} + \frac{1}{Z_G}\frac{\partial Z_G}{\partial(-\beta)}\langle E\rangle + \mu\langle NE\rangle. \qquad (***)$$

According to Eq. (5.19), the first term on the right-hand side would give the energy fluctuation variance in the Gibbs (canonical) ensemble, i.e. at a fixed number of particles in the system, while the second term may be spelled out by using Eq. (**):

$$\frac{1}{Z_{\text{G}}}\frac{\partial Z_{\text{G}}}{\partial(-\beta)}=\frac{1}{Z_{\text{G}}}\sum_{m,N}\left(E_{m,N}-\mu N\right)\exp\left\{\beta\left(\mu N-E_{m,N}\right)\right\}=\langle E\rangle-\mu\langle N\rangle,$$

so Eq. (***) becomes

$$\left\langle E^2\right\rangle=\left\langle\tilde{E}^2\right\rangle_N+\left(\langle E\rangle-\mu\langle N\rangle\right)\langle E\rangle+\mu\langle NE\rangle\equiv\left\langle\tilde{E}^2\right\rangle_N+\langle E\rangle^2+\mu\left(\langle NE\rangle-\langle N\rangle\langle E\rangle\right).$$

Per Eq. (*) of the solution of the previous problem, the expression in the last parentheses is just $\left\langle\tilde{N}\tilde{E}\right\rangle$, so for the energy fluctuation variance in the grand canonical ensemble, we get

$$\left\langle\tilde{E}^2\right\rangle=\left\langle\tilde{E}^2\right\rangle-\langle E\rangle^2=\left\langle\tilde{E}^2\right\rangle_N+\mu\left\langle\tilde{N}\tilde{E}\right\rangle, \qquad (****)$$

and using the final general result (**) of the same solution,

$$\left\langle\tilde{E}^2\right\rangle=\left\langle\tilde{E}^2\right\rangle_N+\mu T\frac{\partial\langle E\rangle}{\partial\mu}.$$

As Eq. (****) clearly shows, the difference between the results for two statistical ensembles is due to the fact that if μ rather than N is fixed, the number of particles may fluctuate, causing correlated energy fluctuations.

Problem 5.7. For a uniform three-site Ising ring with ferromagnetic coupling (and no external field), in thermal equilibrium at temperature T, calculate the correlation coefficients $K_s \equiv \langle s_k s_{k'}\rangle$ for both $k = k'$ and $k \neq k'$.

Solution: In all Ising models, each "spin" s_k may take only the values ±1, so its square equals 1 in any state of the system, and hence $\langle s_k^2\rangle$ equals 1 for any k and any parameters. However, the *mutual correlation* coefficients $\langle s_k s_{k'}\rangle$,[40] with $k' \neq k$, require calculation.

The energy of a particular state of the ring is given by Eq. (4.78) of the lecture notes with $N = 3$ and $h = 0$:

$$E_m=-J\left(s_1s_2+s_2s_3+s_3s_1\right), \quad \text{with } J>0.$$

This system has $2^3 = 8$ different states. In two of them, the "spins" are all aligned (in either of the two possible directions), so for them $E_m = -3J$. In the remaining six states, one spin is directed against two others, so $E_m = -J(+1 - 1 - 1) \equiv +J$. Hence, the statistical sum is[41]

$$Z=2\exp\left\{\frac{3J}{T}\right\}+6\exp\left\{-\frac{J}{T}\right\},$$

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[40] Note that for an Ising system in an external field, which may have $\eta \equiv \langle s_k\rangle \neq 0$, a more appropriate definition of the correlation coefficient (which ensures its full decay at $|k - k'| \to \infty$) is $K_s \equiv \left\langle\tilde{s}_k\tilde{s}_{k'}\right\rangle \equiv \left\langle s_k s_{k'}\right\rangle-\left\langle s_k\right\rangle\left\langle s_{k'}\right\rangle$.

[41] See also the solution of Problem 4.16.

so the probabilities of having *some* (not *particular*) states of these two groups are equal to

$$W_1 = \frac{2\exp\{3J/T\}}{2\exp\{3J/T\}+6\exp\{-J/T\}}, \qquad W_2 = \frac{6\exp\{-J/T\}}{2\exp\{3J/T\}+6\exp\{-J/T\}}, \qquad \text{with } W_1 + W_2 = 1.$$

Since the product $s_k s_{k'}$ (with $k \neq k'$) may take only two values: (+1) when the spins k and k' are aligned with each other, and (–1) otherwise, we may write

$$K_s \equiv \langle s_k s_{k'} \rangle = (+1)W_+ + (-1)W_- = W_+ - W_-,$$

where $W_\pm$ are the corresponding probabilities, with $W_+ + W_- = 1$. If the spins are all aligned (in the above nomenclature, state group 1), then all $s_k s_{k'} = 1$. However, if one of them is misaligned (group 2), there is only a 1/3 chance that any given pair of spins k and k' is aligned – because this is the chance that the misaligned spin has number $k'' \neq k, k'$, i.e. is not involved in this pair. Hence, $W_+ = W_1 + (1/3)W_2$, while $W_- = 1 - W_+ = (2/3)W_2$, so, finally:

$$K_s = W_+ - W_- = \left(W_1 + \frac{1}{3}W_2\right) - \frac{2}{3}W_2 = \frac{1-\exp\{-4J/T\}}{1+3\exp\{-4J/T\}}, \qquad \text{for any } k' \neq k.$$

This result shows that in the low-temperature limit, $T << J$, the mutual correlation coefficient approaches 1. This is natural because the probability W_1 of the full spin alignment approaches 1, while W_2 is exponentially small. In the opposite limit of high temperatures, $\exp\{-4J/T\} \approx 1 - 4J/T$, and the mutual correlation is low:

$$K_s \approx \frac{J}{T} << 1, \qquad \text{for } k' \neq k.$$

Note, however, that $\langle s_k s_{k'} \rangle$ is positive for any ratio J/T. This is natural, because the ferromagnetic coupling, with $J > 0$, always favors spin alignment.

Problem 5.8.[*] For a field-free 1D Ising system of $N >> 1$ "spins", in thermal equilibrium at temperature T, calculate the correlation coefficient $K_s \equiv \langle s_l s_{l+n} \rangle$, where l and $(l + n)$ are the numbers of two specific spins in the chain.

Hint: Consider a mixed partial derivative of the statistical sum calculated in Problem 4.21 for an Ising chain with an arbitrary set of J_k, over a part of these parameters.

Solution: For this system, the general Eq. (2.7), with the Gibbs-distribution probabilities $W_m = \exp\{-E_m/T\}/Z_N$, becomes

$$K_s = \frac{1}{Z_N} \sum_{\substack{s_k=\pm 1,\text{ for}\\ k=1,2,\ldots,N}} s_l s_{l+n} \exp\left\{\sum_{k=1}^{N-1} \frac{J_k}{T} s_k s_{k+1}\right\} \equiv \frac{1}{Z_N} \sum_{\substack{s_k=\pm 1,\text{ for}\\ k=1,2,\ldots,N}} s_l s_{l+n} \prod_{k=1}^{N-1} \exp\left\{\frac{J_k}{T} s_k s_{k+1}\right\}, \qquad (*)$$

where Z_N was calculated in the solution of Problem 4.21:

$$Z_N = \sum_{\substack{s_k=\pm 1,\text{ for}\\ k=1,2,\ldots,N}} \prod_{k=1}^{N-1} \exp\left\{\frac{J_k}{T} s_k s_{k+1}\right\} = 2\prod_{k=1}^{N-1} \left(2\cosh\frac{J_k}{T}\right). \qquad (**)$$

Let us use the fact that all $s_k^2 = 1$ to rewrite Eq. (*) in the following mathematically equivalent form:

$$K_s = \frac{1}{Z_N} \sum_{\substack{s_k=\pm 1,\text{ for}\\ k=1,2,\ldots,N}} (s_l s_{l+1})(s_{l+1}s_{l+2})\ldots(s_{l+n-1}s_{l+n}) \prod_{k=1}^{N-1} \exp\left\{\frac{J_k}{T} s_k s_{k+1}\right\}, \qquad (***)$$

and compare it with the following mixed partial derivative:

$$D_n \equiv \frac{\partial^n Z_N}{\partial J_l \partial J_{l+1} \ldots \partial J_{l+n-1}}.$$

On one hand, if we differentiate Z_N in the first form of Eq. (**) and then use Eq. (***) for K_s, we get

$$\begin{aligned} D_n &\equiv \sum_{\substack{s_k=\pm 1,\text{ for}\\ k=1,2,\ldots,N}} \frac{\partial^n}{\partial J_l \partial J_{l+1} \ldots \partial J_{l+n-1}} \prod_{k=1}^{N-1} \exp\left\{\frac{J_k}{T} s_k s_{k+1}\right\} \\ &= \frac{1}{T^n} \sum_{\substack{s_k=\pm 1,\text{ for}\\ k=1,2,\ldots,N}} (s_l s_{l+1})(s_{l+1}s_{l+2})\ldots(s_{l+n-1}s_{l+n}) \prod_{k=1}^{N-1} \exp\left\{\frac{J_k}{T} s_k s_{k+1}\right\} \equiv \frac{1}{T^n} K_s Z_N. \end{aligned}$$

On the other hand, if we use Z_N in the last form of Eq. (**) instead, then the same derivative is

$$\begin{aligned} D_n &\equiv \frac{\partial^n}{\partial J_l \partial J_{l+1} \ldots \partial J_{l+n-1}} 2 \prod_{k=1}^{N-1} \left(2\cosh\frac{J_k}{T}\right) \\ &= 2 \prod_{k=1}^{l-1} \left(2\cosh\frac{J_k}{T}\right) \prod_{k=l}^{l+n-1} \left(\frac{1}{T} 2\sinh\frac{J_k}{T}\right) \prod_{k=l+n}^{N-1} \left(2\cosh\frac{J_k}{T}\right). \end{aligned}$$

Comparing these two expressions for D_n, with Z_N again taken from the second form of Eq. (**), we get a surprisingly simple result:

$$K_s = \prod_{k=l}^{l+n-1} \sinh\frac{J_k}{T} \Big/ \prod_{k=l}^{l+n-1} \cosh\frac{J_k}{T} \equiv \prod_{k=l}^{l+n-1} \tanh\frac{J_k}{T},$$

which is valid for arbitrary coupling coefficients J_k (both inside and outside of the interval $[l, l+n]$) and arbitrary positions of the sites l and $(l+n)$ in the open chain.[42]

For a particular case of a uniform chain, the result becomes even simpler, and depends only on the distance n between the involved sites:

$$K_s = K_s(n) = \tanh^n \frac{J}{T} \equiv \exp\left\{-\frac{n}{n_\text{c}}\right\}, \qquad (***)$$

where the constant n_c (not necessarily an integer),

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[42] This result is also valid for a closed Ising ring, but only if the site distance n is much smaller than the ring's length N. (This is why for a ring with $N = 3$, considered in the previous problem, Eq. (****) gives the correct result only in the limit $J << T$ when strong fluctuations suppress the difference between open strings and closed rings.) For a uniform ring with $N >> 1$ sites, the general expression for K_s may be calculated (even for $h \neq 0$) by using the transfer matrix approach – see, e.g., Sec. 5.3 in the book by Yeomans, cited in the lecture notes.

$$n_c \equiv -\frac{1}{\ln(\tanh J/T)} \to \begin{cases} 1/\ln(T/J) << 1, & \text{for } J << T, \\ \exp\{2J/T\}/2 >> 1, & \text{for } J >> T, \end{cases}$$

plays the role of the correlation radius of this 1D system – cf. Eq. (4.30) whose pre-exponential factor, as well as Eq. (4.31), are valid only for systems with nonvanishing T_c.

Problem 5.9. Within the framework of the Weiss molecular-field approximation, calculate the variance of spin fluctuations in the d-dimensional Ising model. Use the result to derive the conditions of quantitative validity of the approximation.

Solution: Since in the Ising model, the variable $s_k^2 = (\pm 1)^2 \equiv 1$ in any state of the system, its statistical average also equals 1 within any (reasonable :-) approach to the model – including the Weiss approximation. Combining this fact with Eq. (4.69) of the lecture notes, we get

$$\left\langle \tilde{s}_k^2 \right\rangle = \left\langle s_k^2 \right\rangle - \left\langle s_k \right\rangle^2 = \left\langle s_k^2 \right\rangle - \eta^2 = 1 - \tanh^2(h_{\text{ef}}/T) \equiv \frac{1}{\cosh^2(h_{\text{ef}}/T)}.$$

(Actually, we could get this result also from Eq. (*) of the model solution of Problem 3, with the replacement $h \to h_{\text{ef}}$, which is the essence of Weiss' approach.)

The key assumption of the Weiss theory is $\left\langle \tilde{s}_k^2 \right\rangle << \eta^2$. Reviewing the dependence of $h_{\text{ef}} \equiv h + 2Jd\eta$ on the parameters of the system, which was discussed in Sec. 4.4 (see, in particular, Figs. 4.8 and 4.9), we may conclude that for stable stationary states, this strong inequality is fulfilled (and hence the theory is asymptotically correct) at:

(i) low temperatures, $T << 2Jd$ (meaning, within that theory, that $T << T_c$) at any field h, and
(ii) high external fields, $h^2 >> T^2$, at any ratio $2Jd/T \equiv T_c/T$.

As was mentioned in Sec. 4.3, long-range interactions between the "spins" s_k suppress the fluctuations and thus broaden the region of validity of the molecular-field approximation.

Problem 5.10. Calculate the variance of energy fluctuations in a quantum harmonic oscillator with frequency ω, in thermal equilibrium at temperature T, and express it via the average energy.

Solution: Plugging the result given by Eq. (2.72) of the lecture notes for the average energy E of the oscillator, in the form

$$\langle E \rangle = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}, \qquad (*)$$

where $\beta \equiv 1/T$, into the general Eq. (5.19), we get

$$\left\langle \tilde{E}^2 \right\rangle = -\frac{\partial \langle E \rangle}{\partial \beta} = -\frac{\partial}{\partial \beta}\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} = \left(\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right)^2 e^{\beta\hbar\omega} \equiv \left(\frac{\hbar\omega}{e^{\hbar\omega/T} - 1}\right)^2 e^{\hbar\omega/T}. \qquad (**)$$

It is straightforward to verify that Eqs. (*) and (**) are simply related:

$$\left\langle \tilde{E}^2 \right\rangle = \hbar\omega \langle E \rangle + \langle E \rangle^2. \qquad (***)$$

This means, in particular, that the r.m.s. fluctuation of energy is always larger than its average value:

$$\delta E \geq \langle E \rangle .$$

Note, however, that this relation, as well as Eq. (***) as such,[43] are valid only if E is referred to the ground-state energy $\hbar\omega/2$ of the oscillator (as it is in Eq. (2.72) of the lecture notes); it is *invalid* for the total energy given by Eq. (2.80), where the energy is referred to the minimum of $U(x)$:

$$E_{\text{total}} \equiv E + \frac{\hbar\omega}{2} .$$

For this reference point, Eq. (***) takes a different form:

$$\left\langle \tilde{E}^2 \right\rangle = \langle E_{\text{total}} \rangle^2 - \left(\frac{\hbar\omega}{2} \right)^2 ,$$

so the relation between the r.m.s. fluctuation of energy and its average is opposite:

$$\delta E \leq \langle E_{\text{total}} \rangle .$$

Problem 5.11. The spontaneous electromagnetic field inside a closed volume V is in thermal equilibrium at temperature T. Assuming that V is sufficiently large, calculate the variance of fluctuations of the total energy of the field, and express the result via its average energy and temperature. How large should the volume V be for your results to be quantitatively valid? Evaluate this limitation for room temperature.

Solution: As was discussed in Sec. 2.6(i) of the lecture notes, the spontaneous electromagnetic field in a sufficiently large closed volume V has the following average energy:

$$\langle E \rangle = \frac{\pi^2}{15} \frac{VT^4}{\hbar^3 c^3} \equiv \frac{\pi^2}{15} \frac{V}{\hbar^3 c^3} \beta^{-4} . \qquad (*)$$

Applying to this result the general Eq. (5.19), we get

$$\left\langle \tilde{E}^2 \right\rangle = -\frac{\partial}{\partial \beta} \langle E \rangle = \frac{\pi^2}{15} \frac{V}{\hbar^3 c^3} 4\beta^{-5} \equiv 4T \times \frac{\pi^2}{15} \frac{VT^4}{\hbar^3 c^3}$$

Now using Eq. (*) again, we may reduce the result to a very simple form:

$$\left\langle \tilde{E}^2 \right\rangle = 4T \langle E \rangle ,$$

which shows that the relative r.m.s. fluctuation of the energy,

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[43] That formula was first obtained as early as 1909 by A. Einstein from Planck's radiation law (which does not take the ground state energy into account) and is reproduced in some textbooks without proper qualification. Please note again that the ground state energy is not only measurable but also responsible for several important phenomena – see the discussion in Sec. 2.6 of the lecture notes.

$$\frac{\delta E}{\langle E\rangle} \equiv \frac{\langle \tilde{E}^2\rangle^{1/2}}{\langle E\rangle} = 2\left(\frac{T}{\langle E\rangle}\right)^{1/2} \propto \frac{1}{T^{3/2}V^{1/2}},$$

decreases with the growth of both temperature and volume. (This result has important implications for accurate measurements of the fundamental anisotropy of the cosmic microwave background radiation.)

Proceeding to the second task of the assignment, note that Eq. (*) is strictly valid only if the volume V is much larger than the cube of the wavelength, i.e. if $V >> c^3/\omega^3$, for all substantial frequencies. As was discussed in Sec. 2.6(i), in thermal equilibrium, their scale is given by the relation (2.87): $\hbar\omega_{\max} \sim T$, so the required condition is

$$V >> \left(\frac{c}{\omega_{\max}}\right)^3 \sim \left(\frac{\hbar c}{T}\right)^3.$$

For room temperature ($T \equiv k_B T_K \approx 1.38\times 10^{-23}$J/K×300K $\approx 4\times 10^{-21}$J), the right-hand side of this relation is of the order of 10^{-15}m$^3 \equiv (10\ \mu\text{m})^3$, i.e. is small on the human scale, but not quite microscopic either.

<u>Problem 5.12</u>. Express the r.m.s. uncertainty of the occupancy N_k of a certain quantum state with energy ε_k by non-interacting:

(i) classical particles,
(ii) fermions, and
(iii) bosons,

in thermodynamic equilibrium, via the state's average occupancy $\langle N_k\rangle$, and compare the results.

Solutions: As was discussed in Sec. 2.8 of the lecture notes, for a statistical ensemble of non-interacting particles, we may use the grand canonical distribution for the sub-ensemble of particles on the same energy level. Hence we may apply Eq. (5.24), which was derived from this distribution, to the level occupancy N_k:

$$\langle \tilde{N}_k^2\rangle = T\frac{\partial\langle N_k\rangle}{\partial\mu}. \qquad (*)$$

(i) For classical particles, the dependence of $\langle N_k\rangle$ on the chemical potential μ is given by the same formula (5.25) as for the total number of particles:

$$\langle N_k\rangle \propto \exp\left\{\frac{\mu}{T}\right\},$$

so we may repeat the (very simple) derivation of Eq. (5.27) to get a similar result:

$$\langle \tilde{N}_k^2\rangle = \langle N_k\rangle, \qquad \text{i.e. } \delta N_k = \langle N_k\rangle^{1/2}. \qquad (**)$$

(ii)-(iii) For fermions and bosons, $\langle N_k\rangle$ is given by the very similar expressions (2.115) and (2.118), which may be merged into a single formula (just as it was done in Sec. 3.2):

$$\langle N_k\rangle = \frac{1}{\exp\{(\varepsilon_k-\mu)/T\}\pm 1}, \qquad (***)$$

with the upper sign for fermions and the lower sign for bosons. Now applying Eq. (*) to this formula, we get

$$\left\langle \tilde{N}_k^2 \right\rangle = \frac{\exp\{(\varepsilon_k - \mu)/T\}}{\left[\exp\{(\varepsilon_k - \mu)/T\} \pm 1\right]^2}. \qquad (****)$$

Expressing the exponent participating in both parts of this fraction, from Eq. (***),

$$\exp\{(\varepsilon_k - \mu)/T\} = \frac{1}{\langle N_k \rangle} \mp 1,$$

and plugging this expression into Eq. (****), we get the following final result:

$$\left\langle \tilde{N}_k^2 \right\rangle = \langle N_k \rangle \left(1 \mp \langle N_k \rangle\right), \qquad \text{i.e. } \delta N_k = \left[\langle N_k \rangle \left(1 \mp \langle N_k \rangle\right)\right]^{1/2}.$$

Comparing it with Eq. (**), we see that, for a given average value $\langle N_k \rangle$ of the level occupancy, its fluctuations in the case of fermions are smaller, and in the case of bosons, larger than those for classical particles. (Both results tend to each other at $\langle N_k \rangle \to 0$, i.e. in the classical limit – see Eq. (3.1) of the lecture notes.)

Problem 5.13. Write a general expression for the variance of the number of particles in the ideal gases of bosons and fermions, at fixed V, T, and μ. Spell out the result for the degenerate Fermi gas.

Solution: Combining the general Eq. (5.24) of the lecture notes,

$$\left\langle \tilde{N}^2 \right\rangle = T \frac{\partial \langle N \rangle}{\partial \mu},$$

with Eq. (3.40) for the average number of particles in an ideal gas,

$$\langle N \rangle = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon-\mu)/T} \pm 1}, \qquad (*)$$

(where the upper sign is for the fermions and the lower one is for the bosons), we get

$$\left\langle \tilde{N}^2 \right\rangle = T \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \varepsilon^{1/2} d\varepsilon \frac{\partial}{\partial \mu} \frac{1}{e^{(\varepsilon-\mu)/T} \pm 1} = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{e^{(\varepsilon-\mu)/T} \varepsilon^{1/2} d\varepsilon}{\left[e^{(\varepsilon-\mu)/T} \pm 1\right]^2}.$$

For the degenerate Fermi gas, this integral (with the upper sign) may be worked out explicitly, but in this case, it is easier to return to Eq. (*) because in the limit $T \to 0$, the Fermi distribution becomes just a step function tapering off at $\varepsilon = \mu = \varepsilon_F$ (see the discussion in Sec. 3.3), and hence

$$\langle N \rangle\big|_{T \to 0} = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\mu \varepsilon^{1/2} d\varepsilon = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \frac{2}{3} \mu^{3/2},$$

so

$$\left\langle \tilde{N}^2 \right\rangle = T \frac{\partial \langle N \rangle}{\partial \mu} = \frac{gVm^{3/2}T}{\sqrt{2}\pi^2\hbar^3} \mu^{1/2}, \quad \text{for } T << \mu.$$

Now by using Eq. (3.43) for the 3D density of states $g_3(\varepsilon) \equiv dN_{\text{states}}/d\varepsilon$ in the same volume, this expression may be rewritten in a physically transparent form:

$$\langle \tilde{N}^2 \rangle = Tg_3(\mu) \equiv Tg_3(\varepsilon_F),$$

which is in full accord with the physical picture of fluctuations limited to a ~T-thin energy layer at the Fermi surface.

Problem 5.14. Express the variance of the number of particles, $\langle \tilde{N}^2 \rangle_{V,T,\mu}$, of a single-phase system in equilibrium, via its isothermal compressibility $\kappa_T \equiv -(1/V)(\partial V/\partial P)_{T,N}$.

Solution: Per Eq. (5.24) of the lecture notes, the requested variance

$$\langle \tilde{N}^2 \rangle_{V,T,\mu} = T\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{V,T}.$$

However, as was proved in the solution of Problem 1.10, the isothermal compressibility of a single-phase system may be expressed via the same partial derivative:

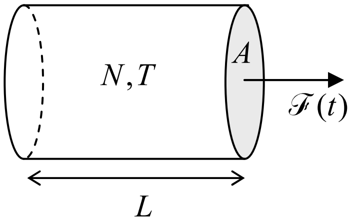
$$\kappa_T = \frac{V}{\langle N \rangle^2}\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{V,T}.$$

Comparing these expressions, we get

$$\langle \tilde{N}^2 \rangle_{V,T,\mu} = \kappa_T T \frac{\langle N \rangle^2}{V}.$$

Note that Eq. (5.24) was derived for the *grand canonical* ensemble of fixed-volume systems, so our result is also valid only for such an ensemble, i.e. if the chemical potential μ does not fluctuate significantly. (As a reminder, in a *canonical* ensemble, μ may fluctuate but the number N of particles does not fluctuate at all, by definition.)

Problem 5.15.* Calculate the low-frequency spectral density of fluctuations of the pressure P of an ideal classical gas, in thermal equilibrium at temperature T, and estimate their variance. Compare the former result with the solution of Problem 3.2.



Hint: You may consider a cylindrically shaped container of volume $V = LA$ (see the figure on the right), and start by using the Maxwell distribution of velocities to calculate the spectral density of the force $\mathscr{F}(t)$ exerted by the confined particles on its plane lid of area A, approximating the force with a delta-correlated process.

Solution: Let us first consider one particle of the gas and the force $f(t)$ it exerts on the lid in the direction normal to its plane – see the figure above. By the delta function's definition, the constant c in the approximation $\langle f(t) f(t+\tau)\rangle = c\delta(\tau)$ may be calculated as the following integral:

$$c = \int \langle f(t) f(t+\tau) \rangle d\tau,$$

over an interval larger than the collision duration τ_c but smaller than the time interval $\Delta t = 2L/|v|$ between two sequential collisions, where v is the component of the particle's velocity component in the direction normal to the lid. Due to the particles' independence, we may replace, in the above formula, the averaging over a statistical ensemble of similar particles (with the same $|v|$) with that over the time interval Δt:

$$\langle ... \rangle = \frac{1}{\Delta t}\int (...)dt \, .$$

Introducing, instead of τ, a new variable $t' \equiv t + \tau$, we get

$$c = \int \left[\frac{1}{\Delta t}\int f(t) f(t+\tau)dt \right] d\tau \equiv \frac{1}{\Delta t}\int dt \int dt' f(t) f(t') \equiv \frac{1}{\Delta t}\left[\int f(t)dt\right]^2 .$$

The time integral in the last expression is just the momentum transferred from the particle to the lid during one elastic collision, equal to $2m|v|$, so

$$c = \frac{1}{\left(2L/|v|\right)}\left(2m|v|\right)^2 = \frac{2m^2}{L}|v|^3, \qquad \text{i.e. } \langle f(t) f(t+\tau)\rangle = \frac{2m^2}{L}|v|^3 \delta(\tau) \, . \qquad (*)$$

For such a short-pulse process as $f(t)$ (see, e.g., Fig. 5.4 of the lecture notes), its time average,

$$\overline{f} \equiv \frac{1}{\Delta t}\int f(t)dt = \frac{1}{\left(2L/|v|\right)} 2m|v| \equiv \frac{mv^2}{L} \, ,$$

is negligible in comparison with its r.m.s. fluctuation:

$$\overline{f} \ll \delta f \, , \qquad (**)$$

(this almost evident fact will be proved *a posteriori*, in just a minute), so Eq. (*) may be rewritten as

$$\langle \tilde{f}(t)\tilde{f}(t+\tau)\rangle = c\delta(\tau), \qquad \text{with } c = \frac{2m^2}{L}|v|^3 .$$

Per to Eq. (5.62), this delta-correlated process has the following low-frequency spectral density:

$$S_f(0) = \frac{c}{2\pi} = \frac{m^2}{\pi L}|v|^3 .$$

Now we may prove Eq. (**) by making the estimate of the r.m.s. fluctuation, given by Eq. (5.60):

$$\delta f \equiv \langle \tilde{f}^2 \rangle^{1/2} \sim \left[2S_f(0)\omega_{\max}\right]^{1/2} ,$$

where $\omega_{\max}$ is the frequency where the spectral density becomes substantially smaller than its low-frequency value. Besides a numerical factor of the order of 1 (its exact calculation would require a specific model of the particle collisions with the lid), this frequency is just the reciprocal collision time τ_c, so

$$\delta f \sim \left[\frac{2\pi S_f(0)}{\tau_c}\right]^{1/2} = \left(\frac{2m^2|v|^3}{L\tau_c}\right)^{1/2} = \overline{f}\left(\frac{2L}{|v|\tau_c}\right)^{1/2} \equiv \overline{f}\left(\frac{\Delta t}{\tau_c}\right)^{1/2} .$$

For the gas to behave ideally, the intervals Δt between lid hits by molecules have to be much longer than the hit duration τ_c, so the last factor has to be much larger than 1, thus proving Eq. (**).

The spectral densities of independent force fluctuations from different molecules (each with its own velocity v) just add up, so for the low-frequency spectral density of the net force we get

$$S_{\mathscr{F}}(0) = N\langle S_f(0)\rangle = \frac{m^2 N}{\pi L}\langle |v|^3 \rangle .$$

This statistical average may be readily calculated from the properly normalized Maxwell distribution (3.5), i.e. the Gaussian distribution of each velocity component, with the variance $\langle v^2\rangle = \langle p^2\rangle/m^2 = T/m$:

$$\langle |v|^3 \rangle = 2\int_0^\infty v^3 w(v)dv = \frac{2}{(2\pi)^{1/2}(T/m)^{1/2}}\int_0^\infty v^3 \exp\left\{-\frac{mv^2}{2T}\right\}dv = \left(\frac{2m}{\pi T}\right)^{1/2}\left(\frac{2T}{m}\right)^2 \int_0^\infty \xi^3 \exp\left\{-\xi^2\right\}d\xi .$$

This is a table integral,[44] equal to 1!/2 = ½, so we get

$$\langle |v|^3 \rangle = \left(\frac{8T^3}{\pi m^3}\right)^{1/2},$$

and, finally, the spectral density of the pressure $P(t) = \mathscr{F}(t)/A$ is

$$S_P(0) = \frac{S_{\mathscr{F}}(0)}{A^2} = \frac{N}{\pi A V}\left(\frac{8mT}{\pi}\right)^{1/2} T . \qquad (***)$$

An approximate but fair estimate of the pressure fluctuation variance may now be achieved, as above, by replacing the integral participating in the last form of Eq. (5.60) with the product $S_P(0)\omega_{\max} \sim S_P(0)/\tau_c$:[45]

$$\langle \tilde{P}^2 \rangle \sim \frac{2S_P(0)}{\tau_c} = \frac{2N}{\pi A V}\left(\frac{8mT}{\pi}\right)^{1/2}\frac{T}{\tau_c} \sim \frac{NT^2}{V^2}\times\frac{L}{\tau_c}\left(\frac{m}{T}\right)^{1/2} \equiv \frac{NT^2}{V^2}\times\frac{L}{\tau_c\langle v^2\rangle^{1/2}} .$$

This estimate differs, by the last factor, from the so-called "thermodynamic" formula cited in a footnote in Sec. 5.3 of the lecture notes. Indeed, for a classical ideal gas, with the average pressure $\langle P\rangle = NT/V$, held at fixed temperature T, and hence with $(-\partial\langle P\rangle/\partial V)_T = NT/V^2$, that formula yields

$$\langle \tilde{P}^2 \rangle = \frac{NT^2}{V^2} . \qquad \text{(WRONG!)} \qquad (****)$$

The difference is due to the short-pulse nature of the pressure force (which cannot be accounted for in the way the "thermodynamic" formula is usually derived), which extends the pressure fluctuation bandwidth to frequencies $\sim 1/\tau_c$, much higher than the value $\sim\langle v^2\rangle^{1/2}/L \sim \langle 1/\Delta t\rangle$ implied by that formula.

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[44] See, e.g., MA Eq. (6.9e) with $n = 1$.

[45] Note that Eq. (**) for the force imposed by a single molecule, which was proved above, does *not* mean that $\delta P \ll \langle P\rangle$. Indeed, due to the independence of molecular hits, $\delta P \propto N^{1/2}\delta\mathscr{F}$, while $\langle P\rangle \propto N\langle\mathscr{F}\rangle$, so for the usual "astronomical" values $N \sim 10^{23}$, the ratio $\delta P/\langle P\rangle \propto 1/N^{1/2}$ is much smaller than 1.

(This fact and the deficiency of the traditional derivation of Eq. (****) were recognized long ago,[46] but this formula is still being copied from old textbooks to new ones.)

Now let us compare Eq. (***), rewritten for the total force $\mathcal{F} = PA$ exerted by all molecules,

$$S_{\mathcal{F}}(0) = A^2 S_{\mathcal{P}}(0) = \frac{NA}{\pi V}\left(\frac{8mT}{\pi}\right)^{1/2} T ,$$

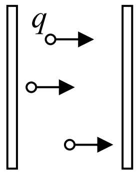
with the drag coefficient calculated in the solution of Problem 3.2,

$$\eta = \frac{NA}{V}\left(\frac{8mT}{\pi}\right)^{1/2} .$$

We see that they are simply related:

$$S_{\mathcal{F}}(0) = \frac{\eta}{\pi} T .$$

In this equality, we may readily recognize the general relation (5.73) between the thermal fluctuations and dissipation, i.e., the classical limit of the fluctuation-dissipation theorem (5.98) – thus providing a good sanity check of Eq. (***).



Problem 5.16. Calculate the low-frequency spectral density of fluctuations of the electric current $I(t)$ due to the random passage of charged particles between two conducting electrodes – see the figure on the right. Assume that the particles are emitted, at random times, by one of the electrodes, and are fully absorbed by the counterpart electrode. Can your result be mapped onto some aspect of the electromagnetic blackbody radiation?

Hint: For the current $I(t)$, use the same delta-correlated-process approximation as for the force $\mathcal{F}(t)$ in the previous problem.

Solution: At the given conditions, the current $I(t)$ is a sum of short independent pulses, with a duration τ_c of the order of the time of the particle's passage between the electrodes. On a time scale much larger than τ_c, we can write.

$$\langle I(t)I(t+\tau)\rangle = C\delta(\tau) .$$

Integrating both parts of this equation over the time of one current pulse, and transforming it exactly as in the model solution of the previous problem, we get

$$C = \int \langle I(t)I(t+\tau)\rangle d\tau = \nu\left[\int I(t)dt\right]^2 > 0,$$

where ν is the average (cyclic) frequency of singe-electron passage events. But the integral in the brackets is just the electric charge q of one particle. Taking into account that the product $q\nu$ is equal to the time-averaged ("dc") current $\bar{I}$, we get

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[46] See, e.g., R. Burgess, *Phys. Lett. A* **44**, 37 (1973) and references therein. In brief, the "thermodynamic" derivation implies a continuous, uniform spread of the momentum $2m|v|$ transferred from each particle to the piston during one hit, over the whole time period $\Delta t = 2L/|v|$ between the adjacent hits. Such a spread could be achieved, for example, by replacing the usual hard piston with a conducting, voltage-biased lid inducing an electric field that would press charged particles of the gas to the opposite lid of the gas-confining cylinder. I am not aware of any practical implementation of such a system.

$$C = \nu q^2 = \left| q\bar{I} \right|, \qquad \text{i.e. } \langle I(t)I(t+\tau)\rangle = \left| q\bar{I} \right| \delta(\tau).$$

(Since, unlike in the previous problem, all the pulse "areas" $\int I(t)dt$ are equal to q and hence to each other, their statistical averaging is unnecessary.) Now Eq. (5.62) of the lecture notes immediately yields a constant low-frequency spectral density:

$$S_I(\omega) = S_I(0) = \frac{\left| q\bar{I} \right|}{2\pi}, \qquad \text{for } \omega << 2\pi\nu. \qquad (*)$$

By using Eq. (5.61), this expression may be recast into its common form

$$\left\langle \tilde{I}^2 \right\rangle_{\Delta\nu} = 2\left| q\bar{I} \right| \Delta\nu.$$

This is the famous *Schottky formula* for the shot noise, which was briefly mentioned in Sec. 5.5 of the lecture notes – see Eq. (5.82) and its discussion. (It was first derived in 1918 by W. Schottky using a different approach, based on the Poisson probability distribution (5.31) of the number of particles passing through the system during a time interval $\Delta t >> \tau_c$.)

Now proceeding to the electromagnetic radiation, let some source of it (say, a set of similar atoms being continuously excited to an energy level $E_e = E_g + \hbar\omega$) emit its quanta, each with energy $\hbar\omega$, independently of each other, and the radiation backflow be negligible. Then replacing the above arguments for the electric current $I(t)$ with those for the power flow $\mathscr{P}(t)$ of the radiation (time-averaged over a time interval much larger than $\hbar\omega/\mathscr{P}$), we may expect the spectral density of its fluctuations (frequently called the *photon shot noise*) to be expressed by a formula similar to Eq. (*):

$$S_{\mathscr{P}}(0) = \frac{\hbar\omega}{2\pi}\overline{\mathscr{P}}.$$

Both the detailed quantum theoretical analysis of radiation and experiments (mostly, in optical photon counting) confirm this result. Unfortunately, its more formal derivation would require much more time than I have in this series, so I have to refer the reader to special literature.[47]

Problem 5.17. Perhaps the simplest model of the diffusion is the 1D *discrete random walk*: each time interval τ, a particle leaps, with equal probability, to any of the two adjacent sites of a 1D lattice with a spatial period a. Prove that the particle's displacement during a time interval $t >> \tau$ obeys Eq. (5.77) of the lecture notes, and calculate the corresponding diffusion coefficient D.

Solution: The particle's displacement at time $t = N\tau$, i.e. after N random leaps, is obviously

$$\Delta q = \sum_{n=1}^{N} a s_n, \qquad (*)$$

where s_n is a random number that may take just two values, ±1, with equal probabilities $W_\pm = ½$, and hence with a vanishing statistical average:[48] $\langle s_n \rangle = 0$; as a result, $\langle \Delta q \rangle = 0$ as well. From Eq. (*), we can calculate the displacement squared, and its statistical average:

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[47] See, e.g., either M. Lax, *Fluctuation and Coherent Phenomena in Classical and Quantum Physics*, Gordon and Breach, 1968, or W. Louisell, *Quantum Statistical Properties of Radiation*, Wiley, 1990.

$$\left\langle \Delta q^2 \right\rangle = \left\langle \sum_{n,n'=1}^{N} a s_n a s_{n'} \right\rangle \equiv a^2 \sum_{n,n'=1}^{N} \left\langle s_n s_{n'} \right\rangle . \tag{**}$$

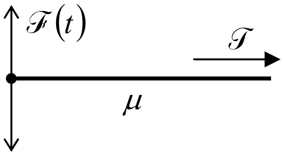
Since different values s_n are statistically independent, any mutual correlation coefficient $\langle s_n s_{n'} \rangle$ with $n \neq n'$ is equal to the product of averages, and hence to zero.[49] As a result, nonvanishing contributions to the right-hand side of Eq. (**) are given only by N terms with $n = n'$, i.e. $\langle s_n^2 \rangle$. But s_n^2 equals 1 for any sign of s_n, so Eq. (**) reduces to

$$\left\langle \Delta q^2 \right\rangle = a^2 N \equiv \frac{a^2}{\tau} t.$$

Due to the condition $t >> \tau$, this result is approximately valid not only for discrete values $N\tau$ (where it is exact), but also for any times t. Comparing it with Eq. (5.77), we see that this model indeed describes the 1D diffusion, with the following diffusion coefficient:

$$D = \frac{a^2}{2\tau}.$$

In agreement with common sense, D grows both with the jump size a, and with the frequency $1/\tau$ of the jumps.



Problem 5.18.[50] A long uniform string, of mass μ per unit length, is attached to a firm support, and stretched with a constant force ("tension") $\mathscr{T}$ – see the figure on the right. Calculate the spectral density of the random force $\mathscr{F}(t)$ exerted by the string on the support point, within the plane normal to its length, in thermal equilibrium at temperature T.

Hint: You may assume that the string is so long that transverse waves propagating along it from the support point never come back.

Solution: Temporarily, let us ignore the fluctuations, and assume that the support point is being slightly moved, in the plane normal to the string, following some externally-fixed law $\mathbf{q}_0(t)$ independent of the string motion. (This motion may be two-dimensional, so generally, it has to be described with a 2D vector.) Such displacement imposes the boundary condition,

$$\mathbf{q}(0,t) = \mathbf{q}_0(t), \tag{*}$$

on the transverse waves $\mathbf{q}(z, t)$ that are excited, by this motion, to propagate along the string. (Here z is the axis directed along the string, with the origin at the attachment point.) According to classical mechanics,[51] if such waves are not too large ($|\partial \mathbf{q}(z, t)/\partial z| << 1$), their dynamics obeys the linear wave equation

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[48] This "Markovian" process is evidently memory-free, and hence ergodic, so this averaging may be understood as either that over an ensemble of many different random walks, or over an ensemble of many sequential leaps, within a very long walk of the same particle.

[49] Note that a similar argument was used in Sec. 5.1 of the lecture notes to derive Eq. (5.12).

[50] This problem, conceptually important for the quantum mechanics of open systems, was also given in Chapter 7 of the QM part of this series.

[51] See, e.g., CM Sec. 6.4, in particular Eq. (6.40), with $m = \mu d$, $\kappa_{\text{ef}} = \mathscr{T}/d$, and an arbitrary constant d.

$$\mu\frac{\partial^2\mathbf{q}}{\partial t^2}=\mathscr{T}\frac{\partial^2\mathbf{q}}{\partial z^2}.$$

At the condition given in the *Hint*,[52] the solution of this equation, satisfying the boundary condition (*), has the form of a wave,

$$\mathbf{q}(z,t)=\mathbf{q}_0\left(t-\frac{z}{v}\right), \qquad (**)$$

traveling from the wall with velocity $v=(\mathscr{T}/\mu)^{1/2}$. This wave of string displacements is accompanied by the following wave of the transverse force:[53]

$$\mathscr{F}(z,t)=-\mathcal{Z}\frac{\partial\mathbf{q}(z,t)}{\partial t}=-\mathcal{Z}\frac{\partial\mathbf{q}_0(t-z/v)}{\partial t}, \qquad \text{where } \mathcal{Z}=(\mu\mathscr{T})^{1/2},$$

exerted by the "right" part of the string (as seen from the given point z) on its "left" part. (The constant $\mathcal{Z}$ is called the *wave impedance* of the system.)

Applying this result to the point $z = 0$, we see that the string provides, for the support point's motion, a damping (drag) force described by Eq. (5.64) of the lecture notes, $\mathscr{F}=-\eta d\mathbf{q}_0(t)/dt$, with the drag coefficient $\eta=\mathcal{Z}$, i.e. has the generalized susceptibility $\chi(\omega)=i\omega\eta=i\omega\mathcal{Z}$ – see Eqs. (5.89)-(5.90).[54] Since this result is valid regardless of the actual motion $\mathbf{q}_0(t)$, we may use it to spell out Eq. (5.98) for our particular case:

$$S_{\mathscr{F}}(\omega)=\mathcal{Z}\frac{\hbar\omega}{2\pi}\coth\frac{\hbar\omega}{2T}.$$

In human-scale systems, the divergence of this result at $\omega\to\infty$ is cut off (at least) by the violation of the already mentioned condition $|\partial\mathbf{q}(z,t)/\partial z| \ll 1$ of its validity. Indeed, according to Eq. (**), the derivative on its left-hand side of this inequality equals $-[\partial\mathbf{q}(z,t)/\partial t]/v$, and for a sinusoidal oscillation with an amplitude A and frequency ω, its magnitude grows with frequency as $A\omega/v$.

Problem 5.19.[55] Each of the two 3D isotropic harmonic oscillators, with mass m, resonance frequency ω_0, and damping coefficient $\delta > 0$, has the electric dipole moment $\mathbf{d} = q\mathbf{s}$, where $\mathbf{s}$ is the vector of the oscillator's displacement from its equilibrium position. Use the Langevin formalism to calculate the average potential of electrostatic interaction (a particular case of the so-called *London dispersion force*) of these oscillators separated by distance $r \gg (T/m)^{1/2}/\omega_0$, in thermal equilibrium at

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[52] This condition is quite realistic if the waves propagate with some attenuation. – see, e.g., CM Sec. 6.6. (If this attenuation is nonvanishing but not too high, it does not affect the forthcoming fluctuation analysis.)

[53] See, e.g., CM Eqs. (6.45) and (6.47).

[54] This result should not be too surprising, because the support point's motion induces traveling waves of the string, which carry away from it ("to infinity") the mechanical power $\mathscr{P}\propto(\partial q/\partial t)^2$ – see. e.g. CM Eq. (6.49).

[55] This system, with an arbitrary temperature, was the subject of QM Problem 7.6, with Problem 5.20 of that course serving as the background. However, the method used in the model solutions of those problems requires one to prescribe, to the oscillators, different frequencies ω_1 and ω_2 at first, and only after this more general problem has been solved, pursue the limit $\omega_1\to\omega_2$, while neglecting dissipation altogether. The goal of this problem is to show that the result of that solution is valid even at nonvanishing damping.

temperature $T >> \hbar\omega_0$. Also, explain why the approach used to solve a very similar Problem 2.18 is not directly applicable to this case.

Hint: You may like to use the following integral: $\int_0^\infty \frac{1-\xi^2}{\left[\left(1-\xi^2\right)^2+(\alpha\xi)^2\right]^2}d\xi = \frac{\pi}{4\alpha}$.

Solution: If the interaction between the oscillators is negligible, in the classical limit, each of them may be described by the Langevin equation (5.65) with $\kappa = m\omega_0^2$, which is valid for each Cartesian component of the displacement vector **s**. Merging these equations into the vector form, and multiplying all terms by the ratio q/m, for the electric dipole moment $\mathbf{d} = q\mathbf{s}$ of the oscillator, we get

$$\ddot{\mathbf{d}} + 2\delta\dot{\mathbf{d}} + \omega_0^2\mathbf{d} = \frac{q}{m}\tilde{\mathscr{F}}(t). \qquad (*)$$

Since the Langevin forces exerted on each dipole by their dissipative environments are random, independent, and isotropic, so are the spontaneously induced dipole moments $\mathbf{d}_{1,2}$. As a result, the energy of their electrostatic interaction,[56]

$$U = \frac{1}{4\pi\varepsilon_0 r^3}\left(d_{1x}d_{2x} + d_{1y}d_{2y} - 2d_{1z}d_{2z}\right), \qquad \text{for } r >> s_{1,2},$$

vanishes at its direct statistical averaging.

A non-zero average London dispersion force appears in the next order in the small parameter $(q^2/4\pi\varepsilon_0 r^3)$, and may be conveniently described as a result of the fact that the Lorentz force $\mathscr{F} = q\mathscr{E}$ of the electric field[57]

$$\mathscr{E} = \frac{3\mathbf{r}(\mathbf{r}\cdot\mathbf{d}) - \mathbf{d}r^2}{4\pi\varepsilon_0 r^5} \equiv \frac{1}{4\pi\varepsilon_0 r^3}\left(-d_x\mathbf{n}_x - d_y\mathbf{n}_y + 2d_z\mathbf{n}_z\right), \qquad (**)$$

of each random dipole $\mathbf{d} = \mathbf{d}_{1,2}$, at the location $\mathbf{r}_{2,1}$ of the counterpart dipole, induces in it a proportional and correlated component $\tilde{\mathbf{d}}_{2,1} \propto \mathscr{E}_{1,2}(\mathbf{r}_{2,1})$ of its dipole moment, so the statistical averages $\left\langle \mathscr{E}_1\cdot\tilde{\mathbf{d}}_2\right\rangle$ and $\left\langle \mathscr{E}_2\cdot\tilde{\mathbf{d}}_1\right\rangle$ do not vanish, contributing to the average interaction energy[58]

$$\langle U\rangle = -\frac{1}{2}\left\langle \overline{\mathscr{E}_1\cdot\tilde{\mathbf{d}}_2}\right\rangle - \frac{1}{2}\left\langle \overline{\mathscr{E}_2\cdot\tilde{\mathbf{d}}_1}\right\rangle.$$

Let us calculate the first term of this sum, by using the fact that the differential equation (*) is linear, and it is hence it is useful to Fourier-expand both its right-hand side and its solution – for example, as in Eq. (5.52) of the lecture notes:

$$\tilde{\mathscr{F}}(t) = \int_{-\omega}^{+\infty}\tilde{\mathscr{F}}_\omega e^{-i\omega t}d\omega, \qquad \mathbf{d}(t) = \int_{-\omega}^{+\infty}\mathbf{d}_\omega e^{-i\omega t}d\omega.$$

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[56] See, e.g., EM Eq. (3.16), in which the dipole moments are denoted as $\mathbf{p}_{1,2}$.

[57] See, e.g., EM Eq. (3.13). In the second form of this expression, the z-axis is assumed to be directed along the vector **r**.

[58] See, e.g., EM Eq. (3.15b). Note the factors ½, which are due to the induced nature of the moments $\tilde{\mathbf{d}}_{2,1}$.

Then for the Fourier amplitudes at an arbitrary frequency ω, Eq. (*) yields the relation (see also Eq. (5.67) of the lecture notes):

$$\mathbf{d}_{1\omega} = \frac{q}{m}\frac{\mathscr{F}_{1\omega}}{\left(\omega_0^2 - \omega^2\right) - 2i\delta\omega}.$$

From the similar Fourier image of Eq. (**) (which is also linear, though algebraic rather than differential), the complex amplitude of the electric field at the location $\mathbf{r}_2 \equiv \mathbf{r}$ of the dipole 2 is

$$\mathscr{E}_{1\omega} = \frac{3\mathbf{r}\left(\mathbf{r}\cdot\mathbf{d}_{1\omega}\right) - \mathbf{d}_{1\omega}r^2}{4\pi\varepsilon_0 r^5} \equiv \frac{1}{4\pi\varepsilon_0 r^3}\left(-d_{1x\omega}\mathbf{n}_x - d_{1y\omega}\mathbf{n}_y + 2d_{1z\omega}\mathbf{n}_z\right).$$

The Lorentz force $\mathscr{F} = q\mathscr{E}$ of this field should be added to the right-hand side of Eq. (*) written for the second dipole. Since this force is independent of the environment-induced force $\tilde{\mathscr{F}}_2(t)$ and the equation is linear, we may use it, in the form,

$$\ddot{\tilde{\mathbf{d}}}_2 + 2\delta\dot{\tilde{\mathbf{d}}}_2 + \omega_0^2\tilde{\mathbf{d}}_2 = \frac{q}{m}q\mathscr{E}_1,$$

to calculate the field-induced part of the dipole moment. The similar Fourier expansion yields

$$\tilde{\mathbf{d}}_{2\omega} = \frac{q^2}{m}\frac{\mathscr{E}_{1\omega}}{\left(\omega_0^2 - \omega^2\right) - 2i\delta\omega}. \qquad (***)$$

At this point, we have to be careful because the interaction energy $\langle U\rangle$ is a quadratic rather than a linear form, so we have to calculate it using all components of their Fourier extensions. Performing absolutely the same calculation as at the derivation of Eq. (5.60) of the lecture notes, we get

$$\langle U_{12}\rangle \equiv -\frac{1}{2}\left\langle\overline{\mathscr{E}_1\cdot\tilde{\mathbf{d}}_2}\right\rangle = -\frac{1}{2}\int_{-\omega}^{+\infty} S_{12}(\omega)d\omega, \qquad (****)$$

where $S_{12}(\omega)$ is the mutual spectral density of the operands, which is defined similarly to Eq. (5.57):

$$\left\langle\mathscr{E}_{1\omega}\cdot\tilde{\mathbf{d}}^*_{2\omega'}\right\rangle = S_{12}(\omega)\delta(\omega - \omega').$$

(In plain English, Eq. (****) says that the contributions of all frequencies to the average interaction of the dipoles are additive.) In order to calculate $S_{12}(\omega)$, we may use Eq. (***) and then Eq. (**), getting

$$\begin{aligned}\left\langle\mathscr{E}_{1\omega}\cdot\tilde{\mathbf{d}}^*_{2\omega'}\right\rangle_{\omega'\approx\omega} &= \frac{q^2}{m}\frac{1}{\left(\omega_0^2 - \omega^2\right) + 2i\delta\omega}\left\langle\mathscr{E}_{1\omega}\cdot\mathscr{E}^*_{1\omega'}\right\rangle_{\omega'\approx\omega} \\ &= \frac{q^2}{m}\frac{1}{\left(\omega_0^2 - \omega^2\right) + 2i\delta\omega}\frac{1}{\left(4\pi\varepsilon_0 r^3\right)^2}\left(\left\langle d_{x\omega}d^*_{x\omega'}\right\rangle + \left\langle d_{y\omega}d^*_{y\omega'}\right\rangle + 4\left\langle d_{z\omega}d^*_{z\omega'}\right\rangle\right),\end{aligned}$$

where in the last expression, the index 1 has been dropped for notation brevity, because the participating averages do not depend on the dipole number. Since all Cartesian components of the spontaneously fluctuating dipole **d** described by Eq. (*) have similar statistics, the expression in the last parentheses is just six times one of them – say $\langle dx_\omega dx_{\omega'}\rangle$, with

$$d_{x\omega}=\frac{q}{m}\frac{\mathcal{F}_{x\omega}}{\left(\omega_0^2-\omega^2\right)-2i\delta\omega},\qquad \text{i.e. } \left\langle d_{x\omega}d^*_{x\omega'}\right\rangle_{\omega'\approx\omega}=\left(\frac{q}{m}\right)^2\frac{\left\langle \mathcal{F}_{x\omega}\mathcal{F}^*_{x\omega'}\right\rangle_{\omega'\approx\omega}}{\left(\omega_0^2-\omega^2\right)^2+4\delta^2\omega^2},$$

so

$$\left\langle \mathscr{E}_{1\omega}\cdot\tilde{\mathbf{d}}^*_{2\omega'}\right\rangle_{\omega'\approx\omega}=\frac{q^2}{m}\left(\frac{q}{m}\right)^2\frac{1}{\left(\omega_0^2-\omega^2\right)+2i\delta\omega}\frac{1}{\left(4\pi\varepsilon_0 r^3\right)^2}6\left\langle d_{x\omega}d^*_{x\omega'}\right\rangle_{\omega'\approx\omega}$$

$$=\frac{q^2}{m}\left(\frac{q}{m}\right)^2\frac{1}{\left(\omega_0^2-\omega^2\right)+2i\delta\omega}\frac{q^2}{\left(4\pi\varepsilon_0 r^3\right)^2}6\frac{\left\langle \mathcal{F}_{x\omega}\mathcal{F}^*_{x\omega'}\right\rangle_{\omega'\approx\omega}}{\left(\omega_0^2-\omega^2\right)^2+4\delta^2\omega^2}.$$

According to its definition (5.55), the *autocorrelation* function on the right-hand side of this relation does not change at the simultaneous change of signs of the frequencies ω and ω':

$$\left\langle \mathcal{F}_{x\omega}\mathcal{F}^*_{x\omega'}\right\rangle_{\omega'\approx\omega}=S_{\mathcal{F}_x}(\omega)\delta(\omega-\omega'),\qquad \text{with } S_{\mathcal{F}_x}(-\omega)=S_{\mathcal{F}_x}(\omega).$$

Hence the *mutual* correlation function has to change the sign of its imaginary part at such frequency change. As a result, Eq. (****) may be recast as follows:

$$\left\langle U_{12}\right\rangle=-\frac{1}{2}\int_0^{+\infty}\left[S_{12}(\omega)+S^*_{12}(\omega)\right]d\omega\equiv-\int_0^{\infty}\operatorname{Re}S_{12}(\omega)d\omega,$$

so adding the independent and equal contribution $\langle U_{21}\rangle$, for the full interaction energy we get

$$\left\langle U\right\rangle=-2\int_0^{\infty}\operatorname{Re}\frac{q^2}{m}\left(\frac{q}{m}\right)^2\frac{1}{\left(\omega_0^2-\omega^2\right)+2i\delta\omega}\frac{1}{\left(4\pi\varepsilon_0 r^3\right)^2}6\frac{S_{\mathcal{F}_x}(\omega)}{\left(\omega_0^2-\omega^2\right)^2+4\delta^2\omega^2}d\omega$$

$$\equiv-12\left(\frac{q^2}{4\pi\varepsilon_0 r^3}\right)^2\frac{1}{m^3}\int_0^{\infty}\frac{\left(\omega_0^2-\omega^2\right)}{\left[\left(\omega_0^2-\omega^2\right)^2+4\delta^2\omega^2\right]^2}S_{\mathcal{F}_x}(\omega)d\omega.$$

So far, our result is valid for arbitrary temperatures. At $T \gg \hbar\omega_0$ (and in thermal equilibrium), we may use Eq. (5.73a), i.e. the classical limit of the fluctuation-dissipation theorem, for the spectral density of force:

$$S_{\mathcal{F}_x}(\omega)=\frac{\eta}{\pi}T\equiv\frac{2m\delta}{\pi}T\,.$$

With this simplification, we may use the integral provided in the *Hint*,[59] with $\alpha = 2\delta/\omega_0$, to spell out the result:

$$\left\langle U\right\rangle=-12\left(\frac{q^2}{4\pi\varepsilon_0 r^3}\right)^2\frac{1}{m^3}\int_0^{\infty}\frac{\left(\omega_0^2-\omega^2\right)}{\left[\left(\omega_0^2-\omega^2\right)^2+4\delta^2\omega^2\right]^2}\frac{2m\delta}{\pi}T\,d\omega$$

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[59] Actually, it may be readily worked out by differentiation, over a parameter, of the following (generally useful) table integral:

$$\int_0^{\infty}\frac{d\xi}{(a\xi)^2+2b\xi+1}=\frac{\pi}{2^{3/2}(a+b)^{1/2}},\qquad \text{for } a+b>0,$$

but I did not want to distract the reader's attention from physics.

$$\equiv -12\left(\frac{q^2}{4\pi\varepsilon_0 r^3}\right)^2 \frac{1}{m^3}\frac{2m\delta}{\pi}T\frac{1}{\omega_0^3}\int_0^\infty \frac{\left(1-\xi^2\right)}{\left[\left(1-\xi^2\right)^2+\left(2\delta/\omega_0\right)^2\xi^2\right]^2}d\xi$$

$$= -12\left(\frac{q^2}{4\pi\varepsilon_0 r^3}\right)^2 \frac{1}{m^3}\frac{2m\delta}{\pi}T\frac{1}{\omega_0^3}\frac{\pi}{4\left(2\delta/\omega_0\right)} \equiv -3\left(\frac{q^2}{4\pi\varepsilon_0 r^3 m\omega_0^2}\right)^2 T.$$

Remarkably, this final result does not depend on the oscillator's damping δ, making it valid even at $\delta \to 0$. In this limit, it coincides with the classical limit of the result obtained in the solution of QM Problem 7.6. (The result for an arbitrary $\hbar\omega_0/T$ ratio, obtained in that solution, also follows from our general formula, but only for $\delta << \omega_0$.)

Note that an attempt[60] to solve this problem by a direct calculation of the average $\langle E\rangle$ value of the total energy of the system,

$$E = \frac{p_1^2}{2m}+\frac{p_2^2}{2m}+\frac{\kappa s_1^2}{2}+\frac{\kappa s_2^2}{2}+U = \frac{p_1^2}{2m}+\frac{p_2^2}{2m}+\frac{\kappa s_1^2}{2}+\frac{\kappa s_2^2}{2}-\frac{q^2}{4\pi\varepsilon_0 r^3}\left(s_{1x}s_{2x}+s_{1y}s_{2y}-2s_{1z}s_{2z}\right),$$

by using the same classical approach as was used for the solution of the (conceptually, very similar) Problem 2.18, yields a surprising result:

$$\langle E\rangle = 6T\ .$$

This equality is in accord with the equipartition theorem, describing the sum of classical contributions $T/2$ by the 12 half-degrees of freedom of the two *non-interacting* 3D oscillators, but gives no average interaction energy. The explanation of this result may be found in the solution of QM Problem 3.20: a simple coordinate transform shows that our system is exactly equivalent to that of six non-interacting 1D harmonic oscillators with slightly different frequencies, which depend on the interaction parameter $\mu \equiv q^2/4\pi\varepsilon_0 r^3 m\omega_0^2 << 1$. At $T \sim \hbar\omega_0$, the average energy of each oscillator, and hence the net average energy $\langle E\rangle$ of the system does depend on $\mu \propto r^{-3}$ describing the interaction energy. However, if when pursuing the limit $T >> \hbar\omega_0$, we take the energy of each 1D oscillator equal exactly T from the very beginning, as we implicitly do in the classical approach, this dependence is lost, together with the $\langle U\rangle$ calculated above.

Problem 5.20.* Within the van der Pol approximation,[61] calculate the major statistical properties of small fluctuations of classical self-oscillations (including their linewidth), at:

(i) a free ("autonomous") run of the oscillator, and
(ii) its phase being locked by an external sinusoidal force,

assuming that the fluctuations are caused by a noise with a smooth spectral density $S_f(\omega)$.

Solution: In the van der Pol approximation, the solution of the (weakly nonlinear) differential equation describing self-oscillations is looked for in the quasi-sinusoidal form[62]

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[60] This is a very useful additional exercise, highly recommended to the reader.

[61] See, e.g., CM Secs. 5.2-5.5. Note that in quantum mechanics, a similar approach is called the *rotating-wave approximation* (RWA) – see, e.g., QM Secs. 6.5, 7.6, 9.2, and 9.4.

$$q(t) = A(t)\cos\Psi(t) \equiv A(t)\cos[\Omega t - \varphi(t)], \qquad (*)$$

with slowly changing amplitude $A(t)$ and phase $\varphi(t)$. In the absence of fluctuations, and at sufficiently weak phase-locking force, the dynamics of $\varphi(t)$, i.e. of the difference between the full phase Ψ of the oscillator and that of the phase-locking force of frequency Ω, may be described by the following *reduced* (or "van der Pol", or "RWA") *equation*:[63]

$$\dot{\varphi} = \xi + \Delta\cos\varphi, \qquad (**)$$

where $\xi \equiv \Omega - \Omega_0$ is the *detuning* (the difference between Ω and the own frequency Ω_0 of the oscillator), and the parameter Δ is proportional to the phase-locking force's amplitude. (As it follows from an elementary analysis of Eq. (**), this parameter, in particular, determines the frequency range of phase-locking in the absence of fluctuations: $\Omega_{\max} - \Omega_{\min} = 2\,|\,\Delta\,|$.)

In order to account for fluctuations, we need to recall that the right-hand side of the reduced equation (**) results from the following time averaging,[64]

$$\frac{1}{\Omega A}\overline{f^{(0)}\cos\Psi},$$

of the right-hand side $f(t)$ of the initial differential equation of motion taken in the "0th approximation" that ignores the relatively slow evolution of A and φ. As was discussed in Sec. 5.5 of the lecture notes, within the Langevin formalism, a noise source is described as an additional term, $\tilde{f}(t)$, in the right-hand of that initial equation of motion, so we need to add, to the right-hand side of the reduced equation (**), the following term:

$$\frac{1}{\Omega A}\overline{\tilde{f}\cos(\Omega t - \varphi)} \equiv \frac{1}{2\Omega A}\overline{\left\{\int_{-\infty}^{+\infty} f_\omega e^{-i[(\omega+\Omega)t - \varphi]}d\omega + \int_{-\infty}^{+\infty} f_\omega e^{-i[(\omega-\Omega)t + \varphi]}d\omega\right\}}.,$$

where A may be treated as a constant (the average amplitude of the self-oscillations) and f_ω is the Fourier image of $\tilde{f}(t)$ – see Eq. (5.52).

This expression shows that the Langevin term has two components, which differ from the original noise (besides the scaling front factor) only by shifting its frequency spectrum by $\pm\Omega$. In the van der Pol approximation, the time averaging may be carried over any time period Δt much larger than the oscillation period $2\pi/\Omega$, with the only requirement for it to be still much shorter than the shortest time scale of the reduced equation(s) dynamics, in our case of the order of $1/\max[|\,\xi\,|, |\,\Delta\,|]$. This averaging retains only low-frequency components of the averaged function – in our case, the components with the "mathematical" frequencies close to $\pm\Omega$, i.e. the "physical" (positive) frequencies close to Ω. If the initial noise is indeed broadband, its spectral density $S_f(\omega)$, defined by Eq. (5.57), is virtually constant within such a narrow interval. Hence, its addition generalizes the reduced equation (**) as follows:

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[62] See, e.g., CM Eq. (5.41). Note that here, in contrast to CM Sec. 5.4, the capital letters Ω and Ω_0 are used to denote the frequencies of the phase locking force and the oscillator, to distinguish them from the frequencies ω of the Fourier components of fluctuations.

[63] See, e.g., CM Eq. (5.68). In this approximation, the oscillation amplitude $A(t)$ may be considered constant – see CM Eq. (5.71) and its discussion.

[64] See, e.g., the second of CM Eqs. (4.57a).

$$\dot{\varphi} = \xi + \Delta\cos\varphi + \tilde{\xi}(t), \qquad (***)$$

where $\tilde{\xi}(t)$, at the low frequencies of our interest, may be treated as a process with zero average and a constant spectral density

$$S_\xi(\omega) \approx S_\xi(0) = \left(\frac{1}{2\Omega A}\right)^2 S_f(\Omega) + \left(\frac{1}{2\Omega A}\right)^2 S_f(-\Omega) = \frac{1}{2\Omega^2 A^2} S_f(\Omega).$$

According to the discussion at the end of Sec. 5.4 of the lecture notes, the correlation function of such a process may be approximated with Eq. (5.62):

$$K_\xi(\tau) = 2\pi S_\xi(0)\delta(\tau) = 2\Gamma\delta(\tau), \qquad \text{with } \Gamma \equiv \pi S_\xi(0) = \frac{\pi S_f(\Omega)}{2\Omega^2 A^2}. \qquad (****)$$

Now we are ready to consider the two specific cases listed in the problem's assignment.

(i) The free-running ("autonomous") mode of the self-oscillator may be described by Eq. (***) with $\Delta = 0$, giving the linear differential equation

$$\dot{\varphi} = \xi + \tilde{\xi}(t),$$

which may be readily integrated:

$$\varphi(t) = \xi t + \tilde{\varphi}(t) + \text{const}, \qquad \text{where } \tilde{\varphi}(t) \equiv \int_0^t \tilde{\xi}(t')dt',$$

so Eq. (*) yields

$$q(t) = A\cos[\Omega t - \xi t - \tilde{\varphi}(t)] \equiv A\cos[\Omega t - (\Omega - \Omega_0)t - \tilde{\varphi}(t)] \equiv A\cos[\Omega_0 t - \tilde{\varphi}(t)].$$

In the absence of fluctuations, this expression describes coherent self-oscillations at the own frequency Ω_0 of the oscillator:

$$q(t)\Big|_{\tilde{\varphi}=0} = A\cos(\Omega_0 t + \text{const}).$$

The noise $\tilde{\xi}(t)$ induces the fluctuations $\tilde{\varphi}(t)$ of the phase around this deterministic evolution, which obey exactly the same equation as the coordinate fluctuation $\Delta\tilde{q}(t)$ of a free 1D "Brownian particle" in Einstein's problem – see Eq. (5.74). Repeating the calculation that followed this formula in the lecture notes, we see that the phase φ of the autonomous oscillator performs a random walk with the diffusion coefficient proportional to the spectral density of the noise source:

$$\left\langle [\tilde{\varphi}(t+\tau) - \tilde{\varphi}(t)]^2 \right\rangle = 2D\tau, \qquad \text{with } D = \Gamma \equiv \frac{\pi S_f(\Omega)}{2\Omega^2 A^2}.$$

This phase diffusion has important implications for the self-oscillation process $q(t)$. Indeed, let us calculate its correlation function:

$$K_q(\tau) \equiv \langle q(t)q(t+\tau)\rangle = A^2\langle \cos[\Omega_0 t - \tilde{\varphi}(t)]\cos[\Omega_0(t+\tau) - \tilde{\varphi}(t+\tau)]\rangle$$
$$\equiv \frac{A^2}{2}\langle \cos[2\Omega_0 t + \Omega_0\tau - \tilde{\varphi}(t) - \tilde{\varphi}(t+\tau)] + \cos[\tilde{\varphi}(t+\tau) - \tilde{\varphi}(t) - \Omega_0\tau]\rangle.$$

Since in a statistical ensemble of similar autonomous oscillators, the full phase Ψ of the oscillations takes all values (modulo 2π) with equal probability, the statistical average of the first term vanishes, leaving us with

$$K_q(\tau) = \frac{A^2}{2}\left\langle \cos[\tilde{\varphi}(t+\tau) - \tilde{\varphi}(t) - \Omega_0\tau]\right\rangle \equiv \frac{A^2}{2}\operatorname{Re}\left\langle \exp\{i[\tilde{\varphi}(t+\tau) - \tilde{\varphi}(t) - \Omega_0\tau]\}\right\rangle$$

$$\equiv \frac{A^2}{2}\operatorname{Re}\left[\exp\{-i\Omega_0\tau\}\left\langle \exp\left\{i\int_t^{t+\tau}\tilde{\xi}(t')dt'\right\}\right\rangle\right] \equiv \frac{A^2}{2}\operatorname{Re}\left[\exp\{-i\Omega_0\tau\}\left\langle \prod_{n=1}^{N}\exp\left\{i\int_{t+(n-1)\tau/N}^{t+n\tau/N}\tilde{\xi}(t')dt'\right\}\right\rangle\right],$$

where the last representation is exactly valid for any integer $N > 0$. Since in our approximation (****),[65] the function $\tilde{\xi}(t)$ is delta-correlated, the partial integrals in this product are statistically independent, and our statistical average breaks into a product of averages:

$$K_q(\tau) = \frac{A^2}{2}\operatorname{Re}\left[\exp\{-i\Omega_0\tau\}\prod_{n=1}^{N}\varepsilon_n\right], \qquad \text{with } \varepsilon_n \equiv \left\langle \exp\left\{i\int_{t+(n-1)\tau/N}^{t+n\tau/N}\tilde{\xi}(t')dt'\right\}\right\rangle.$$

At sufficiently large N, and hence sufficiently small integration intervals τ/N, the exponent in each ε_n may be expanded into the Taylor series, with only three leading terms kept, so

$$\lim_{N\to\infty}\varepsilon_n = \lim_{N\to\infty}\varepsilon_n\left\langle 1 + i\int_{t+(n-1)\tau/N}^{t+n\tau/N}\tilde{\xi}(t')dt' + \frac{1}{2}\left[i\int_{t+(n-1)\tau/Nt}^{t+n\tau/N}\tilde{\xi}(t')dt'\right]\left[i\int_{t+(n-1)\tau/N}^{t+n\tau/N}\tilde{\xi}(t'')dt''\right]\right\rangle$$

$$\equiv \lim_{N\to\infty}\varepsilon_n\left[1 + i\int_{t+(n-1)\tau/N}^{t+n\tau/N}\left\langle\tilde{\xi}(t')\right\rangle dt' - \frac{1}{2}\int_{t+(n-1)\tau/N}^{t+n\tau/N}dt'\int_{t+(n-1)\tau/N}^{t+n\tau/N}dt''\left\langle\tilde{\xi}(t')\tilde{\xi}(t'')\right\rangle\right].$$

By the definition of the random function $\tilde{\xi}(t)$, its statistical average equals zero, so the second term in the last form of this equality vanishes, while the average in its last term is just the correlation function $K_\xi(t' - t'')$. Thus, plugging it from Eq. (****), we get an expression independent of the time step number n:

$$\lim_{N\to\infty}\varepsilon_n = \lim_{N\to\infty}\left[1 - \Gamma\int_{t+(n-1)\tau/N}^{t+n\tau/N}dt'\int_{t+(n-1)\tau/N}^{t+n\tau/N}dt'\ \delta(t'-t'')\right] = \lim_{N\to\infty}\left[1 - \Gamma\int_{t+(n-1)\tau/N}^{t+n\tau/N}dt''\right] = \lim_{N\to\infty}\left(1 - \Gamma\frac{\tau}{N}\right).$$

Since this result is independent of the running index n, the correlation function of the process $q(t)$ is just

$$K_q(\tau) = \lim_{N\to\infty}\frac{A^2}{2}\operatorname{Re}\left[\exp\{-i\Omega_0\tau\}\left(1 - \Gamma\frac{\tau}{N}\right)^N\right] \equiv \frac{A^2}{2}\cos\Omega_0\tau \times \lim_{N\to\infty}\left(1 - \Gamma\frac{\tau}{N}\right)^N.$$

But the last limit is just $\exp\{-\Gamma\tau\}$,[66] so we finally get a very simple (and very important!) result:

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[65] For our current autonomous case, with $\Delta = 0$, this approximation is valid if the spectral density $S_f(\omega)$ of the noise is virtually constant in a frequency interval (around the self-oscillation frequency Ω_0) that is larger than the oscillation linewidth we are currently calculating – see below.

[66] See, e.g., MA Eq. (1.2a) with $n = -N/\Gamma\tau$.

$$K_q(\tau) = \frac{A^2}{2}\cos\Omega_0\tau \, \exp\{-\Gamma\tau\},$$

with Γ given by Eq. (****).

This formula describes the gradual suppression of the coherence of the self-oscillations on the time scale $1/\Gamma$.[67] Now let us apply to this result the Wiener-Khinchin theorem (5.58):

$$\begin{aligned} S_q(\omega) &= \frac{1}{\pi}\int_0^\infty K_q(\tau)\cos\omega\tau \, d\tau = \frac{A^2}{2\pi}\int_0^\infty \cos\omega\tau\cos\Omega_0\tau \, \exp\{-\Gamma\tau\} d\tau \\ &\equiv \frac{A^2}{4\pi}\operatorname{Re}\int_0^\infty \left[\exp\{i(\omega+\Omega_0)\tau - \Gamma\tau\} + \exp\{i(\omega-\Omega_0)\tau - \Gamma\tau\}\right]d\tau \\ &= \frac{A^2}{4\pi}\operatorname{Re}\left[\frac{1}{-i(\omega+\Omega_0)+\Gamma} + \frac{1}{-i(\omega-\Omega_0)+\Gamma}\right] \equiv \frac{A^2}{2\pi}\frac{\Gamma}{\left(\omega^2-\Omega_0^2\right)+\Gamma^2}. \end{aligned}$$

This expression describes the so-called *Lorentz broadening* of the oscillation line, with the *half-linewidth* equal to the Γ given by Eq. (****). Note again that according to that relation, at small fluctuations (giving $\Gamma << \Omega_0$), for which this delta-correlated approximation of the noise is valid, the linewidth of oscillations at frequencies $\omega \sim \Omega_0$ is determined by the initial noise intensity $S_f(\Omega)$ at close frequencies, but it acts on the oscillator via the intensity $S_\xi(0)$ of frequency fluctuations at much lower frequencies $\omega \sim \Gamma << \Omega_0$. This fact is important because for some self-oscillators (such as dc-voltage-biased Josephson junctions[68]), low-frequency external noise may directly "wobble" the oscillation frequency, and hence provide additional line broadening.

(ii) For a phase-locked oscillator ($\Delta \neq 0$, $|\xi| < |\Delta|$), in the absence of fluctuations, Eq. (**) describes a transient process in which the phase φ approaches a constant:

$$\varphi(t) \to \varphi_0, \qquad \text{with } \cos\varphi_0 = -\frac{\xi}{\Delta}, \text{ i.e. } \Delta\sin\varphi_0 = \left(\Delta^2 - \xi^2\right)^{1/2},$$

so the oscillations $q(t) = A\cos[\Omega t - \varphi(t)]$ settle to the frequency Ω of the external force, rather than to Ω_0 – this is exactly what is called *phase locking* (or "synchronization"). In this case, a small noise (not strong enough to disrupt the phase locking[69]) causes not the unrestricted phase diffusion, but rather small fluctuations of the phase around the stable value φ_0. In order to find their spectral density, we may linearize Eq. (***) by taking $\varphi(t) = \varphi_0 + \tilde{\varphi}(t)$, expanding the nonlinear function $\cos\varphi$ into the Taylor series in small $\tilde{\varphi}(t)$, and keeping only the two leading terms. This yields the linear differential equation

$$\dot{\tilde{\varphi}} + \left(\Delta\sin\varphi_0\right)\tilde{\varphi} = \tilde{\xi}(t),$$

---

[67] Note that this calculation essentially repeats the derivation of Eq. (7.89) in QM Sec. 7.3. This is natural because the quantum state dephasing described in that section is essentially the decoherence of the fundamental oscillations of the quantum-mechanical wavefunction in time (with frequency $E/\hbar$) under the effect of low-frequency external fluctuations imposed by the environment.

[68] See, e.g., brief discussions in EM Sec. 6.5 and QM Secs. 1.6 and 2.8.

[69] For a description of such disruptions, see the solution of Problem 28 below.

which may be solved as was discussed in Sec. 5.5, by the Fourier transform of the functions $\tilde{\varphi}(t)$ and $\tilde{\xi}(t)$. For their Fourier images, the linearized equation yields the relation

$$-i\omega\varphi_\omega + (\Delta\sin\varphi_0)\varphi_\omega = \xi_\omega, \qquad \text{i.e. } \varphi_\omega = \frac{1}{-i\omega + \Delta\sin\varphi_0}\xi_\omega,$$

which enables us to express the spectral density of phase fluctuations via that of the noise source, given by Eq. (***):

$$S_\varphi(\omega) = \left|\frac{1}{-i\omega + \Delta\sin\varphi_0}\right|^2 S_\xi(\omega) \approx \frac{1}{\Delta^2\sin^2\varphi_0 + \omega^2} S_\xi(0) = \frac{S_f(\Omega)}{2\Omega^2 A^2}\frac{1}{(\Delta^2 - \xi^2) + \omega^2}.$$

Plugging this expression into Eq. (5.60), we may readily calculate the fluctuations' variance:[70]

$$\langle\tilde{\varphi}^2\rangle = 2\int_0^\infty S_\varphi(\omega)d\omega = \frac{S_f(\Omega)}{\Omega^2 A^2}\int_0^\infty \frac{d\omega}{(\Delta^2 - \xi^2) + \omega^2} = \frac{\pi S_f(\Omega)}{2\Omega^2 A^2}\frac{1}{(\Delta^2 - \xi^2)^{1/2}}.$$

This result shows that the fluctuations are the smallest at the center of the phase-locking region ($\xi \approx 0$), where the hold of the external force on the oscillators' phase is the most firm, and grow infinitely toward either edge of the region ($\xi \to \pm\Delta$) where the phase locking effect is most fragile. However, in any case, these phase fluctuations, with their infinite variance, are much smaller than those in the autonomous oscillator analyzed in Task (i), and do not result in oscillation line broadening. This is natural because the phase locking essentially does not allow the oscillation's instant frequency $\dot{\Psi} \equiv \Omega - \dot{\varphi}$ to deviate significantly from the frequency Ω of the locking force:

$$S_{\dot{\Psi}}(\omega) = S_{\dot{\varphi}}(\omega) = \omega^2 S_\varphi(\omega) = \frac{S_f(\Omega)}{2\Omega^2 A^2}\frac{\omega^2}{(\Delta^2 - \xi^2) + \omega^2} \to 0, \qquad \text{for } \omega \to 0.$$

Problem 5.21. Calculate the correlation function of the coordinate of a 1D harmonic oscillator with low damping, in thermal equilibrium. Compare the solution with that of the previous problem.

Solution: The spectral density of fluctuations of the oscillator's coordinate is given by Eq. (5.68) of the lecture notes.[71] With the simplification (5.69), valid at low damping and $\omega \approx \omega_0$, it becomes

$$S_q(\omega) = \frac{1}{4m\kappa(\xi^2 + \delta^2)} S_{\mathcal{F}}(\omega_0), \qquad \text{with } \xi \equiv \omega - \omega_0, \text{ and } \delta \equiv \frac{\eta}{2m}.$$

From here, the correlation function may be found using the Fourier transform (5.59):[72]

$$K_q(\tau) = 2\int_{\omega\approx\omega_0} S_q(\omega)\cos\omega\tau\, d\omega = \frac{S_{\mathcal{F}}(\omega_0)}{2m\kappa}\int_{|\xi|<<\omega_0} \cos(\omega_0 + \xi)\tau \frac{d\xi}{\xi^2 + \delta^2}.$$

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[70] If you need to, see MA Eq. (6.5a).

[71] Please note again that, as was noted at the derivation of that result, the direct statistical average of the noise-induced oscillations $q(t)$ vanishes, so the correlation function is the simplest quantitative time-domain characteristic of the noise-induced random oscillations.

[72] Note that this discussion is valid for the general (quantum) case, $\hbar\omega \sim T$, only if both $K_q(\tau)$ and $S_q(\omega)$ are understood in the sense of the symmetrized functions defined by Eqs. (5.95)-(5.96).

Since at low damping ($\delta << \omega_0$), this integral converges rapidly near the point $\omega = \omega_0$, i.e. near $\xi = 0$, we may formally extend the limits of integration over ξ from $-\infty$ to $+\infty$, and get

$$K_q(\tau) = \frac{S_{\mathcal{F}}(\omega_0)}{2m\kappa}\int_{-\infty}^{+\infty}\cos(\omega_0+\xi)\tau\,\frac{d\xi}{\xi^2+\delta^2} = \frac{S_{\mathcal{F}}(\omega_0)}{2m\kappa}\int_{-\infty}^{+\infty}\left[\cos\omega_0\tau\cos\xi\tau - \sin\omega_0\tau\sin\xi\tau\right]\frac{d\xi}{\xi^2+\delta^2}$$
$$= \frac{S_{\mathcal{F}}(\omega_0)}{m\kappa}\cos\omega_0\tau\int_0^{+\infty}\cos\xi\tau\,\frac{d\xi}{\xi^2+\delta^2}.$$

This is a table integral[73] equal to $(\pi/2\delta)\exp\{-\delta\tau\}$, so using the fluctuation-dissipation theorem (5.98) for $S_{\mathcal{F}}(\omega_0)$, within the Ohmic model of dissipation ($\chi(\omega) = i\eta\omega$),

$$S_{\mathcal{F}}(\omega_0) = \eta\frac{\hbar\omega_0}{2\pi}\coth\frac{\hbar\omega_0}{2T},$$

we finally get

$$K_q(\tau) = \frac{S_{\mathcal{F}}(\omega_0)}{m\kappa}\cos\omega_0\tau\times\frac{\pi}{2\delta}e^{-\delta\tau} = \frac{\hbar\omega_0}{2\kappa}\coth\frac{\hbar\omega_0}{2T}e^{-\delta\tau}\cos\omega_0\tau .$$

As a sanity check, at $\tau = 0$, this expression gives the same result for $K_q(0) \equiv \langle q^2\rangle$ as Eq. (2.78) with $\omega = \omega_0 = (\kappa/m)^{1/2}$.

Note that the functional form,

$$K_q(\tau) = K_q(0)\cos\omega_0\tau\, e^{-\delta\tau},$$

of our current result (quantitatively valid only for low damping, $\delta << \omega_0$) is similar to that for the autonomous self-oscillator analyzed in Task (i) of the previous problem, despite the quite different physics of these two processes: the noise "filtration" by a passive oscillator in our current case vs. the noise broadening of the spectral line of an active self-oscillator. The significant difference between these two processes may be revealed by comparing their other statistical measures – for example, the time-averaged probability distributions $w(q)$; such comparison is highly recommended to the reader as an additional exercise.

Note also that this problem may be also solved using a 1D version of Eq. (5.177), by calculating the probability distribution $w(q, p, \tau)$ from the 1D version of the Fokker-Planck equation (5.149). However, as should be clear from the solution of the similar problem for high damping, carried out at the end of Sec. 5.8, this way is substantially longer, so there is no good motivation for applying it to this linear system, for which the Langevin formalism used above gives a much simpler approach.

Problem 5.22. A lumped electric circuit consisting of a capacitor C shortened with an Ohmic resistor R is in thermal equilibrium at temperature T. Use two different approaches to calculate the variance of the thermal fluctuations of the capacitor's electric charge Q. Estimate the effect of quantum fluctuations.

Solution: The simplest approach is to notice that the capacitor's electric energy,

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[73] See, e.g., MA Eq. (6.11).

$$E = \frac{Q^2}{2C},$$

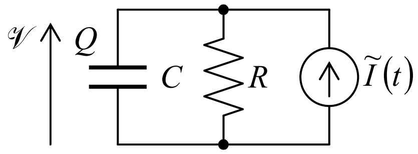
is a quadratic function of Q, so according to the equipartition theorem (2.48), in the thermal-fluctuation (i.e. classical) limit, the average energy of this "half-degree of freedom" has to equal $T/2$:

$$\left\langle \frac{Q^2}{2C} \right\rangle = \frac{T}{2}.$$

Since due to the system's symmetry with respect to the charge's sign, $\langle Q \rangle = 0$, the above relation holds for the charge fluctuations $\tilde{Q} \equiv Q - \langle Q \rangle$ as well, so, finally,

$$\left\langle \tilde{Q}^2 \right\rangle = CT. \qquad (*)$$

A possible concern with this approach is that it ignores the energy of the internal degrees of freedom of the resistor (which, in this system, plays the role of the fluctuation-generating environment). This is why a more prudent approach is to use the Langevin equation together with the Nyquist theorem. The lumped character of the circuit enables us to use for its analysis the usual Kirchhoff rules. For that, the Johnson-Nyquist noise of the physical (noise-inducing) resistor may be represented as a separate fluctuation current source connected in parallel with a noise-free resistor R with current $I = \mathcal{V}/R = Q/CR$ – see the figure on the right.[74] As a result, the Kirchhoff node rule yields



$$\frac{dQ}{dt} = -\frac{Q}{RC} + \tilde{I}(t), \qquad \text{i.e. } \frac{dQ}{dt} + \frac{Q}{\tau} = \tilde{I}(t),$$

where $\tau \equiv RC$ is the charge relaxation time constant. Performing the same transfer to the Fourier images of the fluctuations and then to their spectral densities as was described at the beginning of Sec. 5.5 of the lecture notes for Eq. (5.65), we get

$$Q_\omega = \frac{I_\omega}{-i\omega + \tau^{-1}}, \qquad S_Q(\omega) = \frac{S_I(\omega)}{\left|-i\omega + \tau^{-1}\right|^2} \equiv \frac{S_I(\omega)}{\omega^2 + \tau^{-2}}.$$

Now by using Eq. (5.60) for the charge fluctuation variance, together with the Nyquist formula (5.81c) for $S_I(\omega)$, we get

$$\left\langle \tilde{Q}^2 \right\rangle = 2\int_0^\infty \frac{S_I(\omega)}{\omega^2 + \tau^{-2}} d\omega = \frac{2T}{\pi R}\int_0^\infty \frac{d\omega}{\omega^2 + \tau^{-2}} \equiv \frac{2T}{\pi R}\tau \int_0^\infty \frac{d\xi}{\xi^2 + 1} = \frac{2T}{\pi R}\tau\frac{\pi}{2} \equiv CT,$$

thus confirming the result (*).

The Langevin-equation approach also enables a semi-quantitative discussion of the quantum effects in the system. Indeed, comparing Eqs. (5.92) and (5.98), we see that the transfer from the thermal to the full (thermal + quantum) fluctuations may be achieved by the replacement

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[74] If this point is not quite clear, see, e.g., the model solution of EM Problem 4.2. (Alternatively, we might use a voltage (e.m.f.) fluctuation source, described by Eq. (5.82), connected *in series* with the noise-free resistor. The reader is encouraged to show that this alternative approach gives the same final result.)

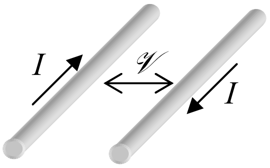
$$T \to \frac{\hbar\omega}{2}\coth\frac{\hbar\omega}{2T}$$

in the spectral density of noise sources. For our current case, it yields

$$\left\langle \tilde{Q}^2 \right\rangle \to \frac{\hbar}{\pi R}\int_0^\infty \omega \coth\frac{\hbar\omega}{2T}\frac{d\omega}{\omega^2+\tau^{-2}}. \qquad (**)$$

Since $\coth\xi \to 1$ at $\xi \to \infty$, this integral diverges on its upper limit, i.e. at frequencies $\omega >> 1/\tau$, $T/\hbar$. At room temperature, the last condition is satisfied at $\omega >> 10^{14}$ s^{-1}. At the frequencies that high, most macroscopic resistors deviate from the simple dispersion-free Ohmic approximation $I = \mathscr{V}/R$, and the spectral density of their noise becomes lower than that given by Eqs. (5.81), making the integral converge. Denoting the frequency of such a cutoff as $\omega_{\max}$, and assuming that it is much higher than $1/\tau$, we may use Eq. (**) to write the estimate

$$\left\langle \tilde{Q}^2 \right\rangle \sim C \times \max\left[T, \frac{\hbar\omega_{\max}}{2}\right].$$



Problem 5.23. Consider a very long, uniform, two-wire transmission line (see the figure on the right) with a wave impedance $\mathscr{Z}$, which allows the propagation of TEM electromagnetic waves with negligible attenuation. Calculate the variance $\langle \mathscr{V}^2 \rangle_{\Delta\nu}$ of spontaneous fluctuations of the voltage $\mathscr{V}$ between the wires within a small interval $\Delta\nu$ of cyclic frequencies, in thermal equilibrium at temperature T.

Hint: As an E&M reminder,[75] in the absence of dispersive materials, TEM waves propagate with a frequency-independent velocity, and with the voltage $\mathscr{V}$ and current I (see the figure above) related as $\mathscr{V}(x,t)/I(x,t) = \pm\mathscr{Z}$, where $\mathscr{Z}$ is the line's wave impedance.

Solution: Since in a traveling TEM wave, the electric and magnetic fields, and hence the local voltage $\mathscr{V}(t)$ and the local current $I(t)$ vary in time simultaneously ("in phase"), the instantaneous power carried by a sinusoidal wave through a cross-section of the transmission line is

$$\mathscr{P}(t) = \mathscr{V}(t)I(t) = \mathscr{V}_\omega \cos(\pm kx - \omega t + \varphi) \times I_\omega \cos(\pm kx - \omega t + \varphi) = \frac{\mathscr{V}_\omega^2}{\mathscr{Z}}\cos^2(\pm kx - \omega t + \varphi), \quad (*)$$

where $\mathscr{V}_\omega$ and I_ω are the voltage and current amplitudes, related by the wave impedance $\mathscr{Z}$, and the two signs describe two possible directions of the wave's propagation. Thus the time-averaged power carried by the wave is

$$\overline{\mathscr{P}} = \frac{\mathscr{V}_\omega^2}{2\mathscr{Z}} \equiv \frac{\overline{\mathscr{V}^2}}{\mathscr{Z}}.$$

For a wave traveling with a velocity c (not necessarily equal to the speed of light), its average energy in the line of length is

$$\overline{E} = \overline{\mathscr{P}}\frac{L}{c} = \frac{\overline{\mathscr{V}^2}L}{c\mathscr{Z}}.$$

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[75] See, e.g., EM Sec. 7.6.

On the other hand, according to Eq. (2.80) of the lecture notes, in thermal equilibrium, the statistical-ensemble average (which in this case includes the time average) of this energy should be equal to

$$\langle E \rangle = \frac{\hbar\omega}{2}\coth\frac{\hbar\omega}{2T},$$

so for each wave mode,

$$\langle \mathscr{V}^2 \rangle = \frac{c\mathscr{Z}}{L}\frac{\hbar\omega}{2}\coth\frac{\hbar\omega}{2T}.$$

Since the velocity c of the TEM waves does not depend on frequency, their wavenumber is related to frequency as $k = \pm\omega/c$, so the number of TEM modes corresponding to a small interval $\Delta\omega \equiv 2\pi\Delta\nu$ of physical (positive) frequencies is

$$\Delta N = 2L\frac{\Delta k}{2\pi} = 2L\frac{\Delta\omega}{2\pi c} \equiv 2L\frac{\Delta\nu}{c},$$

where the front factor 2 describes two possible intervals of k (positive and negative), i.e. two possible directions of wave propagation – see Eq. (*). Since the intensities of waves with different frequencies and directions sum up independently, the required variance of the voltage is

$$\langle \mathscr{V}^2 \rangle_{\Delta\nu} = \langle \mathscr{V}^2 \rangle \Delta N = 2\mathscr{Z}\frac{\hbar\omega}{2}\coth\frac{\hbar\omega}{2T}\Delta\nu, \qquad (**)$$

regardless of c.

Problem 5.24. Now consider a similar long transmission line but terminated, at one end, with an impedance-matching Ohmic resistor $R = \mathscr{Z}$. Calculate the variance $\langle \mathscr{V}^2 \rangle_{\Delta\nu}$ of the voltage across the resistor, and discuss the relation between the result and the Nyquist formula (5.81b), including numerical factors.

Hint: A termination with resistance $R = \mathscr{Z}$ absorbs incident TEM waves without reflection.

Solution: Such an *impedance-matched* resistor cannot chance the wave statistics, and hence Eq. (**) of the model solution of the previous problem, with $\mathscr{Z}$ replaced with R, gives the requested voltage variance. In particular, in the classical limit $\hbar\omega << T$,

$$\langle \mathscr{V}^2 \rangle_{\Delta\nu} = 2RT\Delta\nu. \qquad (*)$$

It may look like this result contradicts the Nyquist formula (5.81b), which gives a twice larger numerical factor.

In order to resolve this paradox, we should notice that in the Langevin-approach analysis of Sec. 5.5, we have represented the environmental force as the sum

$$\mathscr{F} = \langle \mathscr{F} \rangle + \tilde{\mathscr{F}}(t),$$

and then argued that for the Ohmic dissipation, the force's average over a thermally-equilibrium ensemble of environments, with the same motion $q(t)$, may be expressed by Eq. (5.64),

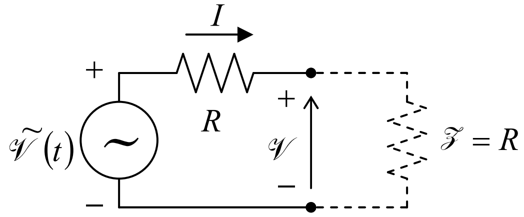
$$\langle \mathscr{F} \rangle = -\eta\dot{q}, \qquad \text{so } \mathscr{F} = -\eta\dot{q} + \tilde{\mathscr{F}}(t).$$

Mapping this formula onto the electric circuit case (see the discussion following Fig. 5.9 of the lecture notes), we get

$$\mathscr{V} = \langle \mathscr{V} \rangle + \tilde{\mathscr{V}}(t) = -RI + \tilde{\mathscr{V}}(t), \qquad (**)$$

where the variance of the second term, within a cyclic frequency interval $\Delta\nu$, is given by Eq. (5.81b),

$$\left\langle \tilde{\mathscr{V}}^2 \right\rangle_{\Delta\nu} = 4RT\Delta\nu. \qquad (***)$$

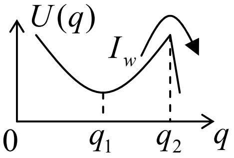


From the point of the electric lumped circuit theory,[76] Eq. (**) is an algebraic description of the equivalent circuit including the deterministic resistor R and an ideal (internal-resistance-free) voltage source with the e.m.f.'s variance given by Eq. (***), connected in series – see the solid-line part of the figure on the right. If the voltage $\mathscr{V}$ is measured with an ideal voltmeter (with infinite internal resistance), then the current I in the circuit vanishes, and the variance of the measured voltage is indeed given by Eq. (***).[77]

However, in our current problem, we are discussing voltage measurements in a different circuit, in which the "noisy" resistor is connected to a semi-infinite transmission line. For TEM waves, the lumped equivalent circuit of this system for *outcoming* waves (those generated by fluctuations in the load resistor and disappearing at infinity) may be obtained[78] by complementing the equivalent circuit with a noise-free resistor of magnitude $\mathscr{Z}$, representing the transmission line – see the dashed-line part of the figure above. This equivalent circuit clearly shows that for $\mathscr{Z} = R$, the random e.m.f. is equally divided between the internal and external resistors, so the variance of the outcoming wave voltage is

$$\left\langle \mathscr{V}_{\rightarrow}^2 \right\rangle_{\Delta\nu} = \left\langle \left(\tilde{\mathscr{V}}/2\right)^2 \right\rangle_{\Delta\nu} = RT\Delta\nu.$$

In equilibrium, *incoming* waves have equal voltage variance, so adding these two (incoherent) contributions, we recover our result (*) obtained from mode counting. By the way, this is exactly the way H. Nyquist first derived his theorem – correctly for the classical limit $\hbar\omega << T$ and with a "small" error for the general, quantum case. This error was corrected later by H. Callen and T. Welton, who used a different approach (and considered a more general situation).



Problem 5.25. An overdamped classical 1D particle escapes from a potential well with a smooth bottom but a sharp top of the barrier – see the figure on the right. Perform the necessary modification of the Kramers formula (5.139).

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[76] See, e.g., EM Secs. 4.1 and 6.6.

[77] By the way, this equivalent circuit gives an alternative way to derive Eq. (5.81c) of the lecture notes. Indeed, if the resistor is connected to an ideal ammeter (with zero internal resistance), we see that the voltage $\mathscr{V}$ vanishes, while the fluctuation current becomes equal to $\tilde{\mathscr{V}} / R$, with the variance

$$\left\langle \tilde{I}^2 \right\rangle = \left\langle \left(\tilde{\mathscr{V}} / R\right)^2 \right\rangle = \left\langle \tilde{\mathscr{V}}^2 \right\rangle / R^2.$$

Together with Eq. (5.81b), this relation immediately gives Eq. (5.81c).

[78] See, e.g., EM Sec. 7.6.

Solution: In this case, the quadratic approximation (5.135) is inapplicable, and has to be replaced with a linear one:

$$U(q \leq q_2) \approx U(q_2) - F(q_2 - q),$$

where $F \equiv dU/dq$ at $q = q_2 - 0$ is the internal slope of the potential at its sharp edge. Now, taking into account the strong inequality (5.127), the integral on the right-hand side of Eq. (5.131) may be calculated as

$$\int_{q'}^{q''} \exp\left\{\frac{U(q) - U(q_1)}{T}\right\} dq \approx \int_{-\infty}^{q_2} \exp\left\{\frac{[U(q_2) - F(q_2 - q)] - U(q_1)}{T}\right\} dq$$
$$\equiv \exp\left\{\frac{U(q_2) - U(q_1)}{T}\right\} \int_{-\infty}^{q_2} \exp\left\{\frac{F}{T}(q - q_2)\right\} dq = \frac{T}{F}\exp\left\{\frac{U_0}{T}\right\}.$$

Comparing this result with Eq. (5.136) for a smooth-edge well, we see that the necessary modification of Eq. (5.139) affects only the pre-exponential coefficient,

$$\left(\frac{2\pi T}{\kappa_2}\right)^{1/2} \to \frac{T}{F}, \qquad \text{i.e. } \frac{2\pi\eta}{(\kappa_1\kappa_2)^{1/2}} \to \left(\frac{2\pi T}{\kappa_1}\right)^{1/2} \frac{\eta}{F},$$

rather than the Arrhenius exponent.

Problem 5.26.* Similar particles, whose spontaneous electric dipole moments $\mathbf{p}$ have a field-independent magnitude p_0, are uniformly distributed in space with a density n so low that their mutual interaction is negligible. Each particle may rotate without substantial inertia but with a kinematic friction torque proportional to its angular velocity. Use the Smoluchowski equation to calculate the complex dielectric constant $\varepsilon(\omega)$ of such a medium, in thermal equilibrium at temperature T, for a weak, linearly-polarized rf electric field.

Solution: According to the E&M basics,[79] the complex dielectric constant of a macroscopically-isotropic medium is

$$\varepsilon(\omega) = \varepsilon_0 + \frac{\mathscr{P}_\omega}{\mathscr{E}_\omega}, \qquad (*)$$

where $\mathscr{P}_\omega$ is the complex amplitude of the polarization $\mathbf{\mathscr{P}}(t)$ of the medium by an rf electric field $\mathbf{\mathscr{E}}(t)$ with frequency ω and complex amplitude $\mathscr{E}_\omega$. In the absence of interactions between the particles, $\mathbf{\mathscr{P}}(t) = n\langle \mathbf{p}(t)\rangle$, where $\mathbf{p}(t)$ is the dipole moment of one particle,[80] so our task is reduced to a calculation of the statistical average of the complex amplitude p_ω of this moment – or more exactly, of its Cartesian component aligned with the field. In a linearly-polarized wave, this direction does not change in time, and we may select it for the z-axis, so the only component we need is

$$p_z = p_0 \cos\theta,$$

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[79] See, e.g., EM Sec. 7.2, in particular Eq. (7.26b).

[80] See, e.g., EM Eq. (3.49).

where θ is the usual polar angle. Since the potential energy of the dipole's interaction with the external field,[81]

$$U = -\mathbf{p}\cdot\mathscr{E}(t) = -p_0\mathscr{E}(t)\cos\theta,$$

also depends (besides time) only on the polar angle,[82] the probability distribution of the particle's orientation also may depend only on this angle and time:

$$w = w(\theta, t).$$

In order to spell out the Smoluchowski equation (5.122) for this function, we need to accept a certain definition of the kinematic friction ("drag") coefficient η for the rotational motion we are considering. Let us define it by quantifying the assumed linear relation between the drag torque $\langle\boldsymbol{\tau}\rangle$ (i.e. the statistical average of the torque $\boldsymbol{\tau}$ exerted on the particle by its environment) and the particle's angular velocity in the following way: $\langle\boldsymbol{\tau}\rangle_\theta = -\eta d\theta/dt$. Then the Langevin equation for the polar angle θ, at negligible inertial effects, is similar to Eq. (5.107) with $m \to 0$ and the replacement $q \to \theta$:

$$\eta\dot{\theta} + \frac{\partial}{\partial\theta}U(\theta,t) = \tilde{\tau}(t), \qquad \text{with } \langle\tilde{\tau}(t)\rangle = 0,$$

where the right-hand side describes the fully random part of $\boldsymbol{\tau}$. With this notation, Eq. (5.122) becomes

$$\eta\frac{\partial w}{\partial t} = \frac{\partial}{\partial\theta}\left(w\frac{\partial U}{\partial\theta}\right) + T\frac{\partial^2 w}{\partial\theta^2} \equiv wp_0\mathscr{E}(t)\cos\theta + \frac{\partial w}{\partial\theta}p_0\mathscr{E}(t)\sin\theta + T\frac{\partial^2 w}{\partial\theta^2}. \qquad (**)$$

In the absence of the external field, $\mathscr{E}(t) = 0$, Eq. (**) equation reduces to the usual diffusion equation (5.114), with the diffusion coefficient D given by the Einstein relation (5.78): $D = T/\eta$, even though for our current angular coordinate, both D and η have dimensionalities different from those at the linear motion. A more important difference is that in our current case, the coordinate space is limited to the segment $0 \leq \theta \leq \pi$, so at $t >> \tau \equiv \eta/T$, the diffusion makes the probability distribution tend to a constant value w_0 defined by the normalization condition. If we, just as was done in the model solution of Problem 2.4, use the condition

$$\oint_{4\pi} w d\Omega \equiv \int_0^{\pi}\sin\theta d\theta\int_0^{2\pi}d\varphi\, w(\theta,t) = 1,$$

then $w_0 = 1/4\pi$.

Next, if $\mathscr{E}(t)$ is different from zero but small in the sense $|p_0\mathscr{E}| << T$, then it is almost obvious from Eq. (**) that it may be satisfied with the following distribution:[83]

$$w(\theta,t) = w_0 + w_1(t)\cos\theta, \qquad \text{with } \left|\frac{w_1}{w_0}\right| \sim \left|\frac{p_0\mathscr{E}}{T}\right| << 1.$$

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[81] See, e.g., EM Eq. (3.15a).

[82] Strictly speaking, it is also important that kinematic friction eventually erases all traces of the past initial conditions (which could depend on the azimuthal angle as well).

[83] Since $\oint_{4\pi}\cos\theta d\Omega = 0$, the term proportional to w_1 does not change the above value of w_0.

Indeed, plugging this expression into Eq. (**) and keeping only the terms of the 1st order in the small parameter w_1/w_0, we see that all retained terms are proportional to $\cos\theta$. Requiring this equality to be valid for all values of θ, we get the following simple ordinary differential equation:

$$\eta \dot{w}_1 = w_0 \mathscr{p}_0 \mathscr{E}(t) - Tw_1 . \qquad (***)$$

Since this equation is linear, it allows for a ready analytical solution even for an arbitrary function $\mathscr{E}(t)$. However, for our limited purposes, we may consider just a sinusoidal ("monochromatic") field,

$$\mathscr{E}(t) = \mathrm{Re}(\mathscr{E}_\omega \exp\{-i\omega t\}),$$

naturally leading (at $t >> \tau$) to a similar solution $w_1(t) = \mathrm{Re}(w_\omega \exp\{-i\omega t\})$. Plugging these expressions into Eq. (***), we get

$$-i\omega\eta w_\omega = w_0 \mathscr{p}_0 \mathscr{E}_\omega - Tw_\omega, \qquad \text{i.e. } w_\omega = w_0 \frac{\mathscr{p}_0 \mathscr{E}_\omega}{T - i\omega\eta}.$$

Now we can calculate the statistical (not time!) average of the needed z-component of the dipole moment:

$$\langle \mathscr{p}_z \rangle = \oint_{4\pi} \mathscr{p}_0 \cos\theta \, w(t) d\Omega = w_1(t) \mathscr{p}_0 \oint_{4\pi} \cos^2\theta d\Omega = \frac{4\pi}{3} \mathscr{p}_0 \,\mathrm{Re}(w_\omega \exp\{-i\omega t\}) \equiv \mathrm{Re}(\mathscr{p}_\omega \exp\{-i\omega t\}),$$

with

$$\mathscr{p}_\omega = \frac{4\pi}{3} \mathscr{p}_0 w_0 \frac{\mathscr{p}_0 \mathscr{E}_\omega}{T - i\omega\eta} = \frac{\mathscr{p}_0^2 \mathscr{E}_\omega}{3(T - i\omega\eta)}.$$

As a sanity check, in the limit $\omega \to 0$, the last expression gives the result

$$\langle \mathscr{p}_z \rangle = \frac{\mathscr{p}_0^2 \mathscr{E}}{3T},$$

similar to that obtained for a classical *magnetic* dipole in the solution of Problem 2.4:

$$\langle \mathscr{m}_z \rangle = \frac{\mathscr{m}_0^2 \mathscr{B}}{3T}.$$

Returning to arbitrary frequencies and plugging the result for $\mathscr{p}_\omega$ into Eq. (*) with $\mathscr{P}_\omega = n\mathscr{p}_\omega$, we get

$$\varepsilon(\omega) = \varepsilon_0 + n \frac{\mathscr{p}_0^2}{3T} \frac{1}{1 - i\omega\tau},$$

where $\tau \equiv \eta/T$ is the already mentioned dipole relaxation time. This expression shows, in particular, that the imaginary part of the complex dielectric constant, which scales the dissipative energy loss in the medium,[84]

$$\varepsilon''(\omega) \equiv \mathrm{Im}[\varepsilon(\omega)] = n \frac{\mathscr{p}_0^2}{3T} \frac{\omega\tau}{1 + \omega^2\tau^2},$$

reaches its maximum at $\omega = 1/\tau$.

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[84] See, e.g., EM Sec. 7.2.

Problem 5.27.* Prove that for systems with relatively low inertia/(i.e. relatively high damping), at not very high temperatures, the Fokker-Planck equation (5.149) reduces to the Smoluchowski equation (5.122) – in the sense described by Eq. (5.153) and the accompanying statement in the lecture notes.

Solution: In the nomenclature used in Sec. 5.6-5.7, the limit we are considering corresponds to either a very small mass m, or a very high drag coefficient η, or both:[85]

$$\frac{\eta}{m} >> \frac{|\kappa|}{\eta}, \qquad \text{where } \kappa \equiv \nabla_q^2 U . \tag{*}$$

Comparing the scale of the terms on the right-hand side of the Fokker-Planck equation (5.149),

$$\frac{\partial w}{\partial t} = -\nabla_q \cdot \left(w \frac{\mathbf{p}}{m} \right) + \nabla_p \cdot \left[w \left(\nabla_q U + \eta \frac{\mathbf{p}}{m} \right) \right] + \eta T \nabla_p^2 w ,$$

in light of Eq. (*), we may see that the character of the evolution of the probability density w in time very much depends on whether the parentheses in the second term of the right-hand side are very close to zero or not. If not (as at most points of the 6D [$\mathbf{q}$, $\mathbf{p}$] space), then this term is much larger than the first one, and the equation may be well approximated as

$$\frac{\partial w}{\partial t} \approx \nabla_p \cdot \left[w \left(\nabla_q U + \eta \frac{\mathbf{p}}{m} \right) \right] + \eta T \nabla_p^2 w \equiv \nabla_p \cdot \left[w \left(\eta \frac{\mathbf{p} - \mathbf{p}_0}{m} \right) \right] + \eta T \nabla_p^2 w, \quad \text{with } \mathbf{p}_0 \equiv -\frac{m}{\eta} \nabla_q U . \tag{**}$$

The right-hand side of this equation differs from the left-hand side of Eq. (5.150), which was analyzed in Sec. 5.7 of the lecture notes, only by the offset of the momentum by $\mathbf{p}_0$ (which is generally a function of $\mathbf{q}$ and t, but is small in the limit $m/\eta \to 0$). Now repeating the calculation that has resulted in Eq. (5.152), we see that Eq. (**) describes a relatively rapid (with the time scale $\Delta t_q \equiv m/\eta$) relaxation,[86] in the momentum space, of the initial distribution $w(\mathbf{q}, \mathbf{p}, t_0)$, to a Gaussian peak centered at $\mathbf{p}_0$:[87]

$$w(\mathbf{q},\mathbf{p},t) \to \exp\left\{ -\frac{[\mathbf{p} - \mathbf{p}_0(\mathbf{q},t)]^2}{2mT} \right\} \mathscr{w}(\mathbf{q},t) , \tag{***}$$

where $\mathscr{w}(\mathbf{q}, t)$ is some function independent of $\mathbf{p}$.

Next, let us quantify the assumption that the temperature is not overly high by accepting that the resulting characteristic spread $\delta p = (mT)^{1/2}$ of the function $w(\mathbf{q}, \mathbf{p}, t)$ in the momentum space is much smaller than $(m/\eta)F$, where F is the scale of the deterministic force $-\nabla U_q$. Then, as a result of the initial fast relaxation of the momentum to the value $\mathbf{p}_0$, the second term on the right-hand side of the Fokker-Planck equation becomes negligible, and in the remaining terms, we may make the replacement $\mathbf{p} \to \mathbf{p}_0$, i.e. $\mathbf{p}/m \to -\nabla_q U/\eta$, so the equation reduces to

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[85] The κ so defined may be interpreted as an effective spring constant, which generally depends on both $\mathbf{q}$ and t.

[86] A good feeling of this time hierarchy may be obtained by reviewing the relaxation dynamics of a fluctuation-free 1D system, for example, a damped pendulum – see, e.g., the model solution of CM Problem 5.20, especially for the case $Q < 1$.

[87] Strictly speaking, this conclusion is restricted by the requirement (well fulfilled in most applications) for the deterministic force $\mathscr{F} = -\nabla U(\mathbf{q}, t)$ to either be time-independent or change slowly on the short time scale Δt_1.

$$\frac{\partial w}{\partial t}=\frac{1}{\eta}\nabla_q\cdot\left(w\nabla_q U\right)+\eta T\nabla_p^2 w.$$

Plugging in the limiting form (***) of the function w and integrating both sides of the resulting equation over the momentum space, we get

$$\frac{\partial \mathscr{w}}{\partial t}=\frac{1}{\eta}\nabla_q\cdot\left(\mathscr{w}\nabla_q U\right)+\eta T\int\nabla_p^2 w\,d^3p,$$

where (by integrating as in Eq. (3.6) of the lecture notes) we may write

$$\mathscr{w}(\mathbf{q},t)\equiv\int w(\mathbf{q},\mathbf{p},t)d^3p=\int w\left[\mathbf{q},\mathbf{p}_0(\mathbf{q},t),t\right]\exp\left\{-\frac{[\mathbf{p}-\mathbf{p}_0(\mathbf{q},t)]^2}{2mT}\right\}d^3p=\left(2\pi mT\right)^{3/2}w\left[\mathbf{q},\mathbf{p}_0(\mathbf{q},t),t\right].$$

In order to carry out the integration in the last term of the equation for $\mathscr{w}$, let us use the following mathematical identity:

$$\nabla_p^2 w\equiv\left(\nabla_p+\frac{1}{\eta}\nabla_q\right)\cdot\left(\nabla_p-\frac{1}{\eta}\nabla_q\right)w+\frac{1}{\eta^2}\nabla_q^2 w. \qquad (****)$$

Now we may notice that our initial Fokker-Plank equation describes a classical system whose Langevin equation of motion is the natural 3D generalization of Eq. (5.107):

$$m\ddot{\mathbf{q}}+\eta\,\dot{\mathbf{q}}+\nabla_q U=\widetilde{\mathscr{F}}(t), \qquad \text{i.e. } \frac{d}{dt}\left(\mathbf{p}+\eta\mathbf{q}\right)=-\nabla_q U+\widetilde{\mathscr{F}}(t).$$

This means that in our limit (*) of a relatively slowly changing force ($1/t_q\equiv|\kappa|/\eta << 1/t_p\equiv\eta/m$), the sum $\mathbf{p}+\eta\mathbf{q}$ evolves as a single variable, so the probability distribution of $w(\mathbf{q},\mathbf{p},t)$ at any certain instant t may be, besides some constant, a function of only the combination $\mathbf{p}+\eta\mathbf{q}$ (and time):[88]

$$w(\mathbf{q},\mathbf{p},t)=f(\mathbf{z},t), \qquad \text{where } \mathbf{z}\equiv\mathbf{p}+\eta\mathbf{q}.$$

Since the operator ($\nabla_p-\eta^{-1}\nabla_q$) of such a function returns zero:

$$\nabla_p f(\mathbf{z},t)=\nabla_z f, \quad \nabla_q f(\mathbf{z},t)=\eta\nabla_z f, \quad \text{so } \left(\nabla_p-\eta\nabla_q\right)=0,$$

the integral over $\mathbf{p}$ of the first term on the right-hand side of Eq. (****) vanishes. Hence we are left with the integral of its last term:

$$\frac{1}{\eta^2}\int\nabla_q^2 w(\mathbf{q},\mathbf{p},t)d^3p\equiv\frac{1}{\eta^2}\nabla_q^2\int w(\mathbf{q},\mathbf{p},t)d^3p=\frac{1}{\eta^2}\nabla_q^2\mathscr{w}(q,t),$$

turning the above equation for $\mathscr{w}$ into the Smoluchowski equation (5.122).

Problem 5.28.* Use the 1D version of the Fokker-Planck equation (5.149) to prove the solution (5.156) of the Kramers problem.

Solution: Obviously, the 1D version of Eq. (5.149) is

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[88] An additional exercise for the reader: prove this statement directly from the Fokker-Planck equation.

$$\frac{\partial w}{\partial t} = -\frac{\partial}{\partial q}\left(w\frac{p}{m}\right) + \frac{\partial}{\partial p}\left[w\left(\frac{\partial U}{\partial q} + \eta\frac{p}{m}\right)\right] + \eta T\frac{\partial^2 w}{\partial p^2}. \qquad (*)$$

Let the potential U be time-independent: $U = U(q)$. Then (as was mentioned in Sec. 5.7 of the lecture notes) in static equilibrium when not only $\partial w/\partial t$ but also the probability current (5.151),

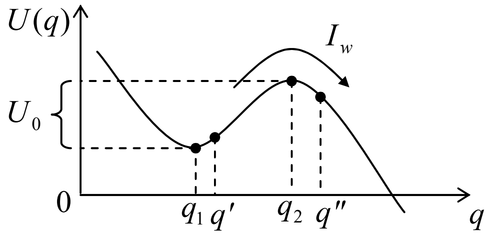
$$j_w = \frac{p}{m}w + T\frac{\partial w}{\partial p},$$

vanish, Eq. (*) has the (easily verifiable) exact stationary solution

$$w = \text{const} \times \exp\left\{-\frac{p^2}{2mT} - \frac{U(q)}{T}\right\},$$

which is just the 1D version of Eq. (3.24) and a natural generalization of Eq. (5.152).

However, to solve the Kramers problem, we need to calculate an exponentially small but still nonvanishing current I_w for a particle in the potential well shown in Fig. 5.10 of the lecture notes (reproduced on the right), again with $T << U_0$. For this, the above expression for w should be modified; let us look for the solution in the following natural form:



$$w(q,p) = w(q_1,0)\,f(q,p)\exp\left\{-\frac{p^2}{2m} - \frac{U(q)}{T}\right\}. \qquad (**)$$

Here $f(q, p)$ is a smooth function that changes only close to the potential barrier's top point q_2, while the value $w(q_1, 0)$ may be chosen to satisfy the following natural generalization of the normalization condition (5.134) without the factor $f(q, p)$:

$$W = \int_{\text{well's bottom}} dq \int_{-\infty}^{+\infty} dp\, w(q,p) \approx w(q_1,0)\int_{-\infty}^{+\infty}\exp\left\{-\frac{\kappa_1\tilde{q}^2}{2T}\right\}d\tilde{q}\int_{-\infty}^{+\infty}\exp\left\{-\frac{p^2}{2mT}\right\}dp = w(q_1,0)\frac{2\pi T}{\omega_1}, \quad \omega_1 \equiv \left(\frac{\kappa_1}{m}\right)^{1/2},$$

where the approximation (5.133) has been used for the potential well's bottom part. Near the barrier's top q_2, a different quadratic approximation is valid – see Eq. (5.135):

$$U(q \approx q_2) - U(q_1) \approx U_0 - \frac{\kappa_2}{2}\tilde{q}^2, \text{ where } \kappa_2 \equiv -\frac{d^2U}{dq^2}\Big|_{q=q_2} > 0, \text{ and } \tilde{q} \equiv q - q_2. \qquad (***)$$

In this approximation, Eq. (*) reduces to

$$-\frac{p}{m}\frac{\partial w}{\partial q} + \left(-\kappa_2\tilde{q} + \eta\frac{p}{m}\right)\frac{\partial w}{\partial p} + \frac{\eta}{m}w + \eta T\frac{\partial^2 w}{\partial p^2} = 0.$$

Now plugging in w in the form (**) and canceling similar multipliers, we get a similar equation for the function $f(q, p)$:

$$-\frac{p}{m}\frac{\partial f}{\partial q} + \left(-\kappa_2\tilde{q} + \eta\frac{p}{m}\right)\frac{\partial f}{\partial p} + \eta T\frac{\partial^2 f}{\partial p^2} = 0.$$

As a sanity check, the equation is evidently satisfied with f = const; however, this expression, corresponding to zero probability current j_w, does not satisfy our boundary conditions. Indeed, in accordance with the discussion in Sec. 5.6 and the above choice of $w(q_1, 0)$, the function f has to satisfy the following boundary conditions:

$$f(q,p) \to \begin{cases} 0, & \text{for } \tilde{q} >> \left(T/\kappa_2\right)^{1/2}, \\ 1, & \text{for } \left(-\tilde{q}\right) >> \left(T/\kappa_2\right)^{1/2}, \end{cases}$$

so it has to change within the region $\tilde{q} \sim \left(T/\kappa_2\right)^{1/2}$. Due to the similarity of the differential equation for f with respect to the coordinate and the momentum, the natural trial solution is

$$f(q,p) = \varphi(\tilde{p}), \qquad \text{where } \tilde{p} \equiv p - \lambda\tilde{q},$$

and λ is a constant coefficient. The solution's substitution into our partial differential equation for $f(q, p)$ turns it into the following ordinary differential equation:

$$\lambda\frac{p}{m}\frac{d\varphi}{d\tilde{p}} + \left(-\kappa_2\tilde{q} + \eta\frac{p}{m}\right)\frac{d\varphi}{d\tilde{p}} + \eta T\frac{d^2\varphi}{d\tilde{p}^2} = 0, \qquad \text{i.e. } \left[\frac{(\lambda-\eta)}{m}p - \kappa_2\tilde{q}\right]\frac{d\varphi}{d\tilde{p}} + \eta T\frac{d^2\varphi}{d\tilde{p}^2} = 0.$$

In order for this equation to be indeed an ordinary one, the expression in the square brackets has to be a function of $\tilde{p} \equiv p - \lambda\tilde{q}$ only. This condition gives us the following characteristic equation for λ:

$$\frac{m\kappa_2}{\lambda - \eta} = \lambda, \qquad \text{i.e. } \lambda^2 - \eta\lambda - m\kappa_2 = 0. \qquad (****)$$

Of the two roots of this quadratic equation,

$$\lambda_\pm = \frac{\eta}{2} \pm \left(\frac{\eta^2}{4} + m\kappa_2\right)^{1/2},$$

only λ_+ allows the function $f(q, p)$ to satisfy our boundary conditions. Indeed, with the characteristic equation satisfied, the differential equation for the function φ becomes

$$\frac{\lambda-\eta}{m}\tilde{p}\frac{d\varphi}{d\tilde{p}} + \eta T\frac{d^2\varphi}{d\tilde{p}^2} = 0, \qquad \text{i.e. } \frac{\lambda-\eta}{m}\tilde{p}\Phi + \eta T\frac{d\Phi}{d\tilde{p}} = 0, \quad \text{where } \Phi \equiv \frac{d\varphi}{d\tilde{p}},$$

and may readily integrated twice:

$$\frac{\lambda-\eta}{m}\int_0^{\tilde{p}}\tilde{p}'d\tilde{p}' + \eta T\int\frac{d\Phi}{\Phi} = 0, \qquad \text{giving } \Phi(\tilde{p}) = C\exp\left\{-\frac{\lambda-\eta}{2m\eta T}\tilde{p}^2\right\},$$

so

$$\varphi(\tilde{p}) \equiv \int_{-\infty}^{\tilde{p}}\Phi(\tilde{p}')dp' = C\int_{-\infty}^{\tilde{p}}\exp\left\{-\frac{\lambda-\eta}{2m\eta T}\tilde{p}'^2\right\}dp', \quad f(q,p) \equiv \varphi(p - \lambda q) = C\int_{-\infty}^{p-\lambda\tilde{q}}\exp\left\{-\frac{\lambda-\eta}{2m\eta T}p'^2\right\}dp'.$$

This solution shows that the fraction in the exponent is positive only for the choice $\lambda = \lambda_+$,:

$$\frac{\lambda_+ - \eta}{2m\eta T} = \frac{1}{2m\eta T}\left[\left(m\kappa_2 + \frac{\eta^2}{4}\right)^{1/2} - \frac{\eta}{2}\right] \equiv \frac{\omega_2'}{2\eta T} > 0,$$

where[89]

$$\omega_2' \equiv \frac{\lambda_+ - \delta}{m} = \left[\omega_2^2 + \left(\frac{\eta}{2m}\right)^2\right]^{1/2} - \frac{\eta}{2m}, \qquad \text{with } \omega_2 \equiv \left(\frac{\kappa_2}{m}\right)^{1/2}.$$

Because of that, the calculated function

$$f(q,p) = C \int_{-\infty}^{p-\lambda_+\tilde{q}} \exp\left\{-\frac{\omega_2' p'^2}{2\eta T}\right\} dp'$$

properly tends to zero at $\tilde{q} \to +\infty$, and to a constant,

$$C \int_{-\infty}^{+\infty} \exp\left\{-\frac{\omega_2' p'^2}{2\eta T}\right\} dp' = C\left(\frac{2\pi\eta T}{\omega_2'}\right)^{1/2},$$

at $\tilde{q} \to -\infty$.[90] Selecting the coefficient C so that this constant equals 1, i.e.

$$C = \left(\frac{\omega_2'}{2\pi\eta T}\right)^{1/2}, \qquad \text{so that } f(q,p) = \left(\frac{\omega_2'}{2\pi\eta T}\right)^{1/2} \int_{-\infty}^{p-\lambda_+\tilde{q}} \exp\left\{-\frac{\omega_2' p'^2}{2\eta T}\right\} dp',$$

we get both of our boundary conditions for this function satisfied.

What remains is to use the calculated function $f(q, p)$, and hence the distribution $w(q, p)$ given by Eq. (**), to find the full probability current

$$I_w(q) = \int_{-\infty}^{+\infty} j_w dp = \int_{-\infty}^{+\infty}\left(w\frac{p}{m} + T\frac{\partial w}{\partial p}\right)dp = \int_{-\infty}^{+\infty} w\frac{p}{m}dp + T\left[w(q,+\infty) - w(q,-\infty)\right] = \int_{-\infty}^{+\infty} w\frac{p}{m}dp.$$

Since any stationary solution of the 1D Fokker-Planck equation keeps the current independent of q, we may calculate it at any point, the most convenient choice being the barrier's top q_2 where $\tilde{q} = 0$, so

$$I_w = \int_{-\infty}^{+\infty} w(q_2, p)\frac{p}{m}dp = w(q_1, 0)\exp\left\{-\frac{U_0}{T}\right\}\frac{1}{m}\int_{-\infty}^{+\infty}\exp\left\{-\frac{p^2}{2mT}\right\} f(q_2, p)\, p\, dp$$

$$= W\frac{\omega_1}{2\pi T}\frac{1}{m}\exp\left\{-\frac{U_0}{T}\right\}\left(\frac{\omega_2'}{2\pi\eta T}\right)^{1/2}\int_{-\infty}^{+\infty}\exp\left\{-\frac{p^2}{2mT}\right\} p\, dp \int_{-\infty}^{p}\exp\left\{-\frac{\omega_2' p'^2}{2\eta T}\right\}dp'.$$

This double integral may be worked out by parts, taking into account that the product of the flipped functions vanishes at both limits $p \to \pm\infty$:

$$\int_{-\infty}^{\infty}\exp\left\{-\frac{p^2}{2mT}\right\} p\, dp \int_{-\infty}^{p}\exp\left\{-\frac{\omega_2' p'^2}{2\eta T}\right\}dp' = -mT\int_{p=-\infty}^{p=+\infty} d\left(\exp\left\{-\frac{p^2}{2mT}\right\}\right)\int_{-\infty}^{p}\exp\left\{-\frac{\omega_2' p'^2}{2\eta T}\right\}dp'$$

---

[89] This formula was given without proof in the lecture notes – see Eq. (5.154). Note that in the classical theory of oscillations, the fraction $\delta \equiv \eta/2m$ is called the *damping coefficient* – see, e.g., CM Sec. 5.1.

[90] Since we actually need the function $f(q, p)$ to approach 1 not at $q \to -\infty$, but at $q \approx q_1$, there is always a finite range of values $p > 0$ for which this boundary condition remains unsatisfied. A careful analysis of this problem (see, e.g., the review paper by V. Mel'nikov cited in Sec. 5.7 of the lecture notes) shows that our result, i.e. the Kramers formula (5.154) is valid only if the damping is not too low: $\eta/m\omega_2 >> T/U_0$.

$$= mT\int_{p=-\infty}^{p=+\infty} \exp\left\{-\frac{p^2}{2mT}\right\} d\left(\int_{-\infty}^{p}\exp\left\{-\frac{\omega_2' p'^2}{2\eta T}\right\}dp'\right) = mT\int_{-\infty}^{+\infty}\exp\left\{-\frac{p^2}{2mT}-\frac{\omega_2' p^2}{2\eta T}\right\}dp$$

$$= mT\pi^{1/2}\left(\frac{1}{2mT}+\frac{\omega_2'}{2\eta T}\right)^{-1/2}.$$

As a result, for the reciprocal lifetime of the metastable state, we get the following expression:

$$\frac{1}{\tau} \equiv \frac{I_w}{W} = \frac{\omega_1}{2\pi T}\frac{1}{m}\left(\frac{\omega_2'}{2\pi\eta T}\right)^{1/2}\exp\left\{-\frac{U_0}{T}\right\} mT\pi^{1/2}\left(\frac{1}{2mT}+\frac{\omega_2'}{2\eta T}\right)^{-1/2} \equiv \frac{\omega_1}{2\pi}\left(\frac{\omega_2'}{\omega_2'+\eta/m}\right)^{1/2}\exp\left\{-\frac{U_0}{T}\right\}.$$

This expression may be further simplified by noticing that using the definition of ω_2', the characteristic equation (****) with $\lambda = \lambda_+$ may be rewritten as

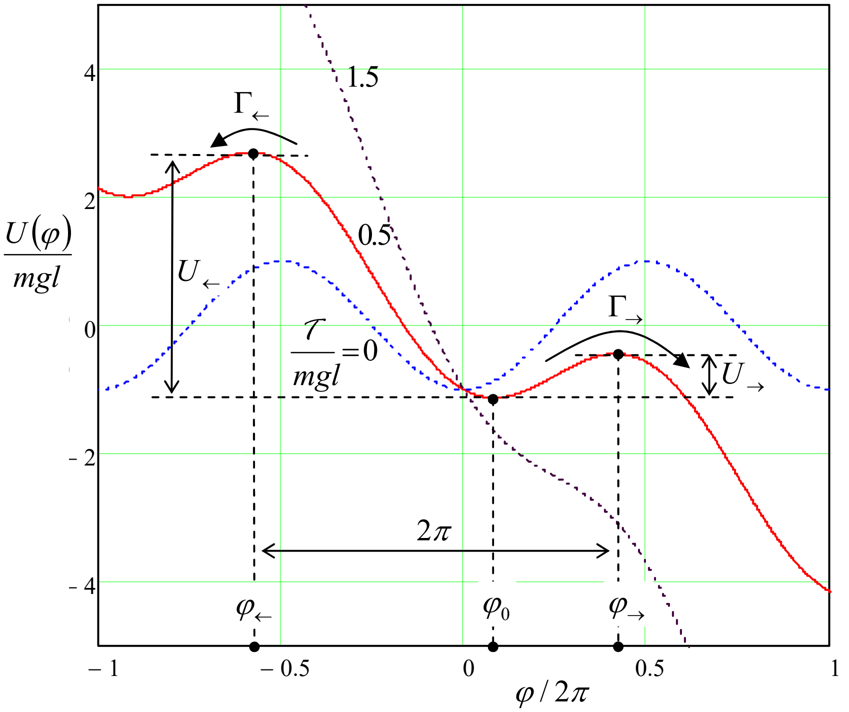
$$\omega_2' + \frac{\eta}{m} = \frac{\kappa_2}{m\omega_2'} \equiv \frac{\omega_2^2}{\omega_2'},$$

so we finally get simply

$$\frac{1}{\tau} = \frac{\omega_1\omega_2'}{2\pi\omega_2}\exp\left\{-\frac{U_0}{T}\right\} \equiv \frac{\omega_1}{2\pi\omega_2}\left[\left(\omega_2^2+\frac{\eta^2}{4m^2}\right)^{1/2} - \frac{\eta}{2m}\right]\exp\left\{-\frac{U_0}{T}\right\},$$

which is the combination of Eqs. (5.111b) and (5.154) of the lecture notes.

Problem 5.29. A constant external torque, applied to a 1D mechanical pendulum with mass m and length l, has displaced it by angle $\varphi_0 < \pi/2$ from the vertical position. Calculate the average rate of the pendulum's rotation induced by relatively small thermal fluctuations of temperature T.



Solution: According to basic classical mechanics, the potential energy of a 1D pendulum placed into a vertical gravity field g and biased with an additional torque $\mathcal{T}$ is

$$U(\varphi) = -mgl\cos\varphi - \mathcal{T}\varphi + \text{const},$$

where φ is the pendulum's deviation from its vertical position. The figure on the right shows plots of this function (frequently called the *washboard potential*) for three representative values of the torque. At $\mathcal{T}$ = 0, the potential is 2π-periodic, so all energy minima (corresponding to the stable static positions of the pendulum) have the same value of U.

However, any nonzero $\mathcal{T}$ leads to a tilt of the potential pattern. If $\mathcal{T}$ is not too large: $|\mathcal{T}| < mgl$, the function $U(\varphi)$ still has a set of minima separated by 2π-intervals of φ, but with the adjacent energy minima offset by $\pm 2\pi\mathcal{T}$. The positions φ_0 of these minima may be found from the usual condition $dU/d\varphi = 0$, giving

$$\sin\varphi_0 = \frac{\mathcal{T}}{mgl}. \qquad (*)$$

This formula is also valid for the (unstable) positions φ_0' of the energy maxima separating the minima (for example, the points $\varphi_{\rightarrow}$ and $\varphi_{\leftarrow} = \varphi_{\rightarrow} - 2\pi$ shown in the figure above for the case $\mathcal{T}/mgl = 0.5$) but from the corresponding values of $d^2U/d\varphi^2 = mgl\cos\varphi$ we see that $\cos\varphi_0 > 0$, while $\cos\varphi_0' < 0$. From here, we can readily calculate the potential energy barriers separating any energy minimum from the two adjacent ones – see the figure above:[91]

$$U_{\rightarrow} \equiv U(\varphi_{\rightarrow}) - U(\varphi_0) = -mgl(\cos\varphi_{\rightarrow} - \cos\varphi_0) - \mathcal{T}(\varphi_{\rightarrow} - \varphi_0) = 2mgl\left[\cos\varphi_0 + \sin\varphi_0(\varphi_0 - \pi/2)\right],$$

$$U_{\leftarrow} \equiv U(\varphi_{\leftarrow}) - U(\varphi_0) = \left[U(\varphi_{\rightarrow}) + 2\pi\mathcal{T}\right] - U(\varphi_0) = U_{\rightarrow} + 2\pi\mathcal{T} = 2mgl\left[\cos\varphi_0 + \sin\varphi_0(\varphi_0 + \pi/2)\right].$$

Small thermal fluctuations not only "wobble" the pendulum near its equilibrium position φ_0, but also lead to rare swings of the pendulum over its top position, i.e. to jumps over one of these potential barriers. Since the jumps over lower barriers are more frequent, the system gradually drifts in a certain direction – if $\mathcal{T} > 0$, then toward larger values of φ – in the figure above, to the right. In order to calculate the speed of this drift, i.e. the average angular velocity $\langle\dot{\varphi}\rangle$, at the eventually approached stationary distribution of the probability, let us select a broad region $\Delta\varphi >> 2\pi$ located well downstream from the initial position of the pendulum. Here, due to the jump randomness, the probabilities W of adjacent well occupation become equal and time-independent, so the probability current is proportional to the difference $(\Gamma_{\rightarrow} - \Gamma_{\leftarrow})$, where $\Gamma_{\rightarrow}$ and $\Gamma_{\leftarrow}$ are the rates (probabilities per unit time) of the jumps over the corresponding barriers – see the labels in the figure above. Since each jump creates, on average, the shift of the angle by 2π in the corresponding direction, the resulting average angular velocity is

$$\langle\dot{\varphi}\rangle = 2\pi(\Gamma_{\rightarrow} - \Gamma_{\leftarrow}). \qquad (**)$$

If the thermal fluctuations are low in the sense $T << \min[U_{\rightarrow}, U_{\leftarrow}]$ and the pendulum's damping is not too low (see below), we may use, for each of the rates, the Arrhenius law (5.111b). Indeed, each rate is just the reciprocal lifetime of the metastable state of the system in the potential well due to the corresponding decay channel:

$$\Gamma_{\rightarrow} = \frac{1}{\tau_{\text{A}}}\exp\left\{-\frac{U_{\rightarrow}}{T}\right\}, \qquad \Gamma_{\leftarrow} = \frac{1}{\tau_{\text{A}}}\exp\left\{-\frac{U_{\leftarrow}}{T}\right\}.$$

Here the effective attempt time τ_{A} is the same for both barriers and is given by the Kramers formula (5.154) with $\omega_1 = \omega_2 \equiv \omega_0$:

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[91] Note that the assignment specifies φ_0 rather than $\mathcal{T}$, so all the results below will be expressed in terms of this angle. In order to express them in terms of torque, one can always use Eq. (*).

$$\frac{1}{\tau_{\mathrm{A}}} \equiv \frac{1}{2\pi}\left[\left(\omega_0^2+\delta^2\right)^{1/2}-\delta\right], \quad \text{where } \omega_0^2=\frac{\kappa}{m}, \quad \kappa \equiv \left|\frac{d^2U}{d(l\varphi)^2}\right|_{\varphi=\varphi_0,\varphi_0'} = \frac{g}{l}\cos\varphi_0, \qquad (***)$$

and δ the damping, i.e. the coefficient in the pendulum's Langevin equation represented in the form

$$\ddot{\varphi}+2\delta\dot{\varphi}+\omega_0^2\sin\varphi=\frac{1}{ml^2}\left[\mathcal{T}+\tilde{\mathcal{T}}(t)\right].$$

So, using the above expressions for the potential barrier heights, we get

$$\langle\dot{\varphi}\rangle=\frac{2\pi}{\tau_{\mathrm{A}}}\left(\exp\left\{-\frac{U_{\rightarrow}}{T}\right\}-\exp\left\{-\frac{U_{\leftarrow}}{T}\right\}\right)=\frac{4\pi}{\tau_{\mathrm{A}}}\exp\left\{-2u\left(\cos\varphi_0+\varphi_0\sin\varphi_0\right)\right\}\sinh\left(\pi u\sin\varphi_0\right),$$

where $u \equiv mgl/T >> 1$.

As was mentioned in Sec. 5.7, the original Kramers formula is only valid if the damping is not too low: $\delta/\omega_0 >> T/U_0$. However, in the system we are discussing now, the requirements for the damping are even higher. Indeed, Eq. (**) implies that the jumps between the adjacent potential wells are single random events independent of each other. In our system, this condition requires the pendulum to settle, after the jump over a barrier, at the bottom of the adjacent well, losing the extra energy to damping fast – before reaching the next potential barrier during the first "swing" over the well. Classical oscillation theory says[92] that for this, the ratio δ/ω_0 has to be larger than 1 or so. The exact threshold for δ/ω_0 is a function of φ_0 but it is not very important, because all the practical applications of this result I am aware of are for strongly overdamped systems, with $\delta/\omega_0 >> 1$. (As it follows from Eq. (***), and as we have seen from the Kramers problem's solution using the Smoluchowski equation in Sec. 5.6, in this limit, the attempt time is independent of m: $\tau_{\mathrm{A}} = 2\pi\eta/\kappa$, where $\eta = 2m\delta$ is the drag coefficient.)[93]

Speaking of important applications of this theory, some of them are:

– phase locking in oscillators,[94] where the sum $(\Gamma_{\rightarrow} + \Gamma_{\leftarrow})$ gives the rate of the spontaneous violations of the locking regime, and

– Josephson junctions,[95] where the difference $(\Gamma_{\rightarrow} - \Gamma_{\leftarrow})$ determines the dc voltage drop across a nominally superconducting junction biased by dc current $I = I_c \sin\varphi_0 < I_c$:

$$\langle V\rangle=\frac{\hbar}{2e}\langle\dot{\varphi}\rangle=\frac{\pi\hbar}{e}\left(\Gamma_{\rightarrow}-\Gamma_{\leftarrow}\right).$$

(In single-flux-quantum digital devices based on the Josephson junctions,[96] the sum $(\Gamma_{\rightarrow} + \Gamma_{\leftarrow})$ gives the full rate of single-bit errors.)

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[92] See, e.g., CM Sec. 5.1.

[93] By the way, in this limit, the simple form of the function $U(\varphi)$ enables an analytical calculation of $\langle\dot{\varphi}\rangle$ for arbitrary ratios $u = mgl/T$ and $\mathcal{T}/mgl$ – even if the latter ratio is larger than 1 by magnitude, so Eq. (*) is no longer valid. This result, first obtained by R. Stratonovich in 1959, may be represented in several forms – see, e.g., Sec. 2 in the review paper by A. Vystavkin *et al.*, *Rev. Phys. Appl.* **9**, 79 (1974).

[94] See, e.g., the model solution of Problem 15(i) and references therein.

[95] See, e.g., CM Problem 2.11, EM Sec. 6.5, and QM Secs. 1.6 and 2.8, and references therein.

[96] See, e.g., P. Bunyk *et al.*, *Int. J. on High Speed Electronics and Systems* **11**, 257 (2001).

Problem 5.30. A classical particle may occupy any of N similar sites. Its interaction with the environment induces random uncorrelated jumps from the occupied site to any other site, with the same time-independent rate Γ. Calculate the correlation function and the spectral density of fluctuations of the instant occupancy $n(t)$ (equal to either 1 or 0) of a site.

Solution: By performing an obvious generalization of the master equations (4.100) for two-state systems to N states, we may write the following system of equations for the probability W_j that the particle occupies the j^{th} site:

$$\dot{W}_j = \sum_{\substack{j'=1 \\ j'\neq j}}^{N} \left(\Gamma_{j'\to j} W_{j'} - \Gamma_{j\to j'} W_j \right).$$

(As was noted in Sec. 4.5 of the lecture notes, such master equations may be valid even for many quantum systems, with the off-diagonal elements $W_{jj'}$ of their density matrices either decayed or uncoupled from the diagonal elements $W_{jj'} \equiv W_j$.[97])

For our current simple case of equal rates ($\Gamma_{j'\to j} = \Gamma_{j\to j'} = \Gamma$), the system reduces to

$$\dot{W}_j = \Gamma \sum_{\substack{j'=1 \\ j'\neq j}}^{N} W_{j'} - (N-1)\Gamma W_j .$$

Since the sum of $W_{j'}$ over all j' (including $j' = j$) should be equal to 1, the sum on the right-hand side of this equation is equal to $(1 - W_j)$, turning it into a linear differential equation for just one variable:

$$\dot{W}_j = \Gamma(1 - W_j) - (N-1)\Gamma W_j \equiv \Gamma\left(1 - N W_j\right).$$

This equation may be readily solved for an arbitrary initial condition, giving the result functionally similar to Eq. (5.171):[98]

$$W(t) = W(0)e^{-N\Gamma t} + W(\infty)\left(1 - e^{-N\Gamma t}\right), \qquad \text{with } W(\infty) = \frac{1}{N}. \qquad (*)$$

The stationary value $W(\infty)$, approached by $W(t)$ at $t \to \infty$, immediately yields the (rather obvious) result for the average site's occupancy (in the stationary state of the system, implied by the assignment):

$$\langle n \rangle = \sum_{n=0,1} n W(\infty) = \frac{1}{N}.$$

Now we can use the general Eq. (5.167) to calculate the correlation function of the instant occupancy:[99]

$$\langle n(t) n(t+\tau) \rangle = \sum_{n=1,0} n W(\infty) \sum_{n'=1,0} n' W(\tau)\Big|_{W(0)=1} .$$

Since one of the two possible occupancy numbers is zero, only one term (with $n = n' = 1$) of the four may give a nonvanishing contribution to this sum:

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[97] See, e.g., QM Sec. 7.6, in particular, the discussion leading to Eq. (7.194).

[98] It is obvious that in this uniform system, all the results are independent of the site number, so from this point on, the index j is dropped.

[99] Please note again the somewhat counter-intuitive dual nature of Eq. (5.167): it expresses an average for a *stationary* process via the probability evolution in a *non-stationary* case – with special initial conditions.

$$\langle n(t)n(t+\tau)\rangle = W(\infty)W(\tau)\big|_{W(0)=1}.$$

From here, by using the general solution (*) with $W(0) = 1$ and the replacement $t \to \tau$, we get

$$\langle n(t)n(t+\tau)\rangle = \left[e^{-N\Gamma\tau} + \frac{1}{N}\left(1-e^{-N\Gamma\tau}\right)\right]\frac{1}{N} \equiv \frac{1}{N}\left[\frac{1}{N} + \left(1-\frac{1}{N}\right)e^{-N\Gamma\tau}\right].$$

As a sanity check, a particular case of this result,

$$\langle n(t)n(t)\rangle \equiv \langle n^2\rangle = \frac{1}{N},$$

may be readily verified by a simpler calculation:

$$\langle n^2\rangle = \sum_{n=1,0} n^2 W(\infty) = \frac{1}{N}.$$

Now we are ready to calculate the correlation function of the occupancy fluctuations:

$$K_n(\tau) \equiv \langle \tilde{n}(t)\tilde{n}(t+\tau)\rangle \equiv \left\langle \left(n(t)-\langle n\rangle\right)\left(n(t+\tau)-\langle n\rangle\right)\right\rangle = \langle n(t)n(t+\tau)\rangle - \langle n\rangle^2$$

$$= \frac{1}{N}\left[\frac{1}{N} + \left(1-\frac{1}{N}\right)e^{-N\Gamma\tau}\right] - \frac{1}{N^2} \equiv \frac{N-1}{N^2}e^{-N\Gamma\tau},$$

and then use the Wiener-Khinchin theorem (5.58) to find their spectral density:

$$S_n(\omega) = \frac{1}{\pi}\int_0^{+\infty} K_n(\tau)\cos\omega\tau\, d\tau = \frac{N-1}{\pi N^2}\operatorname{Re}\int_0^{+\infty} e^{(-N\Gamma+i\omega)\tau}d\tau$$

$$= \frac{N-1}{\pi N^2}\operatorname{Re}\frac{1}{N\Gamma - i\omega} \equiv \frac{N-1}{\pi N}\frac{\Gamma}{(N\Gamma)^2+\omega^2}.$$

This result describes a zero-frequency-centered Lorentzian line (typical for such problems – see, e.g., the two-state problem solved in Sec. 5.8 of the lecture notes), with the cutoff frequency (i.e. the fluctuation bandwidth) $N\Gamma$. As an additional sanity check, the result shows that for a system consisting of just one site ($N = 1$), $S_n(\omega) = 0$, i.e. the site's occupancy does not fluctuate – of course. As a less obvious corollary, the low-frequency fluctuation intensity

$$S_n(0) = \frac{1}{\pi\Gamma}\frac{N-1}{N^3},$$

as a function of N, reaches its maximum already for two sites and then decreases.

Note also that for the particular case $N = 2$, the result is applicable to Ehrenfest's dog-flea system (see Problem 2.1) with just one flea. However, in this particular case, the entropy (whose calculation was the subject of that problem) does not change in time because it has the largest possible value $S = \ln N = \ln 2$ from the very beginning.

Chapter 6. Elements of Kinetics

Problem 6.1. Use the Boltzmann equation in the relaxation-time approximation to derive the Drude formula for the complex ac conductivity $\sigma(\omega)$. Give a physical interpretation of the result's trend at high frequencies.

Solution: For a uniform system in a spatially uniform ac field $\mathscr{E}(t)$, we may neglect, in the Boltzmann-RTA equation (6.18), the term proportional to $\nabla_r w$, but have to retain the term $\partial w/\partial t$. Then, in the same low-field approximation as was used in Sec. 6.2 of the lecture notes to derive Eq. (6.25), we get the following generalization of that relation to our time-dependent case:

$$\frac{\partial \tilde{w}}{\partial t} + \frac{\tilde{w}}{\tau} = -q\mathscr{E}(t)\cdot \mathbf{v}\frac{\partial w_0}{\partial \varepsilon}. \qquad (*)$$

From here, looking for the time dependence of the variables $\mathscr{E}$ and $\tilde{w}$ in the form $\exp\{-i\omega t\}$, we get the following relation between their complex amplitudes:

$$\left(-i\omega + \frac{1}{\tau}\right)\tilde{w}_\omega = -q\mathscr{E}_\omega \cdot \mathbf{v}\frac{\partial w_0}{\partial \varepsilon}, \qquad \text{i.e. } \tilde{w}_\omega = -\frac{1}{1-i\omega\tau}\tau q\mathscr{E}_\omega \cdot \mathbf{v}\frac{\partial w_0}{\partial \varepsilon}.$$

Comparing this result with Eqs. (6.25), we see that the only change due to the non-zero frequency ω is the new factor $(1 - i\omega\tau)$ in the denominator of expressions for the probability perturbation, and hence for the complex amplitude $\mathbf{j}_\omega$ of the electric current $\mathbf{j}$ given by Eq. (6. 26). Hence, the same factor appears in the complex conductivity $\sigma(\omega)$ defined by a relation similar to Eq. (6.28), but for the complex amplitudes $\mathbf{j}_\omega$ and $\mathscr{E}_\omega$:

$$\sigma(\omega) \equiv \frac{\mathbf{j}_\omega}{\mathscr{E}_\omega} = \frac{\sigma(0)}{1-i\omega\tau},$$

where $\sigma(0)$ is given by Eq. (6.29) – and hence by the Drude formula (6.32).

For the interpretation purposes, let us rewrite this result as

$$\sigma(\omega) = \sigma'(\omega) + i\sigma''(\omega), \qquad \text{with } \sigma'(\omega) = \frac{\sigma(0)}{1+(\omega\tau)^2}, \quad \sigma''(\omega) = \frac{\sigma(0)\omega\tau}{1+(\omega\tau)^2}.$$

These formulas show that the real part σ' of the conductivity, responsible in particular for the Joule heat generation, drops fast as soon as the field frequency exceeds the reciprocal relaxation time $1/\tau$ (in most practical conductors, from $\sim 10^{11}$ to $\sim 10^{13}$ s^{-1}), while its imaginary part σ'' first grows with frequency, and then starts dropping as well, but slower – as $1/\omega$. The latter behavior, with a τ-independent imaginary conductivity:

$$\sigma''(\omega) \approx \frac{\sigma(0)}{\omega\tau} \equiv \frac{q^2 n}{m\omega}, \qquad \text{for } \omega\tau >> 1, \qquad (**)$$

corresponds to collision-free oscillations of particle displacements, induced by the external ac field. Hence Eq. (**) does not depend on the scattering model and is very general.

Note also that the frequency dependence of the current density at $\omega\tau >> 1$ is similar to that of the current I flowing through a lumped inductance L (with the voltage $\mathscr{V} = LdI/dt$, and hence $I_\omega = i\mathscr{V}_\omega/\omega L$). Due to this similarity, the σ'' given by Eq. (**) is called the *kinetic inductance* of a conductor, because, in contrast to the usual "magnetic" inductance, it is due to the finite mass m (inertia) of the charge carriers, rather than the magnetic field it induces. This effect is especially noticeable in superconductors, whose linear electrodynamics may be approximately described as that of the usual conductors but with negligible scattering, i.e. with $\tau = \infty$, so Eq. (**), with n and m replaced with certain effective parameters, is valid in a very broad range of frequencies starting from zero.[100]

Problem 6.2. At $t = 0$, similar particles were uniformly distributed in a plane layer of thickness $2a$:

$$n(x,0) = \begin{cases} n_0, & \text{for } -a \le x \le +a, \\ 0, & \text{otherwise.} \end{cases}$$

At $t > 0$, the particles are allowed to propagate by diffusion through an unlimited uniform medium. Use the variable separation method[101] to calculate the time evolution of the particle density distribution.

Solution: In the absence of a drift-inducing field, we may calculate the distribution $n(\mathbf{r}, t)$ using the drift-diffusion equation (6.50) with $\nabla U = 0$. In this case, it is reduced to a simple diffusion equation similar to Eq. (5.116):

$$\frac{\partial n}{\partial t} = D\nabla^2 n, \qquad \text{with } D = \frac{\tau T}{m}.$$

Since this equation is isotropic, the initial 1D distribution $n = n(x, 0)$ results in a 1D distribution $n(x, t)$ at all later times, and its evolution may be described by the 1D version of the diffusion equation:

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}. \qquad (*)$$

Let us look for its solution in the variable-separated form:

$$n(x,t) = \sum_k T_k(t)X_k(x). \qquad (**)$$

Plugging an arbitrary term of this series into Eq. (*) and dividing both sides by DT_kX_k, we obtain

$$\frac{1}{DT_k}\frac{dT_k}{dt} = \frac{1}{X_k}\frac{d^2X_k}{dx^2} = \text{const} \equiv -k^2.$$

Solving the two resulting simple ordinary differential equations for T_k and X_k, we get[102]

$$T_k = a_k \exp\{-Dk^2t\}, \qquad X_k = b_k \cos kx,$$

---

[100] A more detailed discussion of this issue may be found in EM Sec. 6.4.

[101] A detailed introduction to this method (repeatedly used in this series) may be found, for example, in EM Sec. 2.5.

[102] Another possible contribution to the function $X_k(x)$, proportional to $\sin kx$, has been dropped because there is no reason for the function $n(x, t)$ to violate its initial spatial symmetry: $n(-x, t) = n(x, t)$.

with (so far) arbitrary a_k and b_k. Since the length of the diffusion segment ($-\infty \leq x \leq +\infty$) is infinite, the spectrum of the possible values of k is continuous, so plugging these solutions back into Eq. (**), we need to replace the summation over k with integration:

$$n(x,t) = \int_{-\infty}^{+\infty} c_k \exp\{-Dk^2 t\} \cos kx \, dk, \qquad \text{where } c_k \equiv a_k b_k . \tag{***}$$

What remains is to find the function c_k from the initial condition at $t = 0$:

$$\int_{-\infty}^{+\infty} c_k \cos kx \, dk \equiv \frac{1}{2}\int_{-\infty}^{+\infty} c_k \left(e^{ikx} + e^{-ikx}\right) dk = n(x,0) \equiv \begin{cases} n_0, & \text{for } -a \leq x \leq +a, \\ 0, & \text{otherwise.} \end{cases}$$

As usual for the reciprocal Fourier transform, let us multiply both parts of this equation by $e^{-ik'x}$, and integrate the result over the whole x-axis. Changing the order of integration on the left-hand side, we get

$$\frac{1}{2}\int_{-\infty}^{+\infty} dk \, c_k \int_{-\infty}^{+\infty} dx \left[e^{i(k-k')x} + e^{i(k+k')x}\right] = \int_{-\infty}^{+\infty} n(x,0) e^{-ik'x} dx \equiv n_0 \int_{-a}^{+a} \cos k'x \, dx .$$

The inner integral on the left-hand side equals $2\pi[\delta(k - k') + \delta(k + k')]$,[103] so the outer integration is easy, giving

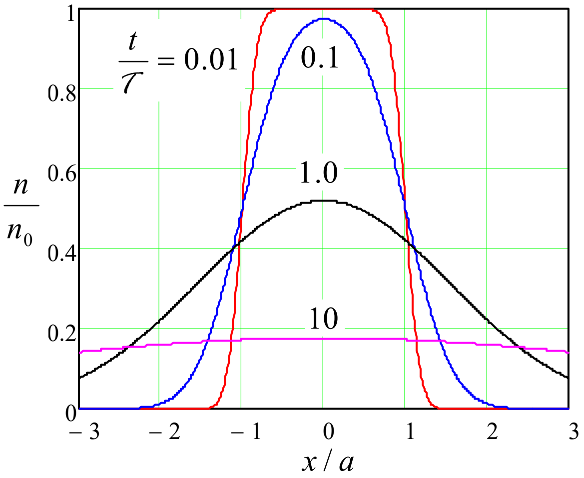
$$\frac{1}{2}\left(c_{k'} + c_{-k'}\right) = \frac{n_0}{2\pi}\int_{-a}^{+a} \cos k'x \, dx \equiv \frac{n_0}{\pi}\frac{\sin k'a}{k'} .$$

Due to the symmetry of the left-hand side of Eq. (***), $c_{k'}$ has to be an even function of k', so (dropping the prime index of k) this result becomes

$$c_k = \frac{n_0}{\pi}\frac{\sin ka}{k} .$$

Plugging this expression into Eq. (***), we may fold the integral in it onto the positive semi-axis. The result is

$$n(x,t) = \frac{2n_0}{\pi}\int_0^{+\infty} \frac{\sin ka}{k} \exp\{-Dk^2 t\} \cos kx \, dk . \tag{****}$$



Plots of this distribution for several values of the normalized time $t/\mathcal{T}$, where $\mathcal{T} \equiv a^2/2D$, are shown in the figure on the right. They show that the initially rectangular distribution of the particle density first smears at the edges very fast, but the later (at $t >> \mathcal{T}$) spread of the particles becomes slower and slower with time. This is very natural in light of the basic law (5.77) of diffusion of a single particle (equivalent to a delta-functional initial distribution of n), in our current notation reading

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[103] If needed, see, e.g., MA Eq. (14.4).

$$\delta x = (2Dt)^{1/2}.$$

Reversing the same statement into the time domain, we may say that the genuine characteristic time of a substantial change of the particle distribution is not the constant $\mathcal{T} \equiv a^2/2D$ but rather the evolving scale $\Delta t \sim (\Delta x)^2/D$, where Δx is the spatial width of the sharp feature(s) of the distribution. (At $t >> \mathcal{T}$, this is the full width $\Delta x \approx \delta x >> a$ of the whole distribution, so $\Delta t \sim t >> \mathcal{T}$.) In this sense, we may say that the process of diffusion does not have a unique time scale.

Problem 6.3. Solve the previous problem using an appropriate Green's function for the 1D version of the diffusion equation, and discuss the relative convenience of the results.

Solution: The spatial-temporal Green's function of any linear, homogeneous, partial differential equation in 1+1 dimensions (one spatial coordinate + time) may be defined by the following general formula for the equation's solution at $t > t_0$:

$$n(x,t) = \int_{-\infty}^{+\infty} n(x_0, t_0) G(x,t;\, x_0, t_0) dx_0 . \qquad (*)$$

Applied to the delta-functional initial conditions, this definition yields

$$n(x,t) = G(x,t;\, x_0,t_0), \qquad \text{if } n(x,t_0) = \delta(x - x_0).$$

However, such a solution (with $t_0 = 0$) of the diffusion equation (*) of the previous problem, similar to Eq. (5.114) of the lecture notes:

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}, \qquad \text{for } -\infty < x < +\infty,$$

was already discussed in Sec. 5.6 – see Eqs. (5.112)-(5.113). From these relations,

$$G(x,t;\, x_0,t_0) = \frac{1}{(2\pi)^{1/2}\delta x(t)} \exp\left\{-\frac{(x-x_0)^2}{2[\delta x(t)]^2}\right\}, \qquad \text{with } \delta x(t) = [2D(t-t_0)]^{1/2},$$

so Eq. (*), also with $t_0 = 0$, becomes

$$n(x,t) = \frac{1}{(4\pi Dt)^{1/2}} \int_{-\infty}^{+\infty} n(x_0, 0) \exp\left\{-\frac{(x-x_0)^2}{4Dt}\right\} dx_0 .$$

For the initial conditions specified in the previous problem,

$$n(x,0) = \begin{cases} n_0, & \text{for } -a \le x \le +a, \\ 0, & \text{otherwise,} \end{cases}$$

we get[104]

---

[104] This integral may be readily expressed via a difference of two values of the so-called *error function*

$$\operatorname{erf}(\zeta) \equiv \frac{2}{\pi^{1/2}} \int_0^{\zeta} \exp\{-\xi^2\} d\xi ;$$

however, for most practical purposes, the explicit integral form (**) is preferable.

$$n(x,t)=\frac{n_0}{(4\pi Dt)^{1/2}}\int_{-a}^{+a}\exp\left\{-\frac{(x-x_0)^2}{4Dt}\right\}dx_0\equiv\frac{n_0}{\pi^{1/2}}\int_{\xi_-}^{\xi_+}\exp\left\{-\xi^2\right\}d\xi\,, \qquad (**)$$

where

$$\xi_\pm\equiv\frac{x\pm a}{\sqrt{2}\delta x(t)},\qquad \delta x(t)\equiv(2Dt)^{1/2}.$$

These formulas yield exactly the same plots of function $n(x, t)$ as shown in the model solution of the previous problem – despite the substantial difference in the expression forms. Indeed, the result (****) of the previous problem is just the Fourier-integral expansion of Eq. (**). However, for practical calculations, there is a big difference between these two integral forms: the real-space integral in Eq. (**) converges faster at relatively small times, $t \ll \mathcal{T}\equiv a^2/2D$, while the reciprocal-space integral obtained in the previous problem's solution by the variable separation, converges faster at $t \gg \mathcal{T}$, when only relatively small values of the effective wave number k, with $|k| \sim 1/(Dt)^{1/2} \ll 1/a$, give noticeable contributions into it.

Problem 6.4. Particles with the same initial spatial distribution as in the two previous problems are now freed at $t = 0$ to propagate ballistically – without scattering. Calculate the time evolution of their density distribution at $t > 0$, provided that initially, the particles were in thermal equilibrium at temperature T. Compare the solution with that of the previous problem.

Solution: Since the particles do not interact and propagate independently of each other, we may calculate their density as

$$n(\mathbf{r},t)=N\int w(\mathbf{r},\mathbf{p},t)d^3p\,,$$

where $w(\mathbf{r}, \mathbf{p}, t)$ is the probability distribution of a single particle. In the absence of scattering and external fields, this distribution is described by the Liouville equation (6.9) with $\mathscr{F} = 0$:[105]

$$\frac{\partial w}{\partial t}+\frac{\mathbf{p}}{m}\cdot\nabla_r w=0\,. \qquad (*)$$

For our 1D initial conditions, $w_i(x, \mathbf{p}) \equiv w(\mathbf{r}, \mathbf{p}, 0) = n(x, 0)\, w_0(\mathbf{p})$, where $w_0(\mathbf{p})$ is the equilibrium (Maxwell) distribution (3.5)-(3.6):

$$w_0(\mathbf{p})=\frac{1}{(2\pi mT)^{3/2}}\exp\left\{-\frac{p_x^2+p_y^2+p_z^2}{2mT}\right\}, \qquad (**)$$

the solution of Eq. (*) may depend only on one spatial coordinate (x), so it is reduced to

$$\frac{\partial w}{\partial t}=-\frac{p_x}{m}\frac{\partial w}{\partial x}\,.$$

This equation is obviously satisfied with any function of one argument, $f_p = f_p(x - p_xt/m)$, describing the ballistic (acceleration-free) propagation of a particle with the initial velocity $v_x = p_x/m$ along the x-axis. This time evolution does not affect the probability distribution in the momentum space and along the transverse coordinates y and z. Hence in our case,

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[105] Note that the same equation follows from the Fokker-Planck equation (5.149) with $\nabla_q U = 0$ and $\eta = 0$.

$$w(\mathbf{r},\mathbf{p},t) = w_{\mathrm{i}}\left(x - \frac{p_x}{m}t, \mathbf{p}\right) = w_0(\mathbf{p})n\left(x - \frac{p_x}{m}t, 0\right),$$

so the spatial distribution we are looking for is

$$n(x,t) \equiv \int w(\mathbf{r},\mathbf{p},t)d^3p = \int w_0(\mathbf{p})n\left(x - \frac{p_x}{m}t, 0\right)d^3p.$$

Now rewriting Eq. (**) as

$$w_0(\mathbf{p}) = \frac{1}{(2\pi mT)^{1/2}}\exp\left\{-\frac{p_x^2}{2mT}\right\}w_\perp(p_y, p_z), \qquad \text{where } \int w_\perp(p_y,p_z)dp_y dp_z = 1,$$

we get the solution valid for any initial distribution $n(x, 0)$:

$$n(x,t) \equiv \frac{1}{(2\pi mT)^{1/2}}\int_{-\infty}^{+\infty} n\left(x - \frac{p_x}{m}t, 0\right)\exp\left\{-\frac{p_x^2}{2mT}\right\}dp_x.$$

For our particular simple distribution, this expression is reduced to

$$n(x,t) \equiv \frac{n_0}{(2\pi mT)^{1/2}}\int_{m(x-a)/t}^{m(x+a)/t} \exp\left\{-\frac{p_x^2}{2mT}\right\}dp_x \equiv \frac{n_0}{\pi^{1/2}}\int_{\xi_-}^{\xi_+}\exp\{-\xi^2\}d\xi,$$

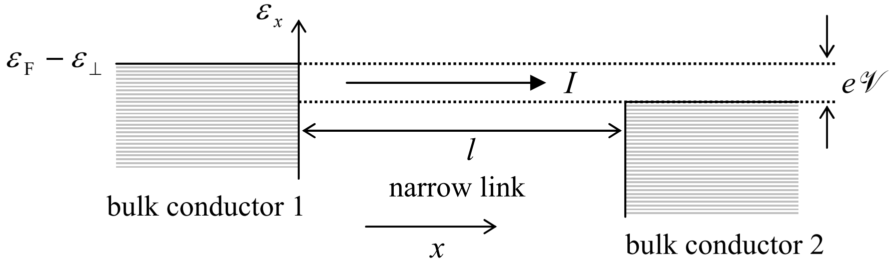
where

$$\xi_\pm \equiv \frac{x \pm a}{\sqrt{2}\Delta x(t)}, \qquad \Delta x(t) \equiv \left(\frac{T}{m}\right)^{1/2} t \equiv \left\langle v_x^2\right\rangle^{1/2} t.$$

Hence, due to the Maxwell distribution (**) of the initial momenta, the functional dependence of the particle density on the spatial coordinates is the same as in the case of diffusion – see Eq. (**) in the solution of the previous problem. However, in our current case of ballistic propagation, the effective width $\Delta x(t)$ of the spatial distribution is directly proportional to t rather than to $t^{1/2}$ as in the case of diffusion, so the time evolution of the particle density is rather different.

Problem 6.5.* Calculate the dc electric conductance of a narrow uniform conducting link between two bulk conductors, in the low-voltage and low-temperature limit, neglecting the electron interaction and scattering inside the link.

Solution: As was discussed in Sec. 3.3 of the lecture notes, at $T \to 0$, any fermions (including electrons) in equilibrium fill all quantum states up to the Fermi energy ε_{F}. Next, as we know from Sec. 6.3 (see, in particular, Fig. 6.5c), if bulk conductors are weakly connected, with no voltage applied between them, their Fermi levels become aligned. The voltage $\mathscr{V}$ applied between the conductors offsets their whole energy spectra by $e\mathscr{V}$, so the single-particle energy diagram of the system looks as sketched in the figure on the right, where the filled energy levels are highlighted.



Since the link is uniform, the longitudinal component ε_x of the electron's energy inside it is conserved.[106] As the energy diagram in the figure above shows, it can move from conductor 1 to conductor 2 only if this energy is within the range[107]

$$\varepsilon_\mathrm{F} - e\mathscr{V} \leq \varepsilon_x + \varepsilon_\perp \leq \varepsilon_\mathrm{F},$$

where $\varepsilon_\perp$ is the energy corresponding to the transverse factor $\psi_\perp(y, z)$ of the wavefunction describing the electron's motion along the channel:

$$\psi(\mathbf{r}) = a\psi_\perp(y,z)\exp\{ik_x x\}.$$

Neglecting, for simplicity, the electron's interaction with the crystal lattice, we may find the wave number k_x from the dispersion relation

$$\frac{\hbar^2 k_x^2}{2m} = \varepsilon_x \equiv \varepsilon - \varepsilon_\perp .$$

If the applied voltage is relatively low, $e\mathscr{V} << \varepsilon_\mathrm{F}$, the number N of different electron states with the same transverse wavefunction $\psi_\perp(y, z)$, may be calculated as

$$N = 2\frac{dN}{d\varepsilon_x}e\mathscr{V}, \qquad (*)$$

where the front factor of 2 is due to two possible electron's spin states with the same "orbital" wavefunction $\psi(\mathbf{r})$, while $dN/d\varepsilon_x$ is the 1D density of the orbital states, which may be calculated as[108]

$$\frac{dN}{d\varepsilon_x} = \frac{dN}{dk_x}\bigg/\frac{d\varepsilon_x}{dk_x} \equiv \frac{l}{2\pi}\bigg/\frac{d\left(\hbar^2 k_x^2/2m\right)}{dk_x} \equiv \frac{l}{2\pi}\bigg/\frac{\hbar^2 k_x}{m} \equiv \frac{l}{2\pi}\bigg/\frac{\hbar(2m\varepsilon_x)^{1/2}}{m}.$$

With this result, Eq. (*) becomes

$$N = \frac{l\, m^{1/2}}{2^{1/2}\pi\hbar\varepsilon_x^{1/2}}e\mathscr{V}. \qquad (**)$$

Each of these traveling-wave states carries the probability current[109]

$$I_w = \frac{\hbar k_x}{m}|\,a\,|^2\int|\psi_\perp(y,z)|^2 dydz .$$

The wave's amplitude $|\,a\,|$ has to be calculated from the normalization condition

$$\int|\,\psi\,|^2 d^3r \equiv \int_0^l \left|ae^{ik_x x}\right|^2 dx\int|\psi_\perp(y,z)|^2 dydz \equiv l\,|\,a\,|^2\int|\psi_\perp(y,z)|^2 dydz = 1 .$$

---

[106] The WKB approximation (discussed, e.g., in QM Sec. 2.4) may be used to show that the result of this analysis is also valid for the so-called "adiabatic" channels whose cross-section is slowly changing along the length. Moreover, strictly speaking, the result is *only* valid for such adiabatic channels, with smoothed interfaces between the bulk conductors and the channel, because only for such a geometry, the electron scattering at the link entrance/exit (the effect swept under the carpet in the provided solution :-) is negligible.

[107] The left inequality ensures that this state in conductor 2 is empty, and hence available for occupation by the traveling electron.

[108] See, e.g., QM Eq. (1.100).

[109] See, e.g., QM Eq. (2.5) with $\partial\varphi/\partial x = k_x$.

From here, we get

$$|a|^2\int\left|\psi_\perp(y,z)\right|^2 dydz = \frac{1}{l}, \qquad \text{i.e. } I_w = \frac{\hbar k_x}{lm} = \frac{1}{l}\left(\frac{2\varepsilon_x}{m}\right)^{1/2}. \qquad (***)$$

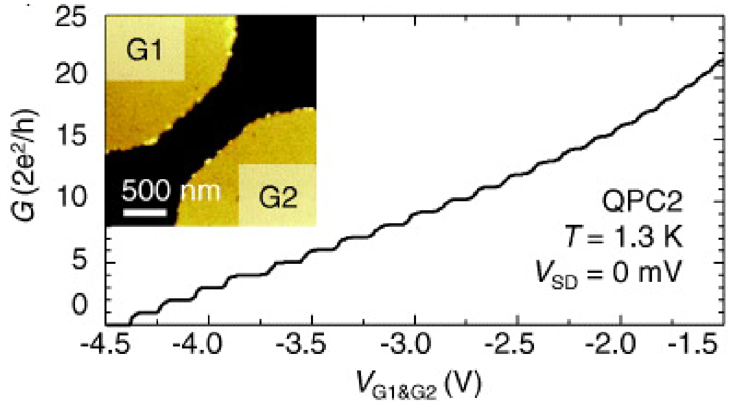
Now we may use Eqs. (**) and (***) to calculate the full electric current carried by one populated transverse mode $\psi_\perp(y, z)$ (sometimes called the *quantum channel* or the "ballistic channel"):

$$I = eNI_w = e\frac{l\,m^{1/2}}{2^{1/2}\pi\hbar\varepsilon_x^{1/2}}e\mathscr{V}\frac{1}{l}\left(\frac{2\varepsilon_x}{m}\right)^{1/2} \equiv \frac{e^2}{\pi\hbar}\mathscr{V}.$$

This means that the electric conductance due to one fully populated quantum channel is given by a wonderfully simple expression:

$$G_\text{q} \equiv \frac{I}{\mathscr{V}} = \frac{e^2}{\pi\hbar} \equiv \frac{2e^2}{h}, \qquad \text{where } h \equiv 2\pi\hbar. \qquad (****)$$

This result had been derived by R. Landauer in 1957 but attracted common attention only in the late 1980s when the effect of longitudinal conductance quantization was observed experimentally in narrow links formed by negatively biased gate electrodes in 2D electron gas in semiconductor heterojunctions – see, e.g., the figure below. As the negative gate voltage is reduced, the link's width w is increased, so the transverse quantization energy $\varepsilon_\perp \approx \pi^2\hbar^2/2mw^2$ + const is reduced, and at certain gate voltage values, new and new quantum channels become populated, increasing the conductance by discrete steps equal to G_q.



The geometry of a typical conductance quantization experiment using a semiconductor heterojunction, and its result. $V_{G1\&G2}$ is the voltage applied to the "gate" electrodes G1 and G2 (marked in the inset) used to squeeze the 2D electron gas from under them and thus form (and control the width of) a quasi-1D conducting link between two broader conducting electrodes. Adapted from C. Rössler *et al.*, *New J. Phys.* **13**, 113006 (2011). © IOP, reproduced with permission.

The most important feature of Eq. (****) is its independence of the electron mass m, channel dimensions, and any other parameters of the used sample. A similar (but, due to the suppression of backscattering by the magnetic field, much more robust and hence more precise) conductance quantization takes place at the quantum Hall effect.[110]

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[110] See, e.g., QM Sec. 3.2. Note also a very similar effect of *thermal* conductance quantization – see, e.g., K. Schwab *et al.*, *Nature* **404**, 974 (2000) and references therein.

Since Eq. (****) was derived neglecting electron scattering, it is also interesting to think about the physics of the channel's conductance G_q, in particular, in the context of the corresponding Joule heat power $\mathscr{P} = I\mathscr{V} = G_q\mathscr{V}^2$. The extra energy $e\mathscr{V}$ picked up by each electron during its passage through the ballistic channel is turned into heat not inside the channel (where, in our simple model, there is no scattering and hence no energy dissipation), but somewhere inside the bulk electrodes, due to a gradual loss of the gained energy via inelastic (e.g., electron-phonon) interactions. This is one more twist of the interplay between the elastic and inelastic scattering at Ohmic conductivity, which was discussed at the end of Sec. 6.2 of the lecture notes.

Problem 6.6. Calculate the effective capacitance (per unit area) of a broad plane sheet of a degenerate 2D electron gas, separated by an insulating gap of thickness d from a well-conducting ground plane.

Solution: Per the solution of Problem 3.20 (see also Problem 3.8), in the degenerate limit ($T << \mu$), the Fermi energy of a gas of N particles, which are confined to a 2D sheet of area A, is

$$\varepsilon_F \equiv \mu\big|_{T\to 0} = \frac{\pi\hbar^2}{m}\frac{N}{A}.$$

At that calculation, the Coulomb interaction effects have been neglected. The most important of these effects[111] is that the distributed electric charge of the gas, with the areal density

$$\sigma \equiv \frac{Q}{A} = \frac{qN}{A},$$

creates a uniform electric field of magnitude $\mathscr{E} = \sigma/\kappa\varepsilon_0$ in the gap between the gas and the ground plane, where κ is the dielectric constant of the material filling the gap.[112] As a result, the electrostatic potential of the layer (relative to that of the ground plane) becomes

$$\phi = \mathscr{E}d = \frac{\sigma d}{\kappa\varepsilon_0} = \frac{qd}{\kappa\varepsilon_0}\frac{N}{A},$$

so the electrochemical potential (6.40) of the layer

$$\mu' \equiv q\phi + \mu = \frac{q^2 d}{\kappa\varepsilon_0}\frac{N}{A} + \frac{\pi\hbar^2}{m}\frac{N}{A} \equiv \sigma q\left(\frac{d}{\kappa\varepsilon_0} + \frac{\pi\hbar^2}{mq^2}\right). \qquad (*)$$

As was discussed in Sec. 6.3, the net electrochemical potential μ' (divided by q) is what we usually measure as the voltage $\mathscr{V}$ – in our current case, between the electron gas and the ground plane. As we know from basic electrostatics, capacitance C is just the ratio $Q/\mathscr{V}$, so the capacitance per unit area (C/A) is the ratio $\sigma/\mathscr{V}$, and Eq. (*) may be represented as

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[111] Another effect is the Coulomb interaction of the electrons within the gas, leading, in particular, to their mutual scattering. In solids, this effect is typically less important, due to the compensating positive charge of the atomic lattice. In contrast, the charge Q discussed in this solution is the uncompensated charge of additional electrons.

[112] If this formula is not evident, please consult EM Secs. 2.2 and 3.4.

$$\left(\frac{C}{A}\right)^{-1}=\frac{d}{\kappa\varepsilon_0}+\frac{\pi\hbar^2}{mq^2}.$$

In the circuit theory language, this means that the effective capacitance C of the 2D electron gas sheet is a connection, *in series*:

$$\frac{1}{C}=\frac{1}{C_\mathrm{e}}+\frac{1}{C_\mathrm{q}},$$

of the usual "electrostatic" capacitance

$$C_\mathrm{e}=\frac{\kappa\varepsilon_0}{d}A,$$

and the so-called *quantum capacitance*[113]

$$C_\mathrm{q}=\frac{mq^2}{\pi\hbar^2}A\cdot$$

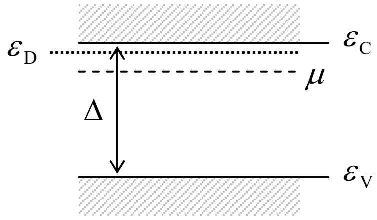
The physics of this effect is pretty straightforward: by its definition, the electrochemical potential is the average energy necessary to add one particle from the environment (in our case, from the ground plane, which serves as a virtually unlimited reservoir of electrons) to the system. In our current case, such addition requires, first, overcoming the Coulomb repulsion of the electrons already in the sheet and, second, giving to the additional electron the Fermi energy of the gas ε_F, to enable it to fill the lowest quantum state not yet occupied – just above ε_F. In the simple model analyzed above, these energy increments are independent, leading to the addition of the two contributions to the effective potential μ', and hence to the addition of the *reciprocal* capacitances describing each of the energy components.

For free electrons (with $|q| = e \approx 1.6\times10^{-19}$ C and $m = m_\mathrm{e} \approx 0.91\times10^{-30}$ kg), the quantum capacitance is quite macroscopic, $C_\mathrm{q}/A \approx 0.67$ F/m^2, and becomes even smaller (so the important fraction $1/C_\mathrm{q}$ becomes *larger*) in semiconductors with lower effective electron mass – e.g., $m \approx 0.2\ m_\mathrm{e}$ in the conduction band of Si. Because of that, its effects may be noticeable in some modern electron devices – most importantly, in the ubiquitous silicon field-effect transistors with their very thin gate-insulating layers. (For comparison with the above estimate of C_q/A, the ratio C_e/A for modern gate-oxide layers is of the order of 0.1 F/m^2.)

Problem 6.7. Give a quantitative description of the dopant atom ionization, which would be consistent with the conduction and valence band occupation statistics, using the same simple model of an n-doped semiconductor as in Sec. 6.4 of the lecture notes (see Fig. 6.7a), and taking into account that the ground state of the dopant atom is typically doubly degenerate, due to two possible spin orientations of the bound electron. Use the results to verify Eq. (6.65), within the displayed limits of its validity.

Solution: For spelling out the electroneutrality condition (6.62),

$$n=p+n_+, \qquad (*)$$



we need to express the concentrations n, p, and n_+ via the parameters μ and T (in equilibrium, common for all components of the system), for given energies ε_V, ε_C, and ε_D – see Fig. 6.7a, which is reproduced on the right. As was argued in Sec. 6.4, at $T << \Delta \equiv \varepsilon_\mathrm{C} - \varepsilon_\mathrm{V}$, Eqs. (6.58):

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[113] Note that both C_e and C_q are always positive, regardless of the charge of the particles (e.g., electrons).

$$n = n_C \exp\left\{\frac{\mu - \varepsilon_C}{T}\right\}, \qquad p = n_V \exp\left\{\frac{\varepsilon_V - \mu}{T}\right\}, \qquad (**)$$

are independent of the dopant excitation statistics, so we need only to express the number n_+ of activated (ionized) dopants via the above parameters and the full concentration n_D of the dopant atoms.

This may be done similarly to the calculation of N_0 in the solution of Problem 3.9. With the assumption given in the assignment, each donor atom may be in either of three different states: one ionized state, without an electron, with a certain energy ε_a, and any of two ground states, with one electron of some spin orientation, with the energy $\varepsilon_a + \varepsilon_D$. Applying the general Eqs. (2.106)-(2.107) to a grand canonical ensemble of such systems, we may find the corresponding probabilities:

$$W_0 = \frac{1}{Z_G}\exp\left\{-\frac{\varepsilon_a}{T}\right\}, \qquad W_1 = \frac{1}{Z_G}\exp\left\{\frac{\mu - (\varepsilon_D + \varepsilon_a)}{T}\right\},$$

where

$$Z_G = \exp\left\{-\frac{\varepsilon_a}{T}\right\} + 2\exp\left\{\frac{\mu - (\varepsilon_D + \varepsilon_a)}{T}\right\} \equiv \exp\left\{-\frac{\varepsilon_a}{T}\right\}\left(1 + 2\exp\left\{\frac{\mu - \varepsilon_D}{T}\right\}\right),$$

so $W_{0,1}$ are independent of the background energy ε_a:

$$W_0 = \frac{1}{1 + 2\exp\{(\mu - \varepsilon_D)/T\}}, \qquad W_1 = \frac{\exp\{(\mu - \varepsilon_D)/T\}}{1 + 2\exp\{(\mu - \varepsilon_D)/T\}}.$$

From here, the average number of ionized atoms (per unit volume) is

$$n_+ = n_D W_0 = \frac{n_D}{1 + 2\exp\{(\mu - \varepsilon_D)/T\}}. \qquad (***)$$

As a sanity check, Eq. (***) shows that at fixed μ and T, the fraction n_+/n_D of the activated donors increases as ε_D is increased – as it should, according to the energy diagram shown above.

With this expression for n_+, the electroneutrality condition (*) takes the form

$$n_C \exp\left\{\frac{\mu - \varepsilon_C}{T}\right\} = n_V \exp\left\{\frac{\varepsilon_V - \mu}{T}\right\} + \frac{n_D}{1 + 2\exp\{(\mu - \varepsilon_D)/T\}}. \qquad (****)$$

Generally, this transcendental equation for μ cannot be solved analytically. However, it may be readily used to plot the electron density n, given by the first of Eqs. (**), as a function of n_D, with the chemical potential μ used as the parameter – see the solid red line in the figure below, calculated for parameters typical for semiconductors. (Note the log-log scale of the plot, covering several orders of magnitude of both densities.) The plot shows that at $T << \Delta$, there are three distinct branches of n as a function of the dopant density n_D.

(i) If the density is very low, $n_D << n_i$,[114] the last term in Eq. (****) is negligible, so the semiconductor remains practically intrinsic, with $n \approx p \approx n_i$ and the chemical potential near the midgap: $\mu \approx (\varepsilon_C + \varepsilon_V)/2$.

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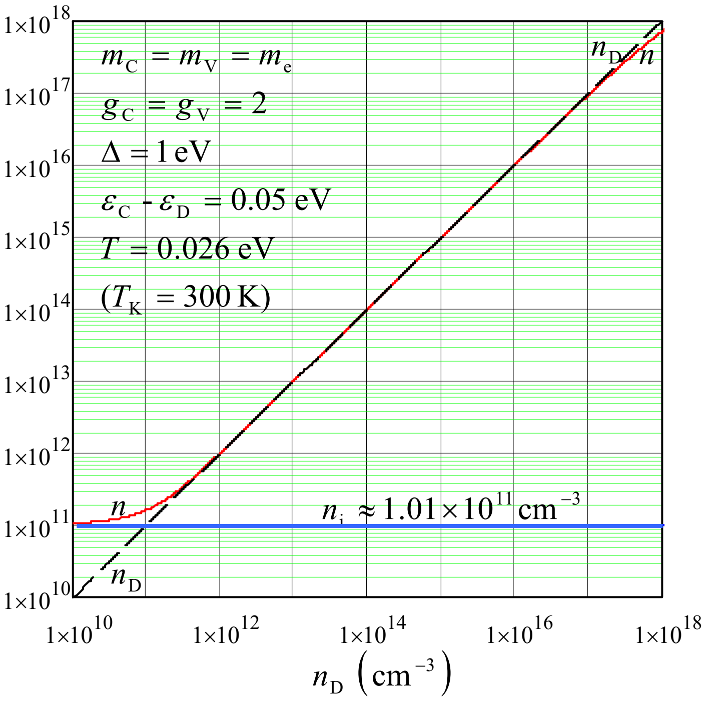
[114] Note again that n_i is a very strong function of temperature – se the second of Eqs. (6.60).

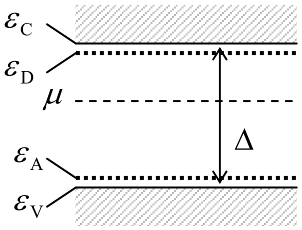


(ii) In the (most typical) case when n_D becomes well above n_i, the density n_+ of activated atoms and the electron density n are virtually equal to n_D (and hence temperature-independent), with the hole density p decreasing and the chemical potential inching toward the conduction band edge – see Eqs. (6.65) of the lecture notes:

$$n \approx n_D, \quad p \approx \frac{n_i^2}{n_D} << n, \quad \mu \approx \varepsilon_C - T\ln\frac{n_C}{n_D}.$$

This result means that the donor atoms may be fully activated even if the apparent ionization energy ($\varepsilon_C - \varepsilon_D$) is much higher than T – as it is in the example shown in the plot above. The mathematical explanation of this counterintuitive fact is given by Eq. (***): what is important for the full activation is for the Fermi level μ to be well (by a few T) below ε_D. The handwaving physical interpretation I can offer is that at $n_D >> n_i$, the relatively abundant electrons with the energy ε_D would readily go down to the Fermi level (playing the role of an effective particle source – cf. Fig. 2.13 of the lecture notes) with a lower energy μ, and from there be re-distributed into the conduction and valence bands – mostly to the former one. (Such interpretation of the Fermi level as a virtually unlimited reservoir of particles is generally useful for semi-quantitative analyses of other systems as well.)

(iii) Finally, if n_D becomes so high that the μ expressed by Eq. (6.65) of the lecture notes enters the T-wide vicinity of the doping level ε_D, the last term in Eq. (****) becomes somewhat lower than n_D, causing a proportional reduction of n – see the deviation of the solid red line from the (straight) dashed one at the top right corner of the figure above. However, as the plot shows, for typical parameter values, this effect is relatively minor, so Eq. (6.65) is almost precise within many orders of magnitude of n_D.



Problem 6.8. Generalize the solution of the previous problem to the case when the n-doping of a semiconductor by n_D donor atoms (per unit volume) is complemented with its simultaneous p-doping by n_A acceptor atoms whose energy $\varepsilon_A - \varepsilon_V$ of activation, i.e. of accepting an additional electron and hence becoming a negative ion, is much lower than the bandgap Δ – see the figure on the right.

Solution: In this case, the electroneutrality condition should also take into account the density n_- of negatively ionized acceptor ions, becoming

$$n + n_- = p + n_+. \qquad (*)$$

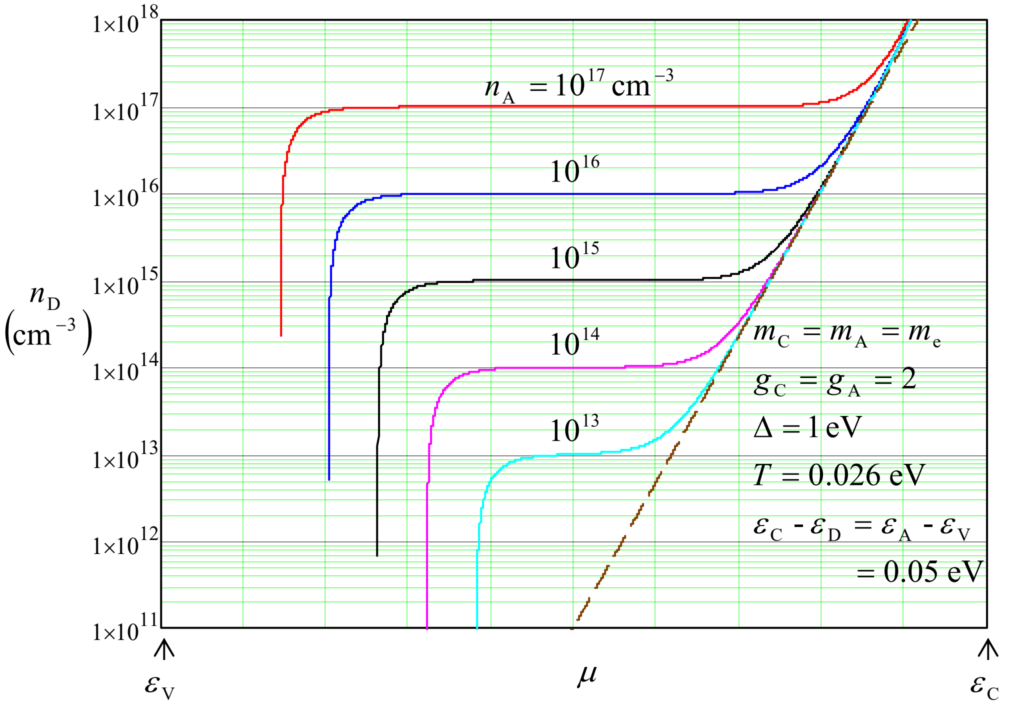
The density n_- may be calculated just like n_+ was in the solution of the previous problem, just taking into account the difference between the electrons and holes by replacing $(\varepsilon_D - \mu)$ with $(\mu - \varepsilon_A)$ – see the figure above. The result is[115]

$$n_- = \frac{n_A}{1 + 2\exp\{(\varepsilon_A - \mu)/T\}}.$$

With this expression, and the formulas for n, p, and n_+ given in the solution of the previous problem, Eq. (*) turns into

$$n_C \exp\left\{\frac{\mu - \varepsilon_C}{T}\right\} + \frac{n_A}{1 + 2\exp\{(\varepsilon_A - \mu)/T\}} = n_V \exp\left\{\frac{\varepsilon_V - \mu}{T}\right\} + \frac{n_D}{1 + 2\exp\{(\mu - \varepsilon_D)/T\}}. \qquad (**)$$

In the general case, this transcendental equation for μ cannot be solved analytically. However, it may be used to plot, for example, the reciprocal dependence of the donor doping level n_D, as a function of the μ it yields, for several values of n_A – see the figure below.



The plots clearly show that at the usual conditions $T << \Delta$ and n_D, $n_A << n_C$, n_V, there are three distinct ranges of doping, where Eq. (**) yields simple results:

(i) At $n_D \approx n_A$, the value of μ is close to the midgap, the exponents in the terms proportional to n_A and n_D are much smaller than 1 (showing that the dopant atoms of both types are fully activated), and Eq. (**) is reduced to

$$n + n_A = p + n_D. \qquad (***)$$

---

[115] Note that in some semiconductors, the degeneracy of electrons on the level ε_A may be different from 2. (In Si, it is equal to 4.) In this case, the factor 2 in the expression for n_-, and hence in Eq. (**), should be replaced with the proper degeneracy factor. However, this change of the pre-exponential factor has virtually no effect on the results presented below, in particular on the plots of μ vs. n_D.

This equation is similar to Eq. (6.63) of the lecture notes, just with n_D replaced with the difference ($n_D - n_A$). With this replacement, its solution is given by Eq. (6.64):

$$n = \frac{n_D - n_A}{2} + \left[\frac{(n_D - n_A)^2}{4} + n_i^2\right]^{1/2}, \qquad p = \frac{n_A - n_D}{2} + \left[\frac{(n_D - n_A)^2}{4} + n_i^2\right]^{1/2} \equiv \frac{n}{n_i^2}, \qquad (****)$$

where n_i is the intrinsic carrier density n_i given by Eq. (6.60):

$$n_i = (n_C n_V)^{1/2} \exp\left\{-\frac{\Delta}{2T}\right\}.$$

The most important feature of this result is that

$$n - p = n_D - n_A,$$

so the sign of ($n - p$), i.e. of the effective charge of carriers, may be controlled by doping. Such *compensated semiconductors* are convenient for some special applications, but in most semiconductor devices, one of the following two limits is used.

(ii) If n_i, $n_A << n_D$ (but n_D is still much lower than the effective density n_C of states in the conduction band), the situation is reduced to the high n-doping analyzed in Sec. 6.4 of the lecture notes, where Eqs. (6.65) are valid:

$$\mu \approx \varepsilon_C - T \ln\frac{n_C}{n_D}, \qquad n \approx n_D, \qquad p \approx \frac{n_i^2}{n_D} << n.$$

The straight dashed line in the figure above shows the first of these approximate equalities. The relatively minor deviations from it in the top right corner of the plots are due to a close approach of μ to ε_D – see the previous problem.

(iii) In the opposite limit of dominating *p-doping* (n_i, $n_D << n_A << n_V$), Eq. (**) is reduced to the equally simple Eqs. (6.67):

$$\mu \approx \varepsilon_V + T \ln\frac{n_V}{n_A}, \qquad n \approx n_A, \qquad n \approx \frac{n_i^2}{n_A} << p,$$

so the carrier densities and the Fermi level are virtually independent of n_D – see the left, nearly-vertical tails of the plots in the figure above.[116]

Problem 6.9. A nearly ideal classical gas of N particles with mass m was in thermal equilibrium at temperature T, in a closed container of volume V. At some moment, an orifice of a very small area A is opened in one of the container's walls, allowing the particles to escape into the surrounding vacuum.[117] In the limit of very low density $n \equiv N/V$, use simple kinetic arguments to calculate the r.m.s. velocity of the escaped particles during the time period when the total number of such particles is still much smaller than N. Formulate the conditions of validity of your results in terms of V, A, and the mean free path l.

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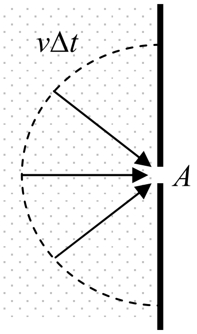
[116] For a more detailed discussion of semiconductor doping statistics (as well as some other issues discussed in Sec. 6.4), I can recommend the classical monograph by W. Shockley, *Electrons and Holes in Semiconductors*, D. Van Nostrand, 1950.

[117] In chemistry and related fields, this process is frequently called *effusion*.

Solution: Assuming that the linear dimensions of the orifice are much smaller than those of the container, so $A << V^{2/3}$, let us calculate the average velocity of the particles that hit the orifice area during a time interval $\Delta t >> A^{1/2}/v_0$, where $v_0 \equiv (3T/m)^{1/2}$ is their r.m.s. velocity in equilibrium – see Eq. (3.9) of the lecture notes. For that, let us also assume that, at the same time, Δt is much less than l/v_0, so the particle collisions on their last path to the orifice may be neglected. In this case, only the particles flying directly toward the orifice may pass through it – see the figure on the right. Moreover, the velocities of such particles should satisfy the condition $v \geq r/\Delta t$, where r is the distance of the particle from the hole at the beginning of the interval Δt. (If the linear size scale of the orifice, $A^{1/2}$, is much smaller than this r, it is not important which exactly part of the hole we are speaking about here.) Hence, as the figure on the right shows, the number of such particles, with velocities within a small range $[v, v + dv]$, is proportional to the volume of the semi-sphere of the radius $r = v\Delta t$, i.e. to $r^3 = (v\Delta t)^3$:

$$dN = \text{const} \times (v\Delta t)^3\, w(v)dv,$$



where the probability density $w(v)$ obeys the 1D Maxwell distribution,

$$w(v) \propto \exp\left\{-\frac{mv^2}{2T}\right\}.$$

(Since the particles from each point may reach the hole area only if they fly in a certain direction, the distribution should be for one Cartesian component of the velocity only.) As a result, we may write

$$dN = c\,(v\Delta t)^3 \exp\left\{-\frac{mv^2}{2T}\right\}dv, \qquad (*)$$

where c is some "constant" – which may still depend on the velocity's direction. Now the average v^2 of the molecules hitting the hole area, from a fixed direction, may be calculated as[118]

$$\langle v^2\rangle = \frac{\int v^2 dN}{\int dN} = \frac{c\int_0^\infty v^2 (v\Delta t)^3 \exp\left\{-\frac{mv^2}{2T}\right\}dv}{c\int_0^\infty (v\Delta t)^3 \exp\left\{-\frac{mv^2}{2T}\right\}dv} = \frac{2T}{m}\frac{\int_0^\infty \xi^5 \exp\left\{-\xi^2\right\}d\xi}{\int_0^\infty \xi^3 \exp\left\{-\xi^2\right\}d\xi} = \frac{2T}{m}\frac{2!/2}{1!/2} = \frac{4T}{m}. \qquad (**)$$

Since this result does not include the velocity's direction, it is valid for the whole particle flux. It also is independent of the time interval Δt, but since particle collisions were neglected at its derivation, it may look like it is only valid for intervals within the initially assumed range

$$\frac{A^{1/2}}{v_0} << \Delta t << \frac{l}{v_0}. \qquad (***)$$

However, if the loss of particles is sufficiently small, as assumed in the assignment, the effusion does not change the statistical distribution of the particles because their diffusive reflections from the container walls and mutual scattering tend to restore the distribution at each point. (The process is frequently called *thermalization*.) Hence Eq. (**) is applicable to each sequential time interval after the orifice opening, even at $t >> A^{1/2}/v_0$. Note, however, that the interval (***) disappears if l is reduced to

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[118] Both involved dimensionless integrals are of the type MA Eq. (6.9e) – with $n = 2$ and $n = 1$, respectively.

approach the scale of the linear sizes of the orifice, $A^{1/2}$. Hence the important condition of validity of our analysis is $A^{1/2} << l$. (We have also neglected possible reflections of the particles from the orifice area – the assumption which is certainly correct if the wall thickness is much smaller than both l and $A^{1/2}$.)

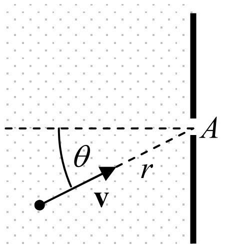
Finally, we have also neglected interparticle collisions/interactions. According to the discussion in Sec. 3.5, this is possible if the gas density n is much smaller than $1/r_0^3$, where r_0 is the linear scale of the particle's size. (This condition is equivalent to $r_0 << l$ – see the solution of Problem 12 below.)

Note that according to Eq. (**), the escaping particles are, on average, hotter than the gas as a whole. Hence the effusion tends to cool the gas, so the maintenance of its temperature would require a flow of heat from the environment.

Problem 6.10. For the system analyzed in the previous problem, calculate the rate of particle flow through the orifice – the so-called *effusion rate*. Discuss the limits of validity of your result.

Solution: Let us calculate the effusion rate, which may be defined as

$$\Gamma \equiv -\frac{dN}{dt} > 0 ,$$



using the same ballistic approach as in the model solution of the previous problem. Consider a small group of particles having a certain velocity **v**, with an angle θ to the direction normal to the wall with the orifice in it – see the figure on the right. The area *dA'* of transverse displacements (normal to the velocity vector **v**), leading to the particle's passage through the orifice, is $A\cos\theta$, while the range dr of the radial distances, leading to such a passage during a small time interval dt, is $dr = vdt$, so the number of such escaping particles is

$$-dN = nw(\mathbf{v})d^3r = nw(\mathbf{v})dA'dr = nA\cos\theta\; w(\mathbf{v})vdt \equiv nAw(\mathbf{v})(v\cos\theta)dt , \qquad (*)$$

where $n \equiv N/V$ is the spatial density of the particles, and $w(\mathbf{v})$ is the 3D Maxwell distribution given by Eqs. (3.5)-(3.6) of the lecture notes, rewritten in terms of velocities $\mathbf{v} = \mathbf{p}/m$:

$$w(\mathbf{v}) \equiv \frac{dW}{d^3v} = m^3\frac{dW}{d^3p} = \left(\frac{m}{2\pi T}\right)^{3/2} \exp\left\{-\frac{mv^2}{2T}\right\}, \qquad \text{so } \int w(\mathbf{v})d^3v = 1 .$$

Since v in Eq. (*) is the magnitude of the particle's velocity, the product $v\cos\theta$ participating in that expression is just its Cartesian component v_n normal to the wall, so the summation of the contributions (*) over all velocities may be represented in the Cartesian form

$$-dN = nAdt\int_0^\infty v_n dv_n \int d^2v_{||} w(\mathbf{v}),$$

where $\mathbf{v}_{||}$ is the velocity within the plane of the wall, and the integration is limited only to the velocities directed toward the wall, i.e. $v_n \geq 0$. Since $w(\mathbf{v})$ may be represented as a product of three similar Cartesian distributions (see Eq. (3.5) again), each of them normalized to 1, the inner integral is

$$\int w(\mathbf{v})d^2v_{||} = w(v_n) \equiv \left(\frac{m}{2\pi T}\right)^{1/2} \exp\left\{-\frac{mv_n^2}{2T}\right\},$$

so we need to actually integrate only in one direction:

$$-dN = nAdt\int_0^\infty w(v_n)v_n dv_n = nAdt\left(\frac{m}{2\pi T}\right)^{1/2}\int_0^\infty \exp\left\{-\frac{mv_n^2}{2T}\right\}v_n dv_n$$

$$\equiv nAdt\left(\frac{m}{2\pi T}\right)^{1/2}\frac{T}{m}\int_0^\infty e^{-\xi}d\xi = nAdt\left(\frac{T}{2\pi m}\right)^{1/2}.$$

Thus, the effusion rate is

$$\Gamma \equiv -\frac{dN}{dt} = An\left(\frac{T}{2\pi m}\right)^{1/2} \equiv \frac{1}{(6\pi)^{1/2}}Anv_0, \qquad (**)$$

where $v_0 = (3T/m)^{1/2}$ is the r.m.s. velocity of the particles – see Eq. (3.9) of the lecture notes.[119]

This result is only valid if the characteristic effusion time $\tau = N/\Gamma$ is sufficiently long:

$$\tau >> \frac{V^{1/3}}{v_0}, \qquad \text{giving } A << V^{2/3},$$

i.e. the condition assumed from the very beginning. Another condition of applicability of Eq. (**) is that the density n of particles and their temperature T are kept constant (which may require a control mechanism with a response time much shorter than τ.) In addition, just as in the previous problem, the result requires the mean free path to be much longer than the linear size of the orifice: $l >> A^{1/2}$, and the wall thickness to be much smaller than both l and $A^{1/2}$. Note that since the mean free path in a typical gas at ambient conditions is very small (e.g., ~70 nm in the air), this condition may be fulfilled only for extremely small orifices. However, it is typically well satisfied in the so-called *molecular ovens* used for emitting ultra-pure atomic and molecular beams into high vacuum (in particular, for epitaxial thin-film deposition[120] and isotope separation), where Eq. (**) serves as the baseline formula for the effusion rate.[121]

Problem 6.11. Use simple kinematic arguments to estimate:

(i) the diffusion coefficient D,
(ii) the thermal conductivity κ, and
(iii) the *shear viscosity* η,

of a nearly ideal classical gas with mean free path l. Compare the result for D with that calculated in Sec. 6.3 of the lecture notes from the Boltzmann-RTA equation.

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[119] Note that the same result (**) may be also obtained in a slightly different way (actually, used in most textbooks), by considering what fraction f of particles, in an elementary volume $d^3r = r^2drd\Omega$, with $r = vt$ and hence $dr = vdt$, has velocities directed toward the orifice (the answer is $f = A\cos\theta/4\pi r^2$), and then integrating the resulting particle number $dN = nfdr^3$ over all velocities in spherical coordinates, with $d^3v = v^2dvd\Omega$. Let me leave the completion of this approach for the reader as a simple but useful additional exercise.

[120] See, e.g., Chapters 6 and 7 in D. Smith, *Thin-Film Deposition*, McGraw-Hill, 1995.

[121] The fact that this rate is proportional to $1/m^{1/2}$ has a special name: the *Graham law*. This law is of particular practical importance for isotope separation, especially because it is valid for the diffusion coefficient as well – see the next problem.

Hint: In fluid dynamics, the shear viscosity (frequently called simply "viscosity") is defined as the coefficient η in the following relation:

$$\frac{d\mathscr{F}_{j'}}{dA_j} = \eta \frac{\partial v_{j'}}{\partial r_j}.$$

Here $d\mathscr{F}_{j'}$ is the j' th Cartesian component of the elementary tangential force exerted by one part of a fluid, separated from its counterpart by an imaginary plane normal to some direction $\mathbf{n}_j$ (with $j \neq j'$, and hence $\mathbf{n}_j \perp \mathbf{n}_{j'}$), dA_j is the elementary area of this interface, and $\mathbf{v}(\mathbf{r})$ is the fluid velocity's distribution.[122]

Solution: The common approach to the calculation of all these kinetic coefficients is to consider, just as mentioned in the *Hint*, an imaginary plane interface normal to some axis $\mathbf{n}_j$. Next, let us consider a subset of particles, with the number dn per unit volume, whose velocities in the direction normal to the interface are within any of two small intervals dv_j around some values $\pm v_j$. If the gas is in equilibrium, then during a small time interval dt, an elementary area dA_j of the interface will be crossed only by the particles with the initial distances $\Delta r_j < |v_j| dt$ from it – half of them in the direction deemed positive (the plus index below), and half in the opposite one (the minus index):

$$dN_\pm = \frac{dn}{2} \left| v_j \right| dt\, dA_j . \qquad (*)$$

This expression is the baseline for all the particular required estimates.

(i) According to Fick's law (see Eqs. (5.118) and (6.48) of the lecture notes), the diffusion coefficient D may be defined via the linear relation between the density $\mathbf{j}_n$ of the particle flow and the small density gradient that causes this flow – the diffusion:

$$\mathbf{j}_n = -D\nabla n .$$

This means that the net rate of the particle flow through area dA_j of our imaginary interface is

$$dI_n \equiv \left(\mathbf{j}_n\right)_j dA_j = -D\frac{\partial n}{\partial r_j} dA_j . \qquad (**)$$

For our model, the left-hand side of this relation is just the sum of the fractions $(dN_+ - dN_-)/dt$ for particles within all possible intervals dv_j. With the direct substitution of Eq. (*) into Eq. (**), we would get zero result, but at a non-zero gradient of n, and hence dn, we have to modify the former relation as

$$\frac{dN_\pm}{dA_j dt} = \left| v_j \right| \frac{dn(\mathbf{r}_\mp)}{2},$$

where $\mathbf{r}_\pm$ are the two points in which a particle crossing the interface had its last scattering events (and hence, on average, equilibrated with other particles at this location). Considering the gradient $\partial(dn)/\partial r_j$ sufficiently small on the scale of dn/l, where l is the mean free path, we may Taylor-expand dn in small $(\mathbf{r}_\mp)_j$ (referred to the point where the particle crosses the interface), and limit the expansion to two leading terms:

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[122] See, e.g., CM Eq. (8.56). Note the difference between the shear viscosity coefficient η considered in this problem and the drag coefficient η whose calculation was the task of Problem 3.2. Despite the similar (traditional) notation, and belonging to the same realm (kinematic friction), these coefficients have different definitions and even different dimensionalities.

$$\frac{dN_{\pm}}{dA_j dt} = |\, v_j \,| \frac{1}{2}\left[dn + \frac{\partial(dn)}{\partial r_j}(\mathbf{r}_{\mp})_j \right].$$

Subtracting these two expressions from each other, we get

$$\frac{dN_{+} - dN_{-}}{dA_j dt} = -|v_j| \frac{1}{2} \frac{\partial(dn)}{\partial r_j} |\, r_j \,|,$$

where r_j is the j^{th} Cartesian component of the vector $\mathbf{r} \equiv \mathbf{r}_+ - \mathbf{r}_-$. Though, nominally, $\mathbf{r}_\pm$ are the positions of the last scattering events of two different particles (before each of them crosses the interface), $\mathbf{r}$ should have *approximately* the same statistics as the vector of a single particle's shift between its two sequential scattering events.[123] By defining τ as the statistical average of the time *before* and hence *after* a scattering event (cf. the classical derivation of the Drude formula in Sec. 6.2.), the j^{th} Cartesian component of such a shift is $2\tau |\, v_j \,|$. Hence for the average over all particles of our subset, we may write

$$\left\langle |v_j||r_j| \right\rangle \approx 2\tau \left\langle v_j^2 \right\rangle, \qquad \text{i.e.} \frac{\left\langle dN_{+} - dN_{-} \right\rangle}{dA_j dt} = -\tau \left\langle v_j^2 \right\rangle \frac{\partial(dn)}{\partial r_j} \ .$$

Now let us sum up $(dN_+ - dN_-)$ over all intervals dv_j. Assuming τ to be independent of the particle energy (as it is in the Boltzmann-RTA approximation),[124] the sum of all products $\tau\langle v_j^2\rangle dn$ yields $\tau\langle v_j^2\rangle n$, where n is the total particle density, while the velocity averaging is over all particles. Due to the gas' isotropy, the last average is just $\langle v^2\rangle/3$, and we get

$$\frac{dI_n}{dA_j} \approx -\frac{\tau}{3}\left\langle v^2 \right\rangle \frac{\partial n}{\partial r_j},$$

so the comparison with Eq. (**) yields[125]

$$D \approx \frac{1}{3}\left\langle v^2 \right\rangle \tau = \frac{1}{3}\left\langle v^2 \right\rangle^{1/2} l\,,$$

where, at the last step, the mean free path' definition (6.51c) was used. This estimate agrees with Eq. (6.51b) of the lecture notes. However, given the approximate treatment of the collision statistics in this analysis, and the phenomenological nature of Eq. (6.17) itself, this exact agreement of the numerical coefficients cannot be considered much more than a lucky coincidence.

(ii) Now let us use the same approach to calculate the thermal conductivity coefficient κ, which may be defined by Eq. (6.105) of the lecture notes. Let us assume that the chemical potential μ of the gas and its electrochemical potential μ' are constant;[126] then this relation is simply

$$\mathbf{j}_{\text{h}} = -\kappa \nabla T, \qquad \text{i.e. } \left(\mathbf{j}_{\text{h}}\right)_j = -\kappa \frac{\partial T}{\partial r_j}, \tag{***}$$

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[123] This assumption is perhaps the largest source of imprecision of the numerical coefficients in the forthcoming estimates.

[124] As the solution of the next problem will show, in many cases this is not a very good assumption and may cost us one more numerical factor of the order of 1.

[125] Note that since $\langle v^2\rangle = 3T/m$, this result means that $D \propto m^{-1/2}$, i.e. the diffusion obeys the same Graham law as the effusion – see the solution of Problem 10.

[126] Per the definition (6.40) of μ', for a gas of charge-free particles, $\mu' = \mu$, so these two conditions are equivalent.

where $\mathbf{j}_\text{h}$ is the energy flow density. In our simple model, we may calculate the j^th Cartesian component of the density as the sum (over all velocities v_j) of the contributions[127]

$$\frac{dN_+\varepsilon(\mathbf{r}_-)-dN_-\varepsilon(\mathbf{r}_-)}{dA_j dt},$$

where $dN_\pm$ now may be taken directly from Eq. (*) but the difference of the particle energies ε on the opposite sides of the interface, due to the gradient $\partial T/\partial r_j$, has to be taken into account. If the gradient is sufficiently small (much smaller than T/l), we may treat the energy just as the particle concentration in the previous task, getting

$$\varepsilon(\mathbf{r}_-)-\varepsilon(\mathbf{r}_+)\approx-\frac{\partial\varepsilon}{\partial r_j}r_j\,.$$

Now the summation of contributions from all particles, again with the assumption of a constant τ, yields

$$\left(\mathbf{j}_\text{h}\right)_j=-n\tau\left\langle v_j^2\frac{\partial\varepsilon}{\partial r_j}\right\rangle.$$

Though one of three Cartesian components of the particle's kinetic energy $\varepsilon = mv^2/2$ is correlated with v_j^2, for a simple estimate, we may ignore this correlation, by taking

$$\left(\mathbf{j}_\text{h}\right)_j\approx-n\tau\left\langle v_j^2\right\rangle\frac{\partial\langle\varepsilon\rangle}{\partial r_j}=-\frac{n}{3}\tau\left\langle v^2\right\rangle c_V\frac{\partial T}{\partial r_j},$$

where $c_V \equiv \partial\langle\varepsilon\rangle/\partial T$ is the specific heat per particle.[128] Now the comparison with Eq. (***) yields

$$\kappa\approx\frac{\tau}{3}n\left\langle v^2\right\rangle c_V=\frac{n}{3}\left\langle v^2\right\rangle^{1/2}c_V l\,.$$

A comparison of this result with that following from the Boltzmann-RTA equation will be the subject of Problem 13 below.

(iii) In statistical physics, the velocity $\mathbf{v}$ in the definition of η, given in the *Hint*, should be understood as the statistical average $\langle\mathbf{v}\rangle$ of the particle velocities:

$$\frac{d\mathscr{F}_{j'}}{dA_j}=\eta\frac{\partial\left\langle v_{j'}\right\rangle}{\partial r_j},\tag{****}$$

where $d\mathscr{F}$ is the *average* force exerted by the "upper" part of the gas (with $r_j > 0$) upon its "lower" counterpart. (The force exerted upon the "upper" part is evidently $-d\mathscr{F}$.) In our model, each particle of the subsets dN_+ and dN_- carries, through the interface, a tangential mechanical momentum with the j'^th component equal to $mv_{j'}$. As a result, the contribution of a subset of dn molecules, with the velocities close to some $\mathbf{v}$, to the net momentum transferred across the area $dA_{j'}$ during the time interval dt in the positive direction, i.e. to $-d\mathscr{F}_{j'}$, may be calculated as

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[127] Comparing this expression with Eq. (6.104) of the lecture notes, please remember that our current calculation is for μ = const, so the terms, proportional to the chemical potential on both sides of the interface, cancel.

[128] As a reminder, according to the equipartition theorem, for free classical particles with negligible thermal excitation of their internal degrees of freedom, i.e. with three half-degrees of freedom, $c_V = 3/2$ – see Eq. (3.31).

$$-d\,\frac{d\mathscr{F}_j}{dA_{j'}} = dN_+ m\langle v_{j'}(\mathbf{r}_-)\rangle - dN_- m\langle v_{j'}(\mathbf{r}_+)\rangle = \frac{dn}{2}\left|v_j\right| dt\; m\langle v_{j'}(\mathbf{r}_-) - v_{j'}(\mathbf{r}_+)\rangle .$$

Now acting just as in the previous tasks of this problem, in the presence of a small gradient $\partial\langle v_{j'}\rangle/\partial r_j$, we may write

$$v_{j'}(\mathbf{r}_-) - v_{j'}(\mathbf{r}_+) \approx -\frac{\partial\langle v_{j'}\rangle}{\partial r_j} r_j .$$

so the summation over all particles gives[129]

$$\frac{d\mathscr{F}_j}{dA_{j'}} \approx \frac{\tau}{3} n\langle v^2\rangle m \frac{\partial\langle v_j\rangle}{\partial r_{j'}} .$$

Comparing this expression with Eq. (****), we get the following estimate of the viscosity coefficient:

$$\eta \approx \frac{\tau}{3} n\langle v^2\rangle m = \frac{n}{3}\langle v^2\rangle^{1/2} ml .$$

<u>Problem 6.12</u>. Use simple kinematic arguments to relate the mean free path l in a nearly ideal classical gas to the full cross-section σ of mutual scattering of its particles.[130] Then use the result to express the thermal conductivity and the viscosity coefficient estimates made in the previous problem, in terms of σ.

Solution: Let us first consider the scattering of a uniform, parallel flux of particles by a single immobile scattering center. By definition,[131] its full cross-section is

$$\sigma \equiv \frac{\text{average number of scattered particles}}{\text{average number of incident particles per unit area}} .$$

In a medium with a relatively low number $n << \sigma^{-3/2}$ of similar scattering centers per unit volume, the scattering events may be considered as independent. Let us consider a plane slab of area A and a small thickness dx, singled out inside such a medium. The average number of scatterers in it is $nAdx$, so the total scattering area, as seen by the incident particles propagating along the x-axis, is $\sigma nAdx$. Due to the assumed scattering event independence, the average fraction of the particles scattered by all these centers is $(\sigma nAdx)/A \equiv \sigma ndx$. This means that the flux j_n of still-unscattered particles is reduced, at the small distance dx, by $j_n\sigma ndx$, giving the following law of its decay along the propagation axis:

$$\frac{\partial j_n}{\partial x} = -\sigma n j_n .$$

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[129] Note that here, the factoring of the averages is more "clean" (less approximate) than in the previous task, because the two Cartesian components of the velocity, v_j and $v_{j'}$, are independent.

[130] I am sorry to use the same letter for the cross-section as for the electric Ohmic conductivity. (Both notations are very traditional.) Let me hope this will not lead to confusion; the conductivity is not discussed in this problem.

[131] This definition is common for particle scattering description in classical and quantum mechanics, and maps onto a similar definition at wave scattering – see, e.g., CM (3.70), EM Eq. (8.39), and QM Eq. (3.59).

On the other hand, the same decay of the incident flux may be described in the language of the relaxation-time approximation – see Eq. (6.17) of the lecture notes. In the picture where the initial flux of the particles had been initially uniform over the volume, and then the scattering was suddenly turned on everywhere, it describes a space-uniform decay of the non-equilibrium part of the probability density w, and all its functionals including j_n, with the time constant τ:

$$\frac{\partial j_n}{\partial t} = -\frac{j_n}{\tau}.$$

The comparison of these two expressions for the same small change dj_n yields the following relation between the passed distance dx in the first case and the passed time dt in the second case

$$\frac{dx}{dt} = \frac{1}{\sigma n \tau}. \qquad (*)$$

If the incident particles move in the same direction with the same velocity v amidst immobile scattering centers, then we may also write $dx/dt = v$. If the particle velocities differ in direction and magnitude, but the scattering centers are still immobile, it is fairer to replace v in this relation with its r.m.s. value (3.9): $dx/dt \rightarrow \langle v^2\rangle^{1/2} = (3T/m)^{1/2}$. However, in the gas where the scatterers are similar particles and move with similar velocities, a better estimate of dx/dt is given by the r.m.s. value of the relative velocity $\mathbf{v}_{\text{rel}} \equiv \mathbf{v}_1 - \mathbf{v}_2$ of the mutually scattering particles. This value may be readily calculated assuming the independence of the directions of the vectors $\mathbf{v}_{1,2}$:

$$\langle v_{\text{rel}}^2 \rangle \equiv \langle (\mathbf{v}_1 - \mathbf{v}_2)^2 \rangle = \langle v_1^2 + v_2^2 - 2\mathbf{v}_1 \cdot \mathbf{v}_2 \rangle = 2\langle v^2 \rangle, \qquad \text{so} \quad \langle v_{\text{rel}}^2 \rangle^{1/2} = \sqrt{2}\langle v^2 \rangle^{1/2},$$

where v without an index refers to the velocity of a single particle in an immobile (“lab”) reference frame. In this case, we may write

$$\frac{dx}{dt} \approx \sqrt{2}\langle v^2 \rangle^{1/2},$$

and comparing this estimate with Eq. (*), get the approximate equality

$$\sqrt{2}\sigma n \tau \langle v^2 \rangle^{1/2} \approx 1.$$

Now using the mean free pass’ definition given by Eq. (6.51b) of the lecture notes, $l \equiv \langle v^2\rangle^{1/2}\tau$, we finally get

$$l \approx \frac{1}{\sqrt{2}n\sigma}, \qquad \text{i.e. } nl = \frac{1}{\sqrt{2}\sigma}. \qquad (**)$$

For an approximate description of collisions between molecules, they may be treated as hard spheres with an effective diameter d_{ef} defined as the smallest impact parameter at which the mutual scattering may be ignored. (This is essentially the hardball model that was discussed in Sec. 3.5 of the lecture notes, with $d_{\text{ef}} \equiv 2r_0$ – see Fig. 3.7.[132]) In this approximation,

$$\sigma = \pi(2r_0)^2 = \pi d_{\text{ef}}^2, \qquad \text{i.e. } l = \frac{1}{\sqrt{2}\pi n d_{\text{ef}}^2}.$$

---

[132] Rather confusingly, it is d_{ef} (rather than r_0) what is often called the *van der Waals radius* of the particle.

For many molecules, d_{ef} is virtually constant within a broad range of kinetic energies ε; in this case, Eq. (**) shows that l is temperature-independent, while the relaxation time τ is not:

$$\tau = l\left\langle v^2\right\rangle^{-1/2} \propto T^{-1/2}.$$

This means, in particular, that the constant-τ approximation used in most of Chapter 6 of the lecture notes cannot work well in this case. Note, however, that this scaling is valid only for a classical gas *and* only within the hardball model.[133]

Now returning to the estimates made in the solution of the previous problem,

$$\kappa \approx \frac{1}{3}n\left\langle v^2\right\rangle^{1/2} c_V l, \qquad \eta \approx \frac{1}{3}n\left\langle v^2\right\rangle^{1/2} ml,$$

we may use Eq. (**) to rewrite them as

$$\kappa \approx \frac{1}{3\sqrt{2}}\left\langle v^2\right\rangle^{1/2}\frac{c_V}{\sigma}, \qquad \eta \approx \frac{1}{3\sqrt{2}}\left\langle v^2\right\rangle^{1/2}\frac{m}{\sigma}. \qquad (***)$$

Note that in view of the approximations used at the derivation of these formulas, it would be naïve to expect them to give quantitative agreement with experiment. A more important role of Eqs. (***) for applications is to give the approximate functional dependence of the kinetic parameters on temperature ($\kappa, \eta \propto T^{1/2}$), and especially to explain their virtual independence of the particle density n. Indeed, since for nearly ideal gases, with their relatively small particle density $n \equiv N/V << \sigma^{-3/2}$, σ is independent of the gas density, so are the heat conductivity and the viscosity coefficient. Note also that somewhat counter-intuitively, the second of Eqs. (***) predicts the viscosity of such gases to grow with temperature (due to the growth of $\langle v^2\rangle \propto T$), and experiment confirms this conclusion. Even more interestingly, for most gases this trend (i.e. a *drop* of η at cooling) continues for a while even beyond the gas condensation point, i.e. in the liquid state of the substance – only to be replaced with the viscosity's rapid (exponential) *increase* as the temperature approaches the liquid's freezing point.

Problem 6.13. Use the Boltzmann-RTA equation to calculate the thermal conductivity of a nearly ideal classical gas, measured in conditions when the applied thermal gradient does not create a net particle flow. Compare the result with that following from the simple kinetic arguments (Problem 11).

Solution: For a non-degenerate gas, the condition specified in the assignment should be taken very seriously. Indeed, let us first forget about it for a minute and calculate κ directly from Eq. (6.107) of the lecture notes:

$$\kappa = \frac{g\tau}{(2\pi\hbar)^3}\frac{4\pi}{3}\int_0^\infty \left(8m\varepsilon^3\right)^{1/2}\frac{(\varepsilon-\mu)^2}{T}\left[-\frac{\partial\langle N(\varepsilon)\rangle}{\partial\varepsilon}\right]d\varepsilon. \qquad (*)$$

For a classical gas, we may use the high-temperature limit of Eqs. (2.115) and (2.118):

$$\langle N(\varepsilon)\rangle = \exp\left\{\frac{\mu-\varepsilon}{T}\right\},$$

---

[133] As perhaps the most important counter-example, at the so-called *Rutherford scattering* of charged particles with the Coulomb interaction $U \propto 1/r$, the total cross-section σ is infinite, at least in the limit $n \to 0$ – see, e.g., CM Eq. (3.73) and the solution of QM Problem 3.8.

giving, in particular:

$$-\frac{\partial\langle N(\varepsilon)\rangle}{\partial\varepsilon}=\frac{1}{T}\exp\left\{\frac{\mu-\varepsilon}{T}\right\}.$$

This exponentially decaying function of ε provides a fast convergence of the integral in Eq. (*) at energies $\sim T$. Since, according to Eq. (3.34), the factor μ in the classical gas is negative, with $|\mu|$ much larger than T, the factor $(\varepsilon-\mu)^2$ in that formula may be approximated with μ^2. As a result, we get

$$\kappa\approx\frac{g\tau}{(2\pi\hbar)^3}\frac{4\pi}{3}\frac{\mu^2}{T}\int_0^\infty\left(8m\varepsilon^3\right)^{1/2}e^{(\mu-\varepsilon)/T}d\varepsilon .$$

This expression differs from Eq. (6.31) for σ (in the corresponding limit for the function $\langle N(\varepsilon)\rangle$) only by the extra factor μ^2/Tq^2, so we immediately may use Eq. (6.32) to write

$$\kappa\approx\frac{\mu^2}{Tq^2}\sigma=\left(\frac{\mu}{T}\right)^2\frac{n\tau T}{m}. \qquad \text{(WRONG!)} \qquad (**)$$

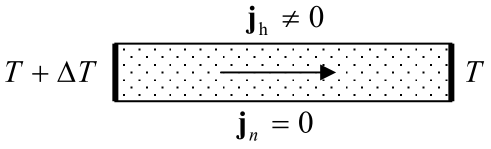
However, in the conditions specified in the assignment, this apparent result is wrong. Indeed, the κ given by Eq. (*) is the coefficient defined by Eq. (6.105); in the absence of the electric field (or just for charge-free particles), i.e. when $\mu'=\mu$, it reads

$$\mathbf{j}_\text{h}=-\frac{\sigma\Pi}{q}\nabla\mu-\kappa\nabla T\equiv-\frac{\sigma\mathcal{S}T}{q}\nabla\mu-\kappa\nabla T, \qquad (***)$$

where the last form is obtained by using Eq. (6.108). This relation is reduced to the Fourier law (6.114),

$$\mathbf{j}_\text{h}=-\kappa\nabla T,$$

only if $\nabla\mu=0$. However, for a gas of uncharged particles, this condition is hard to implement in experiment. It is much easier to ensure that the applied temperature gradient does not result in the net particle flow. (For example, we may heat up one end of a long, sealed tube, which is thermally insulated on its lateral sides – see the figure on the right.[134])



In order to analyze this situation, let us rewrite Eq. (6.97), with $\mu'=\mu$, for the particle flow density $\mathbf{j}_n=\mathbf{j}/q$:

$$\mathbf{j}_n=-\frac{\sigma}{q^2}\nabla\mu-\frac{\sigma\mathcal{S}}{q}\nabla T.$$

It shows that in conditions when there is no particle flow, $\mathbf{j}_n=0$, the application of a temperature gradient unavoidably creates a gradient of the chemical potential:[135]

$$\nabla\mu=-q\mathcal{S}\nabla T.$$

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[134] For a gas of charged particles, for example of electrons in a metal, this condition, $\mathbf{j}_n\equiv\mathbf{j}/q=0$, may be imposed simply by disconnecting a long sample, made of this metal, from an external conducting electric circuit – see, e.g., Fig. 6.12 of the lecture notes.

[135] Note that this is essentially Eq. (6.102), only with $\mu=\mu'$.

Plugging this expression into Eq. (***), we see that the effective thermal conductance differs from the κ given by Eq. (*):

$$\mathbf{j}_{\text{h}} = -\kappa_{\text{ef}}\nabla T, \quad \text{with } \kappa_{\text{ef}} = \kappa - \sigma\mathcal{S}^2 T \leq \kappa, \quad \text{for } \mathbf{j}_n = 0.$$

Per Eqs. (6.101) and (6.110), valid at $T << \varepsilon_{\text{F}}$, for a degenerate Fermi gas, this thermal conductivity reduction is of the order of $\kappa(T/\varepsilon_{\text{F}})^2$, i.e. negligible, so in this case, Eq. (6.109) and hence the Wiedemann-Franz law (6.110) are valid regardless of the measurement conditions. However, for a classical gas, the situation is different. Indeed, by plugging the corresponding formula for $[-\partial\langle N(\varepsilon)/\partial\varepsilon]$ (see above) into Eq. (6.98), and working out two simple integrals,[136] we readily get[137]

$$\mathcal{S} = \frac{1}{q}\left(-\frac{\mu}{T} + \frac{5}{2}\right), \qquad \text{so } \sigma\mathcal{S}^2 T = \frac{n\tau T}{m}\left(-\frac{\mu}{T} + \frac{5}{2}\right)^2.$$

Comparing this expression with Eq. (**), we see that the leading term of the correction, proportional to $(\mu/T)^2 >> 1$, exactly cancels with the crude approximation's result (**). Hence, this "seed" thermal conductivity κ should be re-calculated from Eq. (*) more carefully, by keeping all three terms of the sum $(\varepsilon - \mu)^2 = \varepsilon^2 - 2\varepsilon\mu + \mu^2$. A straightforward calculation,[138] yields the following finite result:

$$\kappa_{\text{ef}} = \frac{5}{2}\frac{n\tau T}{m}, \qquad (****)$$

which is significantly lower than the κ given by Eq. (**).

In order to compare this result with the estimate obtained in the solution of Problem 11, let us rewrite the latter by using Eq. (3.9), $\langle v^2\rangle = 3T/m$:[139]

$$\kappa \approx c_V \frac{n\tau T}{m}.$$

Now we should take into account that at the derivation of Eqs. (6.106)-(6.107) from Eq. (6.104) in Sec. 6.5, the particle's energy ε was associated with its kinetic energy only, thus neglecting the possible thermal excitation of its internal degrees of freedom. Thus for a fair comparison, we should take c_V equal to the corresponding value 3/2, so this estimate becomes

$$\kappa \approx \frac{3}{2}\frac{n\tau T}{m},$$

We see that this result differs from Eq. (****) only by a numerical factor of $(5/2)/(3/2) \approx 1.7$; as was discussed in the model solution of the previous problem, this is not too bad for such a crude estimate, even without a correction for the larger heat capacity of the diatomic nitrogen molecule: $c_V = 5/2$ instead

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[136] They are both of the type MA Eq. (6.7a), one with $s = 7/2$ and the other one with $s = 5/2$ – see also MA Eq. (6.7e).

[137] It is instructive to compare this expression with Eq. (6.101) of the lecture notes, which is valid in the opposite, degenerate limit $T << \mu$.

[138] It involves one more integral of the same type MA Eq. (6.7a), with $s = 9/2$.

[139] Note that at its derivation we have ignored the particle flow, so the comparison of the resulting κ with κ_{ef} is more or less fair – at least within the framework of rather crude assumptions made at the derivation.

of $c_V = 3/2$ implied by our theory. (Let me leave the analysis of how such correction should be made, for the reader's additional exercise.)

Nevertheless, we should remember that, as was noted in the lecture notes, the Boltzmann-RTA equation may give unreliable numerical factors in its results for classical gases, because its assumption of an energy-independent scattering time τ is frequently too crude for the broad distribution of particle energies in such systems.

Problem 6.14. Use the Boltzmann-RTA equation to calculate the shear viscosity of a nearly ideal gas. Spell out the result in the classical limit, and compare it with the estimate made in the solution of Problem 11.

Solution: Per Problem 11, the shear viscosity η of a fluid is defined by the relation

$$\frac{d\mathscr{F}_{j'}}{dA_j} = \eta \frac{\partial \langle v_{j'} \rangle}{\partial r_j},$$

where $d\mathscr{F}$ is the average force exerted by the "upper" part of the gas (with $\mathbf{r}\cdot\mathbf{n}_j > 0$) on its "lower" counterpart. As was discussed in the solution of that problem, in a nearly ideal gas, the equal and opposite force ($-d\mathscr{F}$) exerted on the "upper" part may be calculated as the average momentum being transferred to that part from the "lower" part of the gas, i.e. as

$$-\frac{d\mathscr{F}_{j'}}{dA_j} = \left\langle m v_{j'} \left(d\mathbf{j}_\mathrm{n} \right)_j \right\rangle = m \int v_{j'} v_j w d^3 p, \qquad (*)$$

where $d\mathbf{j}_n = \mathbf{v} w d^3 p$ is the elementary flow of particles with the velocity $\mathbf{v}$ – cf. Eq. (6.26) of the lecture notes. As in other cases discussed in Chapter 6, the unperturbed, isotropic part w_0 of the probability density w gives zero contribution into such an integral, so instead of w, we may use its small perturbation $\tilde{w}$ created by the average velocity's gradient $\nabla\mathbf{v}$. From the Boltzmann-RTA equation (6.18) with $\partial/\partial t = 0$ and $\mathscr{F} = 0$,[140] we get[141]

$$\tilde{w} = -\tau\, \mathbf{v} \cdot \nabla w_0 = -\tau \frac{\partial w_0}{\partial \varepsilon} \mathbf{v} \cdot \nabla \varepsilon,$$

where ε is the internal energy of the particle – in our case of free particles, the kinetic energy due to deviations of their particular velocities from that of the collective motion of the gas:

$$\varepsilon = \frac{m \left(\mathbf{v} - \langle \mathbf{v} \rangle \right)^2}{2}.$$

With the vector $\langle \mathbf{v} \rangle$ directed along the j'th axis and its gradient directed along the jth axis, we may re-write this equality as

$$\varepsilon = \frac{m}{2} \left[v_j^2 + \left(v_{j'} - \langle v_{j'} \rangle \right)^2 + v_{j''}^2 \right], \qquad \text{so} \quad \nabla \varepsilon = -\mathbf{n}_j m \left(v_j - \langle v_{j'} \rangle \right) \frac{\partial \langle v_{j'} \rangle}{\partial r_j}.$$

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[140] In Eq. (6.18), this is the explicit force applied to each particle, not the effective shear force we are calculating.

[141] In contrast to the case of thermal conductance, discussed in Sec. 6.5 of the lecture notes, here we may take $\nabla\mu = 0$ because a velocity gradient in a gas with $\nabla T = 0$ does not create a gradient of the chemical potential.

Now after the differentiation, at the plane of our interest (i.e. at the interface between the "upper" and "lower" parts of the gas), we may take the average gas velocity for the reference, so

$$\nabla\varepsilon = -\mathbf{n}_j m v_j \frac{\partial\langle v_{j'}\rangle}{\partial r_j}, \qquad \text{and} \quad \tilde{w} = m\tau\frac{\partial w_0}{\partial\varepsilon} v_j^2 \frac{\partial\langle v_{j'}\rangle}{\partial r_j}.$$

Plugging this expression into Eq. (*), and then using Eq. (6.19) of the lecture notes, we get

$$\eta = -m^2\tau\int v_j^2 v_{j'}^2 \frac{\partial w_0}{\partial\varepsilon} d^3p = m^2\tau\frac{g}{(2\pi\hbar)^3}\int v_j^2 v_{j'}^2\left[-\frac{\partial\langle N(\varepsilon)\rangle}{\partial\varepsilon}\right]d^3p$$

$$= m^2\tau\frac{g}{(2\pi\hbar)^3}\int_0^\infty\left[-\frac{\partial\langle N(\varepsilon)\rangle}{\partial\varepsilon}\right]p^2dp\oint_{4\pi} v_j^2 v_{j'}^2 d\Omega,$$

where Ω is the solid angle of possible directions of the vector $\mathbf{p}$, and hence of the vector $\mathbf{v} = \mathbf{p}/m$. For the angular integration, we may use the spherical coordinates with the polar z-axis directed, for example, along $\mathbf{n}_j$ and the x-axis directed along $\mathbf{n}_{j'}$, so $v_j = v\cos\theta$, $v_{j'} = v\sin\theta\cos\varphi$, and the integral is

$$\oint_{4\pi} v_j^2 v_{j'}^2 d\Omega = v^4\int_0^\pi \cos^2\theta\sin^2\theta\sin\theta d\theta\int_0^{2\pi}\cos^2\varphi d\varphi = \frac{4\pi}{15}v^4.$$

With the same substitutions as at the derivation of Eq. (6.30), our result reduces to a 1D integral over the particle energy $\varepsilon = p^2/2m$ (so that $p = (2m\varepsilon)^{1/2}$, $dp = (m/2\varepsilon)^{1/2}$):

$$\eta = m^2\tau\frac{g}{(2\pi\hbar)^3}\frac{4\pi}{15}\int_0^\infty\left[-\frac{\partial\langle N(\varepsilon)\rangle}{\partial\varepsilon}\right]v^4p^2dp = m^2\tau\frac{g}{(2\pi\hbar)^3}\frac{4\pi}{15}\left(\frac{32}{m}\right)^{1/2}\int_0^\infty\left[-\frac{\partial\langle N(\varepsilon)\rangle}{\partial\varepsilon}\right]\varepsilon^{5/2}d\varepsilon.$$

In the classical gas limit, both quantum distributions (3.38) are reduced to

$$\langle N(\varepsilon)\rangle = \exp\left\{\frac{\mu-\varepsilon}{T}\right\}, \qquad \text{so} \quad -\frac{\partial\langle N(\varepsilon)\rangle}{\partial\varepsilon} = \frac{1}{T}\exp\left\{\frac{\mu-\varepsilon}{T}\right\},$$

and we may spell our result as

$$\eta = m^2\tau\frac{g}{(2\pi\hbar)^3}\frac{4\pi}{15}\left(\frac{32}{m}\right)^{1/2}\frac{1}{T}\exp\left\{\frac{\mu}{T}\right\}\int_0^\infty\exp\left\{-\frac{\varepsilon}{T}\right\}\varepsilon^{5/2}d\varepsilon$$

$$\equiv m^2\tau\frac{g}{(2\pi\hbar)^3}\frac{4\pi}{15}\left(\frac{32}{m}\right)^{1/2}\frac{1}{T}\exp\left\{\frac{\mu}{T}\right\}T^{7/2}\int_0^\infty\exp\{-\xi\}\xi^{5/2}d\xi.$$

The last integral[142] is equal to $\Gamma(7/2) = (15/8)\pi^{1/2}$, and using Eq. (3.32) of the lecture notes in the form

$$n = \frac{g}{(2\pi\hbar)^3}(2\pi mT)^{3/2}\exp\left\{\frac{\mu}{T}\right\},$$

we, finally, get simply

$$\eta = n\tau T.$$

---

[142] See, e.g., MA Eqs. (6.7a) and (6.7e).

However, taking into account Eq. (3.9), $\langle v^2 \rangle = 3T/m$, this is exactly the estimate obtained in the solution of Problem 11:

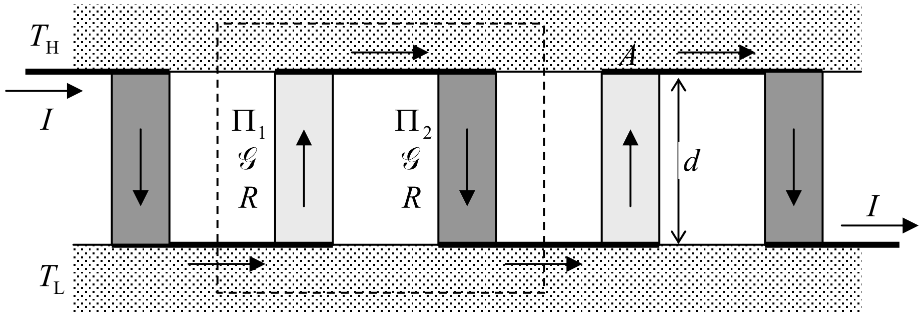
$$\eta = \frac{\tau}{3} n \left\langle v^2 \right\rangle m = n \tau T ,$$

even though, in view of the rather crude approximations made at its derivation, the similarity of the numerical coefficients should not be understood as much more than a lucky coincidence.

Problem 6.15. Use a simple model of a thermoelectric refrigerator ("cooler") based on the Peltier effect to analyze its efficiency. In particular, explain why the fraction ZT given by Eq. (6.113) of the lecture notes may be used as the figure-of-merit of materials for such devices.

Solution: For a simple analysis, let us assume that the temperature difference $\Delta T \equiv T_H - T_L$ supported by the cooler is much smaller than the absolute temperature $T \equiv T_L \approx T_H$ – as it is in most practical thermoelectric systems. Due to this assumption, we may neglect the temperature-induced variations of the transport coefficients Π, σ, and κ in the device.

Let us also neglect the temperature drop across the voltage source in the thermoelectric loop – see Fig. 6.13 of the lecture notes – just as this was done at the derivation of the key Eq. (6.112). In practice, this drop is minimal because a typical cooler comprises a battery of many similar thermoelectric couples connected in parallel for the heat flow but in series for the electric current – see the figure on the right. As the figure shows, each of these couples operates just as the loop shown in Fig. 6.13, and it is sufficient to carry out an analysis of only one of them – say, of the couple inside the dashed-line rectangle.



As was discussed in Sec. 1.4, the cooler's efficiency may be most adequately quantified with its coefficient of performance (COP) defined by Eq. (1.69). For a continuously running (rather than the cyclic) system, it is more natural to count both Q_L and $\mathscr{W}$ in that formula per unit time, and hence rewrite that definition as

$$\text{COP} \equiv -\frac{\mathscr{P}_L}{\mathscr{P}_e}, \qquad (*)$$

where $\mathscr{P}_L$ is the power flow *into* the low-temperature load, and $\mathscr{P}_e$ is the electric power used to run the device. The numerator of this fraction may be calculated as the difference between the sum of two undesirable (positive) heat flows: the flow from the hot plate to the cold one due to the unavoidable thermal conductivity of $\mathscr{G}$ of each element of the couple, and a half of the Joule heat generated in each element,[143] and the beneficial (negative) Peltier-effect power (6.112), with the Peltier coefficients given by Eq. (6.108):

$$\mathscr{P}_L = 2\mathscr{G}\Delta T + I^2 R - \left(\mathscr{S}_1 - \mathscr{S}_2\right) T I.$$

---

[143] The second half of the heat flows into the hot bath.

Here $\mathscr{G}$ and R are, respectively, the thermal conductance and the electric resistance of each element.[144] In the denominator of the fraction (*), we have to account not only for the Ohmic voltage drop $V = IR$ on each element but also for the thermo e.m.f. $\mathscr{V} = \Delta T(\mathscr{S}_1 - \mathscr{S}_2)$ on the thermocouple as a whole due to the Seebeck effect – see Eq. (6.103) of the lecture notes:

$$\mathscr{P}_\text{e} = 2IV + I\mathscr{V} = 2I^2R + I\Delta T(\mathscr{S}_1 - \mathscr{S}_2).$$

Hence, in our model,

$$\text{COP} = \frac{-2\mathscr{G}\Delta T - I^2R + (\mathscr{S}_1 - \mathscr{S}_2)TI}{2I^2R + I\Delta T(\mathscr{S}_1 - \mathscr{S}_2)} \equiv \frac{T}{\Delta T}\,\frac{-1/\text{ZT} - (\Delta T/2T)\xi^2 + \xi}{\xi^2 + \xi}, \qquad (*)$$

where

$$\text{ZT} \equiv \frac{(\mathscr{S}_1 - \mathscr{S}_2)^2}{4\mathscr{G}R}T, \qquad (**)$$

and $\xi \equiv 2RI/(\mathscr{S}_1 - \mathscr{S}_2)\Delta T$ is the normalized current.

This result shows that the COP depends on the device parameters only in the combination ZT. In most practical implementations, two materials of the couple are based on the same semiconductor, but one is *p*-doped and another is *n*-doped. As Eq. (6.98) shows, this makes their Seebeck coefficient signs opposite. A popular choice of dopant concentrations is to make $|\mathscr{S}_1| \approx |\mathscr{S}_2| \equiv \mathscr{S}$, so $|\mathscr{S}_1 - \mathscr{S}_2| \approx 2\mathscr{S}$. Also, if the element's material is uniform, the product $\mathscr{G}R$ is equal to κ/σ independently of the element's geometry.[145] In this case, Eq. (**) is reduced to Eq. (6.113) of the lecture notes.

As the final form of Eq. (*) shows, if ZT is much larger than 1, the second fraction may be made close to 1 by taking the current relatively small ($\xi << 1$), so the COP may approach the front factor $T/\Delta T$, in which we may readily recognize the Carnot value (1.70):

$$(\text{COP})_\text{Carnot} = \frac{T_\text{L}}{T_\text{H} - T_\text{L}}.$$

However, as was mentioned in Sec. 6.5, practical values of ZT are not too high, and to calculate the maximum value of the COP, Eq. (*) should be optimized over the parameter ξ – in, practice, over the current I driving the cooler. Such optimization is easy in the limit $\Delta T/T \to 0$.[146] In this case, the second term in the numerator of Eq. (*) is negligibly small, so the normalized efficiency

$$r \equiv \frac{\text{COP}}{(\text{COP})_\text{Carnot}} = \frac{\xi - 1/\text{ZT}}{\xi^2 + \xi}.$$

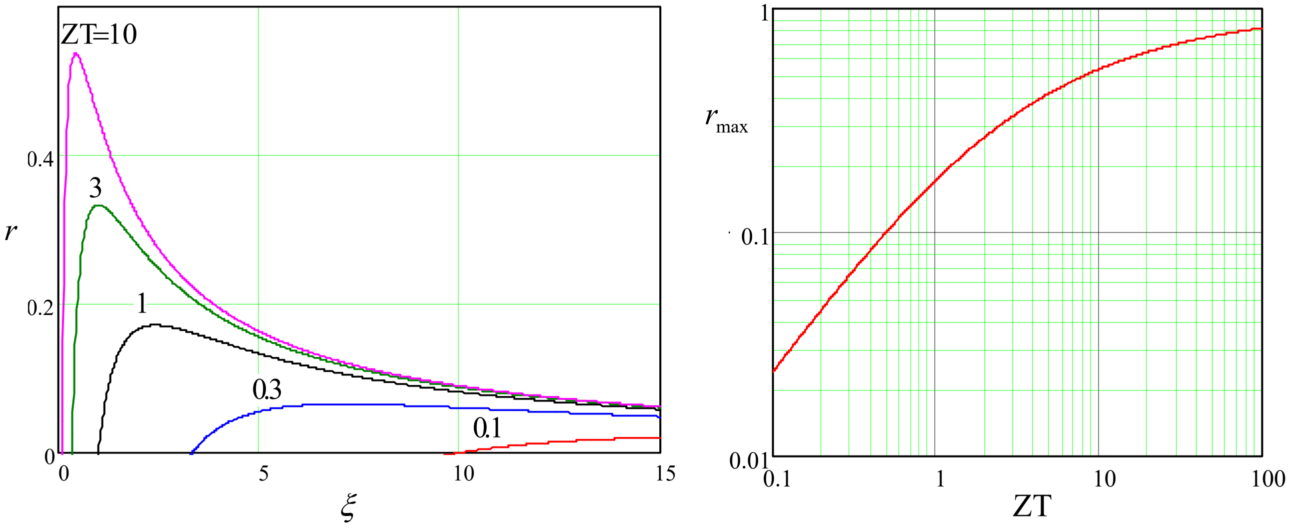
---

[144] In this simple analysis, the values of $\mathscr{G}$ and R are assumed to be similar for both elements of the thermocouple. Additional analysis shows that in the general case, the COP is optimized by taking their products $\mathscr{G}R$ equal to each other; in this case, all the above formulas remain valid.

[145] For example, if the element is a cylinder of length d and the base area A (see the figure above), then $\mathscr{G} = \kappa A/d$ and $R = d/\sigma A$. The reader is challenged to prove the equality $\mathscr{G}R = \kappa/\sigma$ for an arbitrary geometry.

[146] As a reminder, all our analysis is only valid if this fraction is much smaller than 1. Additional analysis shows that the effect of a non-zero (but still small) ratio $\Delta T/T$ on $(\text{COP})_\text{max}$ may be approximately described by either the replacement of the last 1 in the *numerator* of Eq. (***) with the ratio $T_\text{H}/T_\text{L} \approx 1 + \Delta T/T$, or the replacement of the last 1 in its *denominator* with the ratio $T_\text{L}/T_\text{H} \approx 1 - \Delta T/T$.

The left panel of the figure below shows this ratio as a function of ξ for several representative values of ZT.



Note that the COP becomes positive (and hence the device indeed starts working as a cooler) only when the current exceeds a certain value:

$$\xi > \frac{1}{\text{ZT}}, \qquad \text{i.e. when } I > \frac{2\mathscr{G}\Delta T}{(\mathscr{S}_1 - \mathscr{S}_2)T},$$

so the Peltier effect overcomes the unintentional heat leakage from the hot plate to the cold one. The maximum value of the COP ratio,

$$r_{\max} \equiv \frac{(\text{COP})_{\max}}{(\text{COP})_{\text{Carnot}}} = \frac{(ZT+1)^{1/2} - 1}{(ZT+1)^{1/2} + 1}, \qquad (***)$$

is reached at

$$\xi = \xi_{\text{opt}} \equiv \frac{1}{\text{ZT}}\left[(\text{ZT}+1)^{1/2} + 1\right];$$

beyond this value, the COP decreases due to the faster growth of the Joule heat I^2R.

The right panel of the figure above shows the optimized ratio r as a function of ZT, on the appropriate log-log scale. We may see that the state-of-the-art thermoelectric materials with ZT ~ 2 may yield a cooler's efficiency of about one-fourth of the Carnot limit.

<u>Problem 6.16</u>. Use the heat conduction equation (6.119) to calculate the amplitude of day-periodic temperature variations at depth z under the surface of the soil with temperature-independent specific heat c_V and thermal conductivity κ, and negligible thermal expansion. Assume that the incident heat flux is a sinusoidal function of time, with amplitude j_0 per unit area. Estimate the temperature variation amplitude, at depth $z = 1$ m, for a typical dry soil, taking necessary parameters from a reliable source.

Solution: Since the heat conduction equation,

$$\left(\frac{\partial}{\partial t} - D_T \nabla^2\right) T = 0, \qquad \text{where } D_T \equiv \frac{\kappa}{c_V}, \tag{*}$$

is linear, it is natural to look for its solution in the variable-separated form

$$T(\mathbf{r}, t) = \text{Re}\left[T_\omega e^{-\lambda z - i\omega t}\right],$$

where ω is the frequency of the external heat flux. Indeed, by plugging this solution into Eq. (*), we see that it is satisfied, provided that the parameter λ obeys the following characteristic equation:

$$-i\omega - D_T\lambda^2 = 0, \qquad \text{i.e. if } \lambda = \left(\frac{-i\omega}{D_T}\right)^{1/2} \equiv \pm(1-i)\left(\frac{\omega}{2D_T}\right)^{1/2}.$$

By the physical sense of the problem, the temperature variations have to decrease with the depth z, so in the last expression, we need to take the upper sign, giving Re$\lambda > 0$. As a result, our solution takes the form

$$T = \text{Re}\left[A(z) e^{-i(\omega t + \varphi)}\right], \qquad \text{with } A(z) = A(0)\exp\left\{-\left(\frac{\omega}{2D_T}\right)^{1/2} z\right\}, \quad \text{and } \varphi \equiv \left(\frac{\omega}{2D_T}\right)^{1/2} z + \text{const}.$$

Note that it describes not only an exponential decay of the temperature oscillation amplitude $A(z)$ with the depth z but also a simultaneous linear growth of the phase shift φ between these oscillations and their cause – the external heat flux.[147]

What remains is to calculate the constant $A(0)$ by comparing the heat flow at the soil's surface, which follows from our solution:

$$\mathbf{j}_\text{h}\big|_{z=0} = -\kappa\nabla T\big|_{z=0} = -\mathbf{n}_z\kappa\,\text{Re}\left[\left(\frac{-i\omega}{D_T}\right)^{1/2} A(0) e^{-i(\omega t + \varphi)}\right] \equiv -\mathbf{n}_z\kappa\left(\frac{\omega}{D_T}\right)^{1/2} \text{Re}\left[A(0) e^{-i(\omega t + \varphi + \text{const})}\right],$$

with the given external flux $\mathbf{j}_\text{h}(t) = -\mathbf{n}_z j_0 \text{Re}[e^{-i(\omega t + \text{const})}]$. The comparison gives

$$A(0) = \frac{j_0}{\kappa(\omega/D_T)^{1/2}} \equiv j_0\left(\frac{1}{\kappa c_V \omega}\right)^{1/2},$$

so, finally,

$$A(z) = j_0\left(\frac{1}{\kappa c_V\omega}\right)^{1/2} \exp\left\{-\left(\frac{\omega}{2D_T}\right)^{1/2} z\right\} \equiv j_0\left(\frac{1}{\kappa c_V\omega}\right)^{1/2} \exp\left\{-\left(\frac{\omega c_V}{2\kappa}\right)^{1/2} z\right\}. \tag{**}$$

For a realistic numerical estimate of day-periodic variations, we may take j_0 = 0.3 kW/m^2, somewhat smaller than the maximum flux of solar radiation at its normal incidence on the Earth's surface (~1.4 kW/m^2), in order to crudely account for the sunlight reflection and the moderating effect of the atmosphere. For typical dry soil parameters, such an authoritative source as www.engineeringtoolbox.com gives $\kappa \approx$ 1.5 W/m·K, $c_V \equiv C_V/M \approx$ 800 J/kg·K, and $\rho \equiv M/V \approx$ 1,200 kg/m^3, so $c_V \equiv C_V/V = (C_V/M)\times(M/V) \approx 10^6$ J/m^3·K.[148] With these numbers and the frequency ω

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[147] Let me hope that the reader has noticed the complete mathematical similarity between this problem and the standard description of the electromagnetic *skin effect* in conductors – see, e.g., EM Sec. 6.3.

[148] As an exception, I am leaving temperature in SI units, so our answer would be in kelvins as well.

corresponding to the period of 1 day ($\omega \approx 0.727\times10^{-4}$ s^{-1}), for the depth of $z = 1$ m, Eq. (**) yields $A(z) \approx 0.21$ K, much smaller than the amplitude of temperature oscillations at the surface: $A(0) \approx 30$ K. This big ratio, $A(0)/A(z) \sim 150$ (which, in contrast to $A(0)$, is not affected by atmospheric effects and the accepted magnitude of j_0) is natural, taking into account that for our parameters, the characteristic depth of the temperature oscillation decay, $\delta \equiv 1/\text{Re}\lambda = (2\kappa/\omega c_V)^{1/2}$, is about 20 cm. This is why in moderate climates, with the average temperatures well about the water's freezing point, burying water pipes just a few feet below the surface is a reliable way to preserve them from freezing in winter.

Problem 6.17. Use Eq. (6.119) to calculate the time evolution of temperature in the center of a uniform solid sphere of radius R, initially heated to a uniformly distributed temperature T_{ini}, and at $t = 0$ placed into a heat bath that gives the sphere's surface a constant temperature T_0.

Solution: Due to the spherical symmetry of the system, Eq. (6.119),

$$\frac{\partial T}{\partial t} = D_T \nabla^2 T, \qquad \text{with } D_T \equiv \frac{\kappa}{c_V},$$

is reduced to[149]

$$\frac{\partial T}{\partial t} = D_T \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial T}{\partial r}\right).$$

Introducing the temperature's deviation $\tilde{T}(r,t) \equiv T - T_0$ from the boundary value $T(R, t) = T_0$, we may formulate our boundary problem as follows:

$$\frac{\partial \tilde{T}}{\partial t} = D_T \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \tilde{T}}{\partial r}\right), \qquad \text{with } \tilde{T}(R,t) = 0 \quad \text{and } \tilde{T}(r,0) = T_{\text{ini}} - T_0 .$$

Looking for its general solution in the variable-separated form

$$\tilde{T}(r,t) = \sum_n \mathcal{T}_n(t)\mathcal{R}_n(r), \qquad (*)$$

for the n^{th} partial solution, we get

$$\frac{1}{\mathcal{T}_n}\frac{d\mathcal{T}_n}{dt} = D_T \frac{1}{\mathcal{R}_n r^2}\frac{d}{dr}\left(r^2 \frac{d\mathcal{R}_n}{dr}\right) \equiv -\lambda_n ,$$

where λ_n is the variable separation constant. The resulting ordinary differential equation for $\mathcal{T}_n$ is elementary, giving

$$\mathcal{T}_n \propto \exp\{-\lambda_n t\} ,$$

while that for $\mathcal{R}_n$, with the substitution $\mathcal{R}_n(r) = f_n(r)/r$,[150] reduces to the well-known 1D Helmholtz equation,

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[149] If needed, you may consult MA Eq. (10.9) with $\partial/\partial\theta = \partial/\partial\varphi = 0$.

[150] This substitution is frequently used in spherically symmetric problems of other fields of physics as well, especially electrodynamics and quantum mechanics – see, e.g., EM Sec. 8.1, in particular, Eqs. (8.7)-(8.8), and QM Sec. 3.1, in particular Eqs. (3.4)-(3.7).

$$\frac{d^2 f_n}{dr^2} + k_n^2 f_n = 0, \qquad \text{with } k_n^2 \equiv \frac{\lambda_n}{D_T}.$$

This equation, with the boundary conditions $\mathcal{R}_n(0) \neq \infty$ and $\mathcal{R}_n(R) = 0$, i.e. $f_n(0) = f_n(R) = 0$, immediately yields the following eigenfunctions and eigenvalues of the problem:

$$f_n(r) \propto \sin k_n r, \qquad \text{with } k_n = \frac{\pi n}{R}, \quad \lambda_n \equiv D_T k_n^2 = D_T \left(\frac{\pi n}{R}\right)^2,$$

where $n = 1, 2,\ldots$, so the general solution (*) of our boundary problem may be spelled out as

$$\tilde{T}(r,t) = \sum_{n=1}^{\infty} \frac{C_n}{r} \sin\frac{\pi n r}{R} \exp\left\{-n^2 \frac{t}{\tau}\right\}. \qquad (**)$$

Here the constant τ, defined as

$$\tau \equiv \frac{1}{\lambda_1} = \frac{R^2}{\pi^2 D_T} \equiv \frac{R^2 c_V}{\pi^2 \kappa},$$

is the time scale of the thermal relaxation of the sphere, while the expansion coefficients C_n have to be chosen to satisfy the initial condition $\tilde{T}(r,0) = T_{\text{ini}} - T_0$, giving the system of equations

$$\sum_{n=1}^{\infty} \frac{C_n}{r} \sin\frac{\pi n r}{R} = T_{\text{ini}} - T_0, \qquad \text{for } 0 \leq r \leq R.$$

This system may be solved, as usual at the reciprocal Fourier transform, by multiplying both parts of this equation by $r \sin(\pi n' r/R)$, with an arbitrary integer n', and their integration over the interval $[0, R]$. At this integration, all terms with $n' \neq n$ under the sum on the left-hand side vanish due to the eigenfunctions' orthogonality, while the term with $n' = n$ yields $C_n(R/2)$. As a result, we get

$$C_n = \frac{2}{R}(T_{\text{ini}} - T_0)\int_0^R r \sin\frac{\pi n r}{R} dr \equiv 2R(T_{\text{ini}} - T_0)\int_0^1 \sin(\pi n \xi)\, \xi d\xi.$$

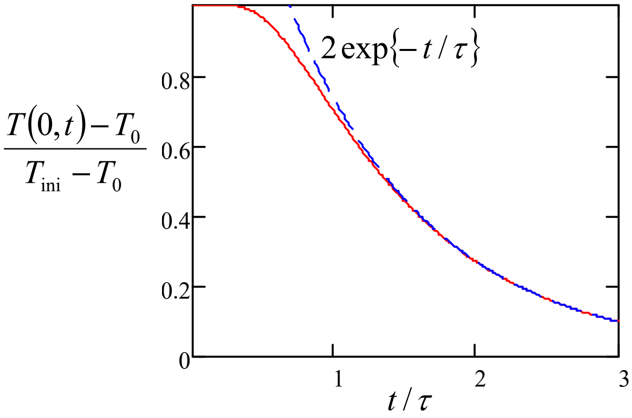
This integral may be readily worked out by parts, giving

$$C_n = 2R(T_i - T_0)\frac{(-1)^{n-1}}{\pi n}.$$

Plugging this C_n into Eq. (**), for the center of the sphere ($r \to 0$), we get the following final result:

$$T(0,t) \equiv T_0 + 2(T_{\text{ini}} - T_0)\sum_{n=1}^{\infty} (-1)^{n-1} \exp\left\{-n^2 \frac{t}{\tau}\right\}.$$

This time dependence is plotted with the solid red line in the figure on the right, while the dashed blue line shows the first term's contribution. The figure shows that the influence of higher terms (with $n > 1$) is significant only during an initial period of the relaxation, where their superposition describes an effective delay of the simple exponential relaxation by ~0.7 τ.



Problem 6.18. Suggest a reasonable definition of the entropy production rate (per unit volume), and calculate this rate for stationary thermal conduction, assuming that it obeys the Fourier law, in a material with negligible thermal expansion. Give a physical interpretation of the result. Does the stationary temperature distribution in a sample correspond to the minimum of the total entropy production in it?

Solution: In contrast to conserved physical variables, the entropy's density $s \equiv dS/dV$ satisfies (as any continuous function of $\mathbf{r}$ and t) only a generalized continuity equation:

$$\frac{\partial s}{\partial t} + \nabla \cdot \mathbf{j}_s = r_s,$$

(where $\mathbf{j}_s$ is the entropy current density), with its right-hand side, generally, not equal to zero. Hence the r_s in this relation may be rationally called the entropy production rate. In a stationary (time-independent) situation, this relation yields

$$r_s = \nabla \cdot \mathbf{j}_s. \qquad (*)$$

According to the fundamental Eq. (1.19), with a temperature-independent volume V, we may write $dS = dQ/T$, so $\mathbf{j}_s$ may be calculated just as $\mathbf{j}_\mathrm{h}/T$, where $\mathbf{j}_\mathrm{h}$ is the heat flow density, and Eq. (*) yields

$$r_s = \nabla \cdot \frac{\mathbf{j}_\mathrm{h}}{T} \equiv \frac{1}{T}\nabla \cdot \mathbf{j}_\mathrm{h} - \frac{1}{T^2}\nabla T \cdot \mathbf{j}_\mathrm{h}. \qquad (**)$$

In contrast to the entropy, the internal energy, and hence (in the absence of mechanical work and the Joule heat generation) its heat-related part u, is a conserved variable, so it satisfies the continuity equation with zero right-hand side:

$$\frac{\partial u}{\partial t} + \nabla \cdot \mathbf{j}_\mathrm{h} = 0,$$

so in a stationary situation, the first term on the right-hand side of Eq. (**) vanishes, and that relation reduces to

$$r_s = -\frac{1}{T^2}\nabla T \cdot \mathbf{j}_\mathrm{h}.$$

Now using the Fourier law (6.114), $\mathbf{j}_\mathrm{h} = -\kappa \nabla T$, we finally get

$$r_s = \kappa \frac{1}{T^2}\nabla T \cdot \nabla T \equiv \kappa \left(\frac{\nabla T}{T}\right)^2. \qquad (***)$$

Next, per Eq. (6.119) of the lecture notes,

$$\frac{\partial T}{\partial t} = D_T \nabla^2 T,$$

the stationary temperature distribution in a uniform sample of volume V obeys the Laplace equation $\nabla^2 T = 0$. However, it is well known,[151] that this equation is equivalent to the requirement of the minimum of the following functional:

$$\int_V (\nabla T)^2 d^3 r.$$

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[151] For proof, see, e.g., the solution of EM Problem 1.16, with the replacement $\phi \to T$.

Comparing this expression with the full rate of entropy production in the sample, per Eq. (***),

$$R_s \equiv \int_V r_s d^3r = \kappa \int_V \left(\frac{\nabla T}{T} \right)^2 d^3r ,$$

we see that if the temperature gradient is so low that $T \approx$ const, the stationary distribution of temperature approximately corresponds to the minimum of R_s – the statement which is sometimes called the *minimum entropy production principle*. However, the same comparison shows that if the temperature of the sample is significantly non-uniform, this principle is not valid. (It may be also violated by the sample's parameter non-uniformity.)