Chapter 3. Ideal and Not-So-Ideal Gases

In this chapter, the general principles of thermodynamics and statistics, discussed in the previous two chapters, are applied to examine the basic physical properties of gases, i.e. collections of identical particles (for example, atoms or molecules) that are free to move inside a certain volume, either not interacting or weakly interacting with each other. We will see that due to the quantum statistics, properties of even the simplest, so-called ideal gases, with negligible direct interactions between particles, may be highly nontrivial.

3.1. Ideal classical gas

Direct interactions of typical atoms and molecules are well localized, i.e. rapidly decreasing when the distance r exceeds a certain scale r_0. In a gas of N particles inside volume V, the average distance r_{ave} between the particles is $(V/N)^{1/3}$. As a result, if the gas density $n \equiv N/V = (r_{\text{ave}})^{-3}$ is much lower than r_0^{-3}, i.e. if $nr_0^3 << 1$, the chance for its particles to approach each other and interact significantly is rather small. The model in which such direct interactions are completely ignored is called the *ideal gas*.

Let us start with a *classical* ideal gas, which may be defined as the ideal gas in whose behavior the quantum effects are also negligible. As was discussed in Sec. 2.8, the condition of that is to have the average occupancy of each quantum state low:

$$\langle N_k \rangle << 1 . \tag{3.1}$$

It may seem that we have already found all properties of such a system, in particular, the equilibrium occupancy of its states – see Eq. (2.111):

$$\langle N_k \rangle = \text{const} \times \exp\left\{ -\frac{\varepsilon_k}{T} \right\} . \tag{3.2}$$

In some sense this is true, but we still need, first, to see what exactly Eq. (2) means for the gas, i.e. a system with an essentially continuous energy spectrum, and, second, to show that, rather surprisingly, the particles' indistinguishability affects some properties of even classical gases.

The first of these tasks is evidently easiest for gas out of any external fields and with no internal degrees of freedom.[1] In this case, ε_k is just the kinetic energy of the particle, which is an isotropic and parabolic function of p:

$$\varepsilon_k = \frac{p^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} . \tag{3.3}$$

Now we have to use two facts from other fields of physics, hopefully well known to the reader. First, in quantum mechanics, the linear momentum **p** is associated with the wavevector **k** of the de Broglie wave,

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[1] In more realistic cases when particles do have internal degrees of freedom, but they are all in a certain (say, ground) quantum state, Eq. (3) is valid as well, with ε_k counted from the fixed (e.g., ground-state) internal energy. The effect of thermal excitation of the internal degrees of freedom will be discussed at the end of this section.

$\mathbf{p} = \hbar\mathbf{k}$. Second, the eigenvalues of $\mathbf{k}$ for *any* waves (including the de Broglie waves) in free space are uniformly distributed in the momentum space, with a constant density of states, given by Eq. (2.82):

$$\frac{dN_{\text{states}}}{d^3k} = \frac{gV}{(2\pi)^3}, \qquad \text{i.e.} \ \frac{dN_{\text{states}}}{d^3p} = \frac{gV}{(2\pi\hbar)^3}, \tag{3.4}$$

where g is the degeneracy of the particle's internal states (for example, for all spin-½ particles, the spin contribution to the internal degeneracy $g = 2s + 1 = 2$). Even regardless of the exact proportionality coefficient between dN_{states} and d^3p, the very fact that this coefficient does not depend on $\mathbf{p}$ means that the probability dW to find the particle in a small region $d^3p = dp_1dp_2dp_3$ of the momentum space is proportional to the right-hand side of Eq. (2), with ε_k given by Eq. (3):

Maxwell distribution

$$\boxed{dW = C\exp\left\{-\frac{p^2}{2mT}\right\}d^3p = C\exp\left\{-\frac{p_1^2+p_2^2+p_3^2}{2mT}\right\}dp_1dp_2dp_3.} \tag{3.5}$$

This is the famous *Maxwell distribution*.[2] The normalization constant C may be readily found from the last form of Eq. (5), by requiring the integral of dW over all the momentum space to equal 1. Namely, such integral is evidently a product of three similar 1D integrals over each Cartesian component p_j of the momentum (j = 1, 2, 3), which may be readily reduced to the well-known dimensionless Gaussian integral,[3] so we get

$$C = \left[\int_{-\infty}^{+\infty}\exp\left\{-\frac{p_j^2}{2mT}\right\}dp_j\right]^{-3} \equiv \left[(2mT)^{1/2}\int_{-\infty}^{+\infty}e^{-\xi^2}d\xi\right]^{-3} = (2\pi mT)^{-3/2}. \tag{3.6}$$

As a sanity check, let us use the Maxwell distribution to calculate the average energy corresponding to each half-degree of freedom:

$$\begin{aligned}\left\langle\frac{p_j^2}{2m}\right\rangle &= \int\frac{p_j^2}{2m}dW = \left[C^{1/3}\int_{-\infty}^{+\infty}\frac{p_j^2}{2m}\exp\left\{-\frac{p_j^2}{2mT}\right\}dp_j\right]\times\left[C^{1/3}\int_{-\infty}^{+\infty}\exp\left\{-\frac{p_{j'}^2}{2mT}\right\}dp_{j'}\right]^2 \\ &= \frac{T}{\pi^{1/2}}\int_{-\infty}^{+\infty}\xi^2e^{-\xi^2}d\xi.\end{aligned} \tag{3.7}$$

The last, dimensionless integral equals $\pi^{1/2}/2$,[4] so, finally,

$$\left\langle\frac{p_j^2}{2m}\right\rangle \equiv \left\langle\frac{mv_j^2}{2}\right\rangle = \frac{T}{2}. \tag{3.8}$$

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[2] This formula had been suggested by J. C. Maxwell as early as 1860, i.e. well before the Boltzmann and Gibbs distributions were developed. Note also that the term "Maxwell distribution" is often associated with the distribution of the particle momentum (or velocity) *magnitude*,

$$dW = 4\pi Cp^2\exp\left\{-\frac{p^2}{2mT}\right\}dp = 4\pi Cm^3v^2\exp\left\{-\frac{mv^2}{2T}\right\}dv, \quad \text{with } 0 \le p, v < \infty,$$

which immediately follows from the first form of Eq. (5), combined with the expression $d^3p = 4\pi p^2dp$ due to the spherical symmetry of the distribution in the momentum/velocity space.

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

[4] See, e.g., MA Eq. (6.9c).

This result is (fortunately :-) in agreement with the equipartition theorem (2.48). It also means that the r.m.s. velocity of each particle is

$$\delta v \equiv \left\langle v^2 \right\rangle^{1/2} = \left\langle \sum_{j=1}^{3} v_j^2 \right\rangle^{1/2} = \left\langle 3 v_j^2 \right\rangle^{1/2} = \left(3 \frac{T}{m} \right)^{1/2}. \qquad (3.9)$$

For a typical gas (say, for N_2, our air's main component), with $m \approx 28 m_p \approx 4.7\times 10^{-26}$ kg, this velocity, at room temperature ($T = k_B T_K \approx k_B \times 300\text{ K} \approx 4.1\times 10^{-21}$ J) is about 500 m/s, comparable with the sound velocity in the same gas – and well above with the muzzle velocity of a typical handgun bullet. Still, it is measurable using even simple table-top equipment (say, a set of two concentric, rapidly rotating cylinders with a thin slit collimating an atomic beam emitted at the axis) that was available in the end of the 19th century. Experiments using such equipment gave convincing early confirmations of the Maxwell distribution.

This is all very simple (isn't it?), but actually the thermodynamic properties of a classical gas, especially its entropy, are more intricate. To show that, let us apply the Gibbs distribution to a gas portion consisting of N particles rather than just one of them. If the particles are exactly similar, the eigenenergy spectrum $\{\varepsilon_k\}$ of each of them is also exactly the same, and each value E_m of the total energy is just the sum of particular energies $\varepsilon_{k(l)}$ of the particles, where $k(l)$, with $l = 1, 2, \ldots N$, is the number of the energy level on which the l^{th} particle resides. Moreover, since the gas is classical, $\langle N_k \rangle << 1$, the probability of having two or more particles in any state may be ignored. As a result, we can use Eq. (2.59) to write

$$Z \equiv \sum_m \exp\left\{-\frac{E_m}{T}\right\} = \sum_{k(l)} \exp\left\{-\frac{1}{T}\sum_l \varepsilon_{k(l)}\right\} \equiv \sum_{k(1)} \sum_{k(2)} \ldots \sum_{k(N)} \prod_l \exp\left\{-\frac{\varepsilon_{k(l)}}{T}\right\}, \qquad (3.10)$$

where the summation has to be carried over all possible states of each particle. Since the summation over each set $\{k(l)\}$ concerns only one of the operands of the product of exponents under the sum, it is very tempting to complete the calculation as follows:

$$Z \to Z_{\text{dist}} = \sum_{k(1)} \exp\left\{-\frac{\varepsilon_{k(1)}}{T}\right\} \cdot \sum_{k(2)} \exp\left\{-\frac{\varepsilon_{k(2)}}{T}\right\} \ldots \cdot \sum_{k(N)} \exp\left\{-\frac{\varepsilon_{k(N)}}{T}\right\} = \left(\sum_k \exp\left\{-\frac{\varepsilon_k}{T}\right\} \right)^N, \qquad (3.11)$$

where the final summation is over all states of one particle. This formula is indeed valid for distinguishable particles.[5] However, if the particles are indistinguishable (again, meaning that they are internally identical *and* free to move within the same spatial region), Eq. (11) has to be modified by what is called the *correct Boltzmann counting*:

Correct Boltzmann counting

$$\boxed{Z = \frac{1}{N!} \left(\sum_k \exp\left\{-\frac{\varepsilon_k}{T}\right\} \right)^N,} \qquad (3.12)$$

that considers all quantum states different only by particle permutations, as the same state.

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[5] Since, by our initial assumption, each particle belongs to the same portion of gas, i.e. cannot be distinguished from others by its spatial position, this requires some internal "pencil mark" for each particle – for example, a specific structure or a specific quantum state of its internal degrees of freedom.

This expression is valid for any set $\{\varepsilon_k\}$ of eigenenergies. Now let us use it for the translational 3D motion of free particles, taking into account that the fundamental relation (4) implies the following rule for the replacement of a sum over quantum states of such motion with an integral:[6]

$$\sum_k (...) \to \int (...) dN_{\text{states}} = \frac{gV}{(2\pi)^3}\int (...) d^3k = \frac{gV}{(2\pi\hbar)^3}\int (...) d^3p\,. \tag{3.13}$$

In application to Eq. (12), this rule yields

$$Z = \frac{1}{N!}\left(\frac{gV}{(2\pi\hbar)^3}\left[\int_{-\infty}^{+\infty} \exp\left\{-\frac{p_j^2}{2mT}\right\} dp_j\right]^3\right)^N. \tag{3.14}$$

The integral in the square brackets is the same one as in Eq. (6), i.e. is equal to $(2\pi mT)^{1/2}$, so finally

$$Z = \frac{1}{N!}\left(\frac{gV}{(2\pi\hbar)^3}(2\pi mT)^{3/2}\right)^N \equiv \frac{1}{N!}\left[gV\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right]^N. \tag{3.15}$$

Now, assuming that $N >> 1$,[7] and applying the Stirling formula, we can calculate the gas' free energy:

$$F = T\ln\frac{1}{Z} = -NT\ln\frac{V}{N} + Nf(T), \tag{3.16a}$$

with[8]

$$\boxed{f(T) \equiv -T\left\{\ln\left[g\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right] + 1\right\}.} \tag{3.16b}$$

Sackur – Tetrode formula

The first of these relations exactly coincides with Eq. (1.45), which was derived in Sec. 1.4 from the equation of state $PV = NT$, using thermodynamic identities. At that stage, this equation of state was just postulated, but now we can *derive* it by calculating the pressure from Eq. (16a), using the second of Eqs. (1.35):

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{NT}{V}. \tag{3.17}$$

So, the equation of state of the ideal classical gas, with density $n \equiv N/V$, is indeed given by Eq. (1.44):

$$P = \frac{NT}{V} \equiv nT\,. \tag{3.18}$$

Hence we may use Eqs. (1.46)-(1.51), derived from this equation of state, to calculate all other thermodynamic variables of the gas. For example, using Eq. (1.47) with $f(T)$ given by Eq. (16b), for the internal energy and the specific heat of the gas we immediately get

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[6] As a reminder, we have already used this rule twice in Sec. 2.6, with particular values of g.

[7] For the opposite limit when $N = g = 1$, Eq. (15) yields the results obtained, by two alternative methods, in the solutions of Problems 2.8 and 2.9. Indeed, for $N = 1$, the "correct Boltzmann counting" factor $N!$ equals 1, so that the particle distinguishability effects vanish – naturally.

[8] This formula was derived (independently) by O. Sackur and H. Tetrode as early as in 1911, i.e. well before the final formulation of quantum mechanics in the late 1920s.

$$E = N\left[f(T) - T\frac{df(T)}{dT}\right] = \frac{3}{2}NT, \qquad c_V \equiv \frac{C_V}{N} = \frac{1}{N}\left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}, \tag{3.19}$$

in full agreement with Eq. (8) and hence with the equipartition theorem.

Much less trivial is the result for entropy (essentially, conjectured in Sec. 1.4):

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = N\left[\ln\frac{V}{N} - \frac{df(T)}{dT}\right]. \tag{3.20}$$

This formula provides the means to resolve the following *gas mixing paradox* (sometimes called the "Gibbs paradox"). Consider two volumes, V_1 and V_2, separated by a partition, each filled with the same gas, with the same density n, at the same temperature T, and hence with the same pressure P. Now let us remove the partition and let the gas portions mix; would the total entropy change? According to Eq. (20), it would not, because the ratio V/N, and hence the expression in the square brackets is the same in the initial and the final state, so the entropy is additive, as any extensive variable should be. This makes full sense if the gas particles in both parts of the volume are truly identical, i.e. the partition's removal does not change our information about the system. However, let us assume that all particles are distinguishable; then the entropy should clearly increase because the mixing would decrease our information about the system, i.e. increase its disorder. A quantitative description of this effect may be obtained using Eq. (11). Repeating for Z_{dist} the calculations made above for Z, we readily get a different formula for entropy:

$$S_{\text{dist}} = N\left[\ln V - \frac{df_{\text{dist}}(T)}{dT}\right], \qquad f_{\text{dist}}(T) \equiv -T\ln\left[g\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right]. \tag{3.21}$$

Please notice that in contrast to the S given by Eq. (20), this entropy includes the term $\ln V$ instead of $\ln(V/N)$, so S_{dir} is *not* proportional to N (at fixed temperature T and density N/V). While for distinguishable particles this fact does not present any conceptual problem, for indistinguishable particles it would mean that entropy was not an extensive variable, i.e. would contradict the basic assumptions of thermodynamics. This fact emphasizes again the necessity of the correct Boltzmann counting in the latter case.

Using Eq. (21), we can calculate the change of entropy due to mixing two gas portions, with N_1 and N_2 distinguishable particles, at a fixed temperature T (and hence at unchanged function f_{dist}):

$$\Delta S_{\text{dist}} = (N_1 + N_2)\ln(V_1 + V_2) - (N_1\ln V_1 + N_2\ln V_2) \equiv N_1\ln\frac{V_1 + V_2}{V_1} + N_2\ln\frac{V_1 + V_2}{V_2}, \tag{3.22}$$

so the change is positive even for $V_1/N_1 = V_2/N_2$. Note that for a particular case, $V_1 = V_2 = V/2$, Eq. (22) reduces to the simple result, $\Delta S_{\text{dist}} = (N_1 + N_2)\ln 2$, which may be readily understood in terms of the information theory. Indeed, allowing each particle of the total number $N = N_1 + N_2$ to spread to a twice larger volume, we lose one bit of information per particle, i.e. $\Delta I = (N_1 + N_2)$ bits for the whole system. Let me leave it for the reader to show that Eq. (22) remains valid if particles in each sub-volume are indistinguishable from each other but different from those in another sub-volume, i.e. for mixing of two different gases.[9] However, it is certainly *not* applicable to the system where *all* particles are identical,

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[9] By the way, if an ideal classical gas consists of particles of several different sorts, its full pressure is a sum of independent *partial pressures* exerted by each component – the so-called *Dalton law*. While this fact was an

stressing again that the correct Boltzmann counting (12) does indeed affect the gas entropy, even though it may be not as consequential as the Maxwell distribution (5), the equation of state (18), and the average energy (19).

In this context, one may wonder whether the change (22) (called the *mixing entropy*) is experimentally observable. The answer is yes. For example, after free mixing of two different gases, and hence increasing their total entropy by ΔS_{dist}, one can use a thin movable membrane that is *semipermeable*, i.e. whose pores are penetrable for particles of one type only, to separate them again, thus reducing the entropy back to the initial value, and measure either the necessary mechanical work $\Delta\mathscr{W} = T\Delta S_{\text{dist}}$ or the corresponding heat discharge into the heat bath. Practically, measurements of this type are easier in *weak solutions*[10] – systems with a small relative concentration $c << 1$ of particles of one sort (*solute*) within much more abundant particles of another sort (*solvent*). The mixing entropy also affects the thermodynamics of chemical reactions in gases and liquids.[11] Note that besides purely thermal-mechanical measurements, the mixing entropy in some conducting solutions (*electrolytes*) is also measurable by a purely electrical method, called *cyclic voltammetry*, in which a low-frequency ac voltage, applied between two solid-state electrodes embedded in the solution, is used to periodically separate different ions, and then mix them again.[12]

Now let us briefly discuss two generalizations of our results for ideal classical gases. First, let us consider such gas in an external field of potential forces. It may be described by replacing Eq. (3) with

$$\varepsilon_k = \frac{p_k^2}{2m} + U(\mathbf{r}_k), \tag{3.23}$$

where $\mathbf{r}_k$ is the position of the k^{th} particular particle, and $U(\mathbf{r})$ is the potential energy of the particle. If the potential $U(\mathbf{r})$ is changing in space sufficiently slowly,[13] Eq. (4) is still applicable, but only to small volumes, $V \to dV = d^3r$ whose linear size is much smaller than the spatial scale of substantial variations of the function $U(\mathbf{r})$. Hence, instead of Eq. (5), we may only write the probability dW of finding the particle in a small volume d^3rd^3p of the 6-dimensional phase space:

$$dW = w(\mathbf{r},\mathbf{p})d^3rd^3p, \qquad w(\mathbf{r},\mathbf{p}) = \text{const} \times \exp\left\{-\frac{p^2}{2mT} - \frac{U(\mathbf{r})}{T}\right\}. \tag{3.24}$$

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important experimental discovery in the early 1800s, for statistical physics this is just a straightforward corollary of Eq. (18) because in an ideal gas, the component particles do not interact.

[10] The statistical mechanics of weak solutions is very similar to that of ideal gases, with Eq. (18) recast into the following formula (derived in 1885 by J. van 't Hoff), $PV = cNT$, for the partial pressure of the solute. One of its corollaries is that the net force (called the *osmotic pressure*) exerted on a semipermeable membrane is proportional to the difference in the solute concentrations it is supporting.

[11] Unfortunately, I do not have time for even a brief introduction to this important field and have to refer the interested reader to specialized textbooks – for example, P. A. Rock, *Chemical Thermodynamics*, University Science Books, 1983; or P. Atkins, *Physical Chemistry*, 5th ed., Freeman, 1994; or G. M. Barrow, *Physical Chemistry*, 6th ed., McGraw-Hill, 1996.

[12] See, e.g., either Chapter 6 in A. Bard and L. Falkner, *Electrochemical Methods*, 2nd ed., Wiley, 2000 (which is a good introduction to electrochemistry as a whole); or Sec. II.8.3.1 in F. Scholz (ed.), *Electroanalytical Methods*, 2nd ed., Springer, 2010.

[13] Quantitatively, the spatial scale of substantial variations of the potential, $|\nabla U(\mathbf{r})/T|^{-1}$, has to be much larger than the *mean free path* l of the gas particles, i.e. the average distance a particle passes between successive collisions with its counterparts. (For more on this notion, see Chapter 6 below.)

Hence, the Maxwell distribution of particle velocities is still valid at each point **r**, so the equation of state (18) is also valid locally. A new issue here is the spatial distribution of the total density,

$$n(\mathbf{r}) \equiv N\int w(\mathbf{r},\mathbf{p})d^3p\,, \tag{3.25}$$

of all gas particles, regardless of their momentum/velocity. For this variable, Eq. (24) yields[14]

$$n(\mathbf{r}) = n(0)\exp\left\{-\frac{U(\mathbf{r})}{T}\right\}, \tag{3.26}$$

where the potential energy at the origin ($\mathbf{r} = 0$) is used as the reference for U. The local gas pressure may be still calculated from the local form of Eq. (18):

$$P(\mathbf{r}) = n(\mathbf{r})T = P(0)\exp\left\{-\frac{U(\mathbf{r})}{T}\right\}. \tag{3.27}$$

A simple example of numerous applications of Eq. (27) is an approximate description of the Earth's atmosphere. At all heights $h \ll R_E \sim 6\times10^6$ m above the Earth's surface (say, above the sea level), we may describe the Earth's gravity effect by the potential $U = mgh$, and Eq. (27) yields the so-called *barometric formula*

Barometric formula

$$\boxed{P(h) = P(0)\exp\left\{-\frac{h}{h_0}\right\}, \qquad \text{with } h_0 \equiv \frac{T}{mg} = \frac{k_B T_K}{mg}.} \tag{3.28}$$

For the same N_2, the main component of the atmosphere, at $T_K = 300$ K, $h_0 \approx 7$ km. This result gives the correct order of magnitude of the atmosphere's thickness, though the exact law of the pressure change differs somewhat from Eq. (28) because electromagnetic radiation flows result in a relatively small deviation of the atmospheric air from the thermal equilibrium, namely a drop of its temperature T with height, with the so-called *lapse rate* of about 2% (~6.5 K) per kilometer.

The second generalization I need to discuss is to particles with internal degrees of freedom. Now ignoring the potential energy $U(\mathbf{r})$, we may describe them by replacing Eq. (3) with

$$\varepsilon_k = \frac{p^2}{2m} + \varepsilon_k', \tag{3.29}$$

where ε_k' describes the internal energy spectrum of the k^{th} particle. If the particles are similar, we may repeat all the above calculations, and see that all their results (including the Maxwell distribution, and the equation of state) are still valid, with the only exception of Eq. (16), which now becomes

$$f(T) = -T\left\{\ln\left[g\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right] + 1 + \ln\left[\sum_{\varepsilon_k'}\exp\left\{-\frac{\varepsilon_k'}{T}\right\}\right]\right\}. \tag{3.30}$$

As we already know from Eqs. (1.50)-(1.51), this change may affect both specific heats of the ideal gas – though not their difference, $c_V - c_P = 1$. They may be readily calculated for usual atoms and molecules, at not very high temperatures (say the room temperature of ~25 meV), because in these conditions, $\varepsilon_k' \gg T$ for most of their internal degrees of freedom, including the electronic and

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[14] In some textbooks, Eq. (26) is also called the *Boltzmann distribution*, though it certainly should be distinguished from Eq. (2.111).

vibrational ones. (The typical energy of the lowest electronic excitations is of the order of a few eV, and that of the lowest vibrational excitations is only an order of magnitude lower.) As a result, these degrees of freedom are "frozen out": they are in their ground states, so their contributions $\exp\{-\varepsilon_k'/T\}$ to the sum in Eq. (30), and hence to the heat capacity, are negligible. In monoatomic gases, this is true for all degrees of freedom besides those of the translational motion, already taken into account by the first term in Eq. (30), i.e. by Eq. (16b), so their specific heat is typically well described by Eq. (19).

The most important exception is the rotational degrees of freedom of diatomic and polyatomic molecules. As quantum mechanics shows,[15] the excitation energy of these degrees of freedom scales as $\hbar^2/2I$, where I is the molecule's relevant moment of inertia. In the most important molecules, this energy is rather low (for example, for N_2, it is close to 0.25 meV, i.e. ~1% of the room temperature), so at usual conditions they are well excited and, moreover, behave virtually as classical degrees of freedom, each giving a quadratic contribution to the molecule's kinetic energy. As a result, they obey the equipartition theorem, each giving an extra contribution of $T/2$ to the energy, i.e. ½ to the specific heat.[16] In polyatomic molecules, there are three such classical degrees of freedom (corresponding to their rotations about the three principal axes[17]), but in diatomic molecules, only two.[18] Hence, these contributions may be described by the following generalization of Eq. (19):

$$c_V = \begin{cases} 3/2, & \text{for monoatomic gases,} \\ 5/2, & \text{for gases of diatomic molecules,} \\ 3, & \text{for gases of polyatomic molecules.} \end{cases} \qquad (3.31)$$

Please keep in mind, however, that as the above discussion shows, this simple result is invalid at very low and very high temperatures. In the latter case, the most frequent violations of Eq. (31) are due to the thermal activation of the vibrational degrees of freedom; for many important molecules, it starts at temperatures of a few thousand K.

3.2. Calculating μ

Now let us discuss the properties of ideal gases of free, indistinguishable particles in more detail, paying special attention to the chemical potential μ – which, for some readers, may still be a somewhat mysterious aspect of the Fermi and Bose distributions. Note again that particle indistinguishability is conditioned by the absence of thermal excitations of their internal degrees of freedom, so in the balance of this chapter such excitations will be ignored, and the particle's energy ε_k will be associated with its "external" energy alone: for a free particle in an ideal gas, with its kinetic energy (3).

Let us start from the classical gas, and recall the conclusion of thermodynamics that μ is just the Gibbs potential per unit particle – see Eq. (1.56). Hence we can calculate $\mu = G/N$ from Eqs. (1.49) and (16b). The result,

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[15] See, e.g., either the model solution of Problem 2.14 (and references therein) or QM Secs. 3.6 and 5.6.

[16] This result may be readily obtained again from the last term of Eq. (30) by treating it exactly like the first one was and then applying the general Eq. (1.50).

[17] See, e.g., CM Sec. 4.1.

[18] This conclusion of the quantum theory may be interpreted as the indistinguishability of the rotations about the molecule's symmetry axis.

$$\mu = -T\ln\frac{V}{N} + f(T) + T = T\ln\left[\frac{N}{gV}\left(\frac{2\pi\hbar^2}{mT}\right)^{3/2}\right], \qquad (3.32a)$$

which may be rewritten as

$$\exp\left\{\frac{\mu}{T}\right\} = \frac{N}{gV}\left(\frac{2\pi\hbar^2}{mT}\right)^{3/2}, \qquad (3.32b)$$

gives us some idea about μ not only for a classical gas but for quantum (Fermi and Bose) gases as well. Indeed, we already know that for indistinguishable particles, the Boltzmann distribution (2.111) is valid only if $\langle N_k \rangle << 1$. Comparing this condition with the quantum statistics (2.115) and (2.118), we see again that the condition of the gas behaving classically may be expressed as

$$\exp\left\{\frac{\mu - \varepsilon_k}{T}\right\} << 1 \qquad (3.33)$$

for all ε_k. Since the lowest value of ε_k given by Eq. (3) is zero, Eq. (33) may be satisfied only if $\exp\{\mu/T\} << 1$. This means that the chemical potential of a classical gas has to be not just negative, but also "strongly negative" in the sense

$$-\mu >> T. \qquad (3.34a)$$

According to Eq. (32), this condition may be represented as

$$T >> T_0, \qquad (3.34b)$$

with T_0 defined as

Quantum scale of temperature

$$\boxed{T_0 \equiv \frac{\hbar^2}{m}\left(\frac{N}{gV}\right)^{2/3} \equiv \frac{\hbar^2}{m}\left(\frac{n}{g}\right)^{2/3} \equiv \frac{\hbar^2}{g^{2/3}mr_{\text{ave}}^2},} \qquad (3.35)$$

where r_{ave} is the average distance between the gas particles:

$$r_{\text{ave}} \equiv \frac{1}{n^{1/3}} = \left(\frac{V}{N}\right)^{1/3}. \qquad (3.36)$$

With the last form of T_0, the condition (34) is very transparent physically: disregarding the factor $g^{2/3}$ (which is typically of the order of 1), it means that the average thermal energy of a particle, which is always of the order of T, has to be much larger than the energy of quantization of particle's motion at the length r_{ave}. An alternative form of the same condition is

$$r_{\text{ave}} >> g^{-1/3} r_c, \quad \text{where } r_c \equiv \frac{\hbar}{(mT)^{1/2}}. \qquad (3.37)$$

In quantum mechanics, the parameter r_c so defined is frequently called the *correlation length*.[19] For a typical gas (say, N_2, with $m \approx 14m_p \approx 2.3\times10^{-26}$ kg) at the standard room temperature ($T = k_B\times300\text{K} \approx 4.1\times10^{-21}$ J), the correlation length r_c is close to 10^{-11} m, i.e. is significantly smaller than the physical size $r_0 \sim 3\times10^{-10}$ m of the molecule. This estimate shows that at room temperatures, as soon as any practical gas is rare enough to be ideal ($r_{\text{ave}} >> r_0$), it is classical. Thus, the only way to observe quantum effects in the translational motion of molecules is by using very deep refrigeration. According to Eq. (37), for

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[19] See, e.g., QM Sec. 7.2 and in particular Eq. (7.37).

the same nitrogen molecule, taking $r_{\text{ave}} \sim 10^2 r_0 \sim 10^{-8}$ m (to ensure that direct interaction effects are negligible), the temperature should be well below 1 mK.

In order to analyze quantitatively what happens with gases when T is reduced to such low values, we need to calculate μ for an arbitrary ideal gas of indistinguishable particles. Let us use the lucky fact that the Fermi-Dirac and the Bose-Einstein statistics may be represented with one formula:

$$\langle N(\varepsilon)\rangle = \frac{1}{e^{(\varepsilon-\mu)/T} \pm 1}, \tag{3.38}$$

where (and everywhere in the balance of this section) the top sign stands for fermions and the lower one for bosons, to discuss fermionic and bosonic ideal gases in one shot.

If we deal with a member of the *grand canonical* ensemble (Fig. 2.13), in which not only T but also μ is externally fixed, we may use Eq. (38) to calculate the *average* number N of particles in volume V. If the volume is so large that $N >> 1$, we may use the general state counting rule (13) to get

$$N = \frac{gV}{(2\pi)^3}\int \langle N(\varepsilon)\rangle d^3k = \frac{gV}{(2\pi\hbar)^3}\int \frac{d^3p}{e^{[\varepsilon(p)-\mu]/T} \pm 1} = \frac{gV}{(2\pi\hbar)^3}\int_0^\infty \frac{4\pi p^2 dp}{e^{[\varepsilon(p)-\mu]/T} \pm 1}. \tag{3.39}$$

In most practical cases, however, the number N of gas particles is fixed by particle confinement (i.e. the gas portion under study is a member of a *canonical* ensemble – see Fig. 2.6), and hence μ rather than N should be calculated. Let us use the trick already mentioned in Sec. 2.8: if N is very large, the relative fluctuation of the particle number, at fixed μ, is negligibly small ($\delta N/N \sim 1/\sqrt{N} << 1$), and the relation between the *average* values of N and μ should not depend on which of these variables is exactly fixed. Hence, Eq. (39), with μ having the sense of the *average* chemical potential, should be valid even if N is *exactly* fixed, so the small fluctuations of N are replaced with (equally small) fluctuations of μ. Physically, in this case the role of the μ-fixing environment for any sub-portion of the gas is played by the rest of it, and Eq. (39) expresses the condition of self-consistency of such chemical equilibrium.

So, at $N >> 1$, Eq. (39) may be used to calculate the average μ as a function of two independent parameters: N (i.e. the gas density $n = N/V$) and temperature T. For carrying out this calculation, it is convenient to convert the right-hand side of Eq. (39) to an integral over the particle's energy $\varepsilon(p) = p^2/2m$, so $p = (2m\varepsilon)^{1/2}$, and $dp = (m/2\varepsilon)^{1/2}d\varepsilon$, getting

$$\boxed{N = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty \frac{\varepsilon^{1/2}d\varepsilon}{e^{(\varepsilon-\mu)/T} \pm 1}.} \tag{3.40}$$

Basic equation for μ

This key result may be represented in two other, sometimes more convenient forms. First, Eq. (40), derived for our current (3D, isotropic and parabolic-dispersion) approximation (3), is just a particular case of the following self-evident state-counting relation

$$N = \int_0^\infty g(\varepsilon)\langle N(\varepsilon)\rangle d\varepsilon, \tag{3.41}$$

where

$$g(\varepsilon) \equiv dN_{\text{states}}/d\varepsilon \tag{3.42}$$

is the temperature-independent density of all quantum states of a particle – regardless of whether they are occupied or not. Indeed, according to the general Eq. (4), for the simple isotopic model (3),

$$g(\varepsilon) = g_3(\varepsilon) \equiv \frac{dN_{\text{states}}}{d\varepsilon} = \frac{d}{d\varepsilon}\left(\frac{gV}{(2\pi\hbar)^3}\frac{4\pi}{3}p^3\right) = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\varepsilon^{1/2}, \tag{3.43}$$

so plugging it into Eq. (41), we return to Eq. (39).

On the other hand, for some calculations, it is convenient to introduce the following dimensionless energy variable: $\xi \equiv \varepsilon/T$, to express Eq. (40) via a dimensionless integral:

$$N = \frac{gV(mT)^{3/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty \frac{\xi^{1/2}d\xi}{e^{\xi-\mu/T} \pm 1}. \tag{3.44}$$

As a sanity check, in the classical limit (34), the exponent in the denominator of the fraction under the integral is much larger than 1, and Eq. (44) reduces to

$$N = \frac{gV(mT)^{3/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty \frac{\xi^{1/2}d\xi}{e^{\xi-\mu/T}} \approx \frac{gV(mT)^{3/2}}{\sqrt{2}\pi^2\hbar^3}\exp\left\{\frac{\mu}{T}\right\}\int_0^\infty \xi^{1/2}e^{-\xi}d\xi, \quad \text{at } -\mu >> T. \tag{3.45}$$

By the definition of the gamma function $\Gamma(\xi)$,[20] the last integral is just $\Gamma(3/2) = \pi^{1/2}/2$, and we get

$$\exp\left\{\frac{\mu}{T}\right\} = N\frac{\sqrt{2}\pi^2\hbar^3}{gV(mT)^{3/2}}\frac{2}{\sqrt{\pi}} = \left(2\pi\frac{T_0}{T}\right)^{3/2}, \tag{3.46}$$

which is exactly the same result as given by Eq. (32), which was obtained earlier in a rather different way – from the Boltzmann distribution and thermodynamic identities.

Unfortunately, in the general case of arbitrary μ, the integral in Eq. (44) cannot be worked out analytically.[21] The best we can do is to use the T_0 defined by Eq. (35), to rewrite Eq. (44) in the following convenient, fully dimensionless form:

$$\frac{T}{T_0} = \left[\frac{1}{\sqrt{2}\pi^2}\int_0^\infty \frac{\xi^{1/2}d\xi}{e^{\xi-\mu/T} \pm 1}\right]^{-2/3}, \tag{3.47}$$

and then use this relation to calculate the ratios T/T_0 and $\mu/T_0 \equiv (\mu/T)\times(T/T_0)$, as functions of μ/T numerically. After that, we may plot the results versus each other, now considering the former ratio as the argument. Figure 1 below shows the resulting plots for both particle types. They show that at high temperatures, $T >> T_0$, the chemical potential is negative and approaches the classical behavior given by Eq. (46) for both fermions and bosons – just as we could expect. However, at temperatures $T \sim T_0$ the type of statistics becomes crucial. For fermions, the reduction of temperature leads to μ changing its sign from negative to positive and then approaching a constant positive value called the *Fermi energy*, $\varepsilon_F \approx 7.595\ T_0$ at $T \to 0$. On the contrary, the chemical potential of a bosonic gas stays negative and then turns into zero at a certain *critical temperature* $T_c \approx 3.313\ T_0$. Both these limits, which are very important for applications, may (and will be :-) explored analytically, separately for each statistics.

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

[21] For the reader's reference only: for the upper sign, the integral in Eq. (40) is a particular form (for s = ½) of a special function called the *complete Fermi-Dirac integral* F_s, while for the lower sign, it is a particular case (for s = 3/2) of another special function called the *polylogarithm* Li_s. (In what follows, I will not use these notations.)

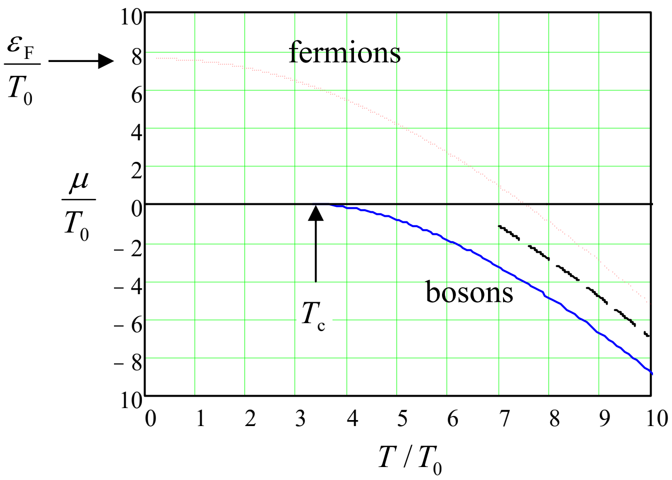

Fig. 3.1. The chemical potential of an ideal gas of $N >> 1$ indistinguishable quantum particles, as a function of temperature at a fixed gas density $n \equiv N/V$ (i.e. fixed $T_0 \propto n^{2/3}$), for two different particle types. The dashed line shows the classical approximation (46), valid only asymptotically at $T >> T_0$.

Before carrying out such analyses (in the next two sections), let me show that rather surprisingly, for any non-relativistic ideal quantum gas, the relation between the product PV and the energy,

$$\boxed{PV = \frac{2}{3}E,} \qquad (3.48)$$

Ideal gas: *PV* vs. *E*

is exactly the same as follows from Eqs. (18) and (19) for the classical gas, and hence does *not* depend on the particle statistics. To prove this, it is sufficient to use Eqs. (2.114) and (2.117) for the grand thermodynamic potential of each quantum state, which may be conveniently represented by a single formula,

$$\Omega_k = \mp T \ln\left(1 \pm e^{(\mu - \varepsilon_k)/T}\right), \qquad (3.49)$$

and sum them over all states k, using the general summation formula (13). The result for the total grand potential of a 3D gas with the dispersion law (3) is

$$\Omega = \mp T \frac{gV}{(2\pi\hbar)^3} \int_0^\infty \ln\left(1 \pm e^{(\mu - p^2/2m)/T}\right) 4\pi p^2 dp = \mp T \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \ln\left(1 \pm e^{(\mu-\varepsilon)/T}\right)\varepsilon^{1/2}\, d\varepsilon. \qquad (3.50)$$

Working out this integral by parts, exactly as we did it with the one in Eq. (2.90), we get

$$\Omega = -\frac{2}{3}\frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{(\varepsilon-\mu)/T} \pm 1} = -\frac{2}{3}\int_0^\infty \varepsilon g_3(\varepsilon)\langle N(\varepsilon)\rangle d\varepsilon. \qquad (3.51)$$

But the last integral is just the total energy E of the gas:

$$\boxed{E = \frac{gV}{(2\pi\hbar)^3}\int_0^\infty \frac{p^2}{2m}\frac{4\pi p^2 dp}{e^{[\varepsilon(p)-\mu]/T} \pm 1} = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{(\varepsilon-\mu)/T} \pm 1} = \int_0^\infty \varepsilon g_3(\varepsilon)\langle N(\varepsilon)\rangle d\varepsilon,} \qquad (3.52)$$

Ideal gas: energy

so for any temperature and any particle type, $\Omega = -(2/3)E$. But since, from thermodynamics, $\Omega = -PV$, we have Eq. (48) proved. This universal relation[22] will be repeatedly used below.

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[22] For gases of diatomic and polyatomic molecules, whose rotational degrees of freedom are usually thermally excited, Eq. (48) is valid only for the translational motion's energy.

3.3. Degenerate Fermi gas

Analysis of low-temperature properties of a *Fermi gas* is very simple in the limit $T = 0$. Indeed, in this limit, the Fermi-Dirac distribution (2.115) is just the step function:

$$\langle N(\varepsilon)\rangle = \begin{cases} 1, & \text{for } \varepsilon < \mu, \\ 0, & \text{for } \mu < \varepsilon, \end{cases} \tag{3.53}$$

– see the bold line in Fig. 2a. Since the function $\varepsilon = p^2/2m$ is isotropic in the momentum space, in that space the particles, at $T = 0$, fully occupy all possible quantum states inside a sphere (called either the *Fermi sphere* or the *Fermi sea*) with some radius p_F (Fig. 2b), while all states above the sea surface are empty. Such *degenerate Fermi gas* is a striking manifestation of the Pauli principle: though in thermodynamic equilibrium at $T = 0$ all particles try to lower their energies as much as possible, only g of them may occupy each translational ("orbital") quantum state. As a result, the sphere's volume is proportional to the particle number N, or rather to their density $n = N/V$.

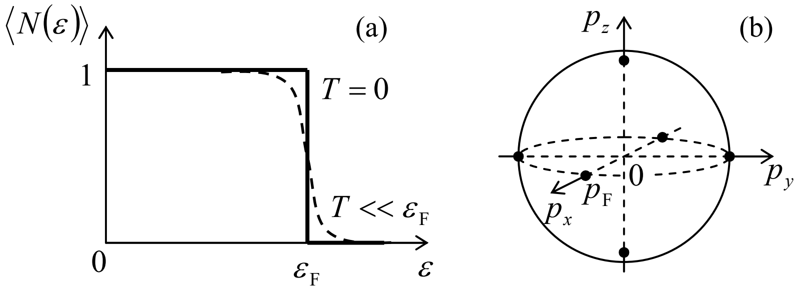

Fig. 3.2. Representations of the Fermi sea: (a) on the Fermi distribution plot, and (b) in the momentum space.

Indeed, the radius p_F may be readily related to the number of particles N using Eq. (39), with the upper sign, whose integral in this limit is just the Fermi sphere's volume:

$$N = \frac{gV}{(2\pi\hbar)^3} \int_0^{p_F} 4\pi p^2 dp = \frac{gV}{(2\pi\hbar)^3} \frac{4\pi}{3} p_F^3 . \tag{3.54}$$

Now we can use Eq. (3) to express via N the chemical potential μ (which, in the limit $T = 0$, bears the special name of the *Fermi energy* ε_F)[23]:

Fermi energy

$$\boxed{\varepsilon_F \equiv \mu\big|_{T=0} = \frac{p_F^2}{2m} = \frac{\hbar^2}{2m}\left(6\pi^2 \frac{N}{gV}\right)^{2/3} \equiv \left(\frac{9\pi^4}{2}\right)^{1/3} T_0 \approx 7.595 T_0 ,} \tag{3.55a}$$

where T_0 is the quantum temperature scale defined by Eq. (35). This formula quantifies the low-temperature trend of the function $\mu(T)$, clearly visible in Fig. 1, and in particular, explains the ratio ε_F/T_0 mentioned in Sec. 2. Note also a simple and very useful relation,

$$\varepsilon_F = \frac{3}{2}\frac{N}{g_3(\varepsilon_F)}, \qquad \text{i.e. } g_3(\varepsilon_F) = \frac{3}{2}\frac{N}{\varepsilon_F}, \tag{3.55b}$$

that may be obtained immediately from the comparison of Eqs. (43) and (54).

The total energy of the degenerate Fermi gas may be (equally easily) calculated from Eq. (52):

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[23] Note that in the electronic engineering literature, μ is usually called the *Fermi level*, for any temperature.

$$E = \frac{gV}{(2\pi\hbar)^3}\int_0^{p_F}\frac{p^2}{2m}4\pi p^2 dp = \frac{gV}{(2\pi\hbar)^3}\frac{4\pi}{2m}\frac{p_F^5}{5} = \frac{3}{5}\varepsilon_F N, \tag{3.56}$$

showing that the average energy, $\langle\varepsilon\rangle \equiv E/N$, of a particle inside the Fermi sea is equal to 3/5 of that (ε_F) of the particles in the most energetic occupied states, on the Fermi surface. Since, according to the basic formulas of Chapter 1, at zero temperature $H = G = N\mu$, and $F = E$, the only thermodynamic variable still to be calculated is the gas pressure P. For it, we could use any of the thermodynamic relations $P = (H - E)/V$ or $P = -(\partial F/\partial V)_T$, but it is even easier to use our recent result (48). Together with Eq. (56), it yields

$$P = \frac{2}{3}\frac{E}{V} = \frac{2}{5}\frac{N\varepsilon_F}{V} = \left(\frac{36\pi^4}{125}\right)^{1/3} P_0 \approx 3.035 P_0, \quad \text{where } P_0 \equiv nT_0 = \frac{\hbar^2 n^{5/3}}{mg^{2/3}}. \tag{3.57}$$

From here, it is straightforward to calculate the isothermal *bulk modulus* (reciprocal compressibility),[24]

$$K_T \equiv -V\left(\frac{\partial P}{\partial V}\right)_T = \frac{2}{3}\varepsilon_F\frac{N}{V}, \tag{3.58}$$

which is frequently simpler to measure experimentally than P.

Perhaps the most important example[25] of the degenerate Fermi gas is the *conduction electrons* in metals – the electrons that belong to the outer shells of isolated atoms but become shared in solid metals, and as a result, can move through the crystal lattice almost freely. Though the electrons (which are fermions with spin $s = ½$ and hence with the spin degeneracy $g = 2s + 1 = 2$) are negatively charged, the Coulomb interaction of the conduction electrons with each other is substantially compensated by the positively charged ions of the atomic lattice, so they follow the simple model discussed above, in which the interaction is disregarded, reasonably well. This is especially true for alkali metals (forming Group 1 of the periodic table of elements), whose experimentally measured Fermi surfaces are spherical within 1% – even within 0.1% for Na.

Table 1 lists, in particular, the experimental values of the bulk modulus for such metals, together with the values given by Eq. (58) using the ε_F calculated from Eq. (55) with the experimental density of the conduction electrons. The agreement is pretty impressive, taking into account that the simple theory described above completely ignores the Coulomb and exchange interactions of the electrons. This agreement implies that, surprisingly, the experimentally observed firmness of solids (or at least metals) is predominantly due to the kinetic energy (3) of the conduction electrons, rather than any electrostatic interactions – though, to be fair, these interactions are the crucial factor defining the equilibrium value

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[24] For a general discussion of this notion, see, e.g., CM Eqs. (7.32) and (7.36).

[25] Recently, nearly degenerate gases (with $\varepsilon_F \sim 5T$) have been formed of weakly interacting Fermi atoms as well – see, e.g., K. Aikawa *et al.*, *Phys. Rev. Lett.* **112**, 010404 (2014), and references therein. Another interesting example of the system that may be approximately treated as a degenerate Fermi gas is the set of $Z >> 1$ electrons in a heavy atom. However, in this system the account of electron interaction via the electrostatic field they create is important. Since for this *Thomas-Fermi model* of atoms, the thermal effects are unimportant, it was discussed already in the quantum-mechanical part of this series (see QM Chapter 8). However, its analysis may be streamlined using the notion of the chemical potential, introduced only in this course – the problem left for the reader's exercise.

of n. Numerical calculations using more accurate approximations (e.g., the Density Functional Theory[26]), which agree with experiment with a few-percent accuracy, confirm this conclusion.[27]

Table 3.1. Experimental and theoretical parameters of electrons' Fermi sea in some alkali metals[28]

Metal	ε_F (eV) Eq. (55)	K (GPa) Eq. (58)	K (GPa) experiment	γ(mcal/mole·K^2) Eq. (69)	γ(mcal/mole·K^2) experiment
Na	3.24	923	642	0.26	0.35
K	2.12	319	281	0.40	0.47
Rb	1.85	230	192	0.46	0.58
Cs	1.59	154	143	0.53	0.77

Looking at the values of ε_F listed in this table, note that room temperatures (T_K ~ 300 K) correspond to T ~ 25 meV. As a result, most experiments with metals, at least in their solid or liquid form, are performed in the limit $T << \varepsilon_F$. According to Eq. (39), at such temperatures, the occupancy step described by the Fermi-Dirac distribution has a non-zero but relatively small width of the order of T – see the dashed line in Fig. 2a. Calculations for this case are much facilitated by the so-called *Sommerfeld expansion formula*[29] for the integrals like those in Eqs. (41) and (52):

Sommerfeld expansion

$$\boxed{I(T) \equiv \int_0^\infty \varphi(\varepsilon)\langle N(\varepsilon)\rangle d\varepsilon \approx \int_0^\mu \varphi(\varepsilon)d\varepsilon + \frac{\pi^2}{6}T^2\frac{d\varphi(\mu)}{d\mu}, \quad \text{for } T << \mu,} \tag{3.59}$$

where $\varphi(\varepsilon)$ is an arbitrary function that is sufficiently smooth at $\varepsilon = \mu$ and integrable at $\varepsilon = 0$. To prove this formula, let us introduce another function,

$$f(\varepsilon) \equiv \int_0^\varepsilon \varphi(\varepsilon')d\varepsilon', \quad \text{so that } \varphi(\varepsilon) = \frac{df(\varepsilon)}{d\varepsilon}, \tag{3.60}$$

and work out the integral $I(T)$ by parts:

$$\begin{aligned} I(T) &\equiv \int_0^\infty \frac{df(\varepsilon)}{d\varepsilon}\langle N(\varepsilon)\rangle d\varepsilon = \int_{\varepsilon=0}^{\varepsilon=\infty}\langle N(\varepsilon)\rangle df \\ &= \left[\langle N(\varepsilon)\rangle f(\varepsilon)\right]_{\varepsilon=0}^{\varepsilon=\infty} - \int_{\varepsilon=0}^{\varepsilon=\infty} f(\varepsilon)\, d\langle N(\varepsilon)\rangle = \int_0^\infty f(\varepsilon)\left[-\frac{\partial\langle N(\varepsilon)\rangle}{\partial\varepsilon}\right]d\varepsilon . \end{aligned} \tag{3.61}$$

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[26] See, e.g., QM Sec. 8.4.

[27] Note also a huge difference between the very high bulk modulus of metals (K ~ 10^{11} Pa) and its very low values in usual, atomic gases (for them, at ambient conditions, K ~10^5 Pa). About four orders of magnitude of this difference is due to that in the particle density N/V, but the balance is due to the electron gas' degeneracy. Indeed, in an ideal classical gas, $K = P = T(N/V)$, so that the factor $(2/3)\varepsilon_F$ in Eq. (58), of the order of a few eV in metals, should be compared with the factor $T \approx 25$ meV in the classical gas at room temperature.

[28] Data from N. Ashcroft and N. D. Mermin, *Solid State Physics*, W. B. Saunders, 1976.

[29] Named after Arnold Sommerfeld, who was the first (in 1927) to apply quantum mechanics to degenerate Fermi gases, in particular to electrons in metals, and may be credited for most of the results discussed in this section.

As evident from Eq. (2.115) and/or Fig. 2a, at $T << \mu$ the function $-\partial\langle N(\varepsilon)\rangle/\partial\varepsilon$ is close to zero for all energies, besides a narrow peak of the unit area, at $\varepsilon \approx \mu$. Hence, if we expand the function $f(\varepsilon)$ in the Taylor series near this point, just a few leading terms of the expansion should give us a good approximation:

$$\begin{aligned} I(T) &\approx \int_0^\infty \left[f(\mu) + \frac{df}{d\varepsilon}\Big|_{\varepsilon=\mu}(\varepsilon-\mu) + \frac{1}{2}\frac{d^2 f}{d\varepsilon^2}\Big|_{\varepsilon=\mu}(\varepsilon-\mu)^2 \right]\left[-\frac{\partial\langle N(\varepsilon)\rangle}{\partial\varepsilon}\right] d\varepsilon \\ &= \int_0^\mu \varphi(\varepsilon')d\varepsilon' \int_0^\infty \left(-\frac{\partial\langle N(\varepsilon)\rangle}{\partial\varepsilon}\right) d\varepsilon + \varphi(\mu)\int_0^\infty (\varepsilon-\mu)\left[-\frac{\partial\langle N(\varepsilon)\rangle}{\partial\varepsilon}\right] d\varepsilon \\ &+ \frac{1}{2}\frac{d\varphi(\mu)}{d\mu}\int_0^\infty (\varepsilon-\mu)^2\left[-\frac{\partial\langle N(\varepsilon)\rangle}{\partial\varepsilon}\right] d\varepsilon . \end{aligned} \qquad (3.62)$$

In the last form of this relation, the first integral over ε equals $\langle N(\varepsilon = 0)\rangle - \langle N(\varepsilon = \infty\rangle = 1$, the second one vanishes (because the function under it is antisymmetric with respect to the point $\varepsilon = \mu$), and only the last one needs to be dealt with explicitly, by working it out by parts and then using a table integral:[30]

$$\int_0^\infty (\varepsilon-\mu)^2\left[-\frac{\partial\langle N(\varepsilon)\rangle}{\partial\varepsilon}\right] d\varepsilon \approx T^2\int_{-\infty}^{+\infty} \xi^2 \frac{d}{d\xi}\left(-\frac{1}{e^\xi+1}\right) d\xi = 4T^2\int_0^{+\infty}\frac{\xi d\xi}{e^\xi+1} = 4T^2\frac{\pi^2}{12} . \qquad (3.63)$$

Being plugged into Eq. (62), this result proves the Sommerfeld formula (59).

The last preparatory step we need to make is to account for a possible small difference (as we will see below, also proportional to T^2) between the temperature-dependent chemical potential $\mu(T)$ and the Fermi energy defined as $\varepsilon_F \equiv \mu(0)$, in the largest (first) term on the right-hand side of Eq. (59):

$$I(T) \approx \int_0^{\varepsilon_F} \varphi(\varepsilon)d\varepsilon + (\mu - \varepsilon_F)\varphi(\mu) + \frac{\pi^2}{6}T^2\frac{d\varphi(\mu)}{d\mu} \equiv I(0) + (\mu - \varepsilon_F)\varphi(\mu) + \frac{\pi^2}{6}T^2\frac{d\varphi(\mu)}{d\mu} . \qquad (3.64)$$

Now, applying this formula to Eq. (41) and the last form of Eq. (52), we get the following results (which are valid for any dispersion law $\varepsilon(\mathbf{p})$ and even any dimensionality of the gas):

$$N(T) = N(0) + (\mu - \varepsilon_F)g(\mu) + \frac{\pi^2}{6}T^2\frac{dg(\mu)}{d\mu}, \qquad (3.65)$$

$$E(T) = E(0) + (\mu - \varepsilon_F)\mu g(\mu) + \frac{\pi^2}{6}T^2\frac{d}{d\mu}\left[\mu g(\mu)\right]. \qquad (3.66)$$

If the number of particles does not change with temperature, $N(T) = N(0)$, as in most experiments, Eq. (65) gives the following formula for finding the temperature-induced change of μ:

$$\mu - \varepsilon_F = -\frac{\pi^2}{6}T^2\frac{1}{g(\mu)}\frac{dg(\mu)}{d\mu} . \qquad (3.67)$$

Note that the change is quadratic in T and negative, in agreement with the numerical results shown with the red line in Fig. 1. Plugging this expression (which is only valid when the magnitude of the change is much smaller than ε_F) into Eq. (66), we get the following temperature correction to the energy:

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[30] See, e.g., MA Eqs. (6.8c) and (2.12b), with $n = 1$.

$$E(T) - E(0) = \frac{\pi^2}{6} g(\mu) T^2, \tag{3.68}$$

where within the accuracy of our approximation, μ may be replaced with ε_F. (Due to the universal relation (48), this result also gives the temperature correction to the Fermi gas' pressure.) Now we may use Eq. (68) to calculate the heat capacity of the degenerate Fermi gas:

Low-T heat capacity

$$\boxed{C_V \equiv \left(\frac{\partial E}{\partial T}\right)_V = \gamma T, \qquad \text{with } \gamma = \frac{\pi^2}{3} g(\varepsilon_F).} \tag{3.69}$$

According to Eq. (55b), in the particular case of a 3D gas with the isotropic and parabolic dispersion law (3), Eq. (69) reduces to

$$\gamma = \frac{\pi^2}{2} \frac{N}{\varepsilon_F}, \qquad \text{i.e. } c_V \equiv \frac{C_V}{N} = \frac{\pi^2}{2} \frac{T}{\varepsilon_F} << 1. \tag{3.70}$$

This important result deserves a discussion. First, note that within the range of validity of the Sommerfeld approximation ($T << \varepsilon_F$), the specific heat of the degenerate gas is much smaller than that of the classical gas, even without internal degrees of freedom: $c_V = 3/2$ – see Eq. (19). The physical reason for such a low heat capacity is that the particles deep inside the Fermi sea cannot pick up thermal excitations with available energies of the order of $T << \varepsilon_F$, because the states immediately above them are already occupied. The only particles (or rather quantum states, due to the particle indistinguishability) that may be excited with such small energies are those at the Fermi surface, more exactly within a surface layer of thickness $\Delta\varepsilon \sim T << \varepsilon_F$; Eq. (70) presents a very vivid manifestation of this fact.

The second important feature of Eqs. (69)-(70) is the linear dependence of the heat capacity on temperature, which decreases with a reduction of T much slower than that of crystal vibrations – see Eq. (2.99). This means that in metals, the specific heat at temperatures $T << T_D$ is dominated by the conduction electrons. Indeed, experiments confirm not only the linear dependence (70) of the specific heat,[31] but also the values of the proportionality coefficient $\gamma \equiv C_V/T$ for cases when ε_F can be calculated independently, for example for alkali metals – see the two rightmost columns of Table 1 above. More typically, Eq. (69) is used for the experimental measurement of the density of states on the Fermi surface, $g(\varepsilon_F)$ – the factor which participates in many theoretical results, in particular in transport properties of degenerate Fermi gases (see Chapter 6 below).

3.4. Bose-Einstein condensation

Now let us explore what happens at the cooling of an ideal gas of *bosons*. Figure 3a shows the same plot as Fig. 1b, i.e. the result of a numerical solution of Eq. (47) with the appropriate (lower) sign in the denominator, on a more appropriate log-log scale. One can see that the chemical potential μ indeed tends to zero at some finite "critical temperature" T_c. It may be found by taking $\mu = 0$ in Eq. (47), thus reducing it to a table integral:[32]

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[31] Solids, with their low thermal expansion coefficients, provide virtually-fixed-volume confinement for the electron gas, so that the specific heat measured at ambient conditions may be legitimately compared with the calculated c_V.

[32] See, e.g., MA Eq. (6.8b) with $s = 3/2$, and then Eqs. (2.7b) and (6.7e).

$$\boxed{T_c = T_0\left[\frac{1}{\sqrt{2}\pi^2}\int_0^\infty \frac{\xi^{1/2}d\xi}{e^\xi - 1}\right]^{-2/3} = T_0\left[\frac{1}{\sqrt{2}\pi^2}\Gamma\left(\frac{3}{2}\right)\zeta\left(\frac{3}{2}\right)\right]^{-2/3} \approx 3.313\, T_0,} \tag{3.71}$$

BEC: critical temperature

explaining the T_c/T_0 ratio which was already mentioned in Sec. 2 and indicated in Figs. 1 and 3.

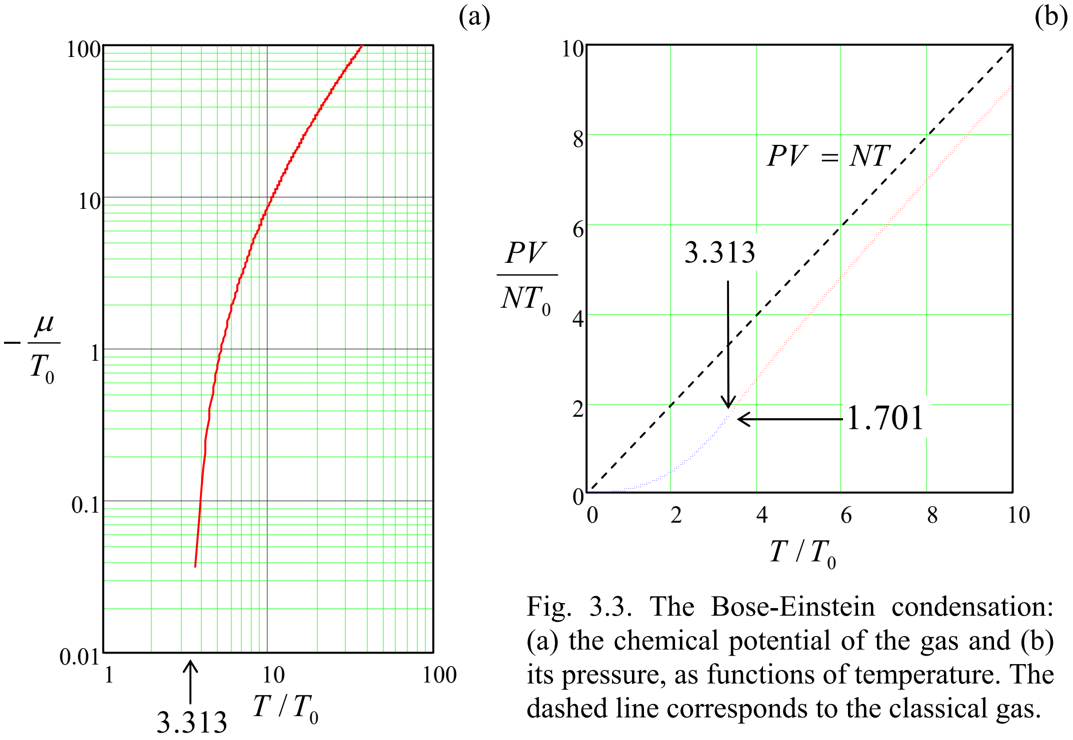

Fig. 3.3. The Bose-Einstein condensation: (a) the chemical potential of the gas and (b) its pressure, as functions of temperature. The dashed line corresponds to the classical gas.

Let us have a good look at the temperature interval $0 < T < T_c$, which cannot be directly described by Eq. (40) (with the appropriate negative sign in the denominator), and hence may look rather mysterious. Indeed, within this range, the chemical potential μ cannot either be negative or equal to zero because according to Eq. (71); in this case, Eq. (40) would give a value of N smaller than the number of particles we actually have. On the other hand, μ cannot be positive either, because the integral (40) would diverge at $\varepsilon \to \mu$ due to the divergence of the factor $\langle N(\varepsilon)\rangle$ – see, e.g., Fig. 2.15.

The only possible resolution of the paradox, suggested by A. Einstein in 1925, is as follows: at $T < T_c$, the chemical potential of each particle of the system still equals exactly zero, but a certain number (N_0 of N) of them are in the ground state (with $\varepsilon \equiv p^2/2m = 0$), forming the so-called *Bose-Einstein condensate*, usually referred to as the BEC. Since the condensate particles do not contribute to Eq. (40) (because of the factor $\varepsilon^{1/2} = 0$), their number N_0 may be calculated by using that formula or, equivalently, Eq. (44) with $\mu = 0$, to find the number ($N - N_0$) of particles still remaining in the gas, i.e. having energies $\varepsilon > 0$:

$$N - N_0 = \frac{gV(mT)^{3/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty \frac{\xi^{1/2}d\xi}{e^\xi - 1}. \tag{3.72}$$

This result is even simpler than it may look. Indeed, let us write it for the case $T = T_c$, when $N_0 = 0$:[33]

$$N = \frac{gV(mT_c)^{3/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty \frac{\xi^{1/2}d\xi}{e^\xi - 1}. \tag{3.73}$$

Dividing both sides of Eqs. (72) and (73), we get an extremely simple and elegant result:

$$\frac{N - N_0}{N} = \left(\frac{T}{T_c}\right)^{3/2}, \qquad \text{so that } N_0 = N\left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right], \quad \text{for } T \leq T_c. \tag{3.74a}$$

Please note that this result is only valid for the particles whose motion, within the volume V, is free – in other words, for a system of free particles confined within a rigid-wall box of volume V. In most experiments with the Bose-Einstein condensation of dilute gases of neutral (and hence very weakly interacting) atoms, they are held not in such a box, but at the bottom of a "soft" potential well, which may be well approximated by a 3D quadratic parabola: $U(\mathbf{r}) = m\omega^2r^2/2$. It is straightforward (and hence left for the reader's exercise) to show that in this case, the dependence of $N_0(T)$ is somewhat different:

$$N_0 = N\left[1 - \left(\frac{T}{T_c^*}\right)^3\right], \quad \text{for } T \leq T_c^*, \tag{3.74b}$$

where T_c^* is a different critical temperature, which now depends on $\hbar\omega$, i.e. on the confining potential's "steepness". (In this case, V is not exactly fixed; however, the effective volume occupied by the particles at $T = T_c^*$ is related to this temperature by a formula close to Eq. (71), so all estimates given above are still valid.) Figure 4 shows one of the first sets of experimental data for the Bose-Einstein condensation of a dilute gas of neutral atoms. Taking into account the finite number of particles in the experiment, the agreement with the simple theory is surprisingly good.

Returning to the spatially uniform Bose system, let us explore what happens below the critical temperature with its other parameters. Formula (52) with the appropriate (lower) sign shows that approaching T_c from higher temperatures, the gas energy and hence its pressure do not vanish – see the red line in Fig. 3b. Indeed, at $T = T_c$ (where $\mu = 0$), that formula yields[34]

$$E(T_c) = gV\frac{m^{3/2}T_c^{5/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty \frac{\xi^{3/2}d\xi}{e^\xi - 1} = gV\frac{m^{3/2}T_c^{5/2}}{\sqrt{2}\pi^2\hbar^3}\Gamma\left(\frac{5}{2}\right)\zeta\left(\frac{5}{2}\right) \approx 0.7701\, NT_c, \tag{3.75}$$

so using the universal relation (48), we get the following pressure value:

$$P(T_c) = \frac{2}{3}\frac{E(T_c)}{V} = \frac{\zeta(5/2)}{\zeta(3/2)}\frac{N}{V}T_c \approx 0.5134\,\frac{N}{V}T_c \approx 1.701P_0, \tag{3.76}$$

which is somewhat lower than, but comparable with $P(0)$ for the fermions – cf. Eq. (57).

---

[33] This is, of course, just another form of Eq. (71). As was mentioned earlier, the dimensionless integral involved in all these three relations is equal to $\Gamma(3/2)\zeta(3/2) \approx 2.315$.

[34] For the involved dimensionless integral see, e.g., MA Eqs. (6.8b) with $s = 5/2$, and then Eqs. (2.7b) and (6.7c).

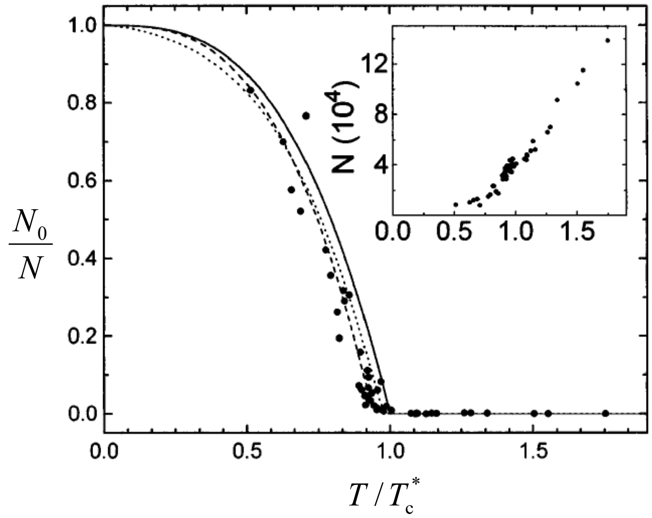

Fig. 3.4. The total number N of trapped ^{87}Rb atoms (inset) and their ground-state fraction N_0/N, as functions of the ratio T/T_c, as measured in one of the pioneering experiments – see J. Ensher *et al.*, *Phys. Rev. Lett.* **77**, 4984 (1996). In this experiment, T_c^* was as low as 0.28×10^{-6} K. The solid line shows the simple theoretical dependence $N(T)$ given by Eq. (74b), while other lines correspond to more detailed theories taking into account the finite number N of trapped atoms. © 1996 APS, reproduced with permission.

Now we can use the same Eq. (52), also with $\mu = 0$, to calculate the energy of the gas at $T < T_c$,

$$E(T) = gV\frac{m^{3/2}T^{5/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty \frac{\xi^{3/2}d\xi}{e^\xi - 1}. \qquad (3.77)$$

Comparing this relation with the first form of Eq. (75), which features the same integral, we immediately get one more simple temperature dependence:

$$\boxed{E(T) = E(T_c)\left(\frac{T}{T_c}\right)^{5/2}, \quad \text{for } T \le T_c.} \qquad (3.78)$$

BEC: energy

From the universal relation (48), we immediately see that the gas pressure follows the same dependence:

$$\boxed{P(T) = P(T_c)\left(\frac{T}{T_c}\right)^{5/2}, \quad \text{for } T \le T_c.} \qquad (3.79)$$

BEC: pressure

This temperature dependence of pressure is shown with the blue line in Fig. 3b. The plot shows that for all temperatures (both below and above T_c) the pressure is lower than that of the classical gas of the same density. Now note also that since, according to Eqs. (57) and (76), $P(T_c) \propto P_0 \propto V^{-5/3}$, while according to Eqs. (35) and (71), $T_c \propto T_0 \propto V^{-2/3}$, the pressure (79) is proportional to $V^{-5/3}/(V^{-2/3})^{5/2} = V^0$, i.e. does not depend on the volume at all! The physics of this result (which is valid at $T < T_c$ only) is that as we decrease the volume at a fixed total number N of particles, more and more of them go to the condensate, decreasing the number $(N - N_0)$ of particles in the gas phase, but not changing its spatial density and pressure. Such behavior is very typical for the coexistence of two different phases of the same matter – see, in particular, the next chapter.

The last thermodynamic variable of major interest is heat capacity, because it may be most readily measured. For temperatures $T \le T_c$, it may be easily calculated from Eq. (78):

$$C_V(T) \equiv \left(\frac{\partial E}{\partial T}\right)_{N,V} = E(T_c)\frac{5}{2}\frac{T^{3/2}}{T_c^{5/2}}, \qquad (3.80)$$

so below T_c, the capacity *increases* with temperature, at the critical temperature reaching the value

$$C_V(T_{\rm c}) = \frac{5}{2}\frac{E(T_{\rm c})}{T_{\rm c}} \approx 1.925\ N, \tag{3.81}$$

which is approximately 28% above that ($3N/2$) of the classical gas. (As a reminder, in both cases we ignore possible contributions from the internal degrees of freedom.) The analysis for $T \geq T_{\rm c}$ is a little bit more cumbersome because differentiating E over temperature – say, using Eq. (52) – one should also take into account the temperature dependence of μ that follows from Eq. (40) – see also Fig. 1. However, the most important feature of the result may be predicted without such calculation (which is left for the reader's exercise). Namely, since at $T >> T_{\rm c}$ the heat capacity has to approach the classical value $1.5N$, a temperature increase from $T_{\rm c}$ up must *decrease* C_V from the value (81), thus forming a sharp maximum (a "cusp") at the critical point $T = T_{\rm c}$ – see Fig. 5.

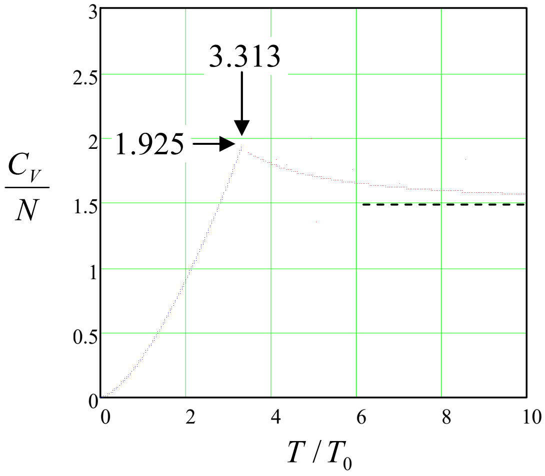

Fig. 3.5. Temperature dependences of the heat capacity of an ideal Bose-Einstein gas, numerically calculated from Eqs. (52) and (40) for $T \geq T_{\rm c}$, and given by Eq. (80) for $T \leq T_{\rm c}$.

Such a cusp is a good indication of the Bose-Einstein condensation in virtually any experimental system, especially because inter-particle interactions (unaccounted for in our simple discussion) typically make this feature even more substantial, frequently turning it into a weak (logarithmic) singularity. Historically, such a singularity was the first noticed, though not immediately understood sign of the Bose-Einstein condensation observed in 1931 by W. Keesom and K. Clusius in liquid ^{4}He at its *λ-point* (called so exactly because of the characteristic shape of the $C_V(T)$ plot) $T = T_{\rm c} \approx 2.17$ K. Other major milestones of the Bose-Einstein condensation research history include:

- the experimental discovery of superconductivity (which was later explained as the result of the Bose-Einstein condensation of electron pairs) by H. Kamerlingh-Onnes in 1911;

- the development of the Bose-Einstein statistics, and predicting the condensation, by S. Bose and A. Einstein, in 1924-1925;

- the discovery of superfluidity in liquid ^{4}He by P. Kapitza and (independently) by J. Allen and D. Misener in 1937, and its explanation as a result of the Bose-Einstein condensation by F. and H. Londons and L. Titza, with further significant elaborations by L. Landau – all in 1938;

- the explanation of superconductivity as a result of electron binding into *Cooper pairs*, with a simultaneous Bose-Einstein condensation of the resulting bosons, by J. Bardeen, L. Cooper, and J. Schrieffer in 1957;

- the discovery of superfluidity of two different phases of ^{3}He, due to the similar Bose-Einstein condensation of pairs of its fermion atoms, by D. Lee, D. Osheroff, and R. Richardson in 1972;

- the first observation of the Bose-Einstein condensation in dilute gases (^{87}Ru by E. Cornell, C. Wieman, *et al.*, and ^{23}Na by W. Ketterle *et al.*) in 1995.

The importance of the last achievement stems from the fact that in contrast to other mentioned Bose-Einstein condensates, in dilute gases (with the typical density n as low as $\sim 10^{14}$ cm^{-3}) the particles interact very weakly, and hence many experimental results are very close to the simple theory described above and its straightforward elaborations – see, e.g., Fig. 4.[35] On the other hand, the importance of other Bose-Einstein condensates, which involve more complex and challenging physics, should not be underestimated – as it sometimes is.

Perhaps the most important feature of any Bose-Einstein condensate is that all N_0 condensed particles are in the same quantum state, and hence are described by exactly the same wavefunction. This wavefunction is substantially less "feeble" than that of a single particle – in the following sense. In the second quantization language,[36] the well-known commutation relations for the generalized coordinates and momenta may be rewritten for the creation/annihilation operators; in particular, for bosons,

$$\left[\hat{a}, \hat{a}^{\dagger}\right] = \hat{I}. \tag{3.82}$$

Since $\hat{a}$ and $\hat{a}^{\dagger}$ are the quantum-mechanical operators of the complex amplitude $a = A\exp\{i\varphi\}$ and its complex conjugate $a^* = A\exp\{-i\varphi\}$, where A and φ are the real amplitude and phase of the wavefunction, Eq. (82) yields the following approximate uncertainty relation (strict in the limit $\delta\varphi << 1$) between the number of particles $N = AA^*$ and the phase φ:

$$\delta N \delta\varphi \geq ½. \tag{3.83}$$

This means that a condensate of $N >> 1$ bosons may be in a state with both phase and amplitude of the wavefunction behaving virtually as c-numbers, with very small relative uncertainties: $\delta N << N$, $\delta\varphi << 1$. Moreover, such states are much less susceptible to unintentional perturbations including the instruments used for measurements. For example, the electric current carried along a superconducting wire by a coherent Bose-Einstein condensate of Cooper pairs may be as high as hundreds of amperes. As a result, the "strange" behaviors predicted by the quantum mechanics are not averaged out as in the usual particle ensembles (see, e.g., the discussion of the density matrix in Sec. 2.1), but may be directly revealed in macroscopic, measurable dynamics of the condensate.

For example, the density **j** of the electric "supercurrent" of the Cooper pairs may be described by the same formula as the well-known usual probability current density of a single quantum particle,[37] just multiplied by the electric charge $q = -2e$ of a single pair, and the pair density n:

$$\mathbf{j} = qn\frac{\hbar}{m}\left(\nabla\varphi - \frac{q}{\hbar}\mathbf{A}\right), \tag{3.84}$$

---

[35] Such controllability of theoretical description has motivated the use of dilute-gas BECs for modeling of renowned problems of many-body physics – see, e.g. the review by I. Bloch *et al.*, *Rev. Mod. Phys.* **80**, 885 (2008). These efforts are assisted by the development of better techniques for reaching the necessary sub-μK temperatures – see, e.g., the recent work by J. Hu *et al.*, *Science* **358**, 1078 (2017). For a more general, detailed discussion see, e.g., C. Pethick and H. Smith, *Bose-Einstein Condensation in Dilute Gases*, 2nd ed., Cambridge U. Press, 2008.

[36] See, e.g., QM Sec. 8.3.

[37] See, e.g., QM Eq. (3.28).

where **A** is the vector potential of the (electro)magnetic field. If a superconducting wire is not extremely thin, the supercurrent does not penetrate into its interior.[38] As a result, the contour integral of Eq. (84), taken along a closed superconducting loop inside its interior (where **j** = 0), yields

$$\frac{q}{\hbar}\oint_C \mathbf{A}\cdot d\mathbf{r} = \Delta\varphi = 2\pi M, \tag{3.85}$$

where M is an integer. But, according to the basic electrodynamics, the integral on the left-hand side of this relation is nothing more than the flux Φ of the magnetic field $\mathscr{B}$ piercing the wire loop area A. Thus we immediately arrive at the famous *magnetic flux quantization* effect:

$$\Phi \equiv \int_A \mathscr{B}_n d^2r = M\Phi_0, \qquad \text{where } \Phi_0 \equiv \frac{2\pi\hbar}{|q|} \approx 2.07\times 10^{-15}\,\text{Wb}, \tag{3.86}$$

which was theoretically predicted in 1950 and experimentally observed in 1961. Amazingly, this effect holds even (citing H. Casimir's famous expression) "over miles of dirty lead wire", sustained by the coherence of the Bose-Einstein condensate of Cooper pairs.

Other prominent examples of such *macroscopic quantum effects* in Bose-Einstein condensates include not only the superfluidity and superconductivity as such, but also the Josephson effect, quantized Abrikosov vortices, etc. Some of these effects are discussed in other parts of this series.[39]

3.5. Gases of weakly interacting particles

Now let us discuss the effects of weak particle interaction effects on the properties of their gas. (Unfortunately, I will have time to do that only very briefly, and only for classical gases.[40]) In most cases of interest, particle interaction may be well described by a certain potential energy U, so in the simplest model, the total energy is

$$E = \sum_{k=1}^{N}\frac{p_k^2}{2m} + U(\mathbf{r}_1,..,\mathbf{r}_k,...,\mathbf{r}_N), \tag{3.87}$$

where $\mathbf{r}_k$ is the radius vector of the k^{th} particle's center.[41] First, let us see how far would the statistical physics allow us to proceed for an arbitrary potential U. For $N >> 1$, at the calculation of the Gibbs statistical sum (2.59), we may perform the usual transfer from the summation over all quantum states of the system to the integration over the $6N$-dimensional space, with the correct Boltzmann counting:

$$Z = \sum_m e^{-E_m/T} \to \frac{1}{N!}\frac{g^N}{(2\pi\hbar)^{3N}}\int \exp\left\{-\sum_{k=1}^{N}\frac{p_j^2}{2mT}\right\}d^3p_1...d^3p_N \int_{r_k\in V}\exp\left\{-\frac{U(\mathbf{r}_1,...\mathbf{r}_N)}{T}\right\}d^3r_1...d^3r_N$$

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[38] This is the *Meissner-Ochsenfeld* (or just "Meissner") *effect* which may be also readily explained using Eq. (84) combined with the Maxwell equations – see, e.g., EM Sec. 6.4.

[39] See EM Secs. 6.4-6.5, and QM Secs. 1.6 and 3.1.

[40] Discussions of the effects of weak interactions on the properties of *quantum* gases may be found, for example, in the textbooks by Huang and by Pathria and Beale – see *References*.

[41] One of the most significant effects *neglected* by Eq. (87) is the influence of atomic/molecular angular orientations on their interactions.

$$\equiv \left(\frac{1}{N!} \frac{g^N V^N}{(2\pi\hbar)^{3N}} \int \exp\left\{ -\sum_{k=1}^{N} \frac{p_j^2}{2mT} \right\} d^3 p_1 ... d^3 p_N \right) \times \left(\frac{1}{V^N} \int_{r_k \in V} \exp\left\{ -\frac{U(\mathbf{r}_1, ...\mathbf{r}_N)}{T} \right\} d^3 r_1 ... d^3 r_N \right). \quad (3.88)$$

But according to Eq. (14), the first operand in the last product is just the statistical sum of an ideal gas (with the same g, N, V, and T), so we may use Eq. (2.63) to write

$$\begin{aligned} F &= F_{\text{ideal}} - T \ln \left[\frac{1}{V^N} \int_{r_k \in V} \exp\left\{ -\frac{U(\mathbf{r}_1, ...\mathbf{r}_N)}{T} \right\} d^3 r_1 ... d^3 r_N \right] \\ &\equiv F_{\text{ideal}} - T \ln \left[1 + \frac{1}{V^N} \int_{r_k \in V} \left(e^{-U/T} - 1 \right) d^3 r_1 ... d^3 r_N \right], \end{aligned} \quad (3.89)$$

where F_{ideal} is the free energy of the ideal gas (i.e. of the same gas but with $U = 0$), given by Eq. (16).

I believe that Eq. (89) is a very convincing demonstration of the enormous power of statistical physics methods. Instead of trying to solve an impossibly complex problem of classical dynamics of $N >> 1$ (think of $N \sim 10^{23}$) interacting particles, and only then calculating appropriate ensemble averages, the Gibbs approach reduces finding the free energy (and then, from thermodynamic relations, all other thermodynamic variables) to the calculation of just one integral on its right-hand side of Eq. (89). Still, this integral is $3N$-dimensional and may be worked out analytically only if the particle interactions are weak in some sense. Indeed, the last form of Eq. (89) makes it especially evident that if $U \to 0$ everywhere, the term in the parentheses under the integral vanishes, and so does the integral itself, and hence the addition to F_{ideal}.

Now let us see what would this integral yield for the simplest, *short-range* interactions, in which the potential U is substantial only when the mutual distance $\mathbf{r}_{kk'} \equiv \mathbf{r}_k - \mathbf{r}_{k'}$ between the centers of two particles is smaller than a certain value $2r_0$, where r_0 may be interpreted as the particle's radius. If the gas is sufficiently dilute, so the radius r_0 is much smaller than the average distance r_{ave} between the particles, the integral in the last form of Eq. (89) is of the order of $(2r_0)^{3N}$, i.e. much smaller than $(r_{\text{ave}})^{3N} \equiv V^N$. Then we may expand the logarithm in that expression into the Taylor series with respect to the small second term in the square brackets, and keep only its first non-zero term:

$$F \approx F_{\text{ideal}} - \frac{T}{V^N} \int_{r_k \in V} \left(e^{-U/T} - 1 \right) d^3 r_1 ... d^3 r_N \, . \quad (3.90)$$

Moreover, if the gas density is so low, the chances for three or more particles to come close to each other and interact (collide) simultaneously are typically very small, so *pair collisions* are the most important ones. In this case, we may recast the integral in Eq. (90) as a sum of $N(N-1)/2 \approx N^2/2$ similar terms describing such pair interactions, each of the type

$$V^{N-2} \int_{r_k, r_{k'} \in V} \left(e^{-U(\mathbf{r}_{kk'})/T} - 1 \right) d^3 r_k d^3 r_{k'} \, . \quad (3.91)$$

It is convenient to think about the $\mathbf{r}_{kk'} \equiv \mathbf{r}_k - \mathbf{r}_{k'}$ as the radius vector of the particle number k in the reference frame with the origin placed at the center of the particle number k' – see Fig. 6a. Then in Eq. (91), we may first calculate the integral over $\mathbf{r}_{k'}$, while keeping the distance vector $\mathbf{r}_{kk'}$, and hence $U(\mathbf{r}_{kk'})$, constant, getting one more factor V. Moreover, since all particle pairs are similar, in the remaining integral over $\mathbf{r}_{kk'}$ we may drop the radius vector's index, so Eq. (90) becomes

$$F = F_{\text{ideal}} - \frac{T}{V^N}\frac{N^2}{2}V^{N-1}\int\left(e^{-U(\mathbf{r})/T}-1\right)d^3r \equiv F_{\text{ideal}} + \frac{T}{V}N^2 B(T), \tag{3.92}$$

where the function $B(T)$, called the *second virial coefficient*,[42] has an especially simple form for spherically symmetric interactions:

Second virial coefficient

$$\boxed{B(T) \equiv \frac{1}{2}\int\left(1-e^{-U(\mathbf{r})/T}\right)d^3r \rightarrow \frac{1}{2}\int_0^\infty 4\pi r^2 dr\left(1-e^{-U(r)/T}\right).} \tag{3.93}$$

From Eq. (92), and the second of the thermodynamic relations (1.35), we already know something particular about the equation of state $P(V, T)$ of such a gas:

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = P_{\text{ideal}} + \frac{N^2T}{V^2}B(T) = T\left[\frac{N}{V}+B(T)\frac{N^2}{V^2}\right]. \tag{3.94}$$

We see that at a fixed gas density $n = N/V$, the pair interaction creates additional pressure, proportional to $(N/V)^2 = n^2$ and a function of temperature, $B(T)T$.

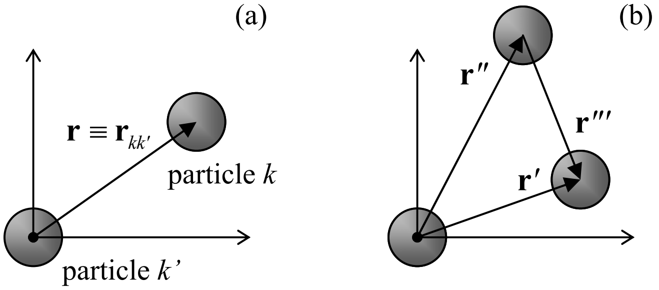

Fig. 3.6. The definition of the interparticle distance vectors at their (a) pair and (b) triple interactions.

Let us calculate $B(T)$ for a few simple models of particle interactions. The solid curve in Fig. 7 shows (schematically) a typical form of the interaction potential between electrically neutral atoms/molecules. At large distances the interaction of particles without their own permanent electrical dipole moment **p**, is dominated by the attraction (the so-called *London dispersion force*) between the correlated components of the spontaneously induced dipole moments, giving $U(r) \rightarrow r^{-6}$ at $r \rightarrow \infty$.[43] At closer distances the potential is repulsive, growing very fast at $r \rightarrow 0$, but its quantitative form is specific for particular atoms/molecules.[44] The crudest description of such repulsion is given by the so-called *hardball* (or "hard-sphere") *model*:

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[42] The term "virial", from the Latin *viris* (meaning "force"), was introduced to molecular physics by R. Clausius. The motivation for the adjective "second" for $B(T)$ is evident from the last form of Eq. (94), with the "first virial coefficient", standing before the N/V ratio and sometimes denoted $A(T)$, equal to 1 – see also Eq. (100) below.

[43] Indeed, independent fluctuation-induced components $\mathbf{p}(t)$ and $\mathbf{p}'(t)$ of dipole moments of two particles have random mutual orientation, so that the time average of their interaction energy, proportional to $\mathbf{p}(t)\cdot\mathbf{p}'(t)/r^3$, vanishes. However, the electric field $\mathscr{E}$ of each dipole **p**, proportional to r^{-3}, induces a correlated component of **p**', also proportional to r^{-3}, giving interaction energy $U(r)$ proportional to $\mathbf{p}'\cdot\mathscr{E} \propto r^{-6}$, with a non-zero statistical average. Quantitative discussions of this effect, within several models, may be found, for example, in QM Chapters 3, 5, and 6.

[44] Note that the particular form of the first term in the approximation $U(r) = a/r^{12} - b/r^6$ (called either the *Lennard-Jones potential* or the "12-6 potential"), that had been suggested in 1924, lacks physical justification, and in professional physics was soon replaced with other approximations, including the so-called *exp-6 model*,

$$U(r)=\begin{cases}+\infty, & \text{for } 0<r<2r_0,\\ 0, & \text{for } 2r_0<r<\infty,\end{cases} \tag{3.95}$$

– see the dashed line and the inset in Fig. 7. (The distance $2r_0$ is sometimes called the *van der Waals radius* of the particle.)

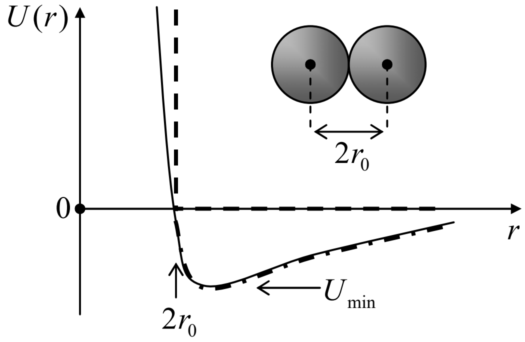

Fig. 3.7. Pair interactions of particles. Solid line: a typical interaction potential; dashed line: its hardball model (95); dash-dotted line: the improved model (97) – all schematically. The inset illustrates the hardball model's physics.

As Eq. (93) shows, in this model the second virial coefficient is temperature-independent:

$$B(T)=b\equiv\frac{1}{2}\int_0^{2r_0}4\pi r^2dr=\frac{2\pi}{3}(2r_0)^3\equiv 4V_0, \qquad \text{where } V_0\equiv\frac{4\pi}{3}r_0^3, \tag{3.96}$$

so the equation of state (94) still gives a linear dependence of pressure on temperature.

A correction to this result may be obtained by the following approximate account of the long-range attraction (see the dash-dotted line in Fig. 7):[45]

$$U(r)=\begin{cases}+\infty, & \text{for } 0<r<2r_0,\\ U(r)<0, \text{ with } |U|\ll T, & \text{for } 2r_0<r<\infty.\end{cases} \tag{3.97}$$

For this improved model, Eq. (93) yields:

$$B(T)\approx b+\frac{1}{2}\int_{2r_0}^{\infty}4\pi r^2dr\frac{U(r)}{T}\equiv b-\frac{a}{T}, \qquad \text{with } a\equiv 2\pi\int_{2r_0}^{\infty}|U(r)|r^2dr>0. \tag{3.98}$$

In this model, the equation of state (94) acquires a temperature-independent term:

$$P=T\left[\frac{N}{V}+\left(\frac{N}{V}\right)^2\left(b-\frac{a}{T}\right)\right]\equiv T\left[\frac{N}{V}+b\left(\frac{N}{V}\right)^2\right]-a\left(\frac{N}{V}\right)^2. \tag{3.99}$$

Still, the correction to the ideal-gas pressure is proportional to $(N/V)^2$ and has to be relatively small for this result to be valid.

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which fits most experimental data much better. However, the Lennard-Jones potential still keeps creeping from one undergraduate textbook to another one, apparently for a not better reason than enabling a simple analytical calculation of the equilibrium distance between the particles at $T\to 0$.

[45] The strong inequality $|U| \ll T$ in this model is necessary not only to make the calculations simpler. A deeper reason is that if $(-U_{\min})$ becomes comparable with T, particles may become trapped in this potential well, forming a different phase – a liquid or a solid. In such phases, the probability of finding more than two particles interacting simultaneously is high, so Eq. (92), on which Eqs. (93)-(94) and Eqs. (98)-(99) are based, becomes invalid.

Generally, the right-hand side of Eq. (99) may be considered as the sum of two leading terms in the general expansion of P into the Taylor series in low density $n = N/V$ of the gas:

Pressure: virial expansion

$$\boxed{P = T\left[\frac{N}{V} + B(T)\left(\frac{N}{V}\right)^2 + C(T)\left(\frac{N}{V}\right)^3 + \ldots\right],} \tag{3.100}$$

where $C(T)$ is called the *third virial coefficient.* It is natural to ask how can we calculate $C(T)$ and the higher virial coefficients. This may be done by a tedious direct analysis of Eq. (90),[46] but the calculations may be streamlined using a different, rather counter-intuitive approach called the *cluster expansion method*.[47]

Let us apply to our system, with the energy given by Eq. (87), the grand canonical distribution. (Just as in Sec. 2, we may argue that if the average number $\langle N\rangle$ of particles in each member of a grand canonical ensemble, with fixed μ and T, is much larger than 1, the relative fluctuations of N are small, so all its thermodynamic properties should be similar to those when N is exactly fixed.) For our current purposes, Eq. (2.109) may be rewritten in the form

$$\Omega = -T\ln\sum_{N=0}^{\infty} Z_N, \quad \text{with } Z_N \equiv e^{\mu N/T}\sum_m e^{-E_{m,N}/T}, \quad E_{m,N} = \sum_{k=1}^{N}\frac{p_k^2}{2m} + U(r_1,\ldots,r_N). \tag{3.101}$$

(Notice that here, as at all discussions of the grand canonical distribution, N means a particular rather than the average number of particles.) Now let us try to forget for a minute that in real systems of interest the number of particles is extremely large, and start to calculate, one by one, the first terms Z_N.

In the term with $N = 0$, both contributions to $E_{m,N}$ vanish, and so does the factor $\mu N/T$, and hence $Z_0 = 1$. In the next term, with $N = 1$, the interaction term vanishes, so $E_{m,1}$ is reduced to the kinetic energy of one particle, giving

$$Z_1 = e^{\mu/T}\sum_k \exp\left\{-\frac{p_k^2}{2mT}\right\}. \tag{3.102}$$

Making the usual transition from the summation to integration, we may write

$$Z_1 = ZI_1, \quad \text{where } Z \equiv e^{\mu/T}\frac{gV}{(2\pi\hbar)^3}\int \exp\left\{-\frac{p^2}{2mT}\right\}d^3p, \quad \text{and } I_1 \equiv 1. \tag{3.103}$$

This is the same simple (Gaussian) integral as in Eq. (6), giving

$$Z = e^{\mu/T}\frac{gV}{(2\pi\hbar)^3}(2\pi mT)^{3/2} = e^{\mu/T}gV\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}. \tag{3.104}$$

Now let us explore the next term, with $N = 2$, which describes, in particular, pair interactions $U = U(\mathbf{r})$, with $\mathbf{r} = \mathbf{r} - \mathbf{r}'$. Due to the assumed particle indistinguishability, this term needs the "correct Boltzmann counting" factor 1/2! – cf. Eqs. (12) and (88):

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[46] L. Boltzmann has used that way to calculate the 3rd and 4th virial coefficients for the hardball model – as much as can be done analytically.

[47] This method was developed in 1937-38 by J. Mayer and collaborators for the classical gas, and generalized to quantum systems in 1938 by B. Kahn and G. Uhlenbeck.

$$Z_2 = e^{2\mu/T}\frac{1}{2!}\sum_{k,k'}\left[\exp\left\{-\frac{p_k^2}{2mT}-\frac{p_{k'}^2}{2mT}\right\}e^{-U(\mathbf{r})/T}\right]. \tag{3.105}$$

Since U is coordinate-dependent, here the transfer from the summation to integration should be done more carefully than in the first term – cf. Eqs. (24) and (88):

$$Z_2 = e^{2\mu/T}\frac{1}{2!}\frac{(gV)^2}{(2\pi\hbar)^6}\int\exp\left\{-\frac{p^2}{2mT}\right\}d^3p\times\int\exp\left\{-\frac{p'^2}{2mT}\right\}d^3p'\times\frac{1}{V}\int e^{-U(\mathbf{r})/T}d^3r. \tag{3.106}$$

Comparing this expression with Eq. (103) for the parameter Z, we get

$$Z_2 = \frac{Z^2}{2!}I_2, \qquad \text{where } I_2 \equiv \frac{1}{V}\int e^{-U(\mathbf{r})/T}d^3r. \tag{3.107}$$

Acting absolutely similarly, for the third term of the grand canonical sum we may get

$$Z_3 = \frac{Z^3}{3!}I_3, \quad \text{where } I_3 \equiv \frac{1}{V^2}\int e^{-U(\mathbf{r}',\mathbf{r}'')/T}d^3r'd^3r'', \tag{3.108}$$

where $\mathbf{r}'$ and $\mathbf{r}''$ are the vectors characterizing the mutual positions of three particles in their "cluster" – see Fig. 6b.

These results may be readily generalized to clusters of arbitrary size N. Plugging the resulting expression for Z_N into the first of Eqs. (101) and recalling that $\Omega = -PV$, we get the equation of state of the gas in the form

$$P = \frac{T}{V}\ln\left(1 + ZI_1 + \frac{Z^2}{2!}I_2 + \frac{Z^3}{3!}I_3 + \ldots\right). \tag{3.109}$$

As a sanity check: at $U = 0$, all integrals I_N are equal to 1, and the expression under the logarithm is just the Taylor expansion of the function e^Z, giving $P = TZ/V$, and $\Omega = -PV = -TZ$. In this case, according to the last of Eqs. (1.62), the average number of particles in the system is $\langle N\rangle = -(\partial\Omega/\partial\mu)_{T,V} = Z$, because since $Z \propto \exp\{\mu/T\}$, $\partial Z/\partial\mu = Z/T$.[48] Thus, in this limit, we have happily recovered the equation of state of the ideal gas.

Returning to the general case of non-zero interactions, let us assume that the logarithm in Eq. (109) may be also represented as a direct Taylor expansion in Z:

Cluster expansion: pressure

$$\boxed{P = \frac{T}{V}\sum_{l=1}^{\infty}\frac{J_l}{l!}Z^l,} \tag{3.110}$$

where J_l are some Z-independent coefficients, still to be calculated. (The lower limit of the sum reflects the fact that according to Eq. (109), at $Z = 0$, $P = (T/V)\ \ln 1 = 0$, so the coefficient J_0 in a more complete version of Eq. (110) would equal 0 anyway.) According to Eq, (1.60), this expansion corresponds to the grand potential

$$\Omega = -PV = -T\sum_{l=1}^{\infty}\frac{J_l}{l!}Z^l. \tag{3.111}$$

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[48] Actually, the fact that in that case $\langle N\rangle = Z$ could have been noted earlier – just by comparing Eq. (104) with Eq. (32b).

Again using the last of Eqs. (1.62), and the already mentioned fact that according to Eq. (104), $\partial Z/\partial\mu = Z/\mu$, we get

Cluster expansion: $\langle N\rangle$

$$\boxed{\langle N\rangle = \sum_{l=1}^{\infty}\frac{J_l}{(l-1)!}Z^l .} \tag{3.112}$$

(Note that this sum differs from that in Eq. (110) "only" by an extra factor l in each term.)

Equations (110) and (112) essentially give the solution of our problem by representing the equation of state of the gas in the parametric form, with the factor Z serving as the parameter. The only remaining conceptual action item is to express the coefficients J_l via the integrals I_N participating in the expansion (109). This may be done using the well-known Taylor expansion of the logarithm function,[49]

$$\ln(1+\xi) = \sum_{l=1}^{\infty}(-1)^{l+1}\frac{\xi^l}{l}. \tag{3.113}$$

Applying it to Eq. (109), we get a Taylor series in Z, starting as

$$P = \frac{T}{V}\left[Z + \frac{Z^2}{2!}(I_2-1) + \frac{Z^3}{3!}\left[(I_3-1)-3(I_2-1)\right]+...\right]. \tag{3.114}$$

Comparing this expression with Eq. (110), we see that

$$\begin{aligned}
J_1 &= 1,\\
J_2 &= I_2 - 1 = \frac{1}{V}\int\left(e^{-U(\mathbf{r})/T}-1\right)d^3r,\\
J_3 &= (I_3-1)-3(I_2-1)\\
&= \frac{1}{V^2}\int\left(e^{-U(\mathbf{r}',\mathbf{r}'')/T} - e^{-U(\mathbf{r}')/T} - e^{-U(\mathbf{r}'')/T} - e^{-U(\mathbf{r}''')/T} + 2\right)d^3r'd^3r'', ...
\end{aligned} \tag{3.115}$$

where $\mathbf{r}''' \equiv \mathbf{r}' - \mathbf{r}''$ – see Fig. 6b. The expression for J_2, describing the pair interactions of particles, shows that besides a factor of $(V/2)$, this is just the second virial coefficient $B(T)$ – cf. Eq. (93). As a reminder, the subtraction of 1 from the integral I_2 in that expression makes the contribution of each elementary 3D volume d^3r into the integral J_2 different from zero only if at this $\mathbf{r}$ two particles interact ($U \neq 0$). Very similarly, in the last of Eqs. (115), the subtraction of three pair-interaction terms from (I_3 – 1) makes the contribution from an elementary 6D volume $d^3r'd^3r''$ into the integral J_3 different from zero only if at that mutual location of particles, all *three* of them interact simultaneously, etc.

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[49] Looking at Eq. (109), one might think that since $\xi = Z + Z^2I_2/2 + \ldots$ is of the order of at least $Z \sim \langle N\rangle$, the expansion (113), which converges only if $|\xi| < 1$, is illegitimate for $\langle N\rangle >> 1$. However, it is justified by the result (114), in which the n^{th} term is of the order of $\langle N\rangle^n(V_0/V)^{n-1}/n!$, so that the series does converge if the gas density is sufficiently low: $\langle N\rangle/V << 1/V_0$, i.e. $r_{\text{ave}} >> r_0$. This is the very beauty of the cluster expansion whose few first terms, perhaps unexpectedly, give good approximation even for gases with $\langle N\rangle >> 1$ particles. The physics behind this trick is that the subtraction of 1 from each exponent of the type $\exp\{-U/T\}$ automatically includes, to the final result, contributions from only minor but the only important parts of the $6N$-dimensional phase space, in which the particles interact. As a result, the sum (114) is over the number of particles in each cluster (not in the whole gas!), with an analytical summation of equal contributions from all possible clusters with the same number l of particles in each of them – just as it is done by Eqs. (92)-(93) for the particular case $l = 2$.

The relations (110), (114), and (115) give the final result of the cluster expansion. To see this result at work, let us eliminate the factor Z from this system of equations, with accuracy up to terms $O(Z^2)$. For that, we need to spell out each of these relations up to terms $O(Z^3)$:

$$\frac{PV}{T} = J_1 Z + \frac{J_2}{2} Z^2 + \frac{J_3}{6} Z^3 + \dots, \tag{3.116}$$

$$\langle N \rangle = J_1 Z + J_2 Z^2 + \frac{J_3}{2} Z^3 + \dots, \tag{3.117}$$

and then divide these two expressions, getting the result

$$\frac{PV}{\langle N \rangle T} = \frac{1 + (J_2/2J_1)Z + (J_3/6J_1)Z^2 + \dots}{1 + (J_2/J_1)Z + (J_3/2J_1)Z^2 + \dots} \approx 1 - \frac{J_2}{2J_1} Z + \left(\frac{J_2^2}{2J_1^2} - \frac{J_3}{3J_1} \right) Z^2 . \tag{3.118}$$

In this approximation, we may again use Eq. (117), now solved for Z with the same accuracy $O(Z^2)$:

$$Z \approx \langle N \rangle - \frac{J_2}{J_1} \langle N \rangle^2 . \tag{3.119}$$

Plugging this expression into Eq. (118), we get the virial expansion (100) with

$$\boxed{B(T) = -\frac{J_2}{2J_1} V, \qquad C(T) = \left(\frac{J_2^2}{J_1^2} - \frac{J_3}{3J_1} \right) V^2 .} \tag{3.120}$$

2nd and 3rd virial coefficients

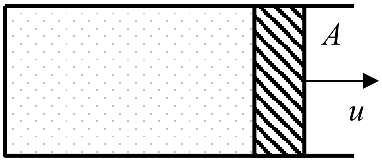
The first of these relations, combined with the first two of Eqs. (115), yields for the 2nd virial coefficient the same Eq. (93) that was obtained from the Gibbs distribution, in particular Eq. (96), $B(T) = 4V_0$, for the hardball model. The second of these results enables the calculation of the 3rd virial coefficient; for the hardball model, $C(T) = 10V_0^2$. (Let me leave the proof of the last result for the reader's exercise.) Evidently, a more complete expansion of Eqs. (110), (114), and (115) may be used to calculate an arbitrary virial coefficient, though starting from the 5th of them, the calculations of the necessary coefficients J_l may be completed only numerically even for the simplest hardball model.

Note that in this model, the virial coefficients $B(T)$, $C(T)$, etc. do not actually depend on temperature. (This is clear already from the above expressions for the integrals I_n and hence J_n.) As a result, by reproducing the calculations (1.45)-(1.47) for Eq. (100), we may readily see that the internal energy E of the gas, in the hardball model, is independent of its volume – just as for the ideal one.

3.6. Exercise problems

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.

Hint: You may assume the simplest geometry of the engine – see Fig. 2.4.



3.2. Use the Maxwell distribution to calculate the *drag coefficient* $\eta \equiv -\partial\langle \mathscr{F} \rangle/\partial u$, where 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.

3.3. Derive the equation of state of an ideal classical gas from the grand canonical distribution.

3.4. Prove that Eq. (22), 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 particles in each of the initial volumes are indistinguishable from each other but different from those in the counterpart volume. For simplicity, you may assume that the masses and internal degeneracy factors of all the particles are equal.

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.

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.

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.

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..

3.9. The inner surfaces of the walls of a closed container of volume V, filled with $N >> 1$ particles, have $N_S >> 1$ 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.

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.

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.

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.[50]

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 a simpler model, in that the Coulomb electron-electron interaction is completely ignored.

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 a degenerate, isotropic 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}.

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 $T << \varepsilon_{\text{F}}$. Compare the results with those for the ideal classical gas.

Hint: You may like to use the solution of Problem 1.9.

3.16. How would the Fermi statistics of an ideal gas affect the barometric formula (28)?

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.[51] Calculate E and also the gas pressure P explicitly in the degenerate gas limit $T \to 0$. In particular, is Eq. (48) valid in this case?

3.18. Use Eq. (49) 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.

3.19.[*] Calculate the speed of sound in an ideal gas of ultra-relativistic fermions of density n at negligible temperature.

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[50] 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 the 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.

[51] 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.)

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 $T/\varepsilon_F << 1$),

neglecting the Coulomb interaction effects.[52]

3.21. Calculate the differential latent heat $\Lambda_{ef} \equiv -N(\partial Q/\partial N_0)_{N,V}$ 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.

3.22.* For a spatially uniform ideal Bose gas, calculate the law of the chemical potential's disappearance at $T \to T_c$ and use the result to prove that at the critical point $T = T_c$, the heat capacity C_V is a continuous function of temperature.

3.23. In Chapter 1, several thermodynamic relations involving entropy have been discussed, including the first of Eqs. (1.39):

$$S = -\left(\partial G / \partial T\right)_P .$$

If we combine this expression with Eq. (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 at 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

$$C_V = T\left(\partial S / \partial T\right)_V .$$

(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. (80), the specific heat for the Bose-Einstein condensate is proportional to $T^{3/2}$, so the integration gives a non-zero entropy $S \propto T^{3/2}$. Resolve this apparent contradiction, and calculate the value of the genuine entropy at $T = T_c$.

3.24. The standard analysis of the Bose-Einstein condensation, outlined in Sec. 4, 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. (71) for the critical temperature of the system of $N >> 1$ particles, are affected by such quantization.

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[52] 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. 1.6, 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.

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. (74b) and calculate the critical temperature T_c^*. Looking at the solution, what is the most straightforward way to detect the condensation in experiment?

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.

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 $U(\boldsymbol{\rho}) = m\omega^2\rho^2/2$, where $\boldsymbol{\rho}$ is the 2D radius vector within the particle confinement plane? If yes, calculate the critical temperature of the condensation.

3.28. Use Eqs. (115) and (120) to calculate the third virial coefficient $C(T)$ for the hardball model of particle interactions.

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.[53]

3.30. A 1D *Tonks' gas* is a set of N classical hard rods of length l confined to a segment of length $L > Nl$, 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 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. (93).

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[53] See, e.g., CM Sec. 8.2.