Chapter 4. Phase Transitions

This chapter gives a brief discussion of the coexistence between different states ("phases") of systems consisting of many similar interacting particles, and transitions between these phases. Due to the complexity of these phenomena, quantitative analytical results in this field have been obtained only for a few very simple models, typically giving rather approximate descriptions of real systems.

4.1. First-order phase transitions

From our everyday experience, say with water ice, liquid water, and water vapor, we know that one chemical substance (i.e. a system of many similar particles) may exist in different stable states – *phases*. A typical substance may have:

(i) a dense *solid phase*, in which interparticle forces keep all atoms/molecules in virtually fixed relative positions, with just small thermal fluctuations about them;

(ii) a *liquid phase*, of comparable density, in which the relative distances between atoms or molecules are almost constant, but these particles are virtually free to move around each other, and

(iii) a *gas phase*, typically of a much lower density, in which the molecules are virtually free to move all around the containing volume.[1]

Experience also tells us that at certain conditions, two different phases may be in thermal and chemical equilibrium – say, ice floating on water at the freezing-point temperature. Actually, in Sec. 3.4 we already discussed a quantitative theory of one such equilibrium: the Bose-Einstein condensate's coexistence with the uncondensed gas of similar particles. However, this is a rather exceptional case when the phase coexistence is due to the quantum nature of the particles (bosons) rather than their direct interaction. Much more frequently, the formation of different phases and transitions between them are due to particle repulsive and attractive interactions, briefly discussed in Sec. 3.5.

Phase transitions are sometimes classified by their *order*.[2] I will start their discussion with the so-called *first-order phase transitions* that feature non-zero *latent heat* Λ – the thermal energy that is necessary to turn one phase into another phase completely, even if temperature and pressure are kept constant.[3] Unfortunately, even the simplest "microscopic" models of particle interaction, such as those discussed in Sec. 3.5, give rather complex equations of state. (As a reminder, even the simplest hardball model leads to the series (3.100), whose higher virial coefficients defy analytical calculation.) This is

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[1] Plasma, in which atoms are partly or completely ionized, is frequently mentioned on one more phase, on equal footing with the three phases listed above, but one has to remember that in contrast to them, a typical electroneutral plasma consists of particles of two very different sorts – positive ions and electrons.

[2] Such classification schemes, started by Paul Ehrenfest in the early 1930s, have been repeatedly modified to accommodate new results for particular systems, and by now only the "first-order phase transition" is still a generally accepted term, but with a definition different from the original one.

[3] For example, for water the latent heat of vaporization at the ambient pressure is as high as $\sim 2.2 \times 10^6$ J/kg, i.e. $\sim$ 0.4 eV per molecule, making this ubiquitous liquid indispensable for fire fighting. (The latent heat of water ice's melting is an order of magnitude lower.)

why I will follow the tradition of discussing the first-order phase transitions on the example of a simple phenomenological model suggested in 1873 by Johannes Diderik van der Waals.

For its introduction, it is useful to recall that in Sec. 3.5 we have derived Eq. (3.99) – the equation of state for a classical gas of weakly interacting particles, which takes into account (albeit approximately) both interaction components necessary for a realistic description of gas condensation/liquefaction: the long-range attraction of the particles and their short-range repulsion. Let us rewrite that result as follows:

$$P + a\frac{N^2}{V^2} = \frac{NT}{V}\left(1 + \frac{Nb}{V}\right). \tag{4.1}$$

As we saw while deriving this formula, the physical meaning of the constant b is the effective volume of space taken by a particle pair collision – see Eq. (3.96). The relation (1) is quantitatively valid only if the second term in the parentheses is small, $Nb \ll V$, i.e. if the total volume excluded from particles' free motion because of their collisions is much smaller than the whole volume V. In order to describe the condensed phase (which I will call "liquid" [4]), we need to generalize this relation to the case $Nb \sim V$. Since the effective volume left for particles' motion is $V - Nb$, it is very natural to make the following replacement: $V \to V - Nb$, in the equation of state of the ideal gas.[5] If we also keep on the left-hand side the term aN^2/V^2, which describes the long-range attraction, we get the so-called *van der Waals equation* of state:

$$\boxed{P + a\frac{N^2}{V^2} = \frac{NT}{V - Nb}.} \tag{4.2}$$

Van der
Waals
equation

Taylor-expanding the right-hand side of this relation in small $Nb/V \ll 1$, we see that its first two terms return us to the microscopically justified Eq. (1); however, already the next term of the expansion gives a virial coefficient $C(T)$ different from the microscopically-derived Eq. (3.120), due to the phenomenological nature of Eq. (2). Let us explore the basic properties of this famous model.

It is frequently convenient to discuss any equation of state in terms of its isotherms, i.e. the $P(V)$ curves plotted at constant T. As Eq. (2) shows, in the van der Waals model, such a plot depends on four parameters: a, b, N, and T, making formulas bulky. To simplify them, it is convenient to introduce dimensionless variables: pressure $p \equiv P/P_c$, volume $v \equiv V/V_c$, and temperature $t \equiv T/T_c$, all normalized to their so-called *critical values*,

$$P_c \equiv \frac{1}{27}\frac{a}{b^2}, \quad V_c \equiv 3Nb, \quad T_c \equiv \frac{8}{27}\frac{a}{b}, \tag{4.3}$$

whose meaning will be clear in a minute. In this notation, Eq. (2) acquires the following form (historically called the *law of corresponding states*):

$$p + \frac{3}{v^2} = \frac{8t}{3v - 1}, \tag{4.4}$$

so the isotherms $p(v)$ depend on only one parameter, the normalized temperature t – see Fig. 1.

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[4] Due to the phenomenological character of the van der Waals model, one cannot say for sure whether the condensed phase it predicts corresponds to a liquid or a solid. However, for most real substances at ambient conditions, gas coexists with liquid, hence the name.

[5] For the 1D gas of non-zero-size particles ("rods") with hard-core next-neighbor interactions, such replacement gives the exact result - see the solution of Problem 3.30. Unfortunately, this is not true in higher dimensions.
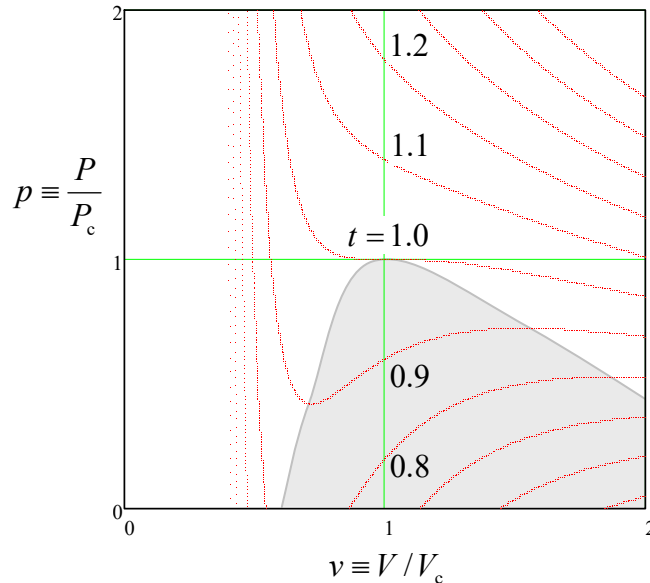
Fig. 4.1. The van der Waals equation of state, plotted on the $[v, p]$ plane for several values of the normalized temperature $t \equiv T/T_c$. Shading shows the range of single-phase instability where $(\partial P/\partial V)_T > 0$.

The most important property of these plots is that the isotherms have qualitatively different shapes in two temperature regions. At $t > 1$, i.e. $T > T_c$, pressure increases monotonically at gas compression (qualitatively, as in an ideal classical gas, with $P = NT/V$, to which the van der Waals system tends at $T >> T_c$), i.e. with $(\partial P/\partial V)_T < 0$ at all points.[6] However, below the critical temperature T_c, any isotherm features a segment with $(\partial P/\partial V)_T > 0$. It is easy to understand that, at least in a constant-pressure experiment (see, for example, Fig. 1.5),[7] these segments describe a mechanically unstable equilibrium. Indeed, if due to a random fluctuation, the volume deviated upward from its equilibrium value, the pressure would also increase, forcing the environment (say, the heavy piston in Fig. 1.5) to allow further expansion of the system, leading to an even higher pressure, etc. A similar deviation of volume downward would lead to a similar avalanche-like decrease. Such avalanche instability would develop further and further until the system has reached one of the stable branches with a negative slope $(\partial P/\partial V)_T$. In the range where the single-phase equilibrium state is unstable, the system as a whole may be stable only if it consists of the two phases (one with a smaller, and another with a higher density $n = N/V$) that are described by the two stable branches – see Fig. 2.
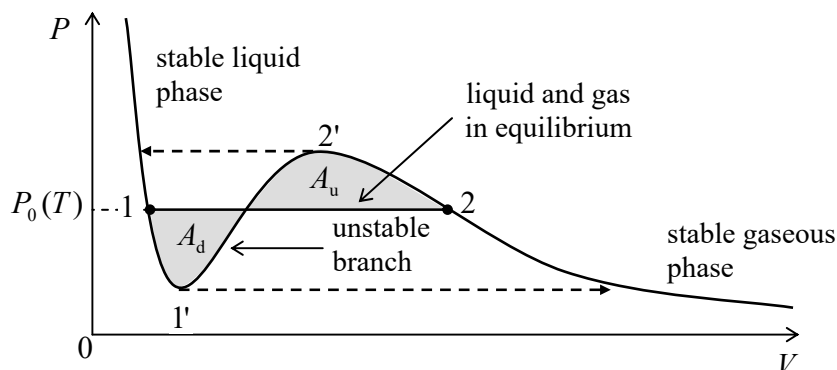

Fig. 4.2. Phase equilibrium at $T < T_c$ (schematically).

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[6] The special choice of the numerical coefficients in Eq. (3) makes the border between these two regions take place exactly at $t = 1$, i.e. at the temperature equal to T_c, with the critical point's coordinates equal to P_c and V_c.
[7] Actually, this assumption is not crucial for our analysis of mechanical stability, because if a fluctuation takes place in a small part of the total volume V, its other parts play the role of a pressure-fixing environment.

In order to understand the basic properties of this two-phase system, let us recall the general conditions of the thermodynamic equilibrium of two systems, which have been discussed in Chapter 1:

$$T_1 = T_2 \text{ (thermal equilibrium)}, \tag{4.5}$$

$$\mu_1 = \mu_2 \text{ ("chemical" equilibrium)}, \tag{4.6}$$

the latter condition meaning that the average energy of a single particle in both systems has to be the same. To those, we should add the evident condition of mechanical equilibrium,

$$P_1 = P_2 \text{ (mechanical equilibrium)}, \tag{4.7}$$

which immediately follows from the balance of the normal forces exerted on any inter-phase boundary.

If we discuss isotherms, Eq. (5) is fulfilled automatically, while Eq. (7) means that the effective isotherm $P(V)$ describing a two-phase system should be a horizontal line – see Fig. 2:[8]

$$P = P_0(T). \tag{4.8}$$

Along this line, the internal properties of each phase do not change; only the particle distribution is: it evolves gradually from all particles being in the liquid phase at point 1 to all particles being in the gas phase at point 2.[9] In particular, according to Eq. (6), the chemical potentials μ of the phases should be equal at each point of the horizontal line (8). This fact enables us to find the line's position: it has to connect points 1 and 2 in that the chemical potentials of the two phases are equal to each other. Let us recast this condition as

$$\int_1^2 d\mu = 0, \quad \text{i.e. } \int_1^2 dG = 0, \tag{4.9}$$

where the integral may be taken along the single-phase isotherm. (For this mathematical calculation, the mechanical instability of states on a certain part of this curve is not important.) By definition, along that curve, $N = \text{const}$ and $T = \text{const}$, so according to Eq. (1.53c), $dG = -SdT + VdP + \mu dN$, for a slow (reversible) change, $dG = VdP$. Hence Eq. (9) yields

$$\int_1^2 VdP = 0. \tag{4.10}$$

This equality means that in Fig. 2, the shaded areas A_d and A_u should be equal. [10]

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[8] Frequently, $P_0(T)$ is called the *saturated vapor pressure*.

[9] A natural question: is the two-phase state with $P = P_0(T)$ the only state existing between points 1 and 2? Indeed, the branches 1-1' and 2-2' of the single-phase isotherm also have negative derivatives $(\partial P/\partial V)_T$ and hence are mechanically stable with respect to small perturbations. However, these branches are actually *metastable*, i.e. have larger Gibbs energy per particle (i.e. μ) than the counterpart phase at the same P, and are hence unstable to *larger* perturbations – such as foreign microparticles (say, dust), protrusions on the confining walls, etc. In very controlled conditions, these single-phase "superheated" and "supercooled" states can survive almost all the way to the zero-derivative points 1' and 2', leading to sudden jumps of the system into the counterpart phase. (At fixed pressure, such jumps go as shown by dashed lines in Fig. 2.) In particular, at the atmospheric pressure, purified water may be supercooled to almost –50°C, and superheated to nearly +270°C. However, at more realistic conditions, unavoidable perturbations result in the two-phase coexistence formation close to points 1 and 2.

[10] This *Maxwell equal-area rule* (also called "Maxwell's construct") was suggested by J. C. Maxwell in 1875 using more complex reasoning.

As the same Fig. 2 figure shows, the Maxwell rule may be rewritten in a different form,

$$\int_{1}^{2}\left[P - P_0(T)\right]dV = 0,$$

(4.11)

which is more convenient for analytical calculations than Eq. (10) if the equation of state may be explicitly solved for P – as it is in the van der Waals model (2). Such calculation (left for the reader's exercise) shows that for that model, the temperature dependence of the saturated vapor pressure at low T is exponential,[11]

$$P_0(T) \propto P_c \exp\left\{-\frac{\Delta}{T}\right\}, \quad \text{with } \Delta = \frac{a}{b} \equiv \frac{27}{8}T_c, \quad \text{for } T \ll T_c,$$

(4.12)

corresponding very well to the physical picture of the particle's thermal activation from a potential well of depth Δ.

The signature parameter of a first-order phase transition, the latent heat of evaporation

$$\Lambda \equiv \int_{1}^{2} dQ,$$

(4.13)

may also be found by a similar integration along the single-phase isotherm. Indeed, using Eq. (1.19), $dQ = TdS$, we get

$$\Lambda = \int_{1}^{2} TdS = T(S_2 - S_1).$$

(4.14)

Let us express the right-hand side of Eq. (14) via the equation of state. For that, let us take the full derivative of both sides of Eq. (6) over temperature, considering the value of $G = N\mu$ for each phase as a function of P and T, and taking into account that according to Eq. (7), $P_1 = P_2 = P_0(T)$:

$$\left(\frac{\partial G_1}{\partial T}\right)_P + \left(\frac{\partial G_1}{\partial P}\right)_T \frac{dP_0}{dT} = \left(\frac{\partial G_2}{\partial T}\right)_P + \left(\frac{\partial G_2}{\partial P}\right)_T \frac{dP_0}{dT}.$$

(4.15)

According to the first of Eqs. (1.39), the partial derivative $(\partial G/\partial T)_P$ is just minus the entropy, while according to the second of those equalities, $(\partial G/\partial P)_T$ is the volume. Thus Eq. (15) becomes

$$-S_1 + V_1\frac{dP_0}{dT} = -S_2 + V_2\frac{dP_0}{dT}.$$

(4.16)

Solving this equation for $(S_2 - S_1)$, and plugging the result into Eq. (14), we get the following *Clapeyron-Clausius formula*:

$$\Lambda = T(V_2 - V_1)\frac{dP_0}{dT}.$$

(4.17)

For the van der Waals model, this formula may be readily used for the analytical calculation of Λ in two limits: $T \ll T_c$ and $(T_c - T) \ll T_c$ – the exercises left for the reader. In the latter limit, $\Lambda \propto (T_c - T)^{1/2}$, naturally vanishing at the critical temperature.

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[11] It is fascinating how well this Arrhenius exponent is hidden in the polynomial van der Waals equation (2)!

Finally, some important properties of the van der Waals' model may be revealed more easily by looking at the set of its isochores $P = P(T)$ for $V = $ const, rather than at the isotherms. Indeed, as Eq. (2) shows, all single-phase isochores are straight lines. However, if we interrupt these lines at the points when the single phase becomes metastable, and complement them with the (very nonlinear!) dependence $P_0(T)$, we get the pattern (called the *phase diagram*) shown schematically in Fig. 3a.
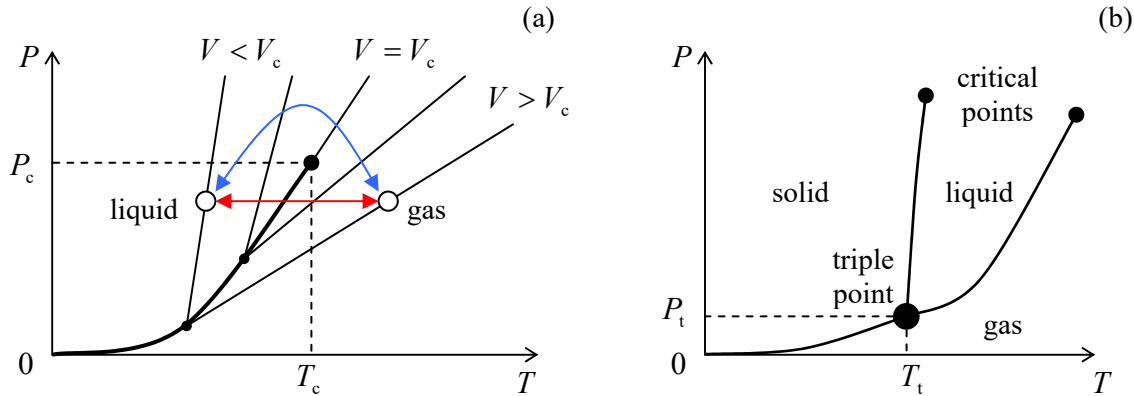

Fig. 4.3. (a) Van der Waals model's isochores, the saturated gas pressure diagram, and the critical point, and (b) the phase diagram of a typical three-phase system (all schematically).

In this plot, one more meaning of the critical point $\{P_c, T_c\}$ becomes very vivid. At fixed pressure $P < P_c$, the liquid and gaseous phases are clearly separated by the saturated pressure line $P_0(T)$, so if we achieve the transition between the phases just by changing temperature (see the red horizontal arrow in Fig. 3a), we have to pass through the phase equilibrium point, being delayed there to either put the latent heat into the system or take it out. However, if we perform the transition between the same initial and final points by changing both the pressure and temperature in a way that we go around the critical point (see the blue arrow in Fig. 3a), no definite point of transition may be observed: the substance stays in a single phase, and it is a subjective judgment of the observer in which region that phase should be called the liquid, and in which region, the gas. For water, the critical point corresponds to the temperature of 647 K (374°C), and the pressure $P_c \approx 22.1$ MPa (i.e. ~200 bars), so a lecture demonstration of its critical behavior would require substantial safety precautions. This is why such demonstrations are typically carried out with other substances such as either diethyl ether,[12] with its much lower T_c (194°C) and P_c (3.6 MPa), or the now-infamous carbon dioxide CO_2, with even lower T_c (31.1°C), though higher P_c (7.4 MPa). Though these substances are colorless and clear in both gas and liquid phases, their separation (by gravity) is still visible, due to small differences in the optical refraction coefficient, at $P < P_c$, but not above P_c.[13]

Thus, in the van der Waals model, two phases may coexist, though only at certain conditions – in particular, $T < T_c$. Now a natural, more general question is whether the coexistence of more than two

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[12] $(CH_3\text{-}CH_2)\text{-}O\text{-}(CH_2\text{-}CH_3)$, historically the first popular general anesthetic.

[13] It is interesting that very close to the critical point the substance suddenly becomes opaque – in the case of ether, whitish. The qualitative explanation of this effect, called the *critical opalescence*, is simple: at this point, the difference of the Gibbs energies per particle (i.e. the chemical potentials) of the two phases becomes so small that unavoidable thermal fluctuations lead to spontaneous appearance and disappearance of relatively large (a-few-μm-scale) single-phase regions in all the volume. A large concentration of boundaries of such randomly-shaped regions leads to strong light scattering.

phases of the same substance is possible. For example, can the water ice, the liquid water, and the water vapor (steam) all be in thermodynamic equilibrium? The answer is essentially given by Eq. (6). From thermodynamics, we know that for a uniform system (i.e. a single phase), pressure and temperature completely define the chemical potential $\mu(P, T)$. Hence, dealing with two phases, we had to satisfy just *one* chemical equilibrium condition (6) for *two* common arguments P and T. Evidently, this leaves us with one extra degree of freedom, so the two-phase equilibrium is possible within a certain range of P at fixed T (or vice versa) – see again the horizontal line in Fig. 2 and the bold line in Fig. 3a. Now, if we want *three* phases to be in equilibrium, we need to satisfy *two* equations for these variables:

$$\mu_1(P,T) = \mu_2(P,T) = \mu_3(P,T).$$

(4.18)

Typically, the functions $\mu(P, T)$ are monotonic, so the two equations (18) have just one solution, the so-called *triple point* $\{P_t, T_t\}$. Of course, this triple point of equilibrium between *three* phases should not be confused with the partial critical points $\{P_c, T_c\}$ for each of the *two*-phase pairs. Fig. 3b shows, very schematically, their relation for a typical three-phase system solid-liquid-gas. For example, water, ice, and water vapor are at equilibrium at a triple point with $P_t \approx 0.612$ kPa[14] and $T_t = 273.16$ K. The practical importance of this particular temperature point is that by an international agreement, it has been accepted for the definition of not only the Kelvin temperature scale but also of the Celsius scale's reference, as 0.01°C, so the absolute temperature zero corresponds to exactly –273.15°C.[15] More generally, triple points of other purified simple substances (such as H_2, N_2, O_2, Ar, Hg, and H_2O) are also used for thermometer calibration, defining the so-called *international temperature scales* including the currently accepted scale ITS-90.

This analysis may be readily generalized to multi-component systems consisting of particles of several (say, L) sorts.[16] If such a mixed system is in a single phase, i.e. is macroscopically uniform, its chemical potential may be defined by a natural generalization of Eq. (1.53c):

$$dG = -SdT + VdP + \sum_{l=1}^{L} \mu^{(l)} dN^{(l)}.$$

(4.19)

The last term reflects the fact that usually, every single phase is not a pure chemical substance, but has particles of all other components, so $\mu^{(l)}$ may depend not only on P and T but also on the *concentrations* $c^{(l)} \equiv N^{(l)}/N$ of particles of each sort. If the total number N of particles is fixed, the number of independent concentrations is $(L - 1)$. For the chemical equilibrium of R phases, all R values of $\mu_r^{(l)}$ ($r =$ 1, 2, …, R) have to be equal for particles of each sort: $\mu_1^{(l)} = \mu_2^{(l)} = \ldots = \mu_R^{(l)}$, with each $\mu_r^{(l)}$ depending on $(L - 1)$ concentrations $c_r^{(l)}$, and also on P and T. This requirement gives $L(R - 1)$ equations for $(L - 1)R$ concentrations $c_r^{(l)}$, plus two common arguments P and T, i.e. for $[(L -1)R + 2]$ independent variables. This means that the number of phases has to satisfy the limitation

Gibbs phase rule

$$L(R-1) \le (L-1)R+2, \quad \text{i.e. } R \le L+2,$$

(4.20)

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[14] Please note that for water, P_t is much lower than the normal atmospheric pressure (1 bar = 101.325 kPa).

[15] Note the recent (2018) re-definition of the "legal" kelvin via joule (see, *Appendix UCA*: *Selected Units and Constants*); however, the new definition is compatible, within experimental accuracy, with that mentioned above.

[16] Perhaps the most practically important example is the air/water system. For its detailed discussion, based on Eq. (19), the reader may be referred, e.g., to Sec. 3.9 in F. Schwabl, *Statistical Mechanics*, Springer (2000). Other important applications include liquid solutions, and metallic *alloys* – solid solutions of metal elements.

where the equality sign may be reached at just one point in the whole parameter space. This is the *Gibbs phase rule*. As a sanity check, for a single-component system, $L = 1$, the rule yields $R \leq 3$ – exactly the result we have already discussed.

4.2. Continuous phase transitions

As Fig. 2 illustrates, if we fix pressure P in a system with a first-order phase transition, and start changing its temperature, then the complete crossing of the transition-point line, defined by the equation $P_0(T) = P$, requires the insertion (or extraction) some non-zero latent heat Λ. Formulas (14) and (17) show that Λ is directly related to non-zero differences between the entropies and volumes of the two phases (at the same pressure). As we know from Chapter 1, both S and V may be represented as the first derivatives of appropriate thermodynamic potentials. This is why P. Ehrenfest called such transitions, involving jumps of potentials' *first* derivatives, the *first-order* phase transitions.

On the other hand, there are phase transitions that have no first derivative jumps at the transition temperature T_c, so the temperature point may be clearly marked, for example, by a jump of the *second* derivative of a thermodynamic potential – for example, the derivative $\partial C / \partial T$ which, according to Eq. (1.24), equals to $\partial^2 E / \partial T^2$. In the initial Ehrenfest classification, this was an example of a *second-order* phase transition. However, most features of such phase transitions are also pertinent to some systems in which the second derivatives of potentials are continuous as well. Due to this reason, I will use a more recent terminology (suggested in 1967 by M. Fisher), in which all phase transitions with $\Lambda = 0$ are called *continuous*.

Most (though not all) continuous phase transitions result from particle interactions. Here are some representative examples:

(i) At temperatures above ~490 K, the crystal lattice of barium titanate ($BaTiO_3$) is cubic, with a Ba ion in the center of each Ti-cornered cube (or vice versa) – see Fig. 4a. However, as the temperature is being lowered below that critical value, the sublattice of Ba ions is displaced along one of six sides of the TiO_3 sublattice, leading to a small deformation of both lattices – which become tetragonal. This is a typical example of a *structural transition*, in this particular case combined with a *ferroelectric transition*, because (due to the positive electric charge of the Ba ions) below the critical temperature the $BaTiO_3$ crystal has a spontaneous electric polarization even in the absence of external electric field.
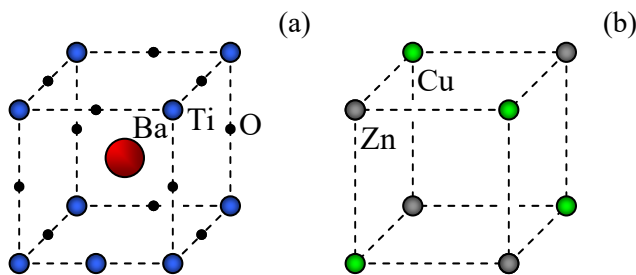

Fig. 4.4. Single cells of crystal lattices of (a) $BaTiO_3$ and (b) CuZn.

(ii) A different kind of phase transition happens, for example, in Cu_xZn_{1-x} alloys (called *brasses*). Their crystal lattice is always cubic, but above certain critical temperature T_c (which depends on x) any of its nodes may be occupied by either a copper atom or a zinc atom, at random. At $T < T_c$, a trend toward ordered atom alternation arises, and at low temperatures, the atoms are fully ordered, as shown in Fig. 4b for the stoichiometric case $x = 0.5$. This is a good example of an *order-disorder* transition.

(iii) At *ferromagnetic* transitions (such as the one taking place, for example, in Fe at 1,388 K) and *antiferromagnetic* transitions (e.g., in MnO at 116 K), lowering of temperature below the critical value[17] does not change atom positions substantially, but results in a partial ordering of atomic spins, eventually leading to their full ordering (Fig. 5).
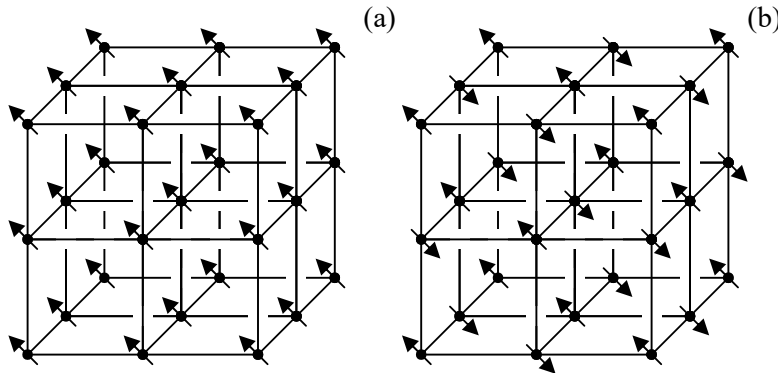

Fig. 4.5. Classical images of fully ordered phases: (a) a ferromagnet, and (b) an antiferromagnet.

Note that, as it follows from Eqs. (1.1)-(1.3), at ferroelectric transitions the role of pressure is played by the external electric field $\mathscr{E}$, and at the ferromagnetic transitions, by the external magnetic field $\mathscr{H}$. As we will see very soon, even in systems with continuous phase transitions, a gradual change of such an external field, at a fixed temperature, may induce jumps between metastable states, similar to those in systems with first-order phase transitions (see, e.g., the dashed arrows in Fig. 2), with non-zero decreases of the appropriate free energy.

Besides these standard examples, some other threshold phenomena, such as the formation of a coherent optical field in a laser, and even the self-excitation of oscillators with negative damping (see, e.g., CM Sec. 5.4), may be treated, at certain conditions, as continuous phase transitions.[18]

The general feature of all these transitions is the gradual formation, at $T < T_c$, of certain *ordering*, which may be characterized by some *order parameter* $\eta \neq 0$. The simplest example of such an order parameter is the magnetization at the ferromagnetic transitions, and this is why continuous phase transitions are usually discussed for certain models of ferromagnetism. (I will follow this tradition but mention in passing other important cases that require a substantial modification of the theory.) Most of such models are defined on an infinite 3D cubic lattice (see, e.g., Fig. 5), with evident generalizations to lower dimensions. For example, the *Heisenberg model* of a ferromagnet (suggested in 1928) is defined by the following Hamiltonian:

Heisenberg
model

$$\hat{H} = -J \sum_{\{k,k'\}} \hat{\boldsymbol{\sigma}}_k \cdot \hat{\boldsymbol{\sigma}}_{k'} - \sum_k \mathbf{h} \cdot \hat{\boldsymbol{\sigma}}_k \,, \qquad (4.21)$$

where $\hat{\boldsymbol{\sigma}}_k \equiv \hat{\mathbf{S}}_k / \hbar$ is the normalized Pauli vector operator[19] acting on the quantum state of the kth spin, while $\mathbf{h}$ is the normalized external magnetic field $\mathscr{B}$:

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[17] For ferromagnets, this point is usually referred to at the *Curie temperature*, and for antiferromagnets, as the *Néel temperature*.

[18] Unfortunately, I will have no time/space for these interesting (and practically important) generalizations, and have to refer the interested reader to the famous monograph by R. Stratonovich, *Topics in the Theory of Random Noise*, in 2 vols., Gordon and Breach, 1963 and 1967, and/or the influential review by H. Haken, *Ferstkörperprobleme* **10**, 351 (1970).

$$\mathbf{h} \equiv \gamma \hbar \mathcal{B} \ .$$

(4.22)

(Here γ is the gyromagnetic ratio of the particle; for an electron, γ is very close to $-e/m_e$, so the effective magnitude $m_0 = \gamma \hbar / 2$ of the spin's magnetic moment is very close to the *Bohr magneton* $\mu_B \equiv e\hbar/2m_e \approx 0.927 \times 10^{-23}$ J/T.) The figure brackets $\{k, k'\}$ in Eq. (21) denote the summation over the pairs of adjacent lattice sites, so the magnitude of the constant J may be interpreted as the maximum coupling energy per "bond" between two adjacent particles. At $J > 0$, the coupling tries to keep spins aligned, i.e. to install the ferromagnetic ordering.[20] The second term in Eq. (21) describes the effect of the external magnetic field, which tries to orient all spin magnetic moments along its direction.[21]

However, even the Heisenberg model, while being rather rudimentary (in particular because its standard form (21) is only valid for spins-½), is still rather complex for analysis. This is why most theoretical results have been obtained for its classical twin, the *Ising model*:[22]

$$E_m = -J \sum_{\{k,k'\}} s_k s_{k'} - h \sum_k s_k \ .$$

(4.23) Ising model

Here E_m are the particular values of the system's energy in each of its 2^N possible states with all possible combinations of the binary classical variables $s_k = \pm 1$, while h is the normalized external magnetic field's magnitude – see Eq. (22). (Despite its classical character, the variable s_k, modeling the field-oriented Cartesian component of the real spin, is usually called "spin" for brevity, and I will follow this tradition.) Somewhat shockingly, even for this toy model, no exact analytical 3D solution that would be valid at arbitrary temperatures has been found yet, and the solution of its 2D version by L. Onsager in 1944 (see Sec. 5 below) is still considered one of the top intellectual achievements of statistical physics. Still, Eq. (23) is very useful for the introduction of the basic notions of continuous phase transitions and methods of their analysis, so for my brief discussion, I will mostly use this model.[23]

Evidently, if $T = 0$ and $h = 0$, the lowest possible energy,

$$E_{min} = -JNd \ ,$$

(4.24)

where d is the lattice dimensionality, is achieved in the "ferromagnetic" phase in which all spins s_k are equal to either $+1$ or -1, so $\langle s_k \rangle = \pm 1$ as well. On the other hand, at $J = 0$, the spins are independent, and if $h = 0$ as well, all s_k are completely random, with a 50% probability to take either of values ± 1, so $\langle s_k \rangle = 0$. Hence in the general case (with arbitrary J and h), we may use the average

$$\eta \equiv \langle s_k \rangle$$

(4.25) Ising model: order parameter

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[19] See, e.g., QM Sec. 4.4.

[20] At $J < 0$, the first term of Eq. (21) gives a reasonable model of an antiferromagnet, but in this case, the external magnetic field effects are more subtle; I will not have time to discuss them.

[21] See, e.g., QM Eq. (4.163).

[22] Named after Ernst Ising who explored the 1D version of the model in detail in 1925, though a similar model was discussed earlier (in 1920) by Wilhelm Lenz.

[23] For more detailed discussions of phase transition theories (including other popular models of the ferromagnetic phase transition, e.g., the *Potts model*), see, e.g., either H. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Oxford U. Press, 1971; or A. Patashinskii and V. Pokrovskii, *Fluctuation Theory of Phase Transitions*, Pergamon, 1979; or B. McCoy, *Advanced Statistical Mechanics*, Oxford U. Press, 2010. For a very concise text, I can recommend J. Yeomans, *Statistical Mechanics of Phase Transitions*, Clarendon, 1992.

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as a good measure of spin ordering, i.e. as the order parameter. Since in a real ferromagnet, each spin carries a magnetic moment, the order parameter η is proportional to the Cartesian component of the system's average magnetization, in the direction of the applied magnetic field.

Now that the Ising model has given us a very clear illustration of the order parameter, let me use this notion for a semi-quantitative characterization of continuous phase transitions. Due to the difficulty of theoretical analyses of most models of the transitions at arbitrary temperatures, their theoretical discussions are focused mostly on a very close vicinity of the critical point T_c. Both experiment and theory show that in the absence of an external field, the function $\eta(T)$ is close to a certain power,

$$\eta \propto \left(-\tilde{t}\right)^{\beta} \equiv \left|\tilde{t}\right|^{\beta}, \qquad \text{for } \tilde{t} < 0, \text{ i.e. } T < T_c, \tag{4.26}$$

of the small deviation from the critical temperature – which is conveniently normalized as

$$\tilde{t} \equiv \frac{T - T_c}{T_c} \equiv t - 1. \tag{4.27}$$

Most other key variables follow a similar temperature behavior, with *critical exponents* frequently being the same for both signs of $\tilde{t}$ – though typically with very different proportionality factors. In particular, the heat capacity at a fixed magnetic field behaves as[24]

$$c_h \propto \left|\tilde{t}\right|^{-\alpha}. \tag{4.28}$$

Similarly, the (normalized) low-field *susceptibility*[25]

$$\chi \equiv \left.\frac{\partial \eta}{\partial h}\right|_{h=0} \propto \left|\tilde{t}\right|^{-\gamma}. \tag{4.29}$$

Two other important critical exponents, ζ and ν, describe the temperature behavior of the *correlation function* $\langle s_k s_{k'} \rangle$, whose dependence on the distance $r_{kk'}$ between two spins may be well fitted by the following law,

$$\langle s_k s_{k'} \rangle \propto \frac{1}{r_{kk'}^{d-2+\zeta}} \exp\left\{-\frac{r_{kk'}}{r_c}\right\}, \tag{4.30}$$

with the *correlation radius*

$$r_c \propto \left|\tilde{t}\right|^{-\nu}. \tag{4.31}$$

Finally, three more critical exponents, usually denoted ε, δ, and μ, describe the external field dependences of, respectively, c, $\eta_\perp$ and r_c at $\tilde{t} \leq 0$. For example, δ may be defined as

$$\eta \propto \left. h^{1/\delta}\right|_{\tilde{t}=0}. \tag{4.32}$$

(Other field exponents are used less frequently, and for their discussion, the interested reader is referred to the special literature that was cited above.)

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[24] The forms of this and other functions of τ are selected to make all critical exponents non-negative.

[25] In most models of ferromagnetic phase transitions, this variable is proportional to the genuine low-field magnetic susceptibility χ_m of the material – see, e.g., EM Eq. (5.111).

The leftmost column of Table 1 shows the ranges of experimental values of these critical exponents for various 3D physical systems featuring continuous phase transitions. One can see that their values vary from system to system, leaving no hope for a universal theory that would describe them all exactly. However, certain combinations of the exponents are much more reproducible – see the four bottom lines of the table.

Table 4.1. Major critical exponents of continuous phase transitions

Exponents and combinations	Experimental range (3D)[a]	Landau's theory	2D Ising model	3D Ising model	3D Heisenberg Model[d]
α	$0 - 0.14$	0[b]	[c]	0.12	-0.14
β	$0.32 - 0.39$	$1/2$	$1/8$	0.31	0.3
γ	$1.3 - 1.4$	1	$7/4$	1.25	1.4
δ	$4 - 5$	3	15	5	$?$
ν	$0.6 - 0.7$	$1/2$	1	0.64	0.7
ζ	0.05	0	$1/4$	0.05	0.04
$(\alpha + 2\beta + \gamma)/2$	1.00 ± 0.005	1	1	1	1
$\delta - \gamma/\beta$	0.93 ± 0.08	1	1	1	$?$
$(2 - \zeta)\nu/\gamma$	1.02 ± 0.05	1	1	1	1
$(2 - \alpha)/\nu d$	$?$	$4/d$	1	1	1

[a] Experimental data are from the monograph by A. Patashinskii and V. Pokrovskii, cited above.
[b] Discontinuity at $T = T_c$ – see below.
[c] Instead of following Eq. (28), in this case, c_h diverges as $\ln|\tilde{t}|$.

[d] With the order parameter η defined as $\langle \sigma_j \cdot \mathscr{B} \rangle / \mathscr{B}$.

Historically the first (and perhaps the most fundamental) of these *universal relations* was derived in 1963 by J. Essam and M. Fisher:

$$\alpha + 2\beta + \gamma = 2 . \tag{4.33}$$

It may be proved, for example, by finding the temperature dependence of the magnetic field value h_t that changes the order parameter by the same amount as a finite temperature deviation $\tilde{t} < 0$ gives at $h = 0$. Comparing Eqs. (26) and (29), we get

$$h_t \propto |\tilde{t}|^{\beta+\gamma} . \tag{4.34}$$

By the physical sense of h_t, we may expect that such a field has to affect the system's free energy[26] F by an amount comparable to the effect of a bare temperature change $\tilde{t}$. Ensemble-averaging the last term

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[26] As was already discussed in Secs. 1.4 and 2.4, there is some dichotomy of terminology for free energies in literature. In models (21) and (23), the magnetic field effects are accounted for at the microscopic level, by the inclusion of the corresponding term into each particular value E_m. From this point of view, the list of macroscopic

of Eq. (23) and using the definition (25) of the order parameter η, we see that the change of F (per particle) due to the field equals $-h_t \eta$ and, according to Eq. (26), scales as $h_t |\tilde{t}|^\beta \propto |\tilde{t}|^{(2\beta + \gamma)}$.

In order to estimate the thermal effect on F, let me first elaborate a bit more on the useful thermodynamic formula already mentioned in Sec. 1.3:

$$C_X = T\left(\frac{\partial S}{\partial T}\right)_X,$$
(4.35)

where X means the variable(s) maintained constant at the temperature variation. In the standard "P-V" thermodynamics, we may use Eqs. (1.35) for $X = V$, and Eqs. (1.39) for $X = P$, to write

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N}, \qquad C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N}.$$
(4.36)

As was just discussed, in the ferromagnetic models of the type (21) or (23), at a constant field h, the role of G is played by F, so Eq. (35) yields

$$C_h = T\left(\frac{\partial S}{\partial T}\right)_{h,N} = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{h,N}.$$
(4.37)

The last form of this relation means that F may be found by double integration of $(-C_h/T)$ over temperature. In the limit $|\tilde{t}| \ll 1$, the factor T may be treated as a constant, so with Eq. (28) for $c_h \propto C_h$, the free energy scales as the double integral of $c_h \propto |\tilde{t}|^{-\alpha}$ over $|\tilde{t}|$, i.e. as $|\tilde{t}|^{(2-\alpha)}$. Requiring this change to be proportional to the same power of $|\tilde{t}|$ as the field-induced part of the energy, we finally get the Essam-Fisher relation (33).

Using similar reasoning, it is straightforward to derive a few other universal relations of critical exponents, including the *Widom relation*:

$$\delta - \frac{\gamma}{\beta} = 1,$$
(4.38)

very similar relations for other high-field exponents ε and μ (which I do not have time to discuss), and the *Fisher relation*:

$$\nu(2 - \zeta) = \gamma.$$
(4.39)

A slightly more complex reasoning, involving the so-called *scaling hypothesis*, yields the following dimensionality-dependent *Josephson relation*

$$\nu d = 2 - \alpha.$$
(4.40)

The second column of Table 1 shows that at least three of these relations are in very reasonable agreement with experiment, so their set may be used as a testbed for various theoretical approaches to continuous phase transitions.

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variables in these systems does not include either P and V or their magnetic analogs, so we may take $G \equiv F + PV$ = F + const, and the equilibrium (at fixed h, T and N) corresponds to the minimum of the *Helmholtz* free energy F.

4.3. Landau's mean-field theory

The highest-level (i.e. the most phenomenological) approach to continuous phase transitions, formally not based on any particular microscopic model (though implying either the Ising model (23) or one of its siblings), is the *mean-field theory* developed in 1937 by L. Landau, on the basis of prior ideas by P. Weiss – to be discussed in the next section. The main idea of this phenomenological approach is to represent the free energy's change ΔF at the phase transition as an explicit function of the order parameter η (25). Since at $T \to T_c$, the order parameter has to tend to zero, this change,

$$\Delta F \equiv F(T) - F(T_c),\qquad\qquad(4.41)$$

may be expanded into the Taylor series in η, and only a few, most important first terms of that expansion retained. In order to keep the symmetry between two possible signs of the order parameter (i.e. between two possible spin directions in the Ising model) in the absence of the external field, at $h = 0$ this expansion should include only even powers of η:

$$\Delta f\big|_{h=0} \equiv \frac{\Delta F}{V}\bigg|_{h=0} = A(T)\eta^2 + \frac{1}{2}B(T)\eta^4 + ...,\qquad \text{at } T \approx T_c.\qquad(4.42)$$

As Fig. 6 shows, at $A(T) < 0$, and $B(T) > 0$, these two terms are sufficient to describe the minimum of the free energy at $\eta^2 > 0$, i.e. to calculate the stationary values of the order parameter; this is why Landau's theory ignores higher terms of the Taylor expansion – which are much smaller at $\eta \to 0$.
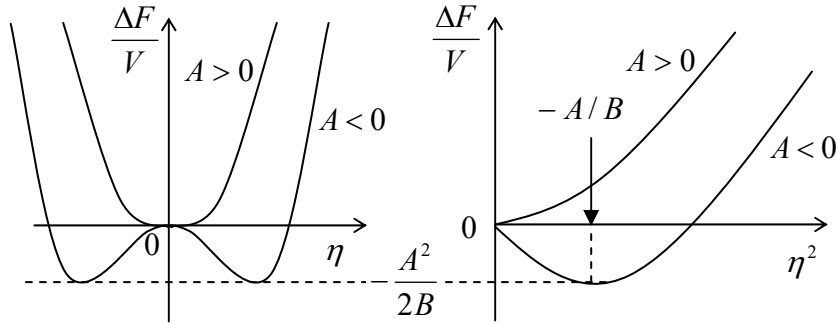

Fig. 4.6. The Landau free energy (42) as a function of (a) η and (b) η^2, for two signs of the coefficient $A(T)$, both for $B(T) > 0$.

Now let us discuss the temperature dependence of the coefficients A and B. As Eq. (42) shows, first of all, the coefficient $B(T)$ has to be positive for any sign of $\tilde{t} \propto (T - T_c)$, to ensure the equilibrium at a finite value of η^2. Thus, it is reasonable to ignore the temperature dependence of B near the critical temperature altogether, i.e. use the approximation

$$B(T) = b > 0.\qquad\qquad(4.43)$$

On the other hand, as Fig. 6 shows, the coefficient $A(T)$ has to change sign at $T = T_c$, to be positive at $T > T_c$ and negative at $T < T_c$, to ensure the transition from $\eta = 0$ at $T > T_c$ to a certain non-zero value of the order parameter at $T < T_c$. Assuming that A is a smooth function of temperature, we may approximate it by the leading term of its Taylor expansion in the difference $\tilde{t} \propto T - T_c < 0$:

$$A(T) = a\tilde{t}, \quad \text{with } a > 0,\qquad\qquad(4.44)$$

so Eq. (42) becomes

$$\Delta f\big|_{h=0} = a\tilde{t}\,\eta^2 + \frac{1}{2}b\eta^4.\qquad\qquad(4.45)$$

In this rudimentary form, the Landau theory may look almost trivial, and its main strength is the possibility of its straightforward extension to the effects of the external field and of spatial variations of the order parameter. First, as the field terms in Eqs. (21) or (23) show, the applied field gives such systems, on average, the energy addition of $-h\eta$ per particle, i.e. $-nh\eta$ per unit volume, where n is the particle density. Second, since according to Eq. (31) (with $\nu > 0$, see Table 1) the correlation radius diverges at $\tilde{t} \to 0$, in this limit, the spatial variations of the order parameter should be slow, $|\nabla\eta| \to 0$. Hence, the effects of the gradient on ΔF may be approximated by the first non-zero term of its expansion into the Taylor series in $(\nabla\eta)^2$. As a result, Eq. (45) may be generalized as

<div style="color:blue; text-align:right; font-size:small;">Landau
theory:
free energy</div>

$$\Delta F = \int \Delta f d^3 r, \qquad \text{with } \Delta f = a\tilde{t}\eta^2 + \frac{1}{2}b\eta^4 - nh\eta + c(\nabla\eta)^2, \tag{4.46}$$

where c is a coefficient independent of η. To avoid the unphysical effect of spontaneous formation of spatial variations of the order parameter, that factor has to be positive at all temperatures and hence may be taken for a constant in a small vicinity of T_c – the only region where Eq. (46) may be expected to provide quantitatively correct results.

Let us find out what critical exponents are predicted by this phenomenological approach. First of all, we may find the equilibrium values of the order parameter from the condition of F having a minimum, $\partial F/\partial \eta = 0$. At $h = 0$, it is easier to use the equivalent equation $\partial F/\partial(\eta^2) = 0$, where F is given by Eq. (45) – see Fig. 6b. This immediately yields

$$|\eta| = \begin{cases} (-a\tilde{t}/b)^{1/2}, & \text{for } \tilde{t} < 0, \\ 0, & \text{for } 0 < \tilde{t}. \end{cases} \tag{4.47}$$

Comparing this result with Eq. (26), we see that in the Landau theory, $\beta = \frac{1}{2}$. Next, plugging the result (47) back into Eq. (45), for the equilibrium (minimal) value of the free energy, we get

$$\Delta f = \begin{cases} -a^2\tilde{t}^2/2b, & \text{for } \tilde{t} < 0, \\ 0, & \text{for } 0 < \tilde{t}. \end{cases} \tag{4.48}$$

From here and Eq. (37), the specific heat,

$$\frac{C_h}{V} = \begin{cases} a^2/bT_c, & \text{for } \tilde{t} < 0, \\ 0, & \text{for } 0 < \tilde{t}, \end{cases} \tag{4.49}$$

has, at the critical point, a discontinuity rather than a singularity, so we need to prescribe zero value to the critical exponent α.

In the presence of a uniform field, the equilibrium order parameter should be found from the condition $\partial f/\partial\eta = 0$ applied to Eq. (46) with $\nabla\eta = 0$, giving

$$\frac{\partial f}{\partial \eta} \equiv 2a\tilde{t}\eta + 2b\eta^3 - nh = 0. \tag{4.50}$$

In the limit of a small order parameter, $\eta \to 0$, the term with η^3 is negligible, and Eq. (50) gives the solution (stable only for $\tilde{t} \geq 0$):

$$\eta = \frac{nh}{2a\tilde{t}}, \tag{4.51}$$

so according to Eq. (29), $\gamma = 1$. On the other hand, at $\widetilde{t} \to 0$ (or at sufficiently high fields at other temperatures), the cubic term in Eq. (50) is much larger than the linear one, and this equation yields

$$\eta = \left(\frac{nh}{2b} \right)^{1/3}, \tag{4.52}$$

so comparison with Eq. (32) yields $\delta = 3$. Finally, according to Eq. (30), the last term in Eq. (46) scales as $c\eta^2/r_c^2$. (If $r_c \neq \infty$, the effects of the pre-exponential factor in Eq. (30) are negligible.) As a result, the gradient term's contribution is comparable[27] with the two leading terms in Δf (which, according to Eq. (47), are of the same order), if

$$r_c \approx \left(\frac{c}{a|\widetilde{t}|} \right)^{1/2}, \tag{4.53}$$

so according to the definition (31) of the critical exponent ν, in the Landau theory it is equal to ½.

The third column in Table 1 summarizes the critical exponents and their combinations in Landau's theory. It shows that these values are somewhat out of the experimental ranges, and while some of their "universal" relations are correct, some are not; for example, the Josephson relation would be only correct at $d = 4$ (not the most realistic spatial dimensionality :-) The main reason for this disappointing result is that describing the spin interaction with the field, the Landau mean-field theory neglects spin randomness, i.e. fluctuations. Though a quantitative theory of fluctuations will be discussed only in the next chapter, we can readily perform their crude estimate. Looking at Eq. (46), we see that its first term is a quadratic function of the effective "half-degree of freedom", η. Hence per the equipartition theorem (2.28), we may expect that the average square of its thermal fluctuations, within a d-dimensional volume with a linear size of the order of r_c, should be of the order of $T/2$ (close to the critical temperature, $T_c/2$ is a good enough approximation):

$$a|\widetilde{t}| \langle \widetilde{\eta}^2 \rangle r_c^d \sim \frac{T_c}{2}. \tag{4.54}$$

In order to be negligible, the variance has to be small in comparison with the average $\eta^2 \sim a|\widetilde{t}|/b$ – see Eq. (47). Plugging in the T-dependences of the operands of this relation, and values of the critical exponents from the Landau theory, for $\tau > 0$ we get the so-called *Levanyuk-Ginzburg criterion* of its validity:

$$\frac{T_c}{2a\tau} \left(\frac{a|\widetilde{t}|}{c} \right)^{d/2} << \frac{a|\widetilde{t}|}{b}. \tag{4.55}$$

We see that for any realistic dimensionality, $d < 4$, the order parameter's fluctuations grow at $\widetilde{t} \to 0$ faster than its average value, and hence the theory becomes invalid.

Thus the Landau mean-field theory is not a perfect approach to finding critical indices at continuous phase transitions in Ising-type systems with their next-neighbor interactions between the particles. However, any long-range interactions between particles increase the correlation radius r_c, and

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[27] According to Eq. (30), the correlation radius may be interpreted as the distance at which the order parameter η relaxes to its equilibrium value if it is deflected from that value at some point. Since the law of such spatial change may be obtained by a variational differentiation of F, for the actual relaxation law, all major terms of (46) have to be comparable.

hence suppress the order parameter fluctuations. As one example, at laser self-excitation, the emerging coherent optical field couples essentially *all* photon-emitting particles in the electromagnetic cavity (resonator). As another example, in superconductors, the role of the correlation radius is played by the Cooper-pair size ξ_0, which is typically of the order of 10^{-6} m, i.e. much larger than the average distance between the pairs ($\sim 10^{-8}$ m). As a result, the mean-field theory remains valid at all temperatures besides an extremely small temperature interval near T_c – for bulk superconductors, of the order of 10^{-6} K.

The real strength of Landau's mean-field theory is that despite its *classical* character, it may be readily generalized to a description of various Bose-Einstein condensates, i.e. *quantum* fluids. Of those generalizations, the most famous is the *Ginzburg-Landau theory* of superconductivity. It was developed in 1950, i.e. even before the microscopic-level explanation of this phenomenon by J. Bardeen, L. Cooper, and R. Schrieffer in 1956-57. In this theory, the real order parameter η is replaced with the modulus of a complex function ψ, physically the wavefunction of the coherent Bose-Einstein condensate of Cooper pairs. Since each pair carries the electric charge $q = -2e$ and has zero spin, it interacts with the magnetic field in a way different from that described by the Heisenberg or Ising models. Namely, as was already discussed in Sec. 3.4, in the magnetic field, the del operator ∇ in Eq. (46) has to be amended with the term $-i(q/\hbar)\mathbf{A}$, where $\mathbf{A}$ is the vector potential of the total magnetic field $\mathscr{B} = \nabla \times \mathbf{A}$, including not only the external magnetic field $\mathscr{H}$ but also the field induced by the supercurrent itself. With the account for the well-known formula for the magnetic field energy, Eq. (46) is now replaced with

GL free energy

$$\Delta f = a\tilde{t}\left|\psi\right|^2 + \frac{1}{2}b\left|\psi\right|^4 - \frac{\hbar^2}{2m}\left|\left(\nabla - i\frac{q}{\hbar}\mathbf{A}\right)\psi\right|^2 + \frac{\mathscr{B}^2}{2\mu_0}, \qquad (4.56)$$

where m is a phenomenological coefficient rather than the actual particle's mass.

The variational minimization of the resulting Gibbs energy density $\Delta g \equiv \Delta f - \mu_0\mathscr{H}\cdot\mathscr{M} \equiv \Delta f - \mathscr{H}\cdot\mathscr{B} + \text{const}$[28] over the variables ψ and $\mathscr{B}$ (which is suggested for the reader's exercise) yields two differential equations:

GL equations

$$\frac{\nabla \times \mathscr{B}}{\mu_0} = q\frac{i\hbar}{2m}\left[\psi\left(\nabla - i\frac{q}{\hbar}\mathbf{A}\right)\psi^* - \text{c.c.}\right], \qquad (4.57a)$$

$$-a\tilde{t}\,\psi = b\left|\psi\right|^2\psi - \frac{\hbar^2}{2m}\left(\nabla - i\frac{q}{\hbar}\mathbf{A}\right)^2\psi. \qquad (4.57b)$$

The first of these *Ginzburg-Landau equations* (57a) should be no big surprise for the reader, because according to the Maxwell equations, in magnetostatics the left-hand side of Eq. (57a) has to be equal to the electric current density, while its right-hand side is the usual quantum-mechanical probability current density multiplied by q, i.e. the density $\mathbf{j}$ of the electric current of the Cooper pair condensate. (Indeed, after plugging $\psi = n^{1/2}\exp\{i\varphi\}$ into that expression, we come back to Eq. (3.84) which, as we already know, explains such macroscopic quantum phenomena as the magnetic flux quantization and the Meissner-Ochsenfeld effect.)

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[28] As an immediate elementary sanity check of this relation, resulting from the analogy of Eqs. (1.1) and (1.3), the minimization of Δg in the absence of superconductivity ($\psi = 0$) gives the correct result $\mathscr{B} = \mu_0\mathscr{H}$. Note that this account of the difference between Δf and Δg is necessary here because (unlike Eqs. (21) and (23)), the Ginzburg-Landau free energy (56) does not take into account the effect of the field on each particle directly.

However, Eq. (57b) is new for us – at least for this course.[29] Since the last term on its right-hand side is the standard wave-mechanical expression for the kinetic energy of a particle in the presence of a magnetic field,[30] if this term dominates that side of the equation, Eq. (57b) is reduced to the stationary Schrödinger equation $E\psi = \hat{H}\psi$, for the ground state of free Cooper pairs, with the energy $E = -a\tilde{t} > 0$. However, in contrast to the usual (single-particle) Schrödinger equation, in which $|\psi|$ is determined by the normalization condition, the Cooper pair condensate density $n = |\psi|^2$ is determined by the thermodynamic balance of the condensate with the ensemble of "normal" (unpaired) electrons, which plays the role of the uncondensed part of the particles in the usual Bose-Einstein condensate – see Sec. 3.4. In Eq. (57b), such balance is enforced by the first term $b|\psi|^2\psi$ on the right-hand side. As we have already seen, in the absence of magnetic field and spatial gradients, such term yields $|\psi| \propto \left(-\tilde{t}\right)^{1/2} \propto (T_c - T)^{1/2}$ – see Eq. (47).

As a parenthetic remark, from the mathematical standpoint, the term $b|\psi|^2\psi$, which is nonlinear in ψ, makes Eq. (57b) a member of the family of the so-called *nonlinear Schrödinger equations*. Another important member of this family is the *Gross-Pitaevskii equation*,

$$-a\tilde{t}\,\psi = b\left|\psi\right|^2\psi - \frac{\hbar^2}{2m}\nabla^2\psi + U(\mathbf{r})\psi,$$

(4.58)

Gross-Pitaevskii equation

which gives a reasonable (albeit approximate) description of gradient and field effects on Bose-Einstein condensates of electrically neutral atoms at $T \approx T_c$. The differences between Eqs. (58) and (57) reflect, first, the zero electric charge q of the atoms (so Eq. (57a) becomes trivial) and, second, the fact that the atoms forming the condensates may be readily placed in external potentials $U(\mathbf{r}) \neq$ const (including the time-averaged potentials of optical traps – see EM Chapter 7), while in superconductors such potential profiles are much harder to create due to the screening of external electric and optical fields by conductors – see, e.g., EM Sec. 2.1.

Returning to the discussion of Eq. (57b), it is easy to see that its last term increases as either the external magnetic field or the density of current passed through a superconductor are increased, increasing the vector potential. In the Ginzburg-Landau equation, this *increase* is matched by a corresponding *decrease* of $|\psi|^2$, i.e. of the condensate density n, until it is completely suppressed. This balance describes the well-documented effect of superconductivity suppression by an external magnetic field and/or the supercurrent passed through the sample. Moreover, together with Eq. (57a), naturally describing the flux quantization (see Sec. 3.4), Eq. (57b) explains the existence of the so-called *Abrikosov vortices* – thin magnetic-field tubes, each carrying one quantum Φ_0 of magnetic flux – see Eq. (3.86). At the core of the vortex, $|\psi|^2$ is suppressed (down to zero at its central line) by the persistent, dissipation-free current of the superconducting condensate that circulates around the core and screens the rest of the superconductor from the magnetic field carried by the vortex.[31] The penetration of such vortices into the so-called type-II superconductors enables them to sustain zero dc resistance up to very high magnetic fields of the order of 20 T, and as a result, to be used in very compact magnets – including those used for beam bending in particle accelerators.

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[29] It is also discussed in EM Sec. 6.5.

[30] See, e.g., QM Sec. 3.1.

[31] See, e.g., EM Sec. 6.5.

Moreover, generalizing Eqs. (57) to the time-dependent case, just as it is done with the usual Schrödinger equation, one can describe other fascinating quantum macroscopic phenomena such as the *Josephson effects*, including the generation of oscillations with frequency $\omega_J = (q/\hbar)\mathscr{V}$ by weak links between two superconductors, biased by dc voltage $\mathscr{V}$. Unfortunately, time/space restrictions do not allow me to discuss these effects in any detail in this course, and I have to refer the reader to special literature.[32] Let me only note that in the limit $T \to T_c$, and for not extremely pure superconductor crystals (in which the so-called non-local transport phenomena may be important), the Ginzburg-Landau equations are exact, and may be derived (and their parameters T_c, a, b, q, and m determined) from the standard "microscopic" theory of superconductivity, based on the initial work by Bardeen, Cooper, and Schrieffer.[33] Most importantly, such derivation proves that $q = -2e$ – the electric charge of a single Cooper pair.

4.4. Ising model: Weiss' molecular-field approximation

The Landau mean-field theory is phenomenological in the sense that even within the range of its validity, it tells us nothing about the value of the critical temperature T_c and other parameters (in Eq. (46), the coefficients a, b, and c), so they have to be found from a particular "microscopic" model of the system under analysis. In this course, we would have time to discuss only the Ising model (23) for various dimensionalities d.

The most simplistic mean-field approach to this model is to assume that all spins are exactly equal, $s_k = \eta$, with an additional condition $\eta^2 \le 1$, ignoring for a minute the fact that in the genuine Ising model, s_k may equal only +1 or –1. Plugging this relation into Eq. (23), we get[34]

$$F = -(NJd)\eta^2 - Nh\eta . \tag{4.59}$$

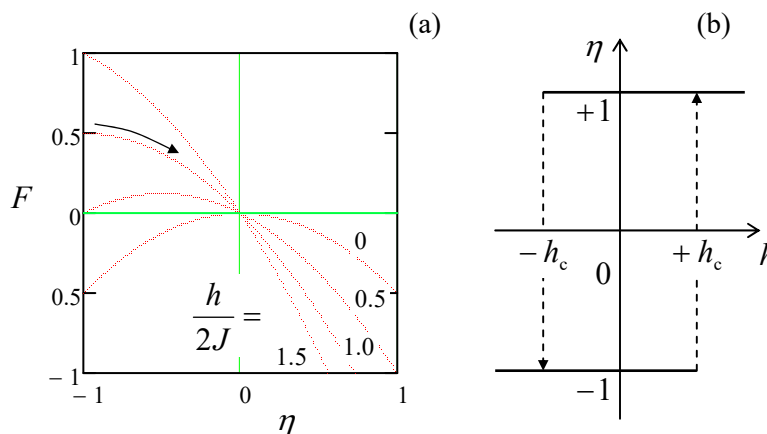This energy is plotted in Fig. 7a as a function of η, for several values of h.

Fig. 4.7. Field dependences of (a) the free energy profile and (b) the order parameter (i.e. magnetization), in the crudest mean-field approach to the Ising model.

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[32] See, e.g., M. Tinkham, *Introduction to Superconductivity*, 2nd ed., McGraw-Hill, 1996. A short discussion of the Josephson effects and Abrikosov vortices may be found in QM Sec. 1.6 and EM Sec. 6.5 of this series.
[33] See, e.g., Sec. 45 in E. Lifshitz and L. Pitaevskii, *Statistical Physics*, Part 2, Pergamon, 1980.
[34] In this naïve approach, we neglect the fluctuations of spin, i.e. their disorder. This full ordering assumption implies $S = 0$, so $F \equiv E - TS = E$, and we may use either notation for the system's energy.

The plots show that at $h = 0$, the system may be in either of two stable states, with $\eta = \pm1$, corresponding to two different spin directions (i.e. two different directions of magnetization), with equal energy.[35] (Formally, the state with $\eta = 0$ is also stationary, because at this point $\partial F/\partial\eta = 0$, but it is unstable because for the ferromagnetic interaction, $J > 0$, the second derivative $\partial^2 F/\partial\eta^2$ is always negative.) As the external field is increased, it tilts the potential profile, and finally at the critical field,

$$h = h_c \equiv 2Jd, \tag{4.60}$$

the state with $\eta = -1$ becomes unstable, leading to the system's jump into the only remaining state with opposite magnetization, $\eta = +1$ – see the arrow in Fig. 7a. Application of the similar external field of the opposite polarity leads to the similar switching, back to $\eta = -1$, at the field $h = -h_c$, so the full field dependence of η follows the hysteretic pattern shown in Fig. 7b.[36]

Such a pattern is the most visible experimental feature of actual ferromagnetic materials, with the *coercive magnetic field* $\mathcal{H}_c$ of the order of 10^3 A/m, and the *saturated* (or "remnant") *magnetization* corresponding to fields $\mathcal{B}$ of the order of a few teslas. The most important property of these materials, also called *permanent magnets*, is their stability, i.e. the ability to retain the history-determined direction of magnetization in the absence of an external field, for a very long time. In particular, this property is the basis of all magnetic systems for data recording, including the ubiquitous hard disk drives with their incredible information density approaching 1 Terabit per square inch.[37]

So, already the simplest mean-field approximation (59) does give a (crude) description of the ferromagnetic ordering. However, it grossly overestimates the stability of these states with respect to thermal fluctuations. Indeed, in this theory, there is no thermally induced randomness at all, until T becomes comparable with the height of the energy barrier separating two stable states,

$$\Delta F \equiv F(\eta = 0) - F(\eta = \pm1) = NJd, \tag{4.61}$$

which is proportional to the number of particles. At $N \to \infty$, this value diverges, and in this sense, the critical temperature is infinite, while numerical experiments and more refined theories of the Ising model show that actually its ferromagnetic phase is suppressed at $T > T_c \sim Jd$ – see below.

The accuracy of this theory may be dramatically improved by even an approximate account for thermally induced randomness. In this approach (suggested in 1907 by Pierre-Ernest Weiss), called the *molecular-field approximation*,[38] random deviations of individual spin values from the lattice average,

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[35] The fact that the stable states always correspond to $\eta = \pm1$, partly justifies the treatment, in this crude approximation, of the order parameter η as a continuous variable.

[36] Since these magnetization jumps are accompanied by (negative) jumps of the free energy F, they are sometimes called first-order phase transitions. Note, however, that in this simple theory, these transitions are between two physically similar *fully-ordered* phases.

[37] For me, it was always shocking how little my graduate physics students knew about this fascinating (and very important) field of modern engineering, which involves so much interesting physics and fantastic electromechanical technology. For getting acquainted with it, I may recommend, for example, the monograph by C. Mee and E. Daniel, *Magnetic Recording Technology*, 2nd ed., McGraw-Hill, 1996.

[38] In some texts, this approximation is called the "mean-field theory". This terminology may lead to confusion, because the molecular-field theory belongs to a different, deeper level of the theoretical hierarchy than, say, the (more phenomenological) Landau-style mean-field theories. For example, for a given microscopic model, the

$$\widetilde{s}_k \equiv s_k - \eta, \qquad \text{with } \eta \equiv \langle s_k \rangle, \tag{4.62}$$

are allowed, but considered small: $|\widetilde{s}_k| \ll \eta$. This assumption allows us, after plugging the resulting expression $s_k = \eta + \widetilde{s}_k$ into the first term on the right-hand side of Eq. (23),

$$E_m = -J \sum_{\{k,k'\}} (\eta + \widetilde{s}_k)(\eta + \widetilde{s}_{k'}) - h \sum_k s_k \equiv -J \sum_{\{k,k'\}} \left[\eta^2 + \eta (\widetilde{s}_k + \widetilde{s}_{k'}) + \widetilde{s}_k \widetilde{s}_{k'} \right] - h \sum_k s_k, \tag{4.63}$$

ignore the last term in the square brackets. Making the replacement (62) in the terms proportional to $\widetilde{s}_k$, we may rewrite the result as

$$E_m \approx E_m' \equiv (NJd)\eta^2 - h_{\text{ef}} \sum_k s_k, \tag{4.64}$$

where h_{ef} is defined as the sum

$$h_{\text{ef}} \equiv h + (2Jd)\eta. \tag{4.65}$$

This sum may be interpreted as an *effective* external field, which (besides the genuine external field h) takes into account the effect that *would be* exerted on spin s_k by its $2d$ next neighbors if they all had non-fluctuating (but possibly continuous) spin values $s_{k'} = \eta$. Such addition to the external field,

<div style="border:1px solid;">

Weiss molecular field

$$h_{\text{mol}} \equiv h_{\text{ef}} - h = (2Jd)\eta, \tag{4.66}$$

</div>

is called the *molecular field* – giving its name to Weiss' approach.

From the point of view of statistical physics, at fixed parameters of the system (including the order parameter η), the first term on the right-hand side of Eq. (64) is merely a constant energy offset, and h_{ef} is just another constant, so

$$E_m' = \text{const} + \sum_k \varepsilon_k, \qquad \text{with } \varepsilon_k = -h_{\text{ef}} s_k \equiv \begin{cases} -h_{\text{ef}}, & \text{for } s_k = +1, \\ +h_{\text{ef}}, & \text{for } s_k = -1. \end{cases} \tag{4.67}$$

Such separability of the energy means that in the molecular-field approximation the fluctuations of different spins are independent of each other, and their statistics may be examined individually, using the energy spectrum ε_k. But this is exactly the two-level system that was the subject of Problems 2.2-2.4. Actually, its statistics is so simple that it is easier to redo it from scratch, rather than to use the results of those exercises (which would require changing notation). Indeed, according to the Gibbs distribution (2.58)-(2.59), the equilibrium probabilities of the states $s_k = \pm 1$ may be found as

$$W_{\pm} = \frac{1}{Z} e^{\pm h_{\text{ef}}/T}, \qquad \text{with } Z = \exp\left\{ +\frac{h_{\text{ef}}}{T} \right\} + \exp\left\{ -\frac{h_{\text{ef}}}{T} \right\} \equiv 2 \cosh \frac{h_{\text{ef}}}{T}. \tag{4.68}$$

From here, we may readily calculate $F = -T \ln Z$ and all other thermodynamic variables, but let us immediately use Eq. (68) to calculate the statistical average of s_j, i.e. the order parameter:

$$\eta \equiv \langle s_j \rangle = (+1)W_+ + (-1)W_- = \frac{e^{+h_{\text{ef}}/T} - e^{-h_{\text{ef}}/T}}{2 \cosh(h_{\text{ef}}/T)} \equiv \tanh \frac{h_{\text{ef}}}{T}. \tag{4.69}$$

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molecular-field approach may be used for the (approximate) calculation of the parameters a, b, and T_c participating in Eq. (46) – the starting point of the Landau theory.

Now comes the punch line of Weiss' approach: plugging this result back into Eq. (65), we may write the condition of *self-consistency* of the molecular-field approach:

$$h_{ef} - h = 2Jd \tanh \frac{h_{ef}}{T} .$$
(4.70)

This is a transcendental equation, which evades an explicit analytical solution, but whose properties may be readily analyzed by plotting both its sides as functions of the same argument, so the stationary state(s) of the system corresponds to the intersection point(s) of these plots.

First of all, let us explore the field-free case ($h = 0$), when $h_{ef} = h_{mol} \equiv 2dJ\eta$, so Eq. (70) is reduced to

$$\eta = \tanh\left(\frac{2Jd}{T}\eta\right),$$
(4.71)

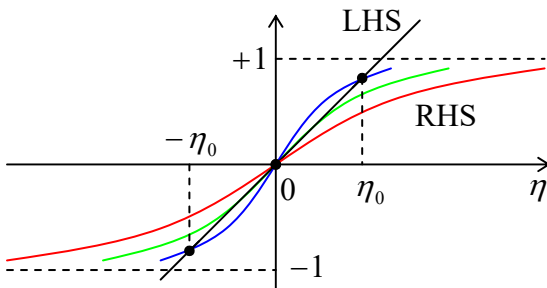giving one of the patterns sketched in Fig. 8, depending on the dimensionless parameter $2Jd/T$.

Fig. 4.8. The ferromagnetic phase transition in Weiss' molecular-field theory: two sides of Eq. (71) sketched as functions of η for three different temperatures: above T_c (red), below T_c (blue), and equal to T_c (green).

If this parameter is small, the right-hand side of Eq. (71) grows slowly with η (see the red line in Fig. 8), and there is only one intersection point with the left-hand side plot, at $\eta = 0$. This means that the spin system has no spontaneous magnetization; this is the so-called *paramagnetic phase*. However, if the parameter $2Jd/T$ exceeds 1, i.e. if T is decreased below the following critical value,

$$T_c = 2Jd ,$$
(4.72)

the right-hand side of Eq. (71) grows, at small η, faster than its left-hand side, so their plots intersect it at three points: $\eta = 0$ and $\eta = \pm\eta_0$ – see the blue line in Fig. 8. It is almost evident that the former stationary point is unstable, while the two latter points are stable. (This fact may be readily verified by using Eq. (68) to calculate F. Now the condition $\partial F/\partial \eta|_{h=0} = 0$ returns us to Eq. (71), while calculating the second derivative, for $T < T_c$ we get $\partial^2 F/\partial \eta^2 > 0$ at $\eta = \pm\eta_0$, and $\partial^2 F/\partial \eta^2 < 0$ at $\eta = 0$). Thus, below T_c the system is in the ferromagnetic phase, with one of two possible directions of the average spontaneous magnetization, so the critical (*Curie*[39]) temperature given by Eq. (72) marks the transition between the paramagnetic and ferromagnetic phases. (Since the stable minimum value of the free energy F is a continuous function of temperature at $T = T_c$, this phase transition is continuous.)

Now let us repeat this graphics analysis to examine how each of these phases responds to an external magnetic field $h \neq 0$. According to Eq. (70), the effect of h is just a horizontal shift of the straight-line plot of its left-hand side – see Fig. 9. (Note a different, here more convenient, normalization of both axes.)

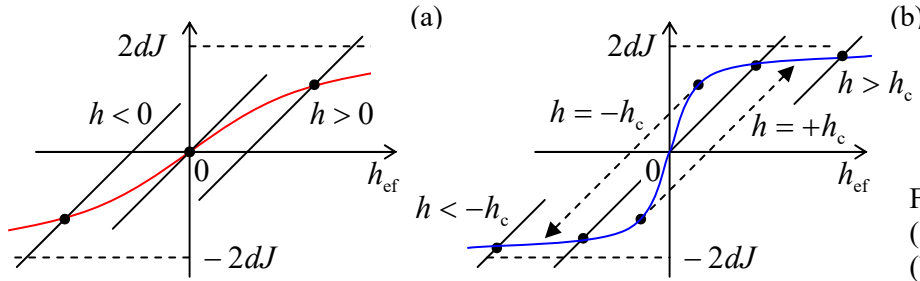[39] Named after Pierre Curie, rather than his (more famous) wife Marie Skłodowska-Curie.

Fig. 4.9 External field effects on (a) a paramagnet ($T > T_c$), and (b) a ferromagnet ($T < T_c$).

In the paramagnetic case (Fig. 9a) the resulting dependence $h_{ef}(h)$ is evidently continuous, but the coupling effect ($J > 0$) makes it steeper than it would be without spin interaction. This effect may be quantified by the calculation of the low-field susceptibility defined by Eq. (29). To calculate it, let us notice that for small h, and hence small h_{ef}, the function tanh is approximately equal to its argument so Eq. (70) is reduced to

$$h_{ef} - h = \frac{2Jd}{T} h_{ef}, \qquad \text{for} \quad \left| \frac{2Jd}{T} h_{ef} \right| \ll 1. \qquad (4.73)$$

Solving this equation for h_{ef}, and then using Eq. (72), we get

$$h_{ef} = \frac{h}{1 - 2Jd/T} \equiv \frac{h}{1 - T_c/T}. \qquad (4.74)$$

Recalling Eq. (66), we can rewrite this result for the order parameter:

$$\eta = \frac{h_{ef} - h}{T_c} = \frac{h}{T - T_c}, \qquad (4.75)$$

so the low-field susceptibility

Curie-
Weiss
law

$$\chi \equiv \frac{\partial \eta}{\partial h}\bigg|_{h=0} = \frac{1}{T - T_c}, \qquad \text{for } T > T_c. \qquad (4.76)$$

This is the famous *Curie-Weiss law*, which shows that the susceptibility diverges at the approach to the Curie temperature T_c.

In the ferromagnetic case, the graphical solution (Fig. 9b) of Eq. (70) gives a qualitatively different result. A field increase leads, depending on the spontaneous magnetization, either to the further saturation of h_{mol} (with the order parameter η gradually approaching 1), or, if the initial η was negative, to a jump to positive η at some critical (coercive) field h_c. In contrast with the crude approximation (59), at $T > 0$ the coercive field is smaller than that given by Eq. (60), and the magnetization saturation is gradual, in a good (semi-quantitative) accordance with experiment.

To summarize, the Weiss molecular-field approach gives an approximate but realistic description of the ferromagnetic and paramagnetic phases in the Ising model, and a very simple prediction (72) of the temperature of the transition between them, for an arbitrary dimensionality d of the cubic lattice. It also enables the calculation of other parameters of Landau's mean-field theory for this model – an exercise left for the reader. Moreover, the molecular-field approximation allows one to obtain similarly reasonable analytical results for some other models of phase transitions – see, e.g., the exercise problems at the end of Sec. 6.

4.5. Ising model: Exact and numerical results

In order to evaluate the main prediction (72) of the Weiss theory, let us now discuss the exact (analytical) and quasi-exact (numerical) results obtained for the Ising model, going from the lowest value of dimensionality, $d = 0$, to its higher values. The zero dimensionality means that the spin has no nearest neighbors at all, so the first term of Eq. (23) vanishes. Hence Eq. (64) is exact, with $h_{ef} = h$, and so is its solution (69). Now we can simply use Eq. (76), with $J = 0$, i.e. $T_c = 0$, reducing this result to the so-called *Curie law*:

$$\chi = \frac{1}{T}. \qquad (4.77)$$

It shows that the system is paramagnetic at any temperature. One may say that for $d = 0$ the Weiss molecular-field theory is exact – or even trivial. (However, in some sense it is more general than the Ising model because as we know from Chapter 2, it gives the exact result for a fully quantum-mechanical treatment of any two-level system, including spin-½.) Experimentally, the Curie law is approximately valid for many so-called *paramagnetic materials*, i.e. 3D systems of particles with spontaneous spins and sufficiently weak interaction between them.

The case $d = 1$ is more complex but has an exact analytical solution. A simple way to obtain it for a uniform chain is to use the so-called *transfer matrix approach*.[40] For this, first of all, we may argue that most properties of a 1D system of $N \gg 1$ spins (say, put at equal distances on a straight line) should not change too much if we bend that line gently into a closed ring (Fig. 10), assuming that spins s_1 and s_N interact exactly as all other next-neighbor pairs. Then the energy (23) becomes

$$E_m = -\left(Js_1s_2 + Js_2s_3 + \ldots + Js_Ns_1\right) - \left(hs_1 + hs_2 + \ldots + hs_N\right). \qquad (4.78)$$
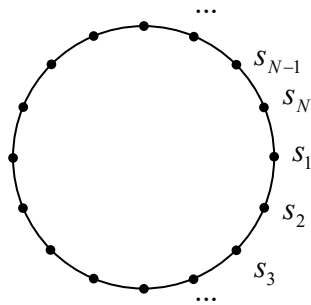

Fig. 4.10. The closed-ring version of the 1D Ising system.

Let us regroup the terms of this sum in the following way:

$$E_m = -\left[\left(\frac{h}{2}s_1 + Js_1s_2 + \frac{h}{2}s_2\right) + \left(\frac{h}{2}s_2 + Js_2s_3 + \frac{h}{2}s_3\right) + \ldots + \left(\frac{h}{2}s_N + Js_Ns_1 + \frac{h}{2}s_1\right)\right], \qquad (4.79)$$

so the group inside each pair of parentheses depends only on the state of two adjacent spins. The corresponding statistical sum,

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[40] This approach was developed in 1941 by H. Kramers and G. Wannier. Note that for the field-free case $h = 0$, an even simpler solution of the problem, valid for chains with an arbitrary number N of "spins" and arbitrary coefficients J_k, is possible. For that, one needs to calculate the explicit relation between the statistical sums Z for systems with N and $(N + 1)$ spins first, and then apply it sequentially to systems starting from $Z = 2$. I am leaving this calculation for the reader's exercise.

$$Z = \sum_{\substack{s_k = \pm 1, \text{ for} \\ k=1,2,\dots N}} \exp\left\{h\frac{s_1}{2T} + J\frac{s_1 s_2}{T} + h\frac{s_2}{2T}\right\} \exp\left\{h\frac{s_2}{2T} + J\frac{s_2 s_3}{T} + h\frac{s_3}{2T}\right\} \dots \exp\left\{h\frac{s_N}{2T} + J\frac{s_N s_1}{T} + h\frac{s_1}{2T}\right\}, \quad (4.80)$$

still has 2^N terms, each corresponding to a certain combination of signs of N spins. However, each operand of the product under the sum may take only four values, corresponding to four different combinations of its two arguments:

$$\exp\left\{h\frac{s_k}{2T} + J\frac{s_k s_{k+1}}{T} + h\frac{s_{k+1}}{2T}\right\} = \begin{cases} \exp\{(J+h)/T\}, & \text{for } s_k = s_{k+1} = +1, \\ \exp\{(J-h)/T\}, & \text{for } s_k = s_{k+1} = -1, \\ \exp\{-J/T\}, & \text{for } s_k = -s_{k+1} = \pm 1. \end{cases} \quad (4.81)$$

These values do not depend on the site number k,[41] and may be represented as the elements $M_{j,j'}$ (with j, $j' = 1, 2$) of the so-called *transfer matrix*

$$M \equiv \begin{pmatrix} \exp\{(J+h)/T\} & \exp\{-J/T\} \\ \exp\{-J/T\} & \exp\{(J-h)/T\} \end{pmatrix}, \quad (4.82)$$

so the whole statistical sum (80) may be recast as a product:

$$Z = \sum_{j_k = 1,2} M_{j_1 j_2} M_{j_2 j_3} \dots M_{j_{N-1} j_N} M_{j_N j_1}. \quad (4.83)$$

According to the basic rule of matrix multiplication, this sum is just

$$Z = \text{Tr}\left(M^N\right). \quad (4.84)$$

Linear algebra tells us that this trace may be represented just as

$$Z = \lambda_+^N + \lambda_-^N, \quad (4.85)$$

where $\lambda_\pm$ are the eigenvalues of the transfer matrix M, i.e. the roots of its characteristic equation,

$$\begin{vmatrix} \exp\{(J+h)/T\} - \lambda & \exp\{-J/T\} \\ \exp\{-J/T\} & \exp\{(J-h)/T\} - \lambda \end{vmatrix} = 0. \quad (4.86)$$

A straightforward solution of this equation yields two roots:

$$\lambda_\pm = \exp\left\{\frac{J}{T}\right\}\left[\cosh\frac{h}{T} \pm \left(\sinh^2\frac{h}{T} + \exp\left\{-\frac{4J}{T}\right\}\right)^{1/2}\right]. \quad (4.87)$$

The last simplification comes from the condition $N \gg 1$ – which we need anyway, to make the ring model sufficiently close to the infinite linear 1D system. In this limit, even a small difference of the exponents, $\lambda_+ > \lambda_-$, makes the second term in Eq. (85) negligible, so we finally get

$$Z = \lambda_+^N = \exp\left\{\frac{NJ}{T}\right\}\left[\cosh\frac{h}{T} + \left(\sinh^2\frac{h}{T} + \exp\left\{-\frac{4J}{T}\right\}\right)^{1/2}\right]^N. \quad (4.88)$$

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[41] This is a result of the "translational" (or rather rotational) symmetry of the system, i.e. its invariance to the index replacement $k \to k + 1$ in all terms of Eq. (78).

From here, we can find the free energy per particle:

$$\frac{F}{N} = \frac{T}{N}\ln\frac{1}{Z} = -J - T\ln\left[\cosh\frac{h}{T} + \left(\sinh^2\frac{h}{T} + \exp\left\{-\frac{4J}{T}\right\}\right)^{1/2}\right], \tag{4.89}$$

and then use thermodynamics to calculate such variables as entropy – see the first of Eqs. (1.35).

However, we are mostly interested in the order parameter defined by Eq. (25): $\eta \equiv \langle s_j \rangle$. The conceptually simplest approach to the calculation of this statistical average would be to use the sum (2.7), with the Gibbs probabilities $W_m = Z^{-1}\exp\{-E_m/T\}$. However, the number of terms in this sum is 2^N, so for $N \gg 1$ this approach is completely impracticable. Here the analogy between the canonical pair $\{-P, V\}$ and other generalized force-coordinate pairs $\{\mathcal{F}, q\}$, in particular $\{\mu_0\mathcal{H}(\mathbf{r}_k), m_k\}$ for the magnetic field, discussed in Secs. 1.1 and 1.4, becomes invaluable – see in particular Eq. (1.3b). (In our normalization (22), and for a uniform field, the pair $\{\mu_0\mathcal{H}(\mathbf{r}_k), m_k\}$ becomes $\{h, s_k\}$.) Indeed, in this analogy the last term of Eq. (23), i.e. the sum of N products $(-hs_k)$ for all spins, with the statistical average $(-Nh\eta)$, is similar to the product PV, i.e. the difference between the thermodynamic potentials F and $G \equiv F + PV$ in the usual "P-V thermodynamics". Hence, the free energy F given by Eq. (89) may be understood as the Gibbs energy of the Ising system in the external field, and the equilibrium value of the order parameter may be found from the last of Eqs. (1.39) with the replacements $-P \rightarrow h$, $V \rightarrow N\eta$:

$$N\eta = -\left(\frac{\partial F}{\partial h}\right)_T, \quad \text{i.e.} \; \eta = -\left[\frac{\partial(F/N)}{\partial h}\right]_T. \tag{4.90}$$

Note that this formula is valid for any model of ferromagnetism, of any dimensionality, if it has the same form of interaction with the external field as the Ising model.

For the 1D Ising ring with $N \gg 1$, Eqs. (89) and (90) yield

$$\eta = \sinh\frac{h}{T}\Bigg/\left(\sinh^2\frac{h}{T} + \exp\left\{-\frac{4J}{T}\right\}\right)^{1/2}, \quad \text{giving} \; \chi \equiv \frac{\partial\eta}{\partial h}\Big|_{h=0} = \frac{1}{T}\exp\left\{\frac{2J}{T}\right\}. \tag{4.91}$$

This result means that the 1D Ising model does *not* exhibit a phase transition, i.e., in this model $T_c = 0$. However, its susceptibility grows, at $T \rightarrow 0$, much faster than the Curie law (77). This gives us a hint that at low temperatures the system is "virtually ferromagnetic", i.e. has the ferromagnetic order with some rare random violations. (Such violations are commonly called *low-temperature excitations*.) This interpretation may be confirmed by the following approximate calculation. It is almost evident that the lowest-energy excitation of the ferromagnetic state of an open-end 1D Ising chain at $h = 0$ is the reversal of signs of all spins in one of its parts – see Fig. 11.
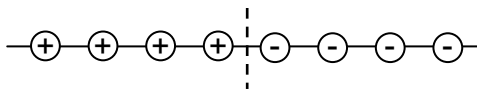

Fig. 4.11. A Bloch wall in an open-end 1D Ising chain.

Indeed, such an excitation (called either the "magnetic domain wall" or just the *Bloch wall*[42]) involves the change of sign of just one product $s_k s_{k'}$, so according to Eq. (23), its energy E_W (defined as

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[42] Named after Felix Bloch who was the first one to discuss such excitations. More complex excitations such as *skyrmions* (see, e.g., A. Fert *et al.*, *Nature Review Materials* **2**, 17031 (2017)) have higher energies.

the difference between the values of E_m with and without the excitation) equals $2J$, regardless of the wall position.[43] Since in the ferromagnetic Ising model, the parameter J is positive, $E_W > 0$. If the system "tried" to minimize its internal energy, having any wall in the system would be energy-disadvantageous. However, thermodynamics tells us that at $T \neq 0$, the system's thermal equilibrium corresponds to the minimum of the free energy $F \equiv E - TS$, rather than just energy E.[44] Hence, we have to calculate the Bloch wall's contribution F_W to the free energy. Since in an open-end linear chain of $N \gg 1$ spins, the wall can take $(N - 1) \approx N$ positions with the same energy E_W, we may claim that the entropy S_W associated with this excitation is $\ln N$, so

$$F_W \equiv E_W - TS_W \approx 2J - T \ln N . \tag{4.92}$$

This result tells us that in the limit $N \to \infty$, and at $T \neq 0$, the Bloch walls are always free-energy-beneficial, thus explaining the absence of the perfect ferromagnetic order in the 1D Ising system. Note, however, that since the logarithmic function changes extremely slowly at large values of its argument, one may argue that a large but finite 1D system should still feature a quasi-critical temperature

$$"T_c" = \frac{2J}{\ln N}, \tag{4.93}$$

below which it would be in a virtually complete ferromagnetic order. (The exponentially large susceptibility (91) is another manifestation of this fact.)

Now let us apply a similar approach to estimate T_c of a 2D Ising model, with open borders. Here the Bloch wall is a line of a certain total length L – see Fig. 12. (For the example presented in that figure, counting from the left to the right, $L = 2 + 1 + 4 + 2 + 3 = 12$ lattice periods.)
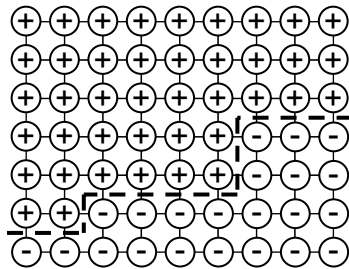

Fig. 4.12. A Bloch wall in a 2D Ising system.

Evidently, the additional energy associated with such a wall is $E_W = 2JL$, while the wall's entropy S_W may be estimated using the following reasoning. A continuous Bloch wall may be thought about as the path of a "Manhattan pedestrian" crossing the system between its nodes. At each junction of straight segments of the path, the pedestrian may select 3 choices of 4 possible directions (except the one that leads backward), so for a path without self-crossings, there are $3^{(L-1)} \approx 3^L$ options for a walk starting from a certain point. Now taking into account that the open borders of a square-shaped lattice with N spins have a length of the order of $N^{1/2}$, and the Bloch wall may start from any of them, there are approximately $M \sim N^{1/2}3^L$ different walks between two borders. Again estimating S_W as $\ln M$, we get

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[43] For the closed-ring model (Fig. 10) such analysis gives an almost similar prediction, with the difference that in that system, the Bloch walls may appear only in pairs, so $E_W = 4J$, and $S_W = \ln[N(N-1)] \approx 2\ln N$.
[44] This is a very vivid application of one of the core results of thermodynamics. If the reader is still uncomfortable with it, they are strongly encouraged to revisit Eq. (1.42) and its discussion.

$$F_W = E_W - TS_W \approx 2JL - T\ln\left(N^{1/2}3^L\right) \equiv L(2J - T\ln 3) - (T/2)\ln N . \qquad (4.94)$$

(Actually, since L scales as $N^{1/2}$ or higher, at $N \to \infty$ the last term in Eq. (94) is negligible.) We see that the sign of the derivative $\partial F_W/\partial L$ depends on whether the temperature is higher or lower than the following critical value:

$$T_c = \frac{2J}{\ln 3} \approx 1.82\, J . \qquad (4.95)$$

At $T < T_c$, the free energy's minimum corresponds to $L \to 0$, i.e. the Bloch walls are free-energy-detrimental, and the system is in the purely ferromagnetic phase.

So, for $d = 2$ the simple estimate predicts a non-zero critical temperature of the same order as the Weiss theory (according to Eq. (72), in this case $T_c = 4J$). The major approximation implied in the calculation leading to Eq. (95) is disregarding possible self-crossings of the "Manhattan walk". The accurate counting of such self-crossings is rather difficult. It had been carried out in 1944 by L. Onsager; since then his calculations have been redone in several easier ways, but even they are rather cumbersome, and I will not have time to discuss them.[45] The final result, however, is surprisingly simple:

$$\boxed{T_c = \frac{2J}{\ln\left(1 + \sqrt{2}\right)} \approx 2.269\, J,} \qquad (4.96)$$ Onsager's exact result

i.e. showing that the simple estimate (95) is off the mark by only ~20%.

The Onsager solution, as well as all alternative solutions of the problem that were found later, are so "artificial" (2D-specific) that they do not give a clear way towards their generalization to other (higher) dimensions. As a result, the 3D Ising problem is still unsolved analytically. Nevertheless, we do know T_c for it with extremely high precision – at least to the 6th decimal place. This has been achieved by numerical methods; they deserve a discussion because of their importance for the solution of other similar problems as well. Conceptually, the task is rather simple: just compute, to the desired precision, the statistical sum of the system (23):

$$Z = \sum_{\substack{s_k = \pm 1,\, \text{for} \\ k = 1, 2, \ldots, N}} \exp\left\{\frac{J}{T}\sum_{\{k, k'\}} s_k s_{k'} + \frac{h}{T}\sum_k s_k\right\} . \qquad (4.97)$$

As soon as this has been done for a sufficient number of values of the dimensionless parameters J/T and h/T, everything is easy; in particular, we can compute the dimensionless function

$$F/T = -\ln Z , \qquad (4.98)$$

and then find the ratio J/T_c as the smallest value of the parameter J/T at which the ratio F/T (as a function of h/T) has a minimum at zero field. However, for any system of a reasonable size N, the "exact" computation of the statistical sum (97) is impossible, because it contains too many terms for any supercomputer to handle. For example, let us take a relatively small 3D lattice with $N = 10\times10\times10 = 10^3$ spins, which still features substantial boundary artifacts even using the periodic boundary conditions, so its phase transition is smeared about T_c by ~ 3%. Still, even for such a crude model, Z would include

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[45] For that, the interested reader may be referred to either Sec. 151 in the textbook by Landau and Lifshitz, or Chapter 15 in the text by Huang.

$2^{1,000} \equiv (2^{10})^{100} \approx (10^3)^{100} \equiv 10^{300}$ terms. Let us suppose we are using a modern exaflops-scale supercomputer performing 10^{18} floating-point operations per second, i.e. $\sim 10^{26}$ such operations per year. With those resources, the computation of just one statistical sum would require $\sim 10^{(300-26)} = 10^{274}$ years. To call such a number "astronomic" would be a strong understatement. (As a reminder, the age of our Universe is close to 1.4×10^{10} years – a very humble number in comparison.)

This situation may be improved dramatically by noticing that any statistical sum,

$$Z = \sum_m \exp\left\{-\frac{E_m}{T}\right\},\tag{4.99}$$

is dominated by terms with lower values of E_m. To find those lowest-energy states, we may use the following powerful approach (belonging to a broad class of numerical *Monte-Carlo techniques*), which essentially mimics one (randomly selected) path of the system's evolution in time. One could argue that for that we would need to know the exact laws of evolution of statistical systems,[46] that may differ from one system to another, even if their energy spectra E_m are the same. This is true, but since the genuine value of Z should be independent of these details, it may be evaluated using *any* reasonable kinetic model that satisfies certain general rules. In order to reveal these rules, let us start from a system with just two states, with energies E_m and $E_{m'} \equiv E_m + \Delta$ – see Fig. 13.
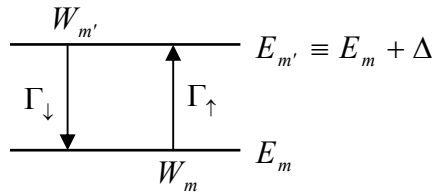

Fig. 4.13. Deriving the detailed balance relation.

In the absence of quantum coherence between the states (see Sec. 2.1), the equations for the time evolution of the corresponding probabilities W_m and $W_{m'}$ should depend only on the probabilities (plus certain constant coefficients). Moreover, since the equations of quantum mechanics are linear, these *master equations* should be also linear. Hence, it is natural to expect them to have the following form,

$$\frac{dW_m}{dt} = W_{m'}\Gamma_\downarrow - W_m\Gamma_\uparrow, \qquad \frac{dW_{m'}}{dt} = W_m\Gamma_\uparrow - W_{m'}\Gamma_\downarrow,\tag{4.100}$$

where the coefficients $\Gamma_\uparrow$ and $\Gamma_\downarrow$ have the physical sense of the *rates* of the corresponding transitions (see Fig. 13); for example, $\Gamma_\uparrow dt$ is the probability of the system's transition into the state m' during an infinitesimal time interval dt, provided that at the beginning of that interval it was in the state m with full certainty: $W_m = 1$, $W_{m'} = 0$.[47] Since for the system with just two energy levels, the time derivatives of the probabilities have to be equal and opposite, Eqs. (100) describe a redistribution of the probabilities between the energy levels, while keeping their sum $W = W_m + W_{m'}$ constant. According to Eqs. (100), at $t \to \infty$, the probabilities settle to their stationary values related as

$$\frac{W_{m'}}{W_m} = \frac{\Gamma_\uparrow}{\Gamma_\downarrow}.\tag{4.101}$$

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[46] Discussion of such laws in the task of *physical kinetics*, which will be briefly reviewed in Chapter 6.
[47] The calculation of these rates for several particular cases is described in QM Secs. 6.6, 6.7, and 7.6 – see, e.g., QM Eq. (7.196), which is valid for a very general model of a quantum system.

Now let us require these stationary values to obey the Gibbs distribution (2.58); from it

$$\frac{W_{m'}}{W_m} = \exp\left\{\frac{E_m - E_{m'}}{T}\right\} = \exp\left\{-\frac{\Delta}{T}\right\} \le 1.\tag{4.102}$$

Comparing these two expressions, we see that the rates have to satisfy the following *detailed balance relation*:

$$\boxed{\frac{\Gamma_\uparrow}{\Gamma_\downarrow} = \exp\left\{-\frac{\Delta}{T}\right\}.}\tag{4.103}$$

Now comes the final step: since the rates of transition between two particular states should not depend on other states and their occupation, Eq. (103) has to be valid for *each* pair of states of any multi-state system. (By the way, this relation may serve as an important sanity check: the rates calculated using any reasonable model of a quantum system have to satisfy it.)

The detailed balance yields only one equation for two rates $\Gamma_\uparrow$ and $\Gamma_\downarrow$; if our only goal is the calculation of Z, the choice of the other equation is not too critical. A very simple choice is

$$\Gamma(\Delta) \propto \gamma(\Delta) \equiv \begin{cases} 1, & \text{if } \Delta < 0, \\ \exp\{-\Delta/T\}, & \text{otherwise,} \end{cases}\tag{4.104}$$

where Δ is the energy change resulting from the transition. This model, which evidently satisfies the detailed balance relation (103), is very popular (despite the unphysical cusp this function has at $\Delta = 0$), because it enables the following simple *Metropolis algorithm* (Fig. 14).
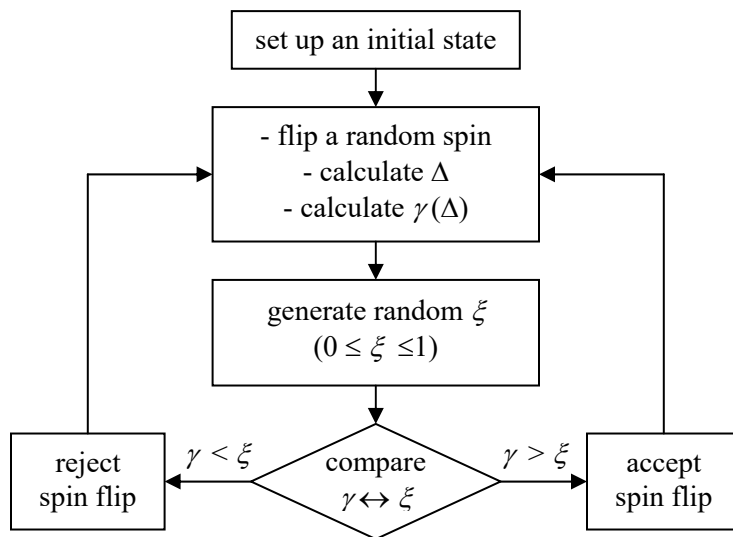

Fig. 4.14. A crude scheme of the Metropolis algorithm for the Ising model simulation.

The calculation starts by setting a certain initial state of the system. At relatively high temperatures, the state may be generated randomly; for example, in the Ising system, the initial state of each spin s_k may be selected independently, with a 50% probability. At low temperatures, starting the calculations from the lowest-energy state (in particular, for the Ising model, from the ferromagnetic state $s_k = \text{sgn}(h) = \text{const}$) may give the fastest convergence. Now one spin is flipped at random, the

corresponding change Δ of the energy is calculated,[48] and plugged into Eq. (104) to calculate $\gamma(\Delta)$. Next, a pseudo-random number generator is used to generate a random number ξ, with the probability density being constant on the segment [0, 1]. (Such functions are available in virtually any numerical library.) If the resulting ξ is less than $\gamma(\Delta)$, the transition is accepted, while if $\xi > \gamma(\Delta)$, it is rejected. Physically, this means that any transition down the energy spectrum ($\Delta < 0$) is always accepted, while those up the energy profile ($\Delta > 0$) are accepted with the probability proportional to $\exp\{-\Delta/T\}$.[49] After sufficiently many such steps, the statistical sum (99) may be calculated approximately as a partial sum over the states passed by the system. (It may be better to discard the contributions from a few first steps, to avoid the effects of the initial state choice.)

This algorithm is extremely efficient. Even with the very modest computers available in the 1980s, it has allowed simulating a 3D Ising system of $(128)^3$ spins to get the following result: $J/T_c \approx$ 0.221650 ± 0.000005. For all practical purposes, this result is exact – so perhaps the largest benefit of the possible future analytical solution of the infinite 3D Ising problem will be a virtually certain Nobel Prize for its author. Table 2 summarizes the values of T_c for the Ising model. Very visible is the fast improvement of the prediction accuracy of the molecular-field approximation, because it is asymptotically correct at $d \to \infty$.

Table 4.2. The critical temperature T_c (in the units of J) of the Ising model
of a ferromagnet ($J > 0$), for several values of dimensionality d

d	Molecular-field approximation – Eq. (72)	Exact value	Exact value's source
0	0	0	Gibbs distribution
1	2	0	Transfer matrix theory
2	4	2.269…	Onsager's solution
3	6	4.513…	Numerical simulation

Finally, I need to mention the *renormalization-group* ("RG") approach,[50] despite its low efficiency for Ising-type problems. The basic idea of this approach stems from the scaling law (30)-(31): at $T = T_c$ the correlation radius r_c diverges. Hence, the critical temperature may be found from the requirement for the system to be *spatially self-similar*. Namely, let us form larger and larger groups ("blocks") of adjacent spins, and require that all properties of the resulting system of the blocks approach those of the initial system, as T approaches T_c.

Let us see how this idea works for the simplest nontrivial (1D) case described by the statistical sum (80). Assuming N to be even (which does not matter at $N \to \infty$), and adding an inconsequential constant C to each exponent (for the purpose that will be clear soon), we may rewrite this expression as

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[48] Note that a flip of a single spin changes the signs of only $(2d + 1)$ terms in the sum (23), i.e. does not require the re-calculation of all $(2d +1)N$ terms of the sum, so the computation of Δ takes just a few multiply-and-accumulate operations even at $N \gg 1$.

[49] The latter step is necessary to avoid the system's trapping in local minima of its multidimensional energy profile $E_m(s_1, s_2,…, s_N)$.

[50] Initially developed in the quantum field theory in the 1950s, it was adapted to statistics by L. Kadanoff in 1966, with a spectacular solution of the so-called *Kubo problem* by K. Wilson in 1972, later awarded with a Nobel Prize.

$$Z = \sum_{s_k = \pm 1} \prod_{k=1,2,\dots N} \exp\left\{\frac{h}{2T}s_k + \frac{J}{T}s_k s_{k+1} + \frac{h}{2T}s_{k+1} + C\right\}. \tag{4.105}$$

Let us group each pair of adjacent exponents to recast this expression as a product over only *even* numbers k,

$$Z = \sum_{s_k = \pm 1} \prod_{k=2,4,\dots N} \exp\left\{\frac{h}{2T}s_{k-1} + s_k\left[\frac{J}{T}(s_{k-1} + s_{k+1}) + \frac{h}{T}\right] + \frac{h}{2T}s_{k+1} + 2C\right\}, \tag{4.106}$$

and carry out the summation over two possible states of the internal spin s_k explicitly:

$$Z = \sum_{s_k = \pm 1} \prod_{k=2,4,\dots N}\left[\begin{array}{l}\exp\left\{\frac{h}{2T}s_{k-1} + \frac{J}{T}(s_{k-1} + s_{k+1}) + \frac{h}{T} + \frac{h}{2T}s_{k+1} + 2C\right\} \\ + \exp\left\{\frac{h}{2T}s_{k-1} - \frac{J}{T}(s_{k-1} + s_{k+1}) - \frac{h}{T} + \frac{h}{2T}s_{k+1} + 2C\right\}\end{array}\right] \tag{4.107}$$

$$\equiv \sum_{s_k = \pm 1} \prod_{k=2,4,\dots N} 2\cosh\left\{\frac{J}{T}(s_{k-1} + s_{k+1}) + \frac{h}{T}\right\}\exp\left\{\frac{h}{2T}(s_{k-1} + s_{k+1}) + 2C\right\}.$$

Now let us require this statistical sum (and hence all statistical properties of the system of two-spin blocks) to be identical to that of the Ising system of $N/2$ spins, numbered by odd k:

$$Z' = \sum_{s_k = \pm 1} \prod_{k=2,4,\dots,N} \exp\left\{\frac{J'}{T}s_{k-1}s_{k+1} + \frac{h'}{T}s_{k+1} + C'\right\}, \tag{4.108}$$

with some different parameters h', J', and C', for all four possible values of $s_{k-1} = \pm 1$ and $s_{k+1} = \pm 1$. Since the right-hand side of Eq. (107) depends only on the sum $(s_{k-1} + s_{k+1})$, this requirement yields only three (rather than four) independent equations for finding h', J', and C'. Of them, the equations for h' and J' depend only on h and J (but not on C),[51] and may be represented in an especially simple form,

$$\boxed{x' = \frac{x(1+y)^2}{(x+y)(1+xy)}, \quad y' = \frac{y(x+y)}{1+xy},} \tag{4.109}$$

if the following notation is used:

$$x \equiv \exp\left\{-4\frac{J}{T}\right\}, \quad y \equiv \exp\left\{-2\frac{h}{T}\right\}. \tag{4.110}$$

Now the grouping procedure may be repeated, with the same result (109)-(110). Hence these equations may be considered as recurrence relations describing repeated doubling of the spin block size. Figure 15 shows (schematically) the *trajectories* of this dynamic system on the phase plane $[x, y]$. (Each trajectory is defined by the following property: for each of its points $\{x, y\}$, the point $\{x', y'\}$ defined by the "mapping" Eq. (109) is also on the same trajectory.) For the ferromagnetic coupling ($J > 0$) and $h > 0$, we may limit the analysis to the unit square $0 \le x, y \le 1$. If this *flow diagram* had a stable fixed point with $x' = x = x_\infty \ne 0$ (i.e. $T/J < \infty$) and $y' = y = 1$ (i.e. $h = 0$), then the first of Eqs. (110) would immediately give us the critical temperature of the phase transition in the field-free system:

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[51] This might be expected because physically C is just a certain constant addition to the system's energy. However, the introduction of that constant was mathematically necessary, because Eqs. (107) and (108) may be reconciled only if $C' \ne C$.

$$T_c = \frac{4J}{\ln(1/x_\infty)}. \tag{4.111}$$

However, Fig. 15 shows that the only fixed point of the 1D system is $x = y = 0$, which (at a finite coupling J) should be interpreted as $T_c = 0$. This is of course in agreement with the exact result of the transfer-matrix analysis but does not provide much additional information.
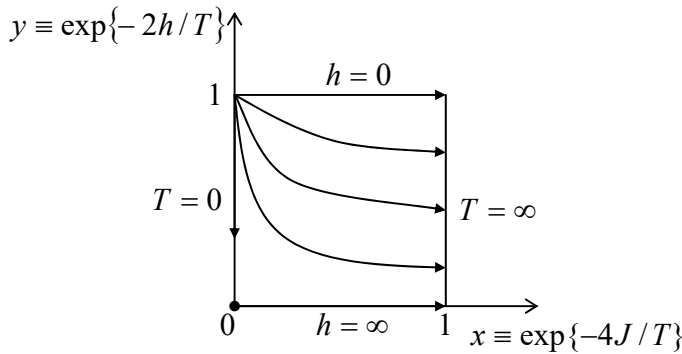

Fig. 4.15. The RG flow diagram of the 1D Ising system (schematically).

Unfortunately, for higher dimensionalities, the renormalization-group approach rapidly becomes rather cumbersome and requires certain approximations whose accuracy cannot be easily controlled. For the 2D Ising system, such approximations lead to the prediction $T_c \approx 2.55\,J$, i.e. to a substantial difference from the exact result (96).

4.6. Exercise problems

4.1. Calculate the entropy, the internal energy, and the specific heat c_V of the van der Waals gas, and discuss the results. For the gas with temperature-independent c_V, find the relation between V and T during an adiabatic process.

4.2. Use two different approaches to calculate the coefficient $(\partial E / \partial V)_T$ for the van der Waals gas and the change of temperature of such a gas, with a temperature-independent C_V, at its very fast expansion.

4.3. For real gases, the Joule-Thomson coefficient $(\partial T / \partial P)_H$ (and hence the gas temperature change at its throttling, see Problem 1.11) inverts its sign at crossing the so-called *inversion curve* $T_{inv}(P)$. Calculate this curve for the van der Waals gas.

4.4. Calculate the difference $C_P - C_V$ for the van der Waals gas, and compare the result with that for an ideal classical gas.

4.5. For the van der Waals model, calculate the temperature dependence of the phase-equilibrium pressure $P_0(T)$ and the latent heat $\Lambda(T)$, in the low-temperature limit $T << T_c$.

4.6. Perform the same tasks as in the previous problem, in the opposite limit: in close vicinity of the critical point T_c.

    <u>4.7</u>. Calculate C_V and C_P for the stable gas-liquid system described by the van der Waals equation, for $V = V_c$ and $0 < T_c - T \ll T_c$.

    <u>4.8</u>. Calculate the critical values P_c, V_c, and T_c for the so-called *Redlich-Kwong model* of the real gas, with the following equation of state:[52]

$$P + \frac{a}{V(V + Nb)T^{1/2}} = \frac{NT}{V - Nb},$$

with constant parameters a and b.

    Hint: Be prepared to solve a cubic equation with particular (numerical) coefficients.

    <u>4.9</u>. Calculate the critical values P_c, V_c, and T_c for the phenomenological *Dieterici model*, with the following equation of state:[53]

$$P = \frac{NT}{V - b}\exp\left\{-\frac{a}{NTV}\right\},$$

with constant parameters a and b. Compare the value of the dimensionless factor P_cV_c/NT_c with those given by the van der Waals and Redlich-Kwong models.

    <u>4.10</u>. In the crude sketch shown in Fig. 3b, the derivatives dP/dT of the phase transitions liquid-gas ("vaporization") and solid-gas ("sublimation"), at the triple point, are different, with

$$\left(\frac{dP_v}{dT}\right)_{T=T_t} < \left(\frac{dP_s}{dT}\right)_{T=T_t}.$$

Is this occasional? What relation between these derivatives can be obtained from thermodynamics?

    <u>4.11</u>. Use the Clapeyron-Clausius formula (17) to calculate the latent heat Λ of the Bose-Einstein condensation, and compare the result with that obtained in the solution of Problem 3.21.

    <u>4.12</u>. As was discussed in Sec. 4.1 of the lecture notes, properties of systems with *first-order phase transitions* (such as the van der Waals gas) change qualitatively at the critical temperature: at $T < T_c$, the system may include two different phases of the same substance. However, since the difference in the density of these phases, in equilibrium, is a *continuous* function of the difference $T_c - T$, this change itself is sometimes considered a *continuous* phase transition between the purely gaseous phase and the mixed gas-liquid "phase". From this viewpoint, what are the most reasonable analogs of the critical exponents β, γ, and δ, which were defined in Sec. 4.2, for such a continuous transition? Evaluate these exponents for the van der Waals model.

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[52] This equation of state, suggested in 1948, describes most real gases better than not only the original van der Waals model, but also other two-parameter alternatives, such as the *Berthelot*, *modified-Berthelot*, and *Dieterici* models, though some approximations with more fitting parameters (such as the *Soave-Redlich-Kwong model*) work even better.

[53] For practical applications, this approximation is currently less popular than the Redlich-Kwong model (also with two fitting parameters), whose analysis was the task of the previous problem.

4.13.

(i) Compose such an effective single-particle Hamiltonian that the corresponding stationary Schrödinger equation coincides with the Gross-Pitaevski equation (58).

(ii) Use this *Gross-Pitaevskii Hamiltonian*, with the particular confining potential $U(\mathbf{r}) = m\omega^2 r^2/2$, to calculate the ground-state energy E of $N \gg 1$ confined particles, by assuming the natural trial solution $\psi \propto \exp\{-r^2/2r_0^2\}$.[54]

(iii) Explore the function $E(r_0)$ for positive and negative values of the constant b, and interpret the results.

(iv) For $b < 0$ with small $|b|$, estimate the largest number N of particles that may form a metastable Bose-Einstein condensate.

4.14. Superconductivity may be suppressed by a sufficiently strong magnetic field. In the simplest case of a bulk, long cylindrical sample of a type-I superconductor, placed into an external magnetic field $\mathscr{H}_{\text{ext}}$ parallel to its axis, this suppression takes a simple form of a simultaneous transition of the whole sample from the superconducting state to the "normal" (non-superconducting) state at a certain value $\mathscr{H}_{\text{c}}(T)$ of the field's magnitude. This *critical field* gradually decreases with temperature from its maximum value $\mathscr{H}_{\text{c}}(0)$ at $T \to 0$ to zero at the critical temperature T_{c}. Assuming that the function $\mathscr{H}_{\text{c}}(T)$ is known, calculate the latent heat of this phase transition as a function of temperature, and spell out its values at $T \to 0$ and $T = T_{\text{c}}$.

Hint: In this particular context, "bulk sample" means a sample much larger than the intrinsic length scales of the superconductor (such as the London penetration depth δ_{L} and the coherence length ξ).[55] For such bulk superconductors, magnetic properties of the superconducting phase may be well described as perfect diamagnetism, with $\mathscr{B} = 0$ inside it.

4.15. In some textbooks, the discussion of thermodynamics of superconductivity is started by displaying, as self-evident, the following formula:

$$F_{\text{n}}(T) - F_{\text{s}}(T) = \frac{\mu_0 \mathscr{H}_{\text{c}}^2(T)}{2} V ,$$

where F_{s} and F_{n} are the free energy values in the superconducting and non-superconducting ("normal") phases, and $\mathscr{H}_{\text{c}}(T)$ is the critical value of the magnetic external field. Is this formula correct, and if not, what qualification is necessary to make it valid? Assume that all the conditions of a simultaneous field-induced phase transition in the whole sample, spelled out in the previous problem, are satisfied.

4.16. Consider a system of $N = 3$ Ising "spins" ($s_k = \pm 1$) with similar ferromagnetic coupling J of each pair of them, in thermal equilibrium.

(i) Calculate the order parameter η and the low-field susceptibility $\chi \equiv \partial \eta/\partial h|_{h=0}$.

(ii) Use the low-temperature limit of the result for χ to predict it for a similar "ring" with an arbitrary N, and verify your prediction by a direct calculation (in this limit).

(iii) Discuss the relation between the last result, in the limit $N \to \infty$, and Eq. (91).

---

[54] This task is essentially the first step of the variational method of quantum mechanics – see, e.g., QM Sec. 2.9.

[55] A discussion of these parameters, as well as of the difference between the type-I and type-II superconductivity, may be found in EM Secs. 6.4-6.5. However, those details are not needed for the solution of this problem.

4.17. Calculate the average energy, entropy, and heat capacity of a uniform three-site ring of Ising-type "spins" ($s_k = \pm 1$), with *antiferromagnetic* coupling (of magnitude J) between the sites, in thermal equilibrium at temperature T, with no external magnetic field. Find the asymptotic behavior of its heat capacity for low and high temperatures, and give an interpretation of the results.

4.18. Using the results discussed in Sec. 5 for the infinite 1D Ising model, calculate the average energy, free energy, entropy, and heat capacity (all per one "spin") as functions of temperature T and external field h. Sketch the temperature dependence of the heat capacity for various values of the h/J ratio, and give a physical interpretation of the result.

4.19. Calculate the specific heat (per "spin") for the d-dimensional Ising problem in the absence of the external field, in the molecular-field approximation. Sketch the temperature dependence of C and compare it with the corresponding plot in the previous problem's solution.

4.20. Prove that in the limit $T \to T_c$, the molecular-field approximation, applied to the Ising model with a spatially constant order parameter, gives results similar to those of Landau's mean-field theory with certain coefficients a and b. Calculate these coefficients and list the critical exponents defined by Eqs. (26), (28), (29), and (32), given by this approximation.

4.21. Assuming that the statistical sum Z_N of a field-free, open-ended 1D Ising system of N "spins" with arbitrary coefficients J_k is known, calculate Z_{N+1}. Then use the result to obtain an explicit expression for Z_N and compare it with Eq. (88).

4.22. Use the molecular-field approximation to calculate the critical temperature and the low-field susceptibility of a d-dimensional cubic lattice of spins, described by the so-called *classical Heisenberg model*:[56]

$$E_m = -J \sum_{\{k,,k'\}} \mathbf{s}_k \cdot \mathbf{s}_{k'} - \sum_k \mathbf{h} \cdot \mathbf{s}_k .$$

Here, in contrast to the (otherwise, very similar) Ising model (23), the spin of each site is described as a classical 3D vector $\mathbf{s}_k = \{s_{xk}, s_{yk}, s_{zk}\}$ of unit length: $s_k^2 = 1$.

4.23. Use the molecular-field approximation to calculate the coefficient a in Landau's expansion (46) for a 3D cubic lattice of spins described by the classical Heisenberg model (whose analysis was the subject of the previous problem).

4.24. Use the molecular-field approximation to calculate the critical temperature of the ferromagnetic transition for the d-dimensional cubic Heisenberg lattice of arbitrary (either integer or half-integer) quantum spins s.

Hint: This model is described by Eq. (4.21) of the lecture notes, with $\hat{\boldsymbol{\sigma}}$ now meaning the vector operator of spin s, in units of Planck's constant $\hbar$.

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[56] This classical model is formally similar to the generalization of the genuine (quantum) Heisenberg model (21) to arbitrary spin s, and serves as its infinite-spin limit.