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Basic Aspects of the Quantum Theory of Solids

Order and Elementary Excitations



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1

Some basic notions of classical and quantum statistical physics

1.1 Gibbs distribution function and partition function

In this short chapter some of the basic notions from thermodynamics and statistical physics are summarized.

The probability to observe a state $|n\rangle$ with energy E_n is

$$w_n = A e^{-E_n/T} ; \quad (1.1)$$

this is called the Gibbs distribution. (Here and below we put the Boltzmann constant $k_B = 1$, i.e. the temperature is measured in units of energy, and vice versa.) The normalization constant A is determined by the condition that the total sum of probabilities of all states is 1:

$$\sum_n w_n = 1 , \quad (1.2)$$

from which we find

$$\frac{1}{A} = \sum_n e^{-E_n/T} \equiv Z . \quad (1.3)$$

Here Z is the partition function

$$Z = \sum_n e^{-E_n/T} = \text{Tr}\left(e^{-\hat{\mathcal{H}}/T}\right) , \quad (1.4)$$

where $\hat{\mathcal{H}}$ is the Hamiltonian of the system. Thus

$$w_n = \frac{e^{-E_n/T}}{Z} . \quad (1.5)$$

The entropy is defined as

$$S = -\langle \ln w_n \rangle = -\frac{\sum_n \ln w_n e^{-E_n/T}}{Z} \quad (1.6)$$

($\langle \dots \rangle$ is the symbol for the average). When we put (1.5) into (1.6), we obtain

$$S = \ln Z + \frac{E}{T}, \quad (1.7)$$

where E is the average energy of the system, $E = \frac{1}{Z} \sum_n E_n e^{-E_n/T}$. We can introduce the quantity

$$F = E - TS = -T \ln Z, \quad (1.8)$$

which is called the (Helmholtz) free energy:

$$F = -T \ln Z = -T \ln \sum_n e^{-E_n/T}. \quad (1.9)$$

1.2 Thermodynamic functions

The Helmholtz free energy, F , is a function of the temperature T and of the density $n = N/V$, or of the volume: $F = F(V, T)$. One can also introduce other so-called thermodynamic potentials, expressed as functions of different variables. These are:

At fixed pressure and temperature – the Gibbs free energy

$$\Phi(P, T) = E - TS + PV = F + PV. \quad (1.10)$$

If instead of the temperature T we chose as free variable its conjugate, the entropy, then we obtain the enthalpy

$$W(P, S) = E + PV. \quad (1.11)$$

Enthalpy is often used in discussions of chemical reactions, thermodynamics of formation of different phases, etc.

The energy itself is also one of the thermodynamic potentials; it is a function of volume and entropy, $E(V, S)$.

Similar to mechanics, where the system at equilibrium tends to a state with minimum energy, many-particle systems at finite temperature tend to minimize the free energy, i.e. the corresponding thermodynamic potential F or Φ .

From these definitions it is clear that, e.g.

$$dF = -S dT - P dV, \quad (1.12)$$

from which we obtain

$$S = - \left(\frac{\partial F}{\partial T} \right)_V , \quad (1.13)$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_T . \quad (1.14)$$

Similarly

$$d\Phi = -S dT + V dP , \quad (1.15)$$

$$S = - \left(\frac{\partial \Phi}{\partial T} \right)_P , \quad (1.16)$$

$$V = \left(\frac{\partial \Phi}{\partial P} \right)_T . \quad (1.17)$$

Other useful thermodynamic quantities are, e.g. the specific heat at constant volume, c_V , and at constant pressure, c_P :

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V , \quad (1.18)$$

$$c_P = \left(\frac{\partial W}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P . \quad (1.19)$$

One can express c_P , c_V through F , Φ , using (1.12), (1.15).

Using the expressions given above, one can obtain useful relations between different thermodynamic quantities, e.g. between the specific heat, the thermal expansion coefficient (the volume coefficient of the thermal expansion $\beta = 3\alpha$, where α is the linear thermal expansion)

$$\beta = + \frac{1}{V} \frac{\partial V}{\partial T} , \quad (1.20)$$

and the compressibility

$$\kappa = - \frac{1}{V} \frac{\partial V}{\partial P} . \quad (1.21)$$

The resulting connection has the form (see, e.g. Landau and Lifshits 1980, Section 16):

$$c_P - c_V = -T \frac{(\partial V / \partial T)_P^2}{(\partial V / \partial P)_T} = VT \frac{\beta^2}{\kappa} . \quad (1.22)$$

Similarly one can also find relations between other thermodynamic quantities; some examples will be given below, especially in Chapter 2.

1.3 Systems with variable number of particles; grand partition function

One can also introduce thermodynamic quantities for systems with variable number of particles N . The thermodynamic potentials introduced above depend on the particle density N/V , i.e.

$$\begin{aligned} F &= N f_1\left(\frac{V}{N}, T\right) \\ \Phi &= N f_2(P, T) \\ E &= N f_3\left(\frac{S}{N}, \frac{V}{N}\right). \end{aligned} \quad (1.23)$$

From these equations we get:

$$\begin{aligned} dF &= -SdT - PdV + \mu dN \\ d\Phi &= -SdT + VdP + \mu dN \\ dE &= TdS - PdV + \mu dN. \end{aligned} \quad (1.24)$$

Here we have introduced the chemical potential μ which is defined by

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial \Phi}{\partial N}\right)_{P,T}. \quad (1.25)$$

From (1.25) and (1.23) we obtain

$$\mu = \frac{\Phi}{N}, \quad (1.26)$$

i.e. the chemical potential is the Gibbs free energy per particle.

One important remark is relevant here. If the number of (quasi)particles N is not conserved, such as for example the number of phonons in a crystal, then the value of N is determined by the condition of minimization of the free energy in N , e.g. $\partial F/\partial N = 0$, etc. One sees then that in such cases the chemical potential is $\mu = 0$. This fact will be used in several places later on. 物理実験。

The chemical potential μ and the number of particles N are **conjugate variables** (like T and S ; P and V). One can introduce a new thermodynamic potential with μ as a variable; it is usually denoted $\Omega(V, T, \mu)$. Using equations (1.3), (1.8) we can write down the **distribution function** (1.1) as

$$w_n = \frac{e^{-E_n/T}}{Z} = \exp\left(\frac{F - E_n}{T}\right). \quad (1.27)$$

For a variable particle number N , it takes the form

$$w_{nN} = \exp\left(\frac{\Omega + \mu N - E_{nN}}{T}\right), \quad (1.28)$$

where we have used this new thermodynamic potential Ω , instead of the free energy:

$$\Omega(V, T, \mu) = F - \mu N. \quad (1.29)$$

Thus Ω is a generalization of the free energy to the case of variable number of particles. Similar to (1.24), we have:

$$d\Omega = -S dT - P dV - N d\mu , \quad (1.30)$$

i.e. the total number of particles is connected to the chemical potential by the relation

$$N = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V}. \quad (1.31)$$

Problem: One can show that $\Omega = -PV$; try to prove this.

Solution: From (1.29) $\Omega = F - \mu N$. But, by (1.26), $\mu N = \Phi$, and, by (1.10), $\Phi = F + PV$. Thus $\Omega = F - \mu N = F - \Phi = -PV$.

Analogously to (1.5), (1.9), we can write down

$$\Omega \equiv -T \ln Z_G \quad (1.32)$$

where Z_{C_1} is called *grand partition function*.

$$Z_{Gr} = \sum_N \left(e^{\mu N/T} \sum_n e^{-E_n N/T} \right). \quad (1.33)$$

$$\sum E_i - \mu N$$

2

General theory of phase transitions

The state of different condensed matter systems is characterized by different quantities: density, symmetry of a crystal, magnetization, electric polarization, etc. Many such states can have a certain ordering. Different types of ordering can be characterized by *order parameters*.

Examples of order parameters are, for instance: for ferromagnets – the magnetization M ; for ferroelectrics – the polarization P ; for structural phase transitions – the distortion $u_{\alpha\beta}$, etc. Typically the system is disordered at high temperatures, and certain types of ordering may appear with decreasing temperature. This is clear already from the general expressions for thermodynamic functions, see Chapter 1: at finite temperatures the state of the system is chosen by the condition of the minimum of the corresponding thermodynamic potential, the Helmholtz free energy (1.8) or the Gibbs free energy (1.10), and from those expressions it is clear that with increasing temperature it is favourable to have the highest entropy possible, i.e. a disordered state. But some types of ordering are usually established at lower temperatures, where the entropy does not play such an important role, and the minimum of the energy is reached by establishing that ordering.

The general order parameter η depends on temperature, and in principle also on other external parameters – pressure, magnetic field, etc. Typical cases of the dependence of the order parameter on temperature are shown in Fig. 2.1. The situation shown in Fig. 2.1(a), where the order parameter changes continuously, is called a *second-order phase transition*, and that shown in Fig. 2.1(b), where η changes in a jump-like fashion, is a *first-order phase transition*. The temperature T_c below which there exists order in a system ($\eta \neq 0$) is called the *critical temperature* (sometimes the Curie temperature, the notion coming from the field of magnetism).

2.1 Second-order phase transitions (Landau theory)

For the second-order phase transitions close to T_c the order parameter η is small, and we can expand the (Gibbs) free energy $\Phi(P, T, \eta)$ in a Taylor series. This

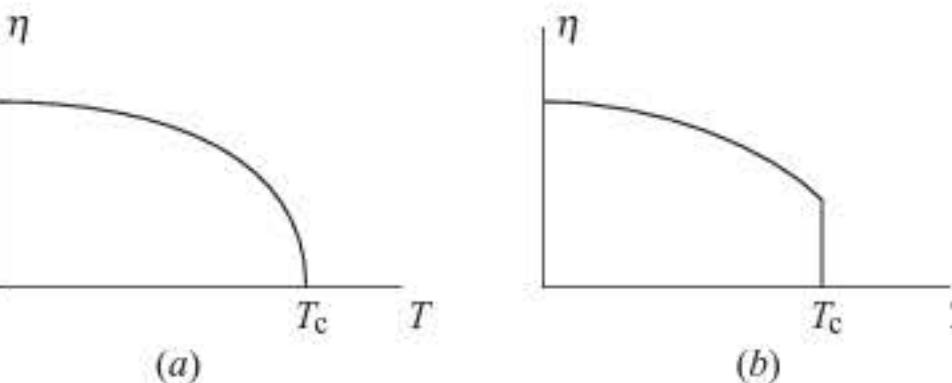


Fig. 2.1

approach was first developed by Landau, and in this section we largely follow the classical presentation of Landau and Lifshits (1980).

The expansion of the free energy in small η is, in general,

$$\Phi = \Phi_0 + \alpha\eta + A\eta^2 + C\eta^3 + B\eta^4 + \dots \quad (2.1)$$

(It will be clear below why we have chosen such an ‘unnatural’ notation with the sequence of coefficients A , C , B .) As mentioned above, the state of the system, in particular the value of the order parameter η (magnetization, or spontaneous polarization, or distortion, etc.) is determined by the condition that the free energy, in this case Φ , has a minimum. The coefficients α , A , C , B are functions of P , T such that the minimum of $\Phi(P, T, \eta)$ as a function of η should correspond to $\eta = 0$ above T_c (disordered state), and to $\eta \neq 0$ (and small) below T_c . From this requirement it is clear that the coefficient α in a system without external fields should be $\alpha = 0$, otherwise $\eta \neq 0$ at all temperatures; in the presence of the linear term in (2.1) the free energy would never have a minimum at $\eta = 0$, which should be the case in a disordered system at $T > T_c$.

The same requirement that $\eta = 0$ above T_c , but $\eta \neq 0$ for $T < T_c$, leads to the requirement that the first nonzero term $A\eta^2$ in the expansion (2.1) should obey the condition

$$\begin{aligned} A(P, T) &> 0 & \text{for } T > T_c \\ A(P, T) &< 0 & \text{for } T < T_c. \end{aligned} \quad (2.2)$$

As a result the dependence of $\Phi(\eta)$ would have the form shown in Fig. 2.2.

Thus at the critical temperature T_c the coefficient $A(P, T)$ should pass through zero and change sign. (We assume that it changes continuously with temperature. We also assume that the other coefficients in equation (2.1) are such that $C = 0$, which is often the case, see Section 2.2 below, and $B > 0$.) Again, making the simplest assumption, we can write close to T_c :

$$A(P, T) = a(T - T_c), \quad (2.3)$$

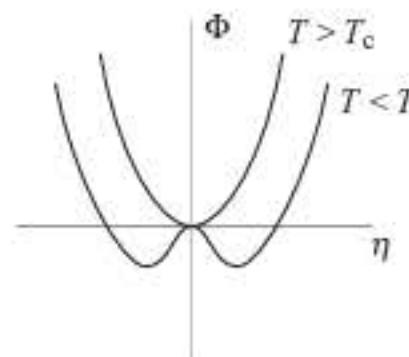


Fig. 2.2

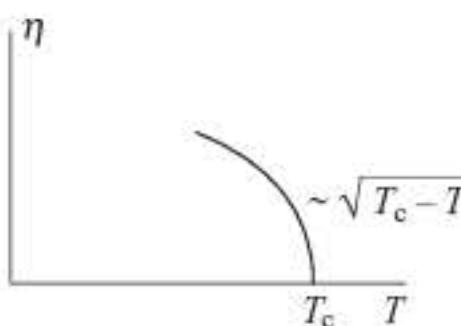


Fig. 2.3

with the coefficient $a > 0$. Then

$$\boxed{\Phi = \Phi_0 + A\eta^2 + B\eta^4 = \Phi_0 + a(T - T_c)\eta^2 + B\eta^4}. \quad (2.4)$$

The behaviour of $\eta(T)$ can be easily found from (2.4) by minimizing the free energy with respect to η :

$$\frac{\partial \Phi}{\partial \eta} = 0 \implies 2A\eta + 4B\eta^3 = 2a(T - T_c)\eta + 4B\eta^3 = 0, \quad (2.5)$$

$$\boxed{\eta^2 = -\frac{A}{2B} = \frac{a}{2B}(T_c - T)}. \quad (2.6)$$

This behaviour is shown in Fig. 2.3.

Here in principle all coefficients may be functions of pressure (or other external variables), $a = a(P)$, $B = B(P)$, $T_c = T_c(P)$. But in practice the dependence of $T_c(P)$ is the most important one; the coefficients a and B can usually be taken as constants.

The equilibrium free energy itself at $T < T_c$ is obtained by putting the equilibrium value of the order parameter (2.6) back into the free energy (2.4):

$$\Phi_{\min} = \Phi_0 - \frac{A^2}{4B} = \Phi_0 - \frac{a^2}{4B}(T_c - T)^2 \quad (2.7)$$

(and $\Phi = \Phi_0$ for $T > T_c$). Thus Φ (and other thermodynamic potentials – e.g. the Helmholtz free energy F if we work at fixed volume V and have a second-order phase transition) are continuous, see Fig. 2.4(a). However the derivatives ($\partial\Phi/\partial T$),

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2.1 Second-order phase transitions

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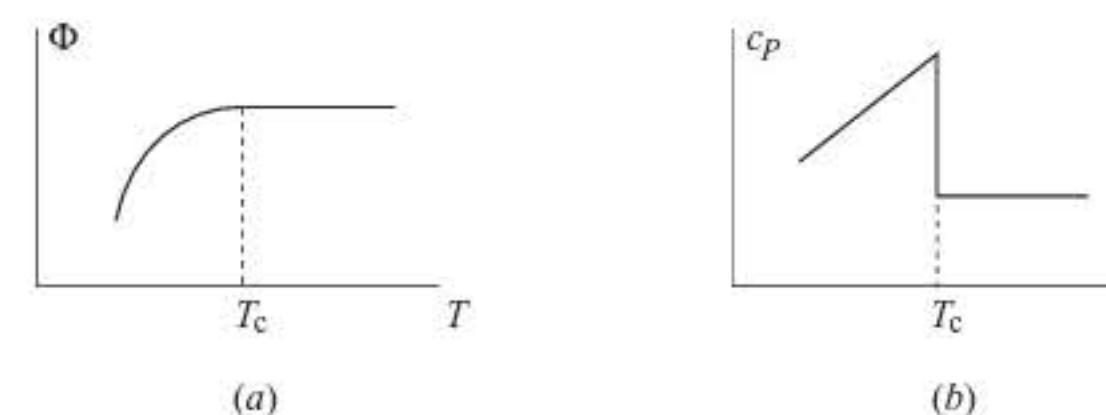


Fig. 2.4

etc. have **kinks** at T_c , and the second derivative would have **jumps**; this is typical behaviour of thermodynamic functions at the second-order phase transitions in the Landau theory.

Problem: Using the definition of specific heat c_P (1.19), equations (1.16), (2.6), (2.7), find the behaviour of specific heat at the second-order phase transition.

Solution: The entropy S , by (1.16) and (2.7), is

$$S = -\frac{\partial \Phi}{\partial T} = \begin{cases} S_0 & (T > T_c) \\ S_0 - \frac{a^2}{2B}(T_c - T) & (T < T_c) \end{cases} \quad (2.8)$$

and, by (1.19), the specific heat is

$$c_P = T \left(\frac{\partial S}{\partial T} \right)_P = \begin{cases} 0 & (T > T_c) \\ a^2 T / 2B & (T < T_c). \end{cases} \quad (2.9)$$

Note that this expression is valid only close to T_c ; at lower temperatures the **specific heat** may and will **deviate** from this simple linear behaviour.

At T_c the entropy has a **kink**, see (2.8), and there exists at T_c a **jump** in the **specific heat at the second-order phase transition**:

$$\Delta c_P = \frac{a^2 T_c}{2B}. \quad (2.10)$$

This behaviour is shown in Fig. 2.4(b).

The total entropy connected with the ordering is

$$S_{\text{ord}} = \int_0^{T_c} \frac{1}{T} c_P(T) dT. \quad (2.11)$$

The experimental measurements of specific heat and of the total entropy of the transition give very important information: the observation of the behaviour of c_P of the type shown in Fig. 2.4 proves that we are dealing with a second-order

phase transition (see however Section 2.5 later), and the measurement of the total entropy of the transition (part of the total entropy, connected with the ordering tells us which degrees of freedom participate in ordering. Thus, e.g. if we have a magnetic ordering of spins $\frac{1}{2}$, the total entropy of the transition in the ideal case should be $S_{\text{tot}} = k_B \ln 2$ (or $k_B \ln(2S + 1)$ for spin S , where $2S + 1$ is the number of possible states of spin S in a fully disordered state, and this entropy has to be removed in the ordered state at $T = 0$). If experimentally one finds S_{tot} smaller than this value, then this means that there is still a certain degree of ordering (or short-range correlations) above T_c . If, however, one finds the value of S_{tot} larger than the expected one, one can conclude that some other degrees of freedom also order at T_c , not only the ones initially assumed. This is an important test, often used experimentally.

Problem: Find the connection between the specific heat jump Δc_P and other properties of the solid (compressibility, thermal expansion).

Solution: By definition, second-order phase transitions are continuous, so that along the transition line there is no jump in volume and in entropy, $\Delta V = 0$, $\Delta S = 0$ (these would be nonzero at the first-order phase transition). Let us differentiate these relations along the curve $T_c(P)$: we thus obtain, e.g. $\alpha \leftarrow \alpha^{\text{sc}}$

$$\Delta \left(\frac{\partial V}{\partial P} \right)_T + \frac{\partial T}{\partial P} \Bigg|_T \Delta \left(\frac{\partial V}{\partial T} \right)_P = 0 . \quad (2.12)$$

Remembering that the thermal expansion coefficient is $\beta = 3\alpha = \frac{1}{V} \frac{dV}{dT}$, and the compressibility $\kappa = -\frac{1}{V} \frac{\partial V}{\partial P}$, we can rewrite equation (2.12) as

$$\Delta\kappa = 3 \frac{dT_c}{dP} \Delta\alpha = \frac{dT_c}{dP} \Delta\beta \quad . \quad (2.13)$$

Similarly, from the condition $\Delta S = 0$, we obtain

$$\Delta \left(\frac{\partial S}{\partial P} \right)_T + \frac{\partial T}{\partial P} \Bigg|_T \Delta \left(\frac{\partial S}{\partial T} \right)_P = 0 . \quad (2.14)$$

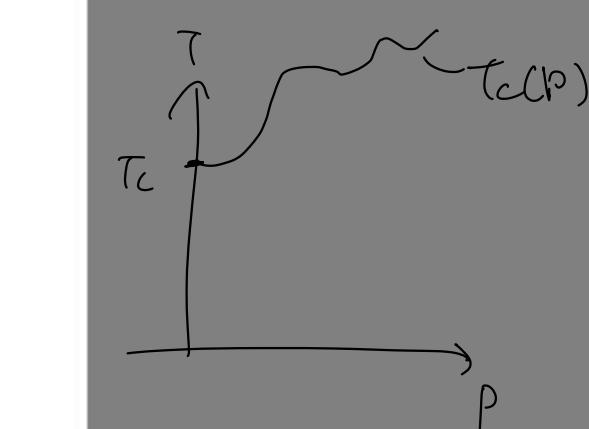
As

$$S = - \left(\frac{\partial \Phi}{\partial T} \right)_n , \quad (2.15)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{\partial^2 \Phi}{\partial T \partial P} = -\frac{\partial}{\partial T} \left(\frac{\partial \Phi}{\partial P}\right) = -\left(\frac{\partial V}{\partial T}\right)_P , \quad (2.16)$$

$\bar{\Phi} = \Phi(T, P)$ 为 Gibbs 的自由能 $G - TS$, $\left(\frac{\partial \bar{\Phi}}{\partial P}\right)_T = V$

$$\overline{F} = F + PV \quad F = -\nabla P - \rho dV - \mu dr$$



$\Delta V \varepsilon$, $T = T_c \varepsilon^{\alpha}$ 定義

$$\left(\frac{d}{dP} \Delta V \right)_{T=T_c} = \Delta \left(\frac{\partial V}{\partial P} \right)_{T_c} + \left(\frac{\partial T}{\partial P} \right)_{T_c} \Delta \left(\frac{\partial V}{\partial T} \right)_P = 0.$$

2.2 (Weak) First-order phase transitions

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this gives the relation

$$\Delta \left(\frac{\partial V}{\partial T} \right)_P = \frac{dT_c}{dP} \frac{\Delta c_P}{T_c} \quad \frac{c_P}{T} = \left(\frac{\partial S}{\partial T} \right)_P \quad (2.17)$$

(here we have used the expression (1.19) for the specific heat c_P). In effect we obtain

$$3\Delta\alpha = \Delta\beta = \frac{dT_c}{dP} \frac{1}{VT_c} \Delta c_P . \quad (2.18)$$

The relations (2.13), (2.18) are known as the Ehrenfest relations. They are the analogues for the second-order phase transition of the well-known Clausius–Clapeyron relations valid for first-order transitions, e.g. the relation between the jump in volume and the latent heat of transition $\Delta Q = T \Delta S$:

$$\Delta V = \frac{\partial T_c}{\partial P} \Delta S = \frac{1}{T_c} \frac{dT_c}{dP} \Delta Q . \quad (2.19)$$

One can easily check that in the limit in which all the jumps at the first-order transition go to zero, i.e. when the first-order phase transition goes over to the second-order one, this expression gives equation (2.18): one can obtain this by applying the operation $\frac{1}{V} \frac{\partial}{\partial T}$ to (2.19) and using $\frac{\partial(\Delta Q)}{\partial T} = \Delta c_P$, and $\beta = 3\alpha = \frac{1}{V} \frac{\partial V}{\partial T}$.

Analogue ... ↗

2.2 (Weak) First-order phase transitions

3/2

Until now we have ignored the cubic term in the expansion (2.1). Very often it is indeed zero, just by symmetry. Thus, in an isotropic ferromagnet the states with positive and negative magnetization should be equivalent, which means that the free energy may contain only terms even in M (which in this case is the order parameter), i.e. the term $C\eta^3$ in this and similar cases should be absent. But there may be other situations, in which such terms are allowed by symmetry and should be present in the expansion (2.1).

Suppose now that the term $C\eta^3$ (cubic invariant) in the free energy (2.1) is nonzero. One can easily analyse the resulting equation for η , analogous to (2.5), and find the properties of the solution. It is also very instructive just to look at the dependence $\Phi(\eta, T)$ in this case, which will immediately tell us what happens. The corresponding set of curves $\Phi(\eta)$ for different temperatures is shown in Fig. 2.5 for the case $C < 0$ (the case $C > 0$ can be studied similarly). For high enough T , when the coefficient A in (2.1) is large, we have only one minimum of $\Phi(\eta)$, at $\eta = 0$ (curve 1 in Fig. 2.5.) With decreasing temperature and, consequently, decreasing coefficient A , the set of curves $\Phi(\eta)$ would look as shown in Fig. 2.5, curves 2–6. At a certain temperature T^* there will appear a second minimum in $\Phi(\eta)$, curve 2.

$T \gg T_c^{(1)}$ ↗ 3
 $A \in \mathcal{K}_F$ ↗ 3 (SLLI)

(A ↗ K_{LL})

$$\Phi(m) = \Phi(-m) \quad \text{even number of terms}$$

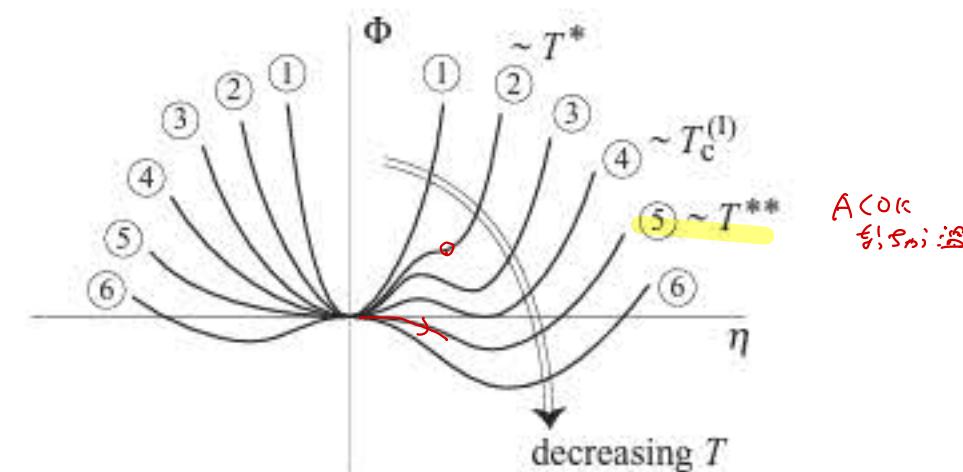


Fig. 2.5

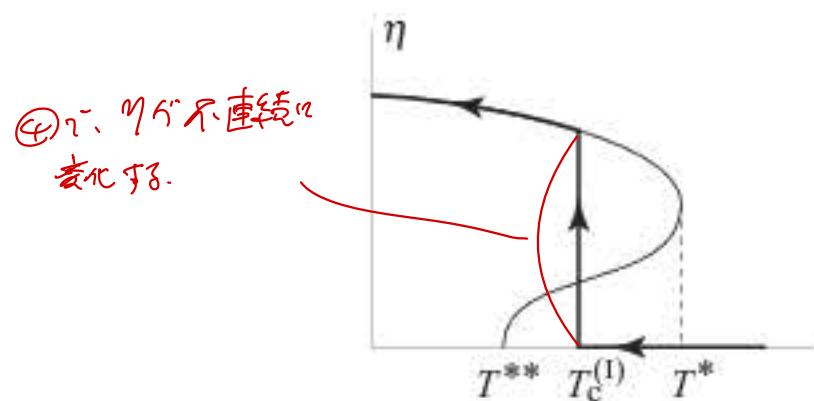


Fig. 2.6

※不安状態

Initially it is just a metastable state, the absolute minimum is still at $\eta = 0$. But with further decrease of temperature, at $T < T_c^{(I)}$, this new state will have free energy lower than the disordered state with $\eta = 0$, curve 4. Note that this will happen when the coefficient A is still positive. If we wait long enough, at this temperature the system would jump from the state $\eta = 0$ to a new minimum with nonzero η , i.e. we will have a first-order transition. The disordered state $\eta = 0$ will still exist as a local minimum, i.e. as a metastable (overcooled) state. At a still lower temperature T^{**} the coefficient A in (2.1) will itself become negative, and the metastable state $\eta = 0$ will cease to exist. The temperatures T^* and T^{**} are the limits of overheating and overcooling in such a first-order transition; they determine the maximum width of hysteresis at such a transition. These points are called spinodal points, and if $T_c^{(I)}$ changes, e.g. under pressure, they will form spinodal lines, or simply spinodals.

Thus the behaviour of $\eta(T)$ has here the form shown in Fig. 2.6. We see that the presence of cubic invariants in the expansion of the free energy (2.1) always leads to first-order phase transitions. Note that here the real critical temperature, the point $T_c^{(I)}$ in Fig. 2.6, is not a singular point of the free energy – it is just the point at which two minima of the free energy in Fig. 2.5 have equal depths. On the other hand, the temperatures T^* and T^{**} (the limits of overheating and overcooling) are

② ⇔ EPH
 $\eta = \rho$

hysteresis (履歴効果)
 ↳ 物質状態の回復速度の違いによる
 变化形式。

Φ (c) 112. 秩序変数の3次元の挙動
 第1 phase transitionは first order (c) 111

2.2 (Weak) First-order phase transition

12

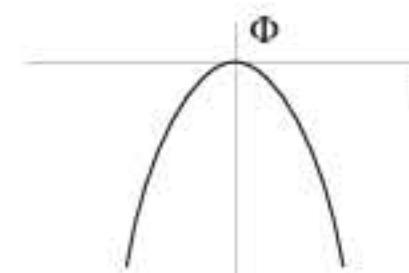


Fig. 2.

文書

singular points, so that, e.g. the susceptibility would not diverge at $T_c^{(I)}$, but it would at T^* and T^{**} .

When do we meet such a situation? The general principle is the following: we should write down in the free energy functional (2.1) *all the terms* permitted by symmetry. Usually one has to check it using *group theory*. And if cubic invariants are allowed by symmetry, then generally speaking they should be present in the expansion (2.1), so that the corresponding transition should be first order.

There are many examples in which this is the case. One is the **structural phase transition** or **charge (or spin) density wave transition** in a **triangular or honeycomb lattice** with the formation of *three equivalent waves* $\eta_n = \eta e^{i\mathbf{Q}_n \cdot \mathbf{r}}$, with the wavevectors $\mathbf{Q}_1, \mathbf{Q}_2, \mathbf{Q}_3$ at 120° to one another, so that $\mathbf{Q}_1 + \mathbf{Q}_2 + \mathbf{Q}_3 = 0$. As a result there exists an invariant $C\eta_1\eta_2\eta_3 = C\eta^3 e^{i(\mathbf{Q}_1+\mathbf{Q}_2+\mathbf{Q}_3)\cdot\mathbf{r}} = C\eta^3$, so that such a phase transition should be *first order*. This is, for example, the situation in transition metal dichalcogenides such as NbSe_3 , TaS_3 , etc.

One can also show in general that at crystallization (formation of a periodic structure from a liquid) the situation is the same – and consequently crystallization or melting, should be a first-order phase transition (Landau).

2.2.1 Another possibility of getting a first-order phase transition

Suppose the coefficient C in (2.1) is zero, and we have

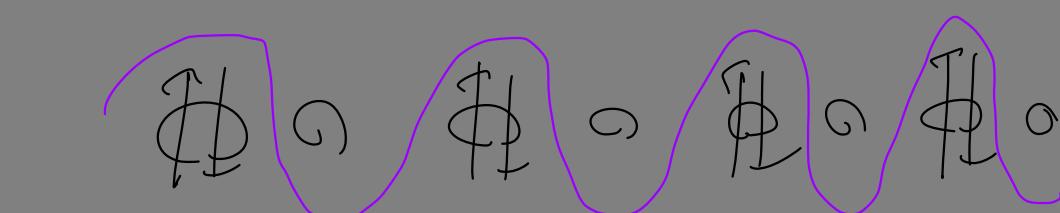
$$\Phi(P, T) = A(P, T)n^2 + B(P, T)n^4 \quad (2.20)$$

We have assumed previously that the coefficients $A(P, T) = a(T - T_c)$ and $B(P, T) > 0$. But the coefficient B is itself a function of pressure, and in principle it may become negative. Then at $T < T_c$, instead of the behaviour shown in Fig. 2.2, we would have the behaviour of the type shown in Fig. 2.7, i.e. the free energy (2.20) would have no minima at finite η . To stabilize the system we then have to include higher order terms in the expansion for the free energy. Thus, e.g. we should write

$$\Phi \equiv An^2 + Bn^4 + Dn^6 \quad (2.21)$$

CDW & cf .. ?

Φ Ε Φ Λ Φ Φ Φ Φ Φ



◎主觀，被打！（空間的行動，時間的行爲）

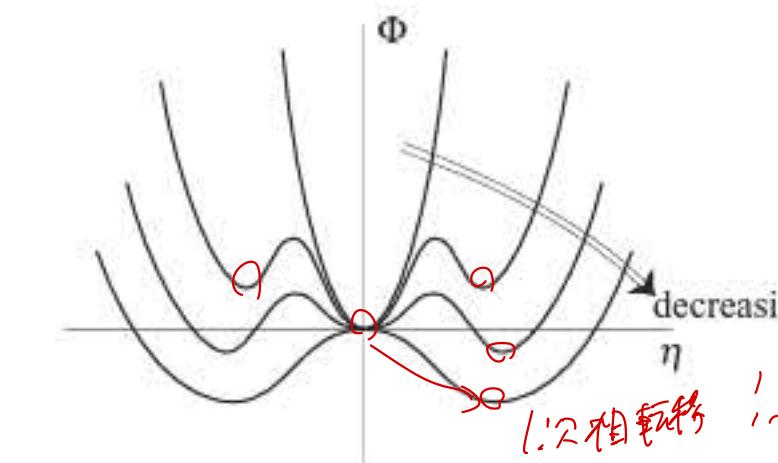


Fig. 2.8

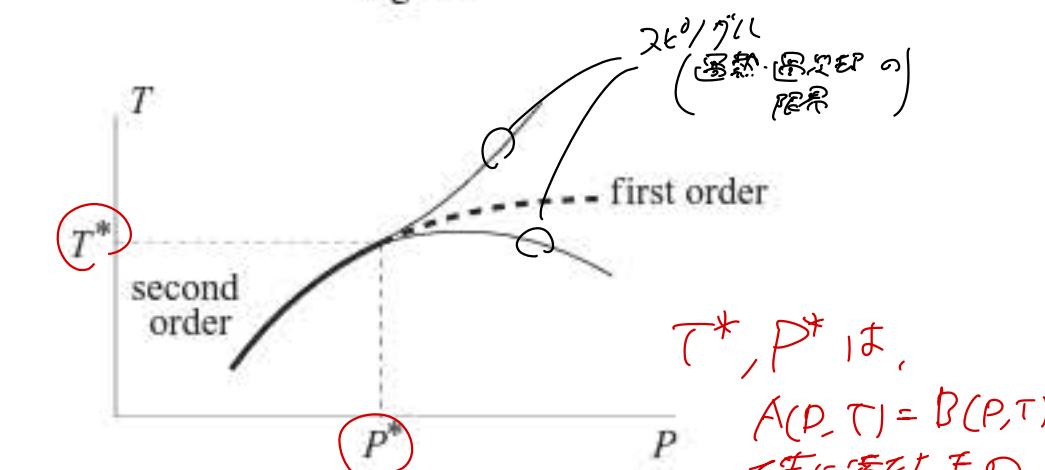


Fig. 2.9

with $D > 0$. Suppose that the coefficient $B < 0$, and that the temperature is slightly above the original T_c (i.e. the coefficient A is positive but small). Then the behaviour of Φ at different temperatures would have the form shown in Fig. 2.8. When we approach the ‘old’ T_c from above, so that $A = a(T - T_c)$ becomes small but is still positive, the term $B\eta^4$ with $B < 0$ starts to be important at small η , leading to the situation with three minima of Φ . That is, in this case the phase transition also becomes **first order**. Thus at the point where $B(P, T)$ changes sign, a second-order phase transition changes to a first-order one. (The point (T^*, P^*) in the (T, P) plane is indeed a *point*: it is the simultaneous solution of two equations $A(P, T) = 0$, $B(P, T) = 0$.) Such a point, at which a second-order phase transition changes to a first-order one, is called a **tricritical point**. Close to it the phase diagram of the system has the form shown in Fig. 2.9. Here we have marked the second-order phase transition by a bold solid line and the first-order transition by a bold dashed one; thin solid lines are spinodals – the lines of overheating and overcooling.

他の自由度との相互作用。

2.3 Interaction with other degrees of freedom

The Landau method of treating phase transitions is very simple, but extremely powerful. It permits us, e.g. to study the influence on the phase transition of the

At the point (P^*, T^*) where $B(P, T)$ changes the sign itself, the phase transition switches from 2nd order to first order.

tricritical point
三相点
(二相転移と一相転移の
交点)

Compressible
圧縮性のもの。

compressibility : 圧縮性 (圧縮性に対する相変化の割合).
④ 热温压系数
 $K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$

2.3 Interaction with other degrees of freedom 15

interaction with other degrees of freedom. Thus, for instance, we can study phase transitions (e.g. magnetic) in a compressible lattice. If u is the deformation, we can write in general (this is a typical situation)

$$\Phi = A\eta^2 + B\eta^4 + \frac{bu^2}{2} + \lambda\eta^2 u. \quad (2.22)$$

elastic energy

elastic + magnetic

u : deformation.

Here the third term is the elastic energy (b is the bulk modulus, i.e. the inverse compressibility), and the last term is the coupling of our order parameter with the deformation, for example the magnetoelastic coupling in the case of magnetic phase transitions.

Minimizing (2.22) with respect to u , we obtain

$$\frac{\partial \Phi}{\partial u} = bu + \lambda\eta^2 = 0, \quad u = -\frac{\lambda\eta^2}{b}. \quad (2.23)$$

Now, we put it back into Φ (2.22):

$$\Phi = A\eta^2 + B\eta^4 + \frac{\lambda^2\eta^4}{2b} - \frac{\lambda^2\eta^4}{b} = A\eta^2 + \left(B - \frac{\lambda^2}{2b} \right) \eta^4. \quad (2.24)$$

Thus we see that if the coupling to the lattice λ is sufficiently strong, or if the lattice compressibility is large (bulk modulus b small), the renormalized coefficient of the η^4 term in (2.24) may become negative – and this, according to Figs. 2.8 and 2.9, makes the transition first order. This is a general rule: coupling to other degrees of freedom gives a tendency to make a phase transition first order (although it may remain second order if this coupling is not strong enough¹).

Note that for the coupling included in equation (2.22) the resulting deformation is $u \sim \eta^2$, see (2.23). Thus, whereas below T_c we have $\eta \sim \sqrt{T_c - T}$ (if the transition remains second order), the corresponding distortion changes linearly, $u \sim (T_c - T)$. In principle this effect can be measured directly. In particular, if the corresponding distortion breaks inversion symmetry and leads to ferroelectricity (i.e. if the polarization $P \sim u$), then the polarization will be proportional to the square of the primary order parameter η and close to T_c would also behave as $T_c - T$. Such systems are known as improper ferroelectrics, in contrast to the ordinary (proper) ferroelectrics in which the polarization itself is the main, primary order parameter, $\eta = P \sim \sqrt{T_c - T}$. A similar situation can exist also in other systems with coupled order parameters. The resulting properties depend on the specific type of coupling between such order parameters η and ζ : coupling of the type of equation (2.22), $\eta^2\zeta$, or of the type $\eta^2\zeta^2$, etc. (The detailed type of

polarization \bar{P}
will be proportional to η^2 .
[Close to T_c , $\propto (T_c - T)$]

¹ A more detailed treatment shows that the tendency to make a first-order transition due to coupling of the order parameter to the lattice is actually much stronger than that obtained above, especially when we take into account coupling to shear strain (Larkin and Pikin).

such coupling is determined by the symmetry properties of corresponding order parameters.)

2.4 Inhomogeneous situations (Ginzburg–Landau theory)

Up to now we have considered only **homogeneous solutions**, i.e. situations in which the order parameter η – e.g. the magnetization – is taken as constant, the same throughout the whole sample, independent of the position. Often one has to consider inhomogeneous situations, for example in the presence of external fields, or close to the surface, etc. Then $\eta = \eta(\mathbf{r})$, and the total free energy should be written as an integral over the whole space, of the type

$$\Phi = \int d^3\mathbf{r} \{ \text{free energy density } \Phi(\mathbf{r}) \}. \quad (2.25)$$



Fig. 2.10

The **free energy density** $\Phi(\mathbf{r})$ contains terms of the type (2.1), with the order parameter $\eta(\mathbf{r})$ taken at a given point. But the variation of η in space also costs **some energy**. Thus, e.g. in a ferromagnet all spins prefer to be parallel, $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$. Variation in space means, e.g. the formation of structures of the type shown in Fig. 2.10 – spirals, or domain walls, etc. It is clear that the **canting of neighbouring spins** costs a certain energy (the usual exchange interaction in a ferromagnet preferring to keep neighbouring spins parallel). For **slow variation** the cost in energy should be proportional to the gradient of the order parameter, $\sim d\eta/d\mathbf{r} = \nabla\eta$. The **only invariant containing** $\nabla\eta$ (for scalar η) is $(\nabla\eta)^2$. Thus, in the same spirit as before, we can write the simplest generalization of equation (2.1) in the form

$$\Phi = \int d^3\mathbf{r} \left\{ A\eta^2(\mathbf{r}) + B\eta^4(\mathbf{r}) + G(\nabla\eta(\mathbf{r}))^2 \right\}. \quad (2.26)$$

This is called a **Ginzburg–Landau (GL) functional** (sometimes also Ginzburg–Landau–Wilson (GLW) functional) – the functional of the function $\eta(\mathbf{r})$. It is widely used, e.g. in the theory of superconductivity (where it was actually introduced), in discussion of domain walls in magnets, etc. **Minimizing this functional in the order parameter** $\eta(\mathbf{r})$ (which in the theory of superconductivity is usually a complex scalar denoted ψ , and which can be viewed as a wavefunction of the superconducting condensate) **gives not the ordinary algebraic self-consistency equation** (2.5), but, due to the presence of the gradient term in (2.26), a differential equation – the famous **Ginzburg–Landau equation**. In the theory of superconductivity it is usually

$\frac{\partial \Phi}{\partial \eta} \propto \nabla^2 \eta - \epsilon T(\mathbf{r})$
($\epsilon = \text{const}$ とある)

gain energy

2.4 Inhomogeneous situations

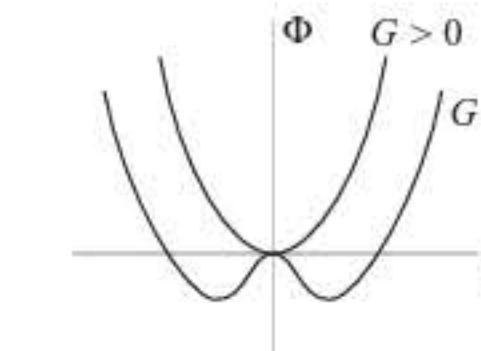


Fig. 2.11

written as

$$\frac{1}{2m} \left(-i\hbar\nabla - \frac{2e}{c} \mathbf{A} \right)^2 \psi + A\psi + 2B|\psi|^2\psi = 0. \quad (2.27)$$

(Here **A** is the vector potential, introduced to describe the behaviour of superconductors in a magnetic field.) We see that the Ginzburg–Landau equation (2.27) has a form similar to the Schrödinger equation, but with a nonlinear term $\sim \psi^3$. Close to T_c , when the order parameter $\psi \rightarrow 0$, this equation can be linearized, and then it is indeed exactly equivalent to the corresponding Schrödinger equation. This analogy is very useful for the treatment of many problems in superconductivity, such as the upper critical magnetic field H_{c2} , the formation and properties of vortices, etc.

Similar equations can also be written down for other physical systems. Thus, the corresponding equation for ferromagnets (known as the Landau–Lifshits equation) is widely used for treating the domain structure of ferromagnets, the dynamics of domain walls, etc.

As we have discussed above, in the usual situation the homogeneous solutions correspond to the minimum energy, which means that the coefficient **G** next to the gradient term in equation (2.26) is positive. But what would happen if the coefficient $G(P, T)$ becomes negative?

Let us suppose that $G < 0$. Then it is favourable to have $\nabla\eta \neq 0$, i.e. the **homogeneous** solution becomes unstable, and there should occur a transition to an inhomogeneous state. For instance, instead of a ferromagnet $\uparrow \uparrow \uparrow \uparrow$ we may have a transition to a **spiral state**. To find such a solution and to describe its properties we have to minimize Φ now with respect to $\nabla\eta$. Again, if the term $G(\nabla\eta)^2$ becomes negative, we have to write down the next terms in the gradient (but still lowest order in η itself), e.g. $E(\nabla^2\eta)^2$ with a positive coefficient E , to stabilize the system.

Thus we would have in the free energy the terms

$$G(\nabla\eta)^2 + E(\nabla^2\eta)^2. \quad (2.28)$$

As a function of $\nabla\eta$, Φ has a form similar to the one shown in Fig. 2.2, see Fig. 2.11. It is convenient to go to the momentum representation: $(\nabla\eta)^2 \rightarrow q^2\eta^2$. Then Φ

運動量表示
(準拠方程式 Fourier 变換して Q → q のこと。)

$T \rightarrow T_c$ で, GL- $e\psi^2$
Schrödinger eq: $-e\psi^2 = -\epsilon_\ell$
(ψ^2 の対応が複雑でない。)

homogeneous \rightarrow

↑ これが (2.28)
(→ R軸が直上の位置).

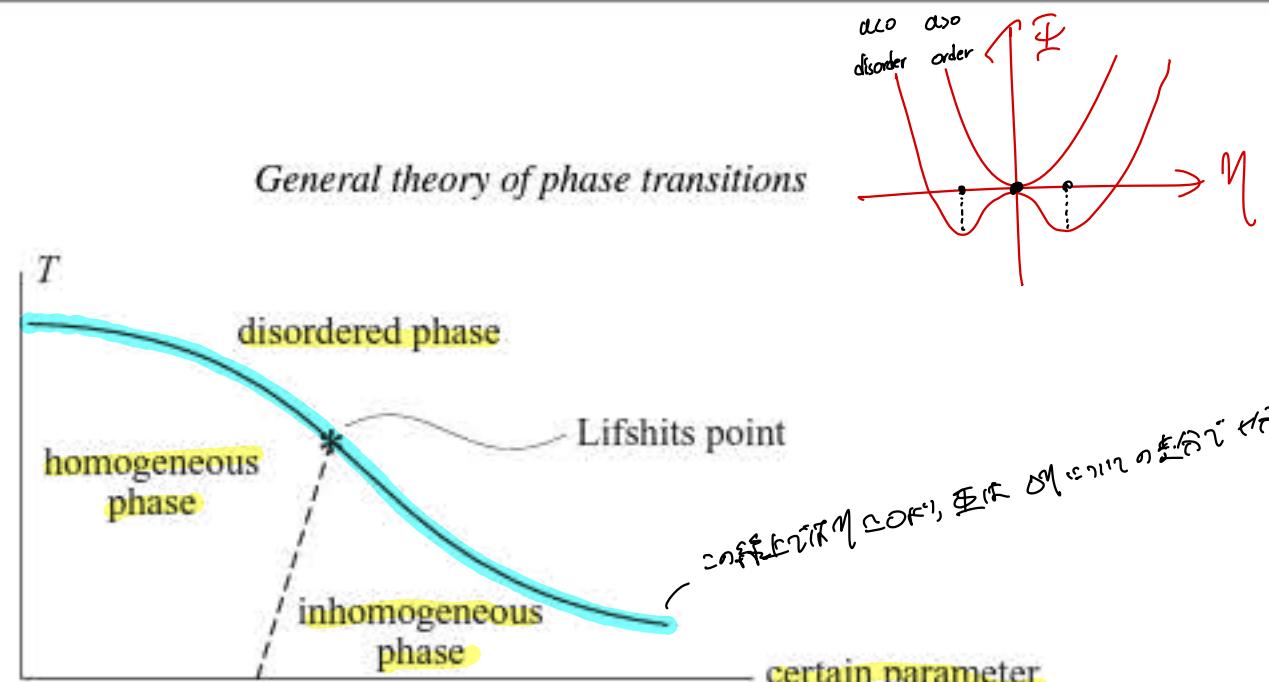


Fig. 2.12

would contain the terms

$$Gq^2\eta^2 + Eq^4\eta^2. \quad (2.29)$$

Now we can find the value of q which minimizes Φ :

$$\frac{\partial\Phi}{\partial q^2} = G\eta^2 + 2Eq^2\eta^2 = 0, \quad (2.30)$$

$$Q^2 = q_{\min}^2 = -\frac{G}{2E} \quad (G < 0). \quad (2.31)$$

That is, in this case the structure with the wavevector Q , or with the period $l = 2\pi/Q$, will be formed. In general the period of this superstructure (lattice, or magnetic, etc.) is **incommensurate** with respect to the underlying lattice period.

The point where the coefficient G changes sign and at which there is a change from **homogeneous** to **inhomogeneous ordering** is called the **Lifshits point**. The typical phase diagram in this case looks like Fig. 2.12. Here the solid lines are second-order phase transitions, and the dashed line is a **first-order transition**. Such is, for example, the phase diagram of CuGeO₃ (spin-Peierls system, see Section 11.2 below) in a magnetic field.

In general, for certain symmetry classes, there may exist in the free energy also **invariants linear** in the derivatives (the so-called *Lifshits invariants*), for example the term $\mathbf{M} \cdot \text{curl } \mathbf{M}$ in magnetic systems. These terms will give **helicoidal** structures even for the case when the coefficient $G > 0$ (instead of (2.29) we will have an equation for the wavevector of a new periodic structure of the type $\text{const} \cdot q + Gq^2\eta^2 = 0$). This is actually the situation in many rare earth metals having different types of such incommensurate magnetic structures. These terms also play a crucial role in magnetically driven ferroelectricity in the so-called **multiferroics**. The microscopic origin of such linear terms is a special problem which we do not discuss here.

$M \times (\partial M)$

$\therefore \cancel{Q}$
 $Q = \frac{2\pi}{l}$

$$\begin{aligned} 1.29(\text{P}) , \Phi &\propto (A + Gq^2 + Eq^4)\eta^2 + B\eta^4 \\ \frac{\partial\Phi}{\partial\eta} &= \eta(A + Gq^2 + Eq^4 + 2B\eta^2) = 0, \\ \eta = 0, \quad \eta &= \pm \sqrt{\frac{A + Gq^2 + Eq^4}{2B}} \end{aligned}$$

$\frac{\partial\Phi}{\partial q^2} =$

(実線上) $(\partial\eta)^4$ の項は η^2 で消す。
Fourier 積分 η^4 が η^2 で消す。

in commensurate
無理数的

希土類金属 rare earth metal の電子局在構造。
磁性電気伝導性
magnetically driven ferroelectricity.

相間長 ξ , 短さ(相間)の長い(遠)

不純物, 境界

$\uparrow \uparrow \uparrow \uparrow \cdots \text{⑩}$

=> 構成部の相間長 ξ でコヒーレンス長 ζ が決まる。

コヒーレンス長が長い $\Rightarrow G_0$ が大きい。

\rightarrow オーダーもが大きい。温度範囲が広い。

$= \langle S_S S_S \rangle$ は S の相間。

時間的相間 ξ 平均
二点関数

物理的相間 ξ
 $\uparrow S_i \downarrow S_j$
 $\uparrow S_i \downarrow S_j$
この相間 $\langle S_i S_j \rangle$

振幅の大きさ $\langle S_i S_j \rangle$ の大きさ。

相間の大きさ $\langle S_i S_j \rangle$ が大きな値を取る最大の
($i-j$)

① 振幅 \uparrow : 平均 $\bar{\eta}$,

$\uparrow S_i$ (FM) $\downarrow S_j$

2. ξ は S_i と S_j の相間 $\langle S_i S_j \rangle$

② つながり、このつなぐが、これがつなぐ。

これに比例して、相間距離 ξ は、

このスピング、どれほどよき影響か (ジョイント形成は?)?

2.5 Fluctuations at the second-order phase transitions

21

It is often convenient to describe fluctuations not in real, but in momentum space. Equation (2.34) then looks as follows:

$$\langle \Delta\eta_q \Delta\eta_{-q} \rangle = \langle |\eta_q|^2 \rangle = \frac{T}{2a|T - T_c|} \frac{1}{(1 + q^2\xi^2)} = \frac{T}{2G} \frac{\xi^2}{(1 + q^2\xi^2)}. \quad (2.36)$$

This is the famous **Ornstein-Zernike** theory of fluctuations. One can also obtain the expression for the susceptibility close to the second-order phase transition. It is given by similar expressions:

$$\chi(T) = \frac{1}{2a(T - T_c)} \Big|_{T > T_c}, \quad \chi(T) = \frac{1}{4a(T_c - T)} \Big|_{T < T_c}, \quad (2.37)$$

i.e. the susceptibility also diverges when $T \rightarrow T_c$ (see also later, Chapter 6, (6.40), (6.44)).

In principle the generalized susceptibility is a function of \mathbf{q} and ω , $\chi(\mathbf{q}, \omega)$ (e.g. the well-known **dielectric function** $\epsilon(\mathbf{q}, \omega)$, which is a response function to the **external electric field** $\mathbf{E}(\mathbf{q}, \omega)$, just as the usual susceptibility of magnetics is a response function with respect to the magnetic field). There exists a very important general connection between $\chi(\mathbf{q}, \omega)$ and the corresponding correlation functions $\langle \eta(\mathbf{r}, 0) \eta(\mathbf{r}', t) \rangle$ or their Fourier transforms. For static susceptibility this relation has the form

$$\chi(\mathbf{q}) = \frac{1}{T} \int \frac{d^3r}{(2\pi)^3} e^{i\mathbf{q} \cdot \mathbf{r}} \langle \eta(\mathbf{0}, t) \eta(\mathbf{r}, t) \rangle. \quad (2.38)$$

For the usual susceptibility, e.g. in magnetic systems for which the order parameter η is the magnetization, or the average spin S , it gives a convenient relation:

$$\chi = \frac{1}{T} \sum_n \langle S_0 \cdot S_n \rangle. \quad (2.39)$$

In general close to T_c , e.g. for $T > T_c$, one obtains from (2.36) and (2.38), that

$$\chi(\mathbf{q}) \Big|_{T > T_c} = \frac{1}{2a(T - T_c)} \frac{1}{(1 + q^2\xi^2(T))} = \frac{1}{2G} \frac{\xi^2(T)}{(1 + q^2\xi^2(T))}, \quad (2.40)$$

which for $\mathbf{q} = 0$ gives (2.37).

2.5.1 Critical indices and scaling relations

All the considerations presented above are valid when we proceed from the expansion (2.26) for the free energy and treat a second-order phase transition in essentially a mean field way. However, as we have already seen above, close to T_c the fluctuations are always strong (and the width of the region in which

$\langle \Delta\eta_q \Delta\eta_{-q} \rangle$ のままで、 $q \rightarrow 0$ のとき零にならなければ。

Fourier 变換して見ると。

実空間の orientation は $q \leftarrow -q$ で保つ。)

局在化の条件から \Rightarrow は ξ の値が T_c で零となる。

すなはち、 $q=0$ の場合 (\mathbf{q} の値が零の場合) は χ が零となる。

DFT の界面の扱い方。

表面

界面

真空

界面

移行領域の界面の扱い方。



Brillouin Zone の構成。

並進対称性 \Rightarrow Brillouin Zone 内に限る。

周期境界条件 \Rightarrow η の離散化。

周期境界条件を広く取る \Leftrightarrow η の离散化を防ぐ。(?)



周期境界条件を広く取る \Leftrightarrow η の离散化を防ぐ。(?)

江漢元

半径は π/a の大きさ、 Brillouin Zone - $\frac{\pi}{a} \sim \frac{\pi}{a}$

この細かさ... 固定条件をし CCC. $\Delta L = \frac{2\pi}{1}$

A horizontal number line with tick marks. Red vertical tick marks are placed at integer values from 1 to 10. A red dot is placed between the 10 and 11 tick marks. A red bracket above the line spans from the 10 mark to the red dot, labeled "....". Above the line, there are two labels: "l=a?" followed by a question mark, and "l=Naive." Below the line, there are two labels: "-pi/a" and "pi/a".

長波長(小さなθ)の場合は ⇒ 小さなスバルが分子、 (?)
短波長(大きなθ) ⇒ 大きなスバルが必要。 (?)

短波長 (たんぱく)

2

General theory of phase transitions

they are important, given by the Ginzburg–Levanyuk criterion, may be sufficiently broad). In this region the description of second-order phase transitions should be modified, and all the anomalies of thermodynamic functions such as specific heat, compressibility, thermal expansion, susceptibility, etc. are very different from those predicted by the Landau theory. This is really the field of the theory of second-order phase transitions, which was especially active in the 1960s and 1970s and which resulted in a rather deep understanding of the phenomena close to T_c for such transitions. This is a very big field in itself, which we cannot cover here; one can find corresponding results and references in many books and review articles, e.g. Chaikin and Lubensky (2000) and Stanley (1987). The basic conclusion of these very elaborate studies is that close to T_c the properties of the system usually have singularities of the type $|T - T_c|^{-\lambda_i}$, where the exponents λ_i (different for different quantities) are called *critical indices*. Thus, e.g. the specific heat behaves as $\tau^{-\alpha}$ where $\tau = |T - T_c|/T_c$; the order parameter itself changes close to T_c as τ^β , the susceptibility χ as $\tau^{-\gamma}$, the correlation length ξ diverges as $\tau^{-\nu}$, etc. (This is the standard notation for these critical exponents.)

The exact values of the critical indices are known only in **very few cases**. A notable example is the exactly soluble two-dimensional Ising model, see Section 6.4.3 below. However, despite the absence of exact solutions in most cases, there exist very powerful general results in this field known as *scaling relations* (Kadanoff; Patashinskii and Pokrovskii). The underlying idea is that when the system approaches T_c , the correlation length diverges and becomes infinitely large. In this case all microscopic details, important at short distances, become irrelevant and the properties of the system become universal. Moreover, as $T \rightarrow T_c$ all length scales become equivalent, and, simply from dimensional arguments, one can show that for instance when one changes all distances by a certain factor, $L \rightarrow kL$, e.g. doubling the size of the system, different quantities would change accordingly. From these arguments one can find the relations between different quantities in the vicinity of the critical temperature. Some examples of these relations are:

$$\alpha + 2\beta + \gamma = 2, \quad (2.4)$$

$$d\,v + \alpha = 2 \quad (2.42)$$

(here d is the space dimensionality), etc. The critical indices may be different from system to system, but relations of the type (2.41), (2.42) are universal. The values of the indices depend only on the dimensionality of the system d and on the symmetry of the order parameter (real or complex scalar; vector; isotropic or anisotropic system, etc.), and for each particular case the critical indices should be the same, independent of the specific physical situation. These are called *universality classes*.

医療界指針下、特定の「-2」回(「-2」)ベ

Tc は ζ の値で決まる。

2) χ -不變性 は、相間長さ比常によじる。

As mentioned above, the values of the critical indices for different universality classes are known exactly only in very few cases. But numerical calculations using powerful computer algorithms have given pretty accurate values of these indices in many cases. Thus, for example, we have:

- For the 2d Ising model: $\alpha = 0$ (logarithmic divergence, which is weaker than any power law divergence); $\beta = \frac{1}{8}$; $\gamma = \frac{7}{4}$; $\nu = 1$.
 - For the 3d Ising model: $\alpha = 0.10$; $\beta = 0.33$; $\gamma = 1.24$; $\nu = 0.63$.
 - For the 3d Heisenberg model: $\alpha = -0.12$; $\beta = 0.36$; $\gamma = 1.39$; $\nu = 0.71$.
 - Compare this with the mean field behaviour following from the Landau theory: $\alpha = 0$ (the specific heat has a jump, equation (2.9), but no divergence at T_c); $\beta = \frac{1}{2}$, see (2.6); $\gamma = 1$ (the well-known Curie–Weiss law, see equation (6.40) below); $\nu = \frac{1}{2}$, see (2.35).

We see that indeed the specific behaviour (divergence) of different quantities as $T \rightarrow T_c$ is different for different cases (different universality classes), but the scaling relations (2.41), (2.42) and others are fulfilled for each of them.

Theoretical methods used to obtain these results are both analytical (those giving scaling relations) and numerical (giving specific values of critical indices for different quantities in different situations). One of the very powerful methods used to treat these problems, and also many others in which the interaction is strong and we do not have any small parameter which would allow us to use perturbation theory or expansion of the type of (2.1), is the renormalization group method. It originates from field theory, but is now widely used in many difficult problems in condensed matter physics, such as the theory of second-order phase transitions, the quantum Hall effect, etc., see, e.g. Chaikin and Lubensky (2000) and Stanley (1987).

2.6 Quantum phase transition

Until now we have considered phase transitions occurring at finite temperatures. The description we used was actually that of classical statistical mechanics. Indeed, even if the physical nature of some phase transition is of essentially quantum origin, such as the superconducting transition in metals or the superfluid transition in liquid ^4He , close to T_c the correlation length ξ becomes very large, see equation (2.35), i.e. it becomes much larger than the distance between particles or the radius of the interaction. In this case the behaviour of the system is essentially classical.

However, there may exist situations in which the critical temperature can be suppressed, e.g. by application of pressure, a magnetic field or some other control parameter g , see Fig. 2.14 (the grey region is here the region of classical fluctuations). In this case, if T_c tends to zero, quantum effects start to play a more and more important role. The state of the system for $g > g_c$ (e.g. pressure $P > P_c$)

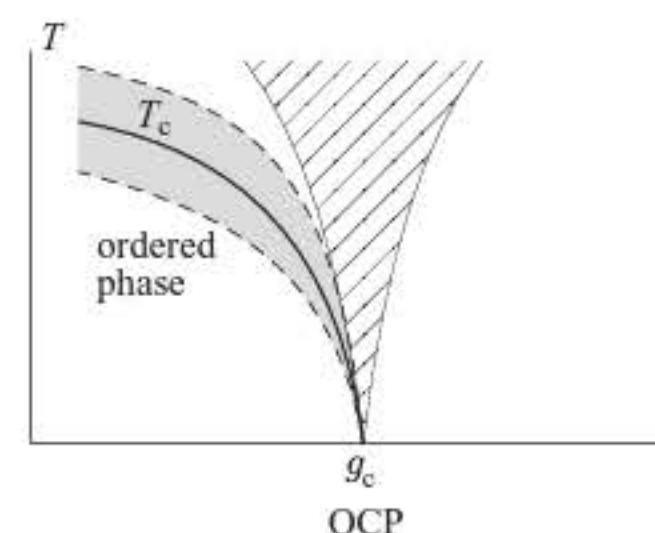


Fig. 2.1

may be disordered even at $T = 0$, not because of classical, but because of quantum fluctuations – we can speak of a quantum disordered phase.

There is here no contradiction with the **Nernst theorem**, which requires that the entropy of the system should tend to zero as $T \rightarrow 0$: the state of such a system at $T = 0$ and $P > P_c$ is a disordered one from the point of view of standard phase transitions (e.g. magnetic ordering may be suppressed for $P > P_c$), but it is a unique quantum state described by a, maybe very complicated, but unique wavefunction. Consequently the entropy of such state is zero. A simple example is given by an ordinary metal (Fermi liquid), as compared, for example, with the ferromagnetic metallic state: although, in contrast to the latter, a normal metal is paramagnetic (Pauli paramagnetism, see Chapter 6 below), it is a unique state – the filled Fermi surface, which has zero entropy. As discussed below, in Section 2.7.3 this determines, for example, the slope of the high-temperature insulator–metal transition in V_2O_3 .

The behaviour of the system close to the point ($T = 0, g = g_c$) in Fig. 2.14 is determined by *quantum fluctuations*, and such a point is called a *quantum critical point* (QCP). One can show that quantum fluctuations dominate the behaviour of the system ‘above’ QCP – in the region of the phase diagram marked by hatching in Fig. 2.14 (of course the intensity of these fluctuations and consequently the amplitude of all the anomalies decreases with increasing temperature). The proximity to a quantum critical point may strongly influence not only thermodynamic, but also transport properties of the corresponding systems, leading, e.g. to a *non-Fermi-liquid behaviour*, see Chapter 10 below. There are even suggestions that the proximity to QCP may be important for the appearance of unconventional superconductivity, in particular for the high- T_c superconductivity in cuprates. More detailed descriptions of these phenomena one can find, e.g. in Sachdev (1999) and in von Löhneysen *et al.* (2007).

g) T_c は、 $T=0$ の disorder state は、「
（無秩序状態）」

① チーリストの定理

T → O₂ S → O

1つの波動 $\psi(x)$ は実数か？

1

\emptyset $\{\}$ $\{\cdot\}$ \emptyset \emptyset $\text{Recl} \in \mathcal{L}.$

2.7 General considerations

2.7.1 Different types of order parameters

There may exist different types of order parameters in different systems. For example, they may be scalars, e.g. periodic density in crystals as compared to a homogeneous liquid; vectors (or pseudovectors), e.g. magnetization in ferromagnets or spontaneous polarization in ferroelectrics. Order parameters may also be complex. An example is a complex scalar – the electron (condensate) wavefunction $\Psi(\mathbf{r})$ in superconductivity. There may also exist more complicated types of order parameters, for example tensor order parameters (liquid crystals, anisotropic superconductivity and superfluidity, e.g. in ^3He and most probably in high-temperature and in heavy-fermion superconductors).

2.7.2 General principle

The general principle is that the free energy should contain *invariants* built in from the order parameter. Thus, for the vector order parameter \mathbf{M} in ordinary magnets, Φ may contain $(\mathbf{M})^2$ or $(\text{div } \mathbf{M})^2 = (\nabla \cdot \mathbf{M})^2$, but, in the absence of an external field, no terms linear in \mathbf{M} or terms $\sim \mathbf{M}^3$ because they break the inversion symmetry (equivalence of the states \mathbf{M} and $-\mathbf{M}$).² Similarly, for the complex scalar order parameter Ψ in isotropic systems the free energy Φ should contain $|\Psi|^2$, but not Ψ^2 , etc.

Symmetry considerations are very powerful, and they determine the form of the Landau free energy expansion. In the general treatment one should always keep all the terms allowed by symmetry, even if we do not know in detail the physical mechanisms responsible for their appearance. This was, for example, the reason why we have included the term $\sim \eta^2 u$ in (2.22), although we did not specify the type of the order parameter or its dependence on the lattice distortion. Of course, the coefficients of such terms *do depend* on the microscopic nature of the ordering, and to calculate these coefficients is a separate, often very difficult problem. However we can deduce many general conclusions even without such a microscopic treatment, using only very general properties such as symmetry.

² For magnetic states there is another, even more powerful restriction. All magnetic states break time reversal invariance; magnetic moments are odd with respect to time inversion. (This becomes clear when one remembers that the standard way to create a magnetic moment is by a current running in a coil; and time inversion means that the current would run in the opposite direction, changing accordingly \mathbf{M} to $-\mathbf{M}$.) But the free energy should of course remain the same under time inversion, from which it follows that magnetic vectors should always enter in even combinations; e.g. \mathbf{M}^2 , $\mathbf{M} \cdot \text{curl } \mathbf{M}$, or $\mathbf{M} \cdot \mathbf{L}$ where \mathbf{L} is the antiferromagnetic vector, see Section 6.2.3.

2.7.3 Broken symmetry and driving force of phase transitions

At second-order phase transitions the symmetry changes (it decreases in the ordered phase). Thus, e.g. in a paramagnetic phase there exists spherical symmetry (free rotation of spins), whereas in a ferromagnet all spins point in the same direction, the spin orientation is fixed, i.e. we have broken spin rotation invariance.

The situation is similar in liquids compared with crystals: in liquids there is continuous translational symmetry (shift by an arbitrary vector), whereas in a crystal there remains only a shift by a vector equal to the lattice period. This means that we have broken the continuous translational symmetry. The low-temperature phase usually has lower symmetry than the high-temperature one.

One should keep in mind an important distinction: there exist cases of a broken *continuous* symmetry, or of a *discrete* one. The examples given above correspond to broken continuous symmetry. But there are also cases of a broken discrete symmetry. Such is, e.g. the case of strongly anisotropic magnets. Suppose that spins can take not an arbitrary orientation, but only two: \uparrow or \downarrow . Again, in the high-temperature disordered phase there is equal probability of finding spins \uparrow or \downarrow at a given site. The low-temperature ordered phase would correspond, e.g. to spins being predominantly \uparrow (at $T = 0$, only \uparrow). This is the so-called Ising ferromagnet. Here a *discrete symmetry* (spin inversion $\uparrow \longleftrightarrow \downarrow$) is broken.

As we have already discussed, it is easy to understand why the system goes to a more disordered phase with increasing temperature. If we start from the low-temperature ordered phase, we see that the transition to a disordered phase is driven by the entropy. According to (1.10) the free energy (for fixed pressure) is $\Phi = E - TS$. At low temperatures, e.g. $T = 0$, to minimize the free energy we should make the (interaction) energy as low as possible, which is reached in the ordered phase. However at high enough temperatures to decrease Φ we should make the entropy nonzero, and this drives the transition to a disordered phase. We thus gain in entropy, losing in energy, which, according to (1.10), becomes favourable with increasing temperature.

We have to include *all* contributions to the entropy. Sometimes it is not easy to understand at first glance why the transition occurs in a certain way. A good example is the insulator–metal transition (Mott transition), e.g. in V_2O_3 , see Chapter 12 below. Briefly, this is a transition between the state with electrons localized each at their own site (Mott–Hubbard insulator) and a metallic state with itinerant electrons. It seems that in this case we should expect the insulating state to be the stable state at low temperatures (electrons localized at their sites, an ‘electronic crystal’), and the metallic phase to be the high-temperature phase (delocalized, moving electrons – an electron liquid), similar to *melting* of an ordinary crystal with increasing temperature. However the actual situation is not so simple.

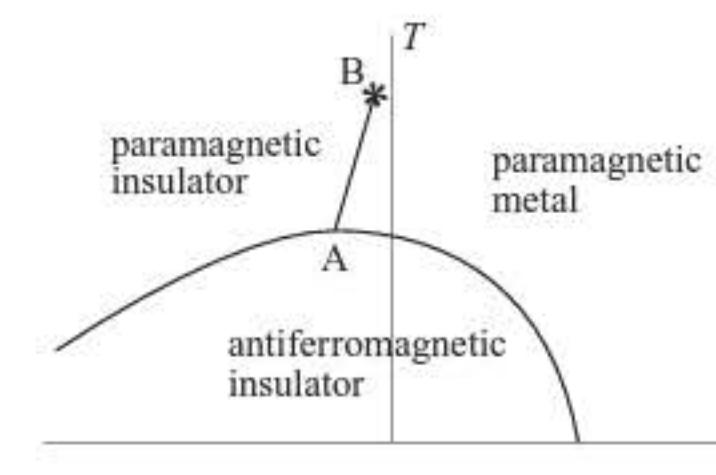


Fig. 2.15

The experimental phase diagram of V_2O_3 looks schematically as shown in Fig. 2.15. We see that the transition between an antiferromagnetic insulator and a metal does indeed occur with increasing temperature. However, the ‘pure’ Mott transition (line AB), not associated with the destruction of magnetic order, is such that with increasing temperature we go from a metal to an insulator! Why? The explanation is most probably that in the metallic phase we have a Fermi surface, and in a sense it is an ‘ordered’ state (a unique state, the entropy of which is small and at $T = 0$ would be zero). But the insulating state with localized electrons also has localized spins, which in the paramagnetic phase are *disordered*, i.e. the paramagnetic insulator has entropy (per site) $k_B \ln(2S + 1)$, higher than that of the metallic Fermi sea. Therefore, according to the general rule, with increasing temperature the system goes over from the state with lower entropy (metallic state) to the one with higher entropy (paramagnetic insulator), although at first glance this looks strange and counter-intuitive. This is not a unique situation, and in each such case we have to think *which entropy* drives the observed transition with increasing temperature.

2.7.4 The Goldstone theorem

There exists one general result which is known as the **Goldstone theorem**. According to this, when there is a *broken continuous symmetry* at the phase transition, there should exist in the *ordered state of the system* (without long-range interaction) a collective mode, an excitation, with *gapless energy spectrum* (the energy starts continuously from 0). There exist many examples of such excitations. Here I give only a few: in an **isotropic ferromagnet** these are spin waves, with the spectrum shown qualitatively in Fig. 2.16. In crystals these are the usual phonons, Fig. 2.17. We will meet many other such examples later in this book.

ゼロのエネルギー領域。

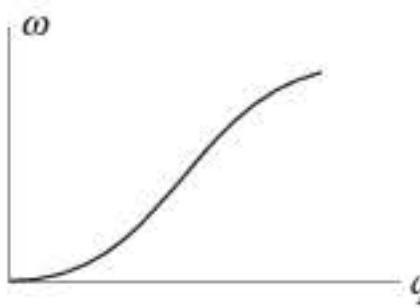


Fig. 2.16
 $q = 0$ or $\omega = 0$ is most important!!

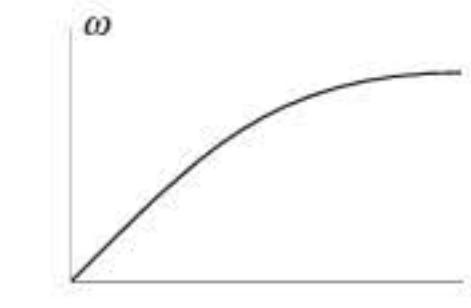


Fig. 2.17

Qualitative explanation

In the case of **broken continuous symmetry** in the ordered phase there exist **infinitely many degenerate states** (e.g. in a ferromagnet all directions of spontaneous magnetization are possible). All these states have the same energy and are equivalent. A collective mode with $q = 0$ describes a transition from one such state to another (e.g. rotation of the total magnetization of the sample as a whole) – and it should cost us **no energy**, hence the spectrum of such excitations $\omega(q)$ should start from $\omega = 0$, i.e. there exists **gapless excitation**. This is the content of the Goldstone theorem; the corresponding gapless modes are often called **Goldstone modes**.

2.7.5 Critical points



In principle there may exist phase transitions *without* a change of symmetry, but only the first-order ones. Such is, for example, the liquid–gas phase transition. The symmetry of both these phases, gas and liquid, is the same, but they differ in density (and of course in many other properties, not related to the phase transition itself). Such a transition can end at a *critical point* (\tilde{P} , \tilde{T}) (Fig. 2.18): here the thick dashed line is a first-order transition, and the thin solid lines are the limits of hysteresis. As in this case there is no change of symmetry across the first-order phase transition, one can in principle go from one phase to another continuously, e.g. from point A to point B in Fig. 2.18, moving around the critical point without crossing the transition line. For the second-order phase transitions this is impossible, because the symmetry of the two phases, the disordered one and the ordered one (or two different ordered phases) is different.

The same situation in (P , V) coordinates has a familiar form, Fig. 2.19, where above the critical point (for $T > \tilde{T}$, $P > \tilde{P}$) the state of the system is unique, and below it the system with fixed total density, or fixed volume in the grey region, would **phase-separate (decompose)** into **different phases** (here gas and liquid), the relative volumes of which will be determined by the well-known **Maxwell construction**. The point (\tilde{P} , \tilde{T}) is the critical point. Above it the P – V isotherms have only negative

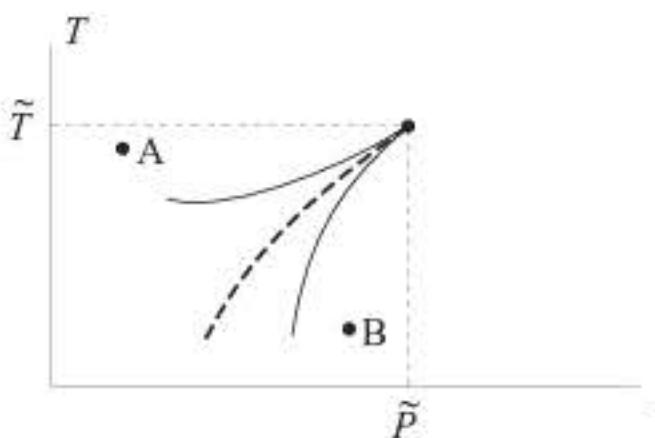


Fig. 2.18

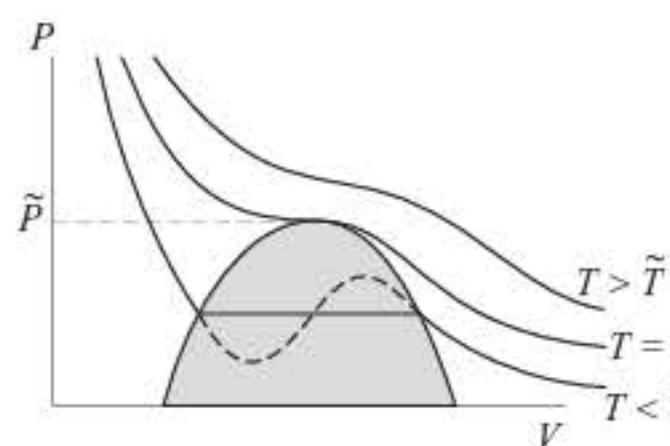


Fig. 2.19

slope, $dP/dV < 0$, the compressibility (1.21) is positive, and the transition (cross-over), e.g. from a liquid to a gas state, is smooth. Inside the grey region in Fig. 2.19 there are parts of P - V isotherms with $dV/dP > 0$, which would imply negative compressibility, i.e. an absolute instability of the corresponding homogeneous state. This is in fact the reason for the phase separation in this region.

Critical points can appear even in solids. This is the situation, e.g. for the isomorphous phase transitions like the γ - α transition in Ce or in a high-temperature metal-insulator transition in V_2O_3 shown in Fig. 2.15, where the point B is such a critical point.

Concluding this chapter, one general remark is in order. We have seen that the Landau approach to phase transitions, although conceptually and technically rather simple, is nevertheless very powerful in describing many quite different situations. It uses the most general arguments such as those of symmetry, etc. and if there are no special indications otherwise, makes the simplest assumptions possible, such as the use of a Taylor expansion in the small parameter η or $\nabla\eta$, to give quite general and very successful descriptions of very complicated phenomena. Such an approach is often very fruitful also in many other fields of physics.

One good example is the treatment by Landau of the extremely complicated phenomenon of turbulence (see Landau and Lifshits, *Fluid Mechanics*, 1987). In this problem it is known that the flow of a liquid remains homogeneous, laminar, if the so-called Reynolds number R is less than a certain critical value R_c , and the flow develops instability (transition to turbulence) for $R > R_c$. Landau again used here, in the absence of a complete theory (which still does not exist!) an expansion in terms of the amplitude Π of a new mode of the motion, which appears for $R > R_c$ and breaks the laminar flow. The expansion again has the form $A\Pi^2 + B\Pi^4$, with $A = \gamma(R_c - R)$, so that the new mode Π is absent for $R < R_c$ and the laminar flow is stable, and $\Pi \neq 0 (\sim \sqrt{R - R_c})$ for $R > R_c$. The analogy with the treatment of the second-order phase transition (cf. (2.1)–(2.6)) is of course apparent. Again, this approach is limited, and the real theory of turbulence should be much more complicated, e.g. it may resemble the theory of second-order phase transitions going beyond Landau's approach and briefly discussed in Section 2.5.1, with critical exponents, etc. or be even more complicated. But the Landau theory gives at least a first orientation in this nontrivial problem. Such an approach is widely used also in many other fields of physics, including elementary particle physics and cosmology.

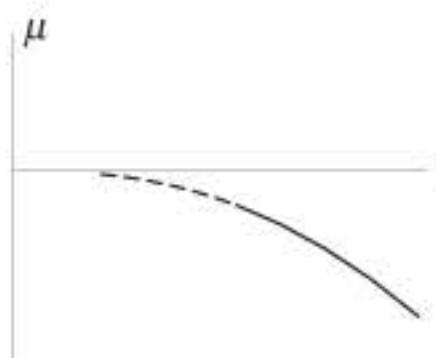


Fig. 3.1

In both cases the total number of particles $N = \sum_k n_k$; this condition determines the chemical potential $\mu(T)$.

Problem: Discuss the cross-over to Boltzmann statistics. Find the asymptotic behaviour of $\mu(T)$ at high temperatures.

Solution: Boltzmann statistics (the classical case) corresponds to the situation in which all $n_k \ll 1$ (no double occupancy, etc.), i.e.

$$\left. \begin{array}{l} e^{(\mu-\varepsilon_k)/T} \ll 1 \\ \text{(or } e^{(\varepsilon_k-\mu)/T} \gg 1 \text{)} \end{array} \right\} n_k \Rightarrow e^{(\mu-\varepsilon_k)/T}. \quad (3.6)$$

The chemical potential μ is obtained from the condition

$$n = \frac{N}{V} = \int n_k \frac{d^3 k}{(2\pi\hbar)^3}. \quad (3.7)$$

Taking the energy spectrum $\varepsilon_k = k^2/2m$, and going over to the variable ε (and then to the dimensionless variable $z = \varepsilon/T$), we obtain:

$$n = \frac{m^{2/3}}{\sqrt{2\pi^2\hbar^3}} \int_0^\infty e^{(\mu-\varepsilon)/T} \sqrt{\varepsilon} d\varepsilon \underset{(\varepsilon/T=z)}{=} e^{\mu/T} \frac{m^{3/2} T^{3/2}}{\sqrt{2\pi^2\hbar^3}} \int_0^\infty \sqrt{z} e^{-z} dz. \quad (3.8)$$

The integral in (3.8) is the gamma function, $\Gamma(\frac{3}{2}) = \frac{\sqrt{\pi}}{2}$.

In effect $n = e^{\mu/T}(T/\tau)^{3/2}$, where τ is a constant (a combination of m , π , \hbar , ...). Inverting this equality, we find

$$e^{\mu/T} = n \left(\frac{T}{\tau} \right)^{-3/2}, \quad (3.9)$$

$$\mu = T \ln n - \frac{3}{2} T \ln \left(\frac{T}{\tau} \right) \quad (3.10)$$

which is valid at $T \gg \tau$. This behaviour is schematically shown in Fig. 3.1; we will need these results later on, in Chapter 5.

Special consideration is required for (quasi)particles, whose number is not conserved. Such is, for instance, the situation for phonons in crystals or for photons – quanta of the electromagnetic field. As mentioned in Chapter 1, in this case the number of particles N itself is determined by the condition of minimization of the corresponding thermodynamic potential, e.g. the free energy, with respect to N . From the definition of the chemical potential (1.25) we then see that in this case the corresponding chemical potential has to be taken as zero for all temperatures.

4

Phonons in crystals

In this chapter we will discuss the first, and probably the best-known example of bosonic systems – phonons in crystals. According to our general scheme, after briefly summarizing the basic facts about noninteracting phonons in a harmonic lattice, we will pay most attention to the next two factors: quantum effects in the lattice dynamics, and especially the interaction between phonons which leads, e.g. to such phenomena as thermal expansion, explains the features of melting, etc. But for completeness we give, at the beginning, a very short summary of the material well known from standard courses of solid state physics.

4.1 Harmonic oscillator

The classical equation for a harmonic oscillator is

$$M\ddot{x} = -Bx . \quad (4.1)$$

Its solution is:

$$x = x_0 e^{i\omega t} , \quad (4.2)$$

where the frequency is

$$\omega = \sqrt{B/M} . \quad (4.3)$$

The Hamiltonian of the harmonic oscillator has the form

$$\mathcal{H} = \frac{p^2}{2M} + \frac{Bx^2}{2} \quad \left(\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x} \right) . \quad (4.4)$$

In quantum mechanics the energy levels are quantized:

$$\varepsilon_n = \left(n + \frac{1}{2} \right) \hbar\omega . \quad (4.5)$$

4.2 Second quantization

The operators of the coordinate \hat{x} and momentum \hat{p} obey the commutation relation

$$[\hat{x}, \hat{p}]_- = \hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar. \quad (4.6)$$

It is convenient to introduce the *annihilation and creation operators* of phonons (in the following we omit the sign $\hat{}$ for the operators):

$$\left. \begin{aligned} b &= \frac{1}{\sqrt{2\hbar M\omega}} (M\omega x + ip) \\ b^\dagger &= \frac{1}{\sqrt{2\hbar M\omega}} (M\omega x - ip). \end{aligned} \right\} \quad (4.7)$$

Problem: Check that b, b^\dagger obey the commutation relation

$$[b, b^\dagger]_- = 1 \quad (4.8)$$

(in future we also omit the minus sign on the commutator $[,]_-$).

Solution:

$$\begin{aligned} [b, b^\dagger] &= \frac{1}{2\hbar M\omega} \left\{ (M\omega)^2 [x, x] + iM\omega [p, x] - iM\omega [x, p] + [p, p] \right\} \\ &= \frac{1}{2\hbar} (-2i[x, p]) = \frac{(-2i)i\hbar}{2\hbar} = 1. \end{aligned} \quad (4.9)$$

We can express x, p through b, b^\dagger , using (4.7):

$$x = \sqrt{\frac{\hbar}{2M\omega}} (b^\dagger + b), \quad p = \frac{i\sqrt{2\hbar M\omega}}{2} (b^\dagger - b). \quad (4.10)$$

From (4.4), (4.10) and using (4.8), we obtain

$$\mathcal{H} = \frac{1}{2}\hbar\omega(bb^\dagger + b^\dagger b) = \hbar\omega b^\dagger b + \frac{1}{2}\hbar\omega = \hbar\omega\left(n + \frac{1}{2}\right), \quad n = b^\dagger b. \quad (4.11)$$

For the eigenstates (the states with certain particular value n) equation (4.11) gives the energy levels (4.5); this is actually the simplest way to obtain the energy spectrum of the harmonic oscillator. Note the presence of $\frac{1}{2}$ in (4.11); this term corresponds to the so-called *zero-point oscillations* and it describes a real physical effect, which, as we will see later, often has very important physical implications.

The states with n excitations $|n\rangle$ obey the relations

$$\begin{aligned} b|n\rangle &= \sqrt{n}|n-1\rangle \\ b^\dagger|n\rangle &= \sqrt{n+1}|n+1\rangle, \end{aligned} \quad (4.12)$$

that is, b is indeed an annihilation operator and b^\dagger is a creation operator; they respectively decrease and increase the number of phonons by 1. For the number



Fig. 4.

operator \hat{n} we have, as we should

$$\hat{n}|n\rangle = b^\dagger b |n\rangle = b^\dagger \sqrt{n} |n-1\rangle = n |n\rangle . \quad (4.13)$$

For the ground state $|0\rangle$ (the state with zero phonons)

$$b|0\rangle = 0. \quad (4.14)$$

From (4.12) we then obtain

$$|n\rangle = \frac{1}{\sqrt{n!}}(b^\dagger)^n |0\rangle . \quad (4.15)$$

Let us now consider not an isolated oscillator, but a linear chain, consisting of atoms with the harmonic interaction: its Hamiltonian is

$$\mathcal{H} = \sum \left[\frac{M\dot{u}_n^2}{2} + \frac{B}{2}(u_n - u_{n+a})^2 \right]. \quad (4.16)$$

(Here we have introduced the deviation of the n -th atom from its equilibrium position $u_n = x_n - x^0$.) The equations of motion have the form

$$M\ddot{\mu}_r \equiv -B(2\mu_r - \mu_{r+1} - \mu_{r-1}), \quad (4.17)$$

We seek the solution in the form $\mu_n \equiv \mu_n e^{iqn}$. Then from (4.17) we get

$$M\ddot{u}_+ \equiv -n(2 - e^{iqa} - e^{-iqa}) \equiv -2B(1 - \cos qa)u_+ \quad (4.18)$$

This is also the equation for the harmonic oscillator, with frequency

$$\omega_q = 2\sqrt{\frac{B}{M}} \sin \frac{qa}{2} \sim_{q \ll 1} \sqrt{\frac{B}{M}} qa \quad (4.19)$$

(compare with (4.1), (4.3))

Problem: Consider a linear chain ‘with the basis’ (two atoms per unit cell – e.g. with different masses M_1 and M_2 , see Fig. 4.1). Find the phonon spectrum.

Solution: For convenience we introduce two variables, u_n and v_n , for the atoms of two kinds, see Fig. 4.2. The equations of motion for u_n and v_n are:

$$\begin{aligned} M_1 \ddot{u}_n &= B(v_n + v_{n-1} - 2u_n) \\ M_2 \ddot{v}_{n-1} &\equiv B(u_{n-1} + u_n - 2v_{n-1}) \end{aligned} \quad (4.20)$$

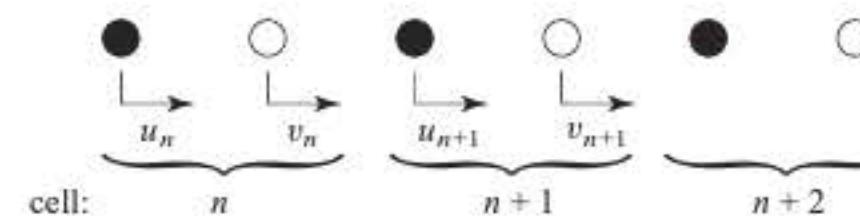


Fig. 4.2

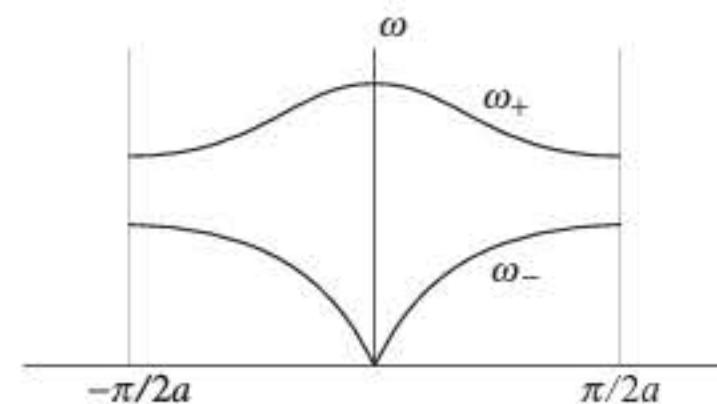


Fig. 4.3

Let us seek the solution in the form $u_n = ue^{iqna-i\omega t}$, $v_n = ve^{iqna-i\omega t}$. The solution of equation (4.20) is now reduced to the diagonalization of the matrix

$$\begin{vmatrix} 2B - M_1\omega^2 & -B(1 + e^{-iqa}) \\ -B(1 + e^{iqa}) & 2B - M_2\omega^2 \end{vmatrix} = 0. \quad (4.21)$$

The eigenenergies are

$$\omega_{\pm}^2(q) = B \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \pm B \sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4 \sin^2 qa}{M_1 M_2}}. \quad (4.22)$$

Thus there exist in this case two branches of phonons, see Fig. 4.3: optical phonons with the spectrum ω_+ , which at $q = 0$ have finite frequency,

$$\omega_+^2(q = 0) = 2B \left(\frac{1}{M_1} + \frac{1}{M_2} \right), \quad (4.23)$$

and ordinary acoustic phonons, whose spectrum is obtained by taking the ‘minus’ sign in equation (4.22),

$$\omega_-(q = 0) = \sqrt{2B/(M_1 + M_2)} \sin qa, \quad (4.24)$$

which for $M_1 = M_2$ coincides with (4.19).

Problem: The same for equal masses, but alternating spring constants, Fig. 4.4.

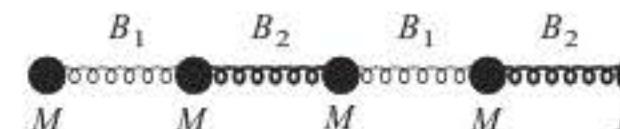


Fig. 4.4

Solution:

$$\omega_{\pm}^2(q) = \frac{B_1 + B_2}{M} \pm \frac{1}{M} \sqrt{B_1^2 + B_2^2 + 2B_1B_2 \cos qa}. \quad (4.25)$$

In the general case the Hamiltonian of the harmonic lattice takes the form

$$\mathcal{H} = \sum_{q,\alpha} \hbar\omega_{q\alpha} \left(b_{q\alpha}^\dagger b_{q\alpha} + \frac{1}{2} \right) + \text{const.} \quad (4.26)$$

where \mathbf{q} is the (quasi)momentum (in the one-dimensional case $-\frac{\pi}{a} < q < \frac{\pi}{a}$; in general \mathbf{q} lies in the first Brillouin zone), and α is the mode index (denoting acoustic or optical modes and the corresponding polarization – one longitudinal, two transverse modes).

4.3 Physical properties of crystals in the harmonic approximation

Phonons are *bosons*. The number of phonons is not fixed, which means that the phonon chemical potential should be taken as zero, see Chapter 3:

$$\mu_{ph} = 0. \quad (4.27)$$

Consequently, the phonon occupation number is (cf. (3.3))

$$\bar{n}_q = \frac{1}{e^{\hbar\omega_q/T} - 1}. \quad (4.28)$$

The energy of the mode \mathbf{q} is $E_q = (n_q + \frac{1}{2})\hbar\omega_q$. Thus the total energy (including the zero-point energy – the term with $\frac{1}{2}$ in (4.26)) is

$$\begin{aligned} E &= \sum_q \hbar\omega_q \left(\frac{1}{e^{\hbar\omega_q/T} - 1} + \frac{1}{2} \right) = \sum_q \frac{\hbar\omega_q}{2} \frac{e^{\hbar\omega_q/T} + 1}{e^{\hbar\omega_q/T} - 1} \\ &= \sum_q \frac{\hbar\omega_q}{2} \coth \frac{\hbar\omega_q}{2T}. \end{aligned} \quad (4.29)$$

General rule

The transformation of the sum in \mathbf{q} to an integral is done as follows:

$$\sum_{\mathbf{q}} \Rightarrow \int \frac{d^d \mathbf{q}}{(2\pi)^d} \quad \begin{cases} \text{in 3d-case } d = 3; \\ \text{similarly in one-dimensional and in} \\ \text{two-dimensional cases } (d = 1, 2) \end{cases} \quad (4.30)$$

By (1.18) the specific heat (per unit volume) is

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{1}{T^2} \int \frac{d^3 \mathbf{q}}{(2\pi)^3} \frac{(\hbar\omega_{\mathbf{q}})^2 e^{\hbar\omega_{\mathbf{q}}/T}}{(e^{\hbar\omega_{\mathbf{q}}/T} - 1)^2}. \quad (4.31)$$

Later, in most cases we put $\hbar = 1$ (as well as the Boltzmann constant $k_B = 1$).

One can introduce the phonon density of states $D(\omega)$: $d^3 \mathbf{q}/(2\pi)^3 = D(\omega) d\omega$, where $D(\omega) d\omega$ is the number of phonon states at energy ω in an interval $d\omega$. Normalization should be such that $\int d\omega D(\omega)$ over the Brillouin zone is equal to the total number of phonon modes per unit cell, i.e. equal to the total number of degrees of freedom. If there are m atoms per unit cell and N_c unit cells, there are $3mN_c = 3N$ modes. Then

$$c_V = 3N \int \frac{(\omega/T)^2 e^{\omega/T}}{(e^{\omega/T} - 1)^2} D(\omega) d\omega. \quad (4.32)$$

Different models for the phonon spectra $\omega(\mathbf{q})$ give different forms of the phonon density of states $D(\omega)$ and consequently in general different phonon specific heat:

- (1) Einstein model, $\omega(\mathbf{q}) = \omega_0 = \text{const.}$ (this is not such a bad approximation for optical phonons). The phonon density of states is then a delta function, and the specific heat is

$$c_V^E = 3N \frac{(\omega_0/T)^2 e^{\omega_0/T}}{(e^{\omega_0/T} - 1)^2} \quad (4.33)$$

or, with $\hbar\omega_0 \equiv \Theta_E$, where Θ_E is the corresponding temperature (we then put Θ_E in (4.33) instead of ω_0 , or simply take ω_0 in kelvin), it is

$$T \rightarrow 0 : \quad c_V^E(T \ll \Theta_E) \simeq 3N \left(\frac{\Theta_E}{T} \right)^2 \exp\left(-\frac{\Theta_E}{T}\right) \quad (4.34)$$

$$T \gg \Theta_E : \quad c_V^E(T \gg \Theta_E) \simeq 3N + O\left(\frac{\Theta_E}{T}\right). \quad (4.35)$$

The expression (4.35) is the Dulong–Petit law, well known from classical physics (we recall that above we put $k_B = 1$; the standard form of the Dulong–Petit law is $c = 3k_B N$).

- (2) Debye model: we approximate the total phonon spectrum by the spectrum of acoustic phonons $\omega(\mathbf{q}) = s\mathbf{q}$, with the appropriate upper cut-off, see the schematic picture in Fig. 4.5. The integration in $\int d^3 \mathbf{q}$ is carried out not over

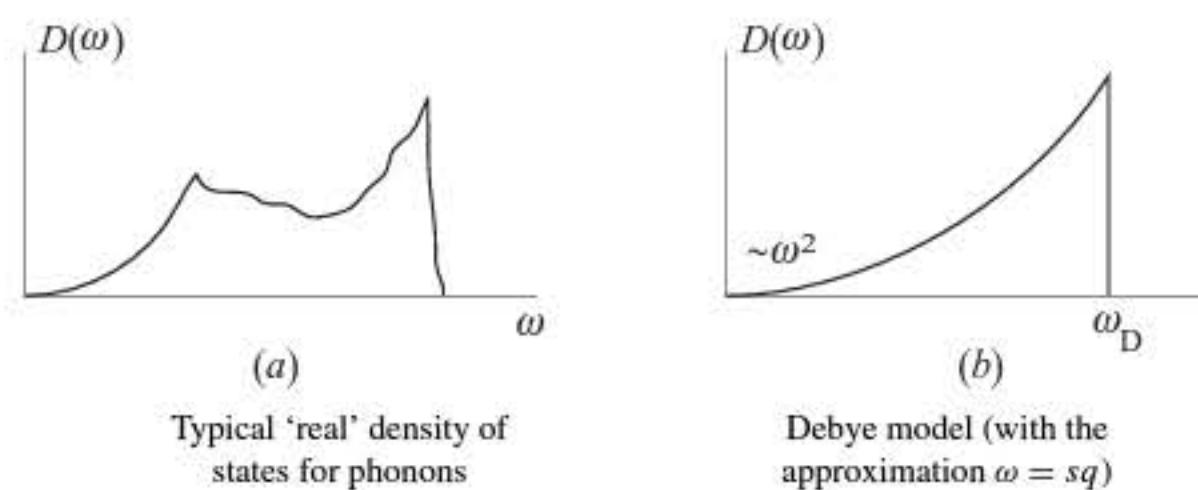


Fig. 4.5

the real Brillouin zone, but over a *sphere*, with the volume equal to the volume of the Brillouin zone.

The number of q -points in the Brillouin zone is N ; their density is $V/(2\pi)^3$; thus

$$N = \frac{V}{(2\pi)^3} \frac{4}{3} \pi q_0^3 \quad (4.36)$$

where q_0 – the Debye wavevector – is the maximum wavevector of the equivalent sphere in q -space.

The maximum frequency $\omega_D = sq_0$ is called the Debye frequency (s is the sound velocity); $\Theta_D = \hbar\omega_D$ is the Debye temperature.

In effect

$$c_V = 3N \left(\frac{T}{\Theta_D} \right)^3 \cdot 3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx . \quad (4.37)$$

(Here we have used that $D(\omega) d\omega$ in (4.29) is

$$D(\omega) d\omega = \frac{4\pi q^2 dq}{\frac{4}{3}\pi q_D^2} = \frac{3\omega^2}{\omega_D^2} d\omega , \quad (4.38)$$

and substituted $k_B\Theta_D$ for $\hbar\omega_D$.)

The limiting behaviour of the specific heat in the Debye model is

$$T \rightarrow 0 \quad (T \ll \Theta_D) : \quad c_V \sim \frac{12\pi^4}{5} N \left(\frac{T}{\Theta_D} \right)^3 , \quad (4.39)$$

$$T \rightarrow \infty \quad (T \gg \Theta_D) : \quad c_V \simeq 3N . \quad (4.40)$$

At high temperatures we have the Dulong–Petit law again. (Actually the cross-over from the low-temperature behaviour $c_V \sim T^3$ to the high-temperature limit occurs not at $T \sim \Theta_D$, but at approximately $T \sim \frac{1}{4}\Theta_D$.) One has to remember that at low temperatures the phonon specific heat is $\sim T^3$; this relation is very important for many experiments.

Problem: Find the free energy of the harmonic crystal.

Solution: The energy of the harmonic crystal is

$$E = \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} \left(n_{\mathbf{q}} + \frac{1}{2} \right), \quad n_{\mathbf{q}} = 1, 2, 3, \dots . \quad (4.41)$$

The partition function is

$$Z = \prod_{\mathbf{q}} \sum_{n_{\mathbf{q}}} \exp \left\{ -\frac{\hbar \omega_{\mathbf{q}}}{T} \left(n_{\mathbf{q}} + \frac{1}{2} \right) \right\} = \prod_{\mathbf{q}} \frac{e^{-\hbar \omega_{\mathbf{q}}/2T}}{1 - e^{-\hbar \omega_{\mathbf{q}}/T}} . \quad (4.42)$$

The free energy (1.9) is then given by the expression

$$F = -T \ln Z = \frac{1}{2} \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} + T \sum_{\mathbf{q}} \ln \left(1 - e^{-\hbar \omega_{\mathbf{q}}/T} \right) = T \sum_{\mathbf{q}} \ln \left[2 \sinh \frac{\hbar \omega_{\mathbf{q}}}{2T} \right] . \quad (4.43)$$

Here we have used a simple transformation

$$\begin{aligned} \ln \left(1 - e^{-\hbar \omega/T} \right) &= \ln \left[2e^{-\hbar \omega/2T} \left(\frac{e^{\hbar \omega/2T} - e^{-\hbar \omega/2T}}{2} \right) \right] \\ &= -\frac{\hbar \omega}{2T} + \ln \left(2 \sinh \frac{\hbar \omega}{2T} \right) . \end{aligned} \quad (4.44)$$

4.4 Anharmonic effects

In general the interatomic interaction, i.e. the potential energy of two atoms with coordinates x_1, x_2 is $v(x_1 - x_2)$. Previously, in the harmonic approximation, we used an expansion in small deviations from the static positions

$$\begin{aligned} v(x_1 - x_2) &= v_0 + \frac{1}{2} B (u_1 - u_2)^2 \\ (x_1 &= x_1^0 + u_1, \quad x_2 = x_2^0 + u_2) , \end{aligned} \quad (4.45)$$

see, e.g. (4.16).

In general there exist *anharmonic terms*, proportional respectively to $(u_1 - u_2)^3$, $(u_1 - u_2)^4$, etc.:

$$v = v_0 + \frac{B}{2} (u_1 - u_2)^2 + \frac{\zeta}{3!} (u_1 - u_2)^3 + \frac{\nu}{4!} (u_1 - u_2)^4 + \dots . \quad (4.46)$$

$$\left(B = \frac{\partial^2 v}{\partial x^2}, \quad \zeta = \frac{\partial^3 v}{\partial x^3}, \quad \nu = \frac{\partial^4 v}{\partial x^4}, \quad \dots \right) . \quad (4.47)$$

The term with the coefficient ζ gives rise to cubic anharmonism, the one with ν to quartic, etc.

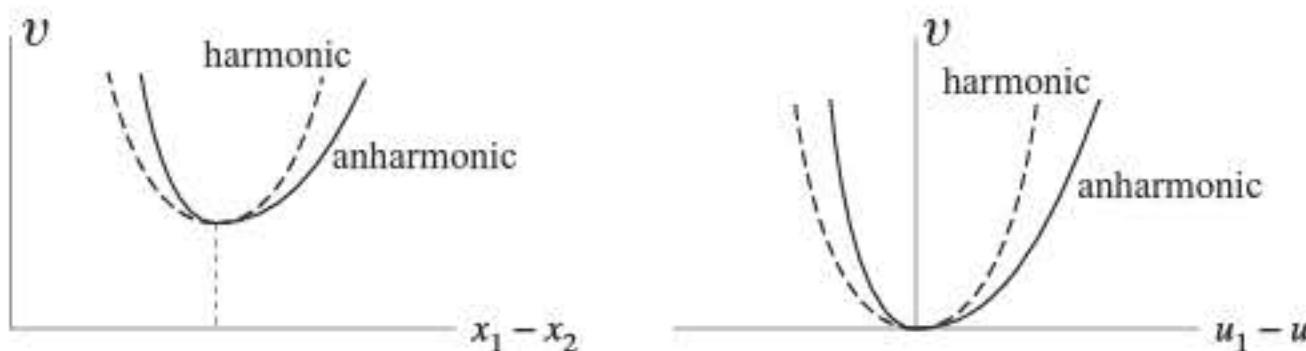


Fig. 4.6

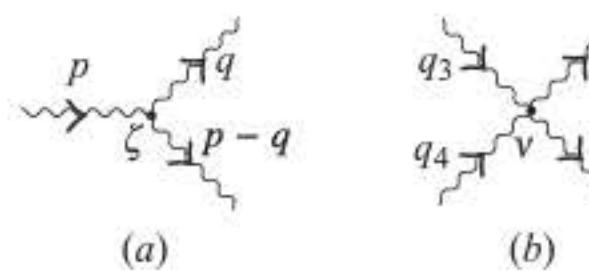


Fig. 4.7

Usually the coefficient ζ is negative, $\zeta < 0$, and the potential looks like the one shown in Fig. 4.6 by the solid line, i.e. it is steeper for negative relative distortion (when two atoms approach one another) and less steep for positive $u_1 - u_2$, when the two atoms move further apart. (This is quite natural: the interaction between atoms becomes stronger when they approach – the overlap of atomic or ionic cores leads to a very strong, almost hard core repulsion; and this interaction is weaker when the distance between atoms becomes large.)

One can also write down the corresponding anharmonic terms in second quantization form, through the operators b , b^\dagger , and add them to the phonon Hamiltonian (4.26). Cubic anharmonism will give rise to terms with the structure $\zeta \sum_{p,q} (b_{p-q}^\dagger b_q^\dagger b_p + \text{h.c.})$, and quartic anharmonism, to terms of the type $v [\sum_{q_1 q_2 q_3 q_4} (b_{q_1}^\dagger b_{q_2}^\dagger b_{q_3} b_{q_4} + \text{h.c.}) + \sum_{k_1 k_2 k_3 k_4} (b_{k_1}^\dagger b_{k_2}^\dagger b_{k_3} b_{k_4} + \text{h.c.})]$, where the momenta involved obey conservation laws $q_1 + q_2 = q_3 + q_4$, $k_1 = k_2 + k_3 + k_4$ (the total momentum of created phonons is equal to the total momentum of annihilated ones).

Anharmonic interactions have several consequences. One is that they lead to phonon–phonon interactions, schematically illustrated in Fig. 4.7. These processes are important, e.g. for thermal conductivity. These graphs, Fig. 4.7(a), 4.7(b), at this stage can be treated simply as pictorial representations of certain processes. Thus, if we depict the phonon by a wavy line, Fig. 4.7(a) corresponds to a process in which in the initial state there was one phonon with momentum p , which as a result of anharmonic interaction is transformed into two other phonons, with momenta q and $p - q$; such processes are allowed by cubic anharmonism. Correspondingly,

Fig. 4.7(b) describes the process of scattering of two phonons with momenta q_3 and q_4 into two others, with momenta q_1, q_2 ; such processes are contained in the quartic term of the Hamiltonian. But one can give these ‘pictures’ much more meaning: they are actually *Feynman diagrams*, which allow one really to *calculate* the probabilities of corresponding processes. This method will be discussed in more detail in Chapter 8, and in Chapters 9–11 we will show how it works in many specific problems.

Another important consequence of anharmonic interactions is their role in thermal expansion and in the melting of crystals. This will be discussed in the following sections.

4.4.1 Thermal expansion

By (4.43) the free energy of a crystal in the harmonic approximation is (putting $\hbar = 1$)

$$F = T \sum_q \ln \left[2 \sinh \frac{\omega_q}{2T} \right]. \quad (4.48)$$

With the inclusion of anharmonicity, i.e. of the phonon–phonon interaction, this is no longer true. But one can still use this expression approximately in the so-called *quasiharmonic approximation*, accounting for anharmonicity in the following way. The phonon frequencies ω_q in the anharmonic crystal in general depend on the specific volume, $\omega_q(V)$ (see Fig. 4.6: the curvature of the potential $v(x)$, d^2v/dx^2 , which according to (4.3), (4.4) determines phonon frequencies, in the anharmonic case depends on x). Usually this dependence is described by the phenomenological relation

$$\frac{V}{\omega} \frac{d\omega}{dV} = \frac{d \ln \omega}{d \ln V} = -\gamma, \quad (4.49)$$

which is called the Grüneisen approximation; γ is the Grüneisen constant (usually, in ordinary crystals, $\gamma \sim 1–2$).

The total free energy as a function of volume can then be written as

$$F(V) = \frac{1}{2\kappa} \left(\frac{\delta V}{V} \right)^2 + T \sum_q \ln \left[2 \sinh \frac{\omega_q(V)}{2T} \right]. \quad (4.50)$$

The first term in (4.50) is the elastic energy after deformation δV , and κ is the lattice compressibility (inverse bulk modulus). In equation (4.50) we considered the situation when we (artificially) fix the volume of the system V , which may differ from the equilibrium volume without phonons by the distortion δV . Then we indeed should include in the total energy the first term of equation (4.50) describing such deformation. The second term gives the phonon contribution to the

free energy, which is calculated by treating the lattice as harmonic, but *at a given volume* V (the expression (4.43) for the phonon contribution, strictly speaking, is valid only for the harmonic crystal). However, whereas in the purely harmonic case the phonon frequencies are constant, independent of the distance between atoms or of the volume, here we assume that they do depend on V , by the relation (4.49). Thus we effectively take into account anharmonic effects, albeit approximately, via the phenomenological Grüneisen relation. Such a scheme is often used in treating anharmonic lattices, and it is called the quasiharmonic approximation. The equilibrium volume V in this scheme should be determined by minimizing the free energy (4.50); due to the presence of the second term the resulting volume would depend on temperature, and this dependence gives thermal expansion.

Differentiating (4.50) in V and using (4.49), we obtain

$$\frac{1}{\kappa} \frac{\delta V}{V} = \sum_{\mathbf{q}} \gamma \frac{\omega_{\mathbf{q}}}{2} \coth \frac{\omega_{\mathbf{q}}}{2T} = \gamma \bar{E}(T), \quad (4.51)$$

where $\bar{E}(T)$ is the average energy of the lattice (cf. (4.29)).

Thus the volume thermal expansion β is:

$$\beta = \frac{1}{V} \frac{\partial(\delta V)}{\partial T} = \kappa \gamma \frac{\partial \bar{E}(T)}{\partial T} = \gamma \kappa c_V = \gamma \frac{c_V}{B}, \quad (4.52)$$

where $B = 1/\kappa$ is the bulk modulus.

The linear thermal expansion coefficient is

$$\alpha = \frac{\partial l}{\partial T} = \frac{1}{3} \beta \quad \left(\text{as } \beta = \frac{1}{V} \frac{\partial V}{\partial T} = \frac{1}{l^3} \frac{\partial(l^3)}{\partial T} = \frac{3}{l} \frac{\partial l}{\partial T} = 3\alpha \right).$$

Thus

$$\boxed{\alpha = \gamma \cdot \frac{c_V}{3B}}. \quad (4.53)$$

This is called the Grüneisen equation. We see that we get nonzero thermal expansion only when we include anharmonic effects (the dependence of the phonon frequencies on interatomic distance or on volume, which is phenomenologically described by the relation (4.49)). For constant phonon frequencies (Grüneisen constant $\gamma = 0$) thermal expansion would be absent.

The Grüneisen equation (4.53) is very useful, as it establishes the relation between different measurable quantities and allows us, e.g. to calculate the thermal expansion if the specific heat and bulk modulus are known. It is often used in practice, to check the consistency of different thermophysical data of real materials.

Why is anharmonism necessary for thermal expansion? The physics of the expansion is illustrated in Figs. 4.8 and 4.9. At low temperatures the system is

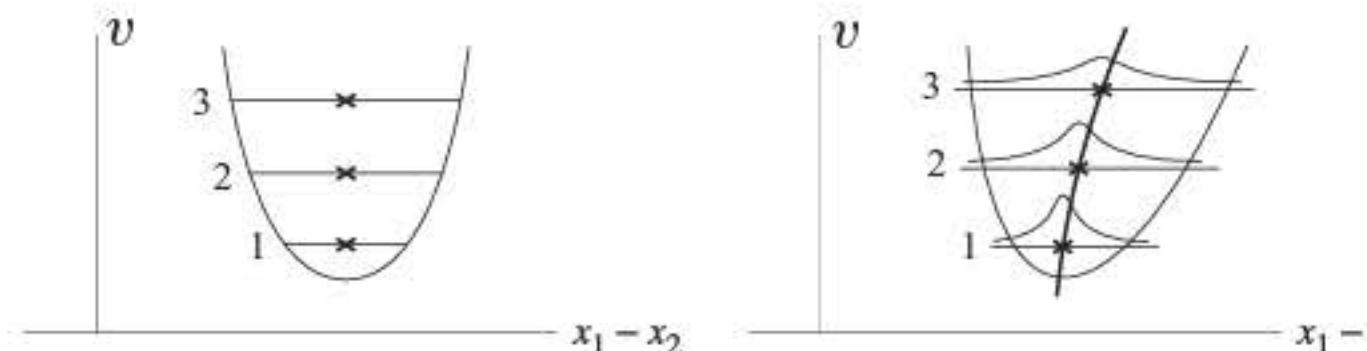


Fig. 4.

Fig. 4.

at the lowest quantum level of the oscillator (state 1). At higher temperatures the average distance between atoms is given by averaging over all occupied higher lying quantum levels. In the harmonic case we have the situation shown in Fig. 4, and the average displacement at each level, i.e. the average lattice parameter, is the same at each quantum level. Thus it does not change with temperature, and in the purely harmonic crystal we would not have any thermal expansion.

On the other hand, in an anharmonic crystal the interaction potential qualitatively looks as shown in Fig. 4.9 (cf. Fig. 4.6). Then with increasing temperature when the higher levels become occupied, the average distance between atoms (lattice parameter) *increases* with temperature – and this is the conventional thermal expansion.

4.4.2 Melting

From (4.49) we see that the dependence of the phonon frequencies on the specific volume can be rewritten as

$$\omega = \omega_0 \left(\frac{V}{V_0} \right)^{-\gamma} . \quad (4.5)$$

As the change of volume (due to thermal expansion) is usually small, we can approximately write instead of (4.54) (and using the definition of thermal expansion $\beta = 3\alpha = \frac{1}{V} \frac{\partial V}{\partial T}$)

$$V \approx V_0(1 + 3\alpha T) \quad (4.5)$$

This means the

$$\omega(T) \approx \omega(1 - 3\omega T) \quad (4.5)$$

Actually, as follows from a more complete treatment, see Section 8.6, the description of phonons always contains not the phonon frequency ω , but rather ω^2 . Consequently, the equation describing the change of phonon frequencies with temperature

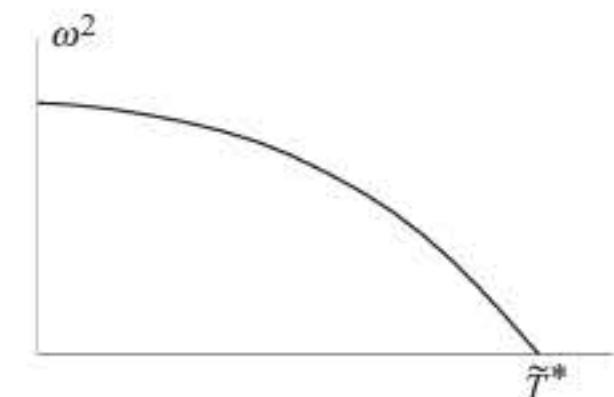


Fig. 4.10

has not the form (4.56), but is rather

$$\omega^2(T) = \omega_0^2(1 - 6\alpha\gamma T). \quad (4.57)$$

The more general equation for $\omega(T)$ is

$$\omega^2(T) = \omega_0^2(1 - cn(T)), \quad (4.58)$$

where $n(T) = 1/(e^{\omega/T} - 1)$ is the average number of excited phonons (this will be shown later); here c is some constant ($\sim \xi^2/B^3$). Then for $\omega \sim \omega_0 < T$

$$\omega^2 = \omega_0^2 \left(1 - \frac{cT}{\omega_0}\right), \quad (4.59)$$

i.e. for high temperatures the expression (4.58) gives the same temperature dependence as (4.56), (4.57).

These expressions give the dependence of ω on T shown in Fig. 4.10. At a certain temperature \tilde{T}^* the phonon frequency $\omega^2 = 0$, and for $T > \tilde{T}^*$ it becomes negative, which means an instability of our system and the transition to a new state, e.g. melting of the crystal.

I remind readers that in quantum mechanics the time dependence of the wavefunction is given by $\psi(t) = \psi(0) \exp i\omega t$. When ω^2 becomes negative, i.e. $\omega t = \pm i|\omega|t$, this would give an exponential growth of the corresponding quantities. In our case, when the phonon frequencies cross zero, this would mean an exponential growth of the number of corresponding phonons, or of the respective distortion, which means absolute instability of the initial state, in this case a crystal. Whether such instability would indeed correspond to melting or to a structural transition to a different crystal structure, depends on which particular phonon mode becomes unstable. If this is the phonon with momentum Q , then this implies the change of the crystal structure with the formation of a superstructure with this wavevector, $u(\mathbf{r}) \sim \exp(iQ \cdot \mathbf{r})$. Melting corresponds in this language to the softening of transverse phonons at $\mathbf{q} = 0$ (in other words, the *shear modulus* becomes negative).

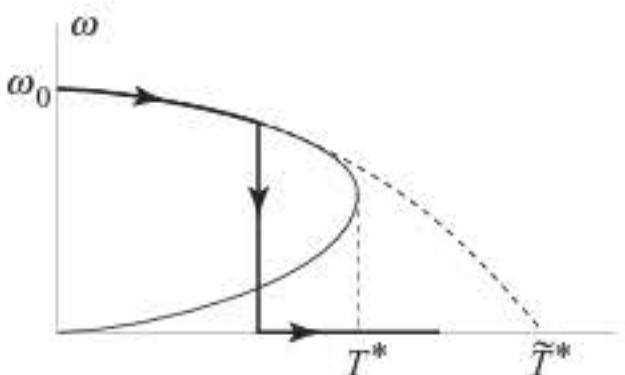


Fig. 4.11

In general, the description of structural phase transitions as an instability of the original crystal structure due to softening of particular phonon modes is known as the *soft mode* concept (Ginzburg, Cochran, Anderson). It is widely used in solid state physics and leads to definite predictions which can be checked experimentally.

Returning to melting, we see that in this approximation the transition would be continuous, i.e. second order (the phonon frequency goes continuously to zero). But on general grounds melting should be a first-order phase transition (one can show that in this case there exist cubic invariants in the Landau free energy expansion, see Section 2.2 above). How can we correct this drawback? It is more correct to take in (4.58) not $n(T) = 1/(e^{\omega_0/T} - 1)$ (which leads to (4.59)), but the number of phonons with an already renormalized, new frequency ω , $1/(e^{\omega/T} - 1)$. Then instead of (4.59) we would obtain

$$\omega = \omega_0(1 - cn(\omega)) = \omega_0 \left(1 - \frac{cT}{\omega}\right) \quad (4.60)$$

(here we have simplified the mathematics by writing the equation not for ω^2 , but for ω ; this is sufficient for our qualitative treatment).

The equation (4.60) is a self-consistent equation for ω . Its solution is

$$\omega = \frac{\omega_0}{2} \pm \sqrt{\frac{\omega_0^2}{4} - cT\omega_0}, \quad (4.61)$$

see Fig. 4.11. We see that in contrast to the previous treatment, the self-consistent solution with real ω exists only up to a temperature $T^* = \omega_0/4c$ (smaller than \tilde{T}^*), after which it becomes complex, i.e. the time dependence of the vibration amplitude (4.2) $\sim e^{+i\omega t}$ is again diverging, which indeed signals an instability of the lattice, in our case melting. And in this theory melting would be a first-order phase transition, with a jump in ω , as it should be. The results are qualitatively the same if we had proceeded from equation (4.58) for ω^2 .

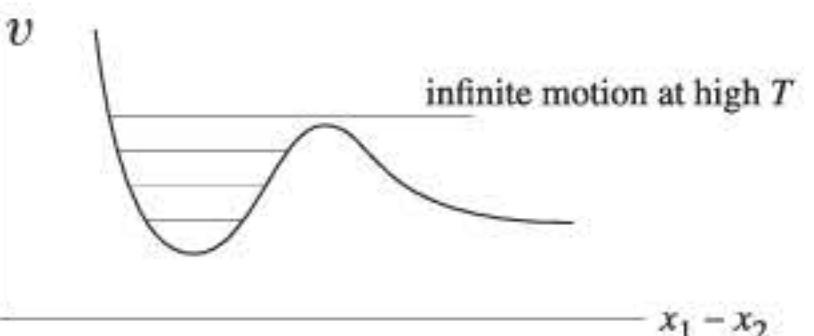


Fig. 4.12

The softening of phonons means at the same time a decrease of the bulk modulus of the lattice, B : as $\omega^2 = B/M$, we get from (4.57)

$$B(T) \simeq B_0(1 - 6\alpha\gamma T). \quad (4.62)$$

But, from the Grüneisen relation (4.53), $\alpha \sim 1/B$, which again gives a self-consistent equation for B (or for ω^2), equivalent to (4.58):

$$B(T) = B_0 \left(1 - \frac{2\gamma^2 c_V T}{B(T)} \right), \quad (4.63)$$

i.e. we again obtain a quadratic equation for $B(T)$ similar to (4.60), which will again give first-order melting.

Once again, strictly speaking an instability of a phonon does not mean necessary melting; it can signal, e.g. a transformation into another crystal structure. To check that we will indeed have melting, we have to show that the *shear modulus* (shear modes for $q \rightarrow 0$) becomes unstable. But qualitatively the picture described is correct, and it is also consistent with other approaches to melting, described below.

Why does melting occur at all? How can one explain it qualitatively? Let us extend Fig. 4.6 a bit. From (4.46), $v = v_0 + \frac{1}{2}Bu^2 - \frac{1}{3!}|\zeta|u^3$, i.e. this potential actually looks as in Fig. 4.12. We see that there exists an infinite motion at high enough temperature! The lattice is no longer stable, which means melting. Thus we again see that the melting is intrinsically connected with the anharmonicity of the lattice.

4.4.3 Another approach to melting. Quantum melting

From equation (4.10) we see that the vibration amplitude can be expressed through the phonon operators as

$$u = \sqrt{\frac{\hbar}{2M\omega}} (b^\dagger + b) \quad (4.64)$$

(for one phonon mode). The average shift from the equilibrium position is of course zero, $\langle u \rangle = 0$, but the square of the average amplitude of vibrations is nonzero:

$$\begin{aligned}\langle u^2 \rangle &= \frac{\hbar}{2M\omega} \langle (b^\dagger + b)^2 \rangle = \frac{\hbar}{2M\omega} \langle b^\dagger b^\dagger + bb + b^\dagger b + bb^\dagger \rangle \\ &= \frac{\hbar}{2M\omega} (2\langle b^\dagger b \rangle + 1) = \frac{\hbar}{M\omega} \left(n + \frac{1}{2} \right)\end{aligned}\quad (4.65)$$

(we use the commutation relation $bb^\dagger - b^\dagger b = 1$).

Thus

$$\langle u^2 \rangle = \frac{\hbar}{M\omega} \left(n + \frac{1}{2} \right) = \frac{\hbar^2}{M\Theta_D} \left(n + \frac{1}{2} \right) \quad (4.66)$$

(there may enter some numerical factors such as 3 because of the presence of several phonon modes). The limiting values of this mean square vibration amplitude are:

$$T \rightarrow 0 : \quad \langle u^2 \rangle \sim \frac{\hbar^2}{2M\Theta_D} \quad \begin{array}{l} \text{(important: note that } \langle u^2 \rangle_{T=0} \neq 0; \\ \text{these are the famous zero-point oscillations)} \end{array} \quad (4.67)$$

$$T \gg \Theta_D : \quad \langle u^2 \rangle \sim \frac{\hbar^2 T}{M\Theta_D^2} \quad \left(\text{actually it is equal to } \frac{9\hbar^2 T}{M\Theta_D^2} \right). \quad (4.68)$$

When the vibration amplitude becomes comparable to the lattice spacing itself, $\langle u^2 \rangle \sim a^2$ (actually when $\langle u^2 \rangle/a^2 \sim 0.2$), melting occurs; this is the *Lindemann criterion* of melting.

The factor $\langle u^2 \rangle$ also enters into the intensity of X-ray scattering in crystals, in the theory of the Mössbauer effect, etc. It enters through the factor e^{-2W} , where

$$W \sim \langle u^2 \rangle, \quad W = \begin{cases} \frac{3}{8} \frac{\hbar^2 K^2}{M\Theta_D} & (T \rightarrow 0) \\ \frac{3}{2} \frac{\hbar^2 K^2 T}{M\Theta_D^2} & (T \gg \Theta_D). \end{cases} \quad (4.69)$$

K is the Umklapp wavevector $\sim \hbar/a$; the quantity W is called the *Debye-Waller factor*.

Thus, in melting an important parameter is

$$\Lambda = \frac{\langle u^2 \rangle}{a^2}, \quad (4.70)$$

the so-called *de Boer* parameter (usually this term is used at $T = 0$, for zero-point vibrations; this is then the *quantum de Boer parameter*). At $T = 0$

$$\langle u^2 \rangle \sim \frac{\hbar}{M\omega} \quad \text{with} \quad \omega = \sqrt{\frac{B}{M}}. \quad (4.71)$$

The stiffness of the lattice B (the bulk modulus) can be estimated as follows: when an atom is shifted from its equilibrium position by a distance $\sim a$ (a is the lattice parameter), the change in potential energy $\sim Ba^2$ is of the order of the typical interaction between atoms $v(a)$, i.e.

$$B \sim \frac{v}{a^2}. \quad (4.72)$$

As a result the quantum de Boer parameter Λ (4.70) becomes

$$\Lambda \sim \frac{\hbar}{a} \frac{1}{\sqrt{Mv}}. \quad (4.73)$$

If $\Lambda \gtrsim 0.2$ – 0.3 , the crystal is unstable with respect to *zero-point motion* even at $T = 0$, which means *quantum melting*. This will also be important for electrons (see the discussion of Wigner crystals and cold melting below, and in Section 11.8).

When will a substance melt by quantum fluctuations and remain liquid down to $T = 0$? According to (4.73), better chances for this exist if:

- the mass of the atom M is small;
- the interaction v is weak.

The best candidate for this is helium: it is light, and He atoms have filled 1s shells (inert atoms), so that the He–He interaction is weak. That is why helium remains liquid down to $T = 0$ (at normal pressure).

Another good candidate could have been hydrogen. It is even lighter than helium. But the effective interaction between hydrogen atoms and even between H₂ molecules is too strong. Nevertheless there have been active experimental attempts to stabilize hydrogen in a liquid phase down to the lowest temperatures, i.e. to prevent its crystallization, with the idea that it would then experience Bose condensation and possibly would become superfluid, as ⁴He. These attempts have not yet succeeded; instead Bose condensation was reached in completely different systems, in optically trapped and supercooled alkali atoms (Rb, Cs, etc.).

As we have said, the condition for quantum melting is determined by the value of the quantum de Boer parameter Λ . Typical values of Λ are: $\Lambda_{^3\text{He}} = 0.5$, $\Lambda_{^4\text{He}} \approx 0.4$, $\Lambda_{\text{H}_2} \approx 0.3$, $\Lambda_{\text{Ne}} \approx 0.1$. (In the book by Ashcroft and Mermin (1976) other values for Λ are given, which is due to the different normalization used there, but the ratio for different elements is the same.)

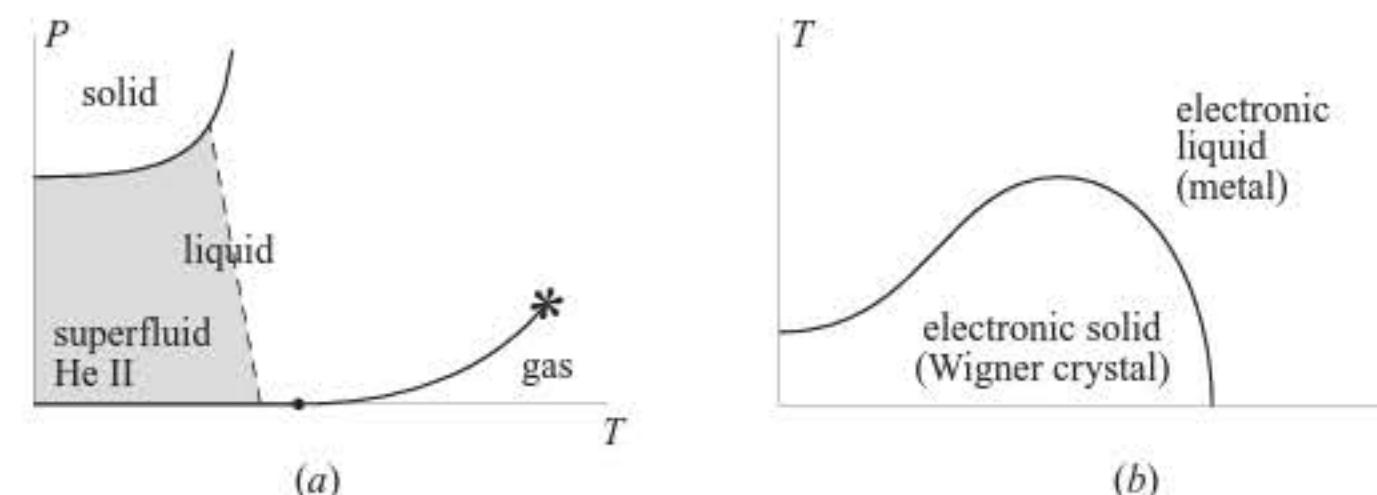


Fig. 4.13

Under pressure the average distance a between atoms decreases, the atom-atom interaction $v(a)$ increases, and Λ may decrease or increase depending on the behaviour of va^2 (see (4.73)). For neutral particles (helium) the interaction v increases faster, Λ decreases, and He becomes solid under pressure (the phase diagram of ${}^4\text{He}$ is shown schematically in Fig. 4.13(a)). For electrons the opposite is true: the characteristic Coulomb interaction between electrons is $v = e^2/a$, and $\Lambda = \hbar/a\sqrt{me^2/a} \sim 1/\sqrt{a}$, where a is the average distance between electrons. Under pressure this distance decreases, the de Boer parameter increases, and there occurs *cold melting* of the electronic (Wigner) crystal (Fig. 4.13(b)).

When helium crystallizes under pressure, it still has a large value of Λ , i.e. large quantum fluctuations. This means that it is a *quantum crystal*, for which quantum effects are important. Thus, for instance, the vacancies in solid He are very mobile, they behave like quasiparticles. There is even discussion of a possible *superfluidity* of vacancies in solid He ('superfluidity in solid' – 'supersolid'). In 2004 there appeared the first experimental indications that it could indeed be true, although this question is still controversial.

Yet another manifestation of quantum effects in solid He is their importance for the exchange interaction, especially in solid ${}^3\text{He}$. The exchange interaction in solid ${}^3\text{He}$ (${}^3\text{He}$ is a fermion!) is usually due to ring exchange in the presence of vacancies, see Fig. 4.14. As a result of this process, after three steps the atoms 1 and 2 interchange their positions. This can be shown to lead to a partial ferromagnetism of solid ${}^3\text{He}$.

4.4.4 Low-dimensional solids; why is our world three-dimensional?

Problem: Using the approach described above (see, e.g. equation (4.65)), discuss what would be the situation with crystals in the one-dimensional (1d) and two-dimensional (2d) cases.

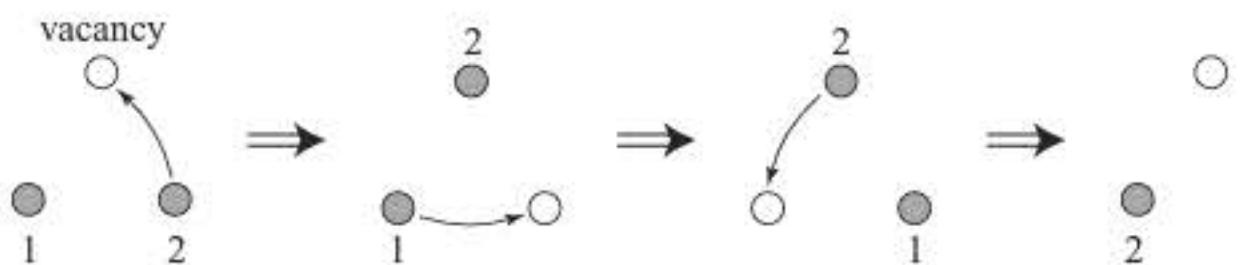


Fig. 4.1

Solution: Similar to the single oscillator case, see (4.65), in a crystal the average vibration amplitude $\langle u^2 \rangle$ is

$$\begin{aligned} \langle u^2 \rangle &= \sum_k \frac{\hbar}{M\omega_k} \left(\langle b_k^\dagger b_k \rangle + \frac{1}{2} \right) = \sum_k \frac{\hbar}{M\omega_k} \left(n_k + \frac{1}{2} \right) \\ &= \int \frac{d^d k}{(2\pi)^d} \frac{\hbar}{M\omega_k} \left(\frac{1}{e^{\omega_k/T} - 1} + \frac{1}{2} \right). \end{aligned} \quad (4.74)$$

1. First consider the case of zero temperature. At $T = 0$, $n_k = 0$, and

$$\langle u^2 \rangle = \int \frac{d^d k}{(2\pi)^d} \frac{\hbar}{M\omega_k} \cdot \frac{1}{2}. \quad (4.75)$$

1(a) At $k \rightarrow 0$, $\omega_k = sk$ (acoustic phonons, s is the sound velocity). Thus for $d = 1$ (one-dimensional system)

$$\langle u^2 \rangle \sim \int \frac{dk}{sk} , \quad (4.76)$$

i.e. $\langle u^2 \rangle$ is logarithmically divergent! This means that in a 1d system even at $T = 0$ $\langle u^2 \rangle \rightarrow \infty$, and as a result *there is no long-range crystalline order* in this case! Zero-point vibrations are so strong that they destroy the ordered state even at $T = 0$! Mathematically this divergence is due to the behaviour of the integral (4.75) at the lower limit of integration $k \rightarrow 0$, or $\omega \rightarrow 0$; this is what is called an infrared divergence. The upper limit of integration is determined by the upper edge of the spectrum, which in solids is finite, so that usually there are no divergences there. Therefore here and in the future we do not specify this upper limit of integration.

1(b) $T = 0$, 2d system. Here $d^2k \sim k dk$, and everything is OK,

$$\langle u^2 \rangle \sim \int \frac{k dk}{sk}, \quad (4.77)$$

the integral is convergent, the mean square vibration amplitude $\langle u^2 \rangle$ is finite, and in general there may exist long-range crystalline order at $T = 0$ in 2d case.

1(c) And of course everything is fine in 3d systems, where $d^3k \sim k^2 dk$

2. $T \neq 0$. Again the behaviour as $k \rightarrow 0$ is critical; thus we consider the region $\omega_k = sk < T$. This part of the spectrum exists if the spectrum is gapless. In this region

$$n_k = \frac{1}{e^{\omega_k/T} - 1} \simeq \frac{1}{\omega_k/T} = \frac{T}{sk},$$

and from (4.74) we get

$$\langle u^2 \rangle \sim \int \frac{d^d k}{\omega_k} \left(\frac{T}{\omega_k} + \frac{1}{2} \right). \quad (4.78)$$

In this expression again the most dangerous part is that close to $k = 0$ or $\omega = 0$, and we can ignore the term with $\frac{1}{2}$ in the integrand.

2(a) 1d case: $\langle u^2 \rangle$ was divergent already at $T = 0$. At $T \neq 0$ it is even more divergent – the corresponding expression for $\langle u^2 \rangle$ would be proportional to $T \int \frac{dk}{s^2 k^2}$ and would diverge not logarithmically, but linearly.

2(b) 2d case: The most dangerous term has the form

$$\langle u^2 \rangle \sim \int \frac{k dk \cdot T}{\omega_k^2} \sim T \int \frac{k dk}{s^2 k^2}, \quad (4.79)$$

i.e. in the 2d case, $\langle u^2 \rangle$ is logarithmically divergent *at any finite T*. Thus *at finite temperature there is no long-range order either in 1d or in 2d systems*.

2(c) 3d case. Here all is ‘quiet’ even at nonzero temperatures:

$$\langle u^2 \rangle \sim T \int \frac{k^2 dk}{s^2 k^2}, \quad (4.80)$$

which is convergent, so that the fluctuations are finite. Luckily for us! Otherwise everything surrounding us, and maybe we ourselves, would not be stable. Our bones, and all other tissues would ‘melt’. (If you like, this may be the physical explanation of why we exist in a three-dimensional world.)

There exists a general theorem – the *Mermin–Wagner theorem* – which states that whenever an ordering corresponds to a breaking of *continuous symmetry*, there is *no long-range order* in one-dimensional and two-dimensional cases *at any nonzero temperature*. Actually this theorem is intrinsically connected with the Goldstone theorem about the presence of gapless Goldstone excitations for a broken continuous symmetry, mentioned above in Section 2.7.4: we saw above that for the divergence of the mean square vibration amplitude $\langle u^2 \rangle$ and consequently for the instability of the crystal, it is crucial that the energy spectrum ω_k which stands in the denominator in equations (4.74)–(4.80) should be gapless, $\omega_k \rightarrow 0$ for $k \rightarrow 0$. All these features are especially important in different magnetic systems, see below, Chapter 6, but also in low-dimensional superconductors, etc.

5

General Bose systems; Bose condensation

5.1 Bose condensation

There exist in nature different kinds of bosons. These may be phonons or photons. Their number is not conserved, and consequently their chemical potential is $\mu = 0$, see the previous chapter.

We meet a different situation in the case of systems of bosons with conserved particle number. These are, for example, atoms or molecules with an *even spin*, such as ${}^4\text{He}$. For these cases in general the chemical potential is $\mu \neq 0$; it is determined by the condition (1.25), that is by the requirement that the total number of particles, or particle density, is fixed. In these cases we meet the phenomenon of *Bose condensation*.

Consider ideal noninteracting bosons with the spectrum $\varepsilon_p = p^2/2m$. From equation (3.3) we obtain the number of bosons in a unit of the phase space $d^3p/(2\pi\hbar)^3$:

$$dn_p = \frac{d^3p}{(2\pi\hbar)^3} \frac{1}{e^{(\varepsilon_p - \mu)/T} - 1}, \quad (5.1)$$

or

$$n = \frac{m^{3/2}}{\sqrt{2\pi^2\hbar^3}} \int_0^\infty \frac{\sqrt{\varepsilon} d\varepsilon}{e^{(\varepsilon - \mu)/T} - 1}. \quad (5.2)$$

To show that the phenomenon of Bose condensation considered below is intrinsically a quantum phenomenon, we keep here the Plank constant \hbar in an apparent way, and do not put it equal to 1, as elsewhere in this book. For a *given density* (given number of particles) equation (5.2) is an equation for the chemical potential $\mu(T)$. At high temperatures, $\mu(T) < 0$ (cf. (3.10) and Fig. 3.1). As discussed in the problem in Chapter 3, the chemical potential μ increases with decreasing temperature, and it tends to zero at a certain temperature T_0 , given by the condition

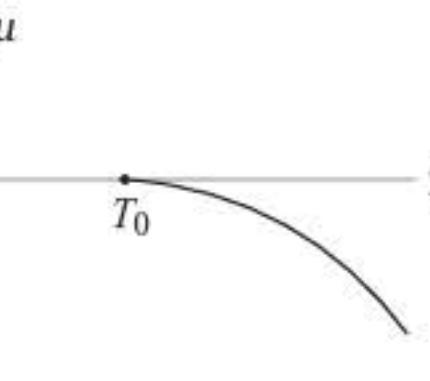


Fig. 5.1

(we use below the dimensionless variable $z = \varepsilon/T$)

$$n = \frac{m^{3/2} T^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\infty \frac{\sqrt{z} dz}{e^z - 1}, \quad (5.3)$$

see Fig. 5.1. The integral in (5.3) is finite; it can be expressed through the Riemann ζ function,

$$\int_0^\infty \frac{z^{x-1} dz}{e^z - 1} = \Gamma(x) \zeta(x), \quad (5.4)$$

where $\Gamma(x)$ is the gamma function.

Similarly, more general integrals of this type are

$$\int_0^\infty \frac{z^{x-1} dz}{e^z + 1} = (1 - 2^{1-x}) \Gamma(x) \zeta(x). \quad (5.5)$$

These formulae will also be useful for fermions later on.

In our case ($x = \frac{3}{2}$) $\Gamma(\frac{3}{2}) = \frac{\sqrt{\pi}}{2}$, $\zeta(\frac{3}{2}) \simeq 2.61$. This finally gives

$$T_0 = \frac{3.31 \hbar^2}{m} n^{2/3}. \quad (5.6)$$

As follows from the general principles of statistical mechanics, the chemical potential $\mu(T)$ for Bose particles should always be negative (or, in general, should lie below the bottom of the corresponding band); otherwise the sum over N (from 0 to ∞) in (1.33), (1.32) would not converge, see Chapter 3 (for free bosons we have to put in (1.33) $E_{nN} = \varepsilon_p N$, where $\varepsilon_p = p^2/2m$).

For $T < T_0$ there is no solution of equation (5.2) with $\mu < 0$, but that is a *necessary requirement* for a Bose system! Indeed the left-hand side of equation (5.3) is constant, whereas the right-hand side goes to zero as $T \rightarrow 0$.

The solution of this apparent paradox is the following: there is a *macroscopic occupation* of the state with $p = 0$ or with $\varepsilon = 0$. The transition from summation over discrete values of p , \sum_p , to the integral $\int d^3 p / (2\pi)^3$, which we usually do

when going from a finite system to a system with infinite volume and which we ‘automatically’ did in writing equation (5.2), is not valid in this case. Due to the macroscopic occupation of one particular state, here the state with $\mathbf{p} = 0$ (which is allowed for bosons!), the number of particles in this state is infinite, and in the corresponding summation over \mathbf{p} the first term ($\mathbf{p} = 0, \varepsilon = 0$) tends to infinity. The remaining sum $\sum_{\mathbf{p} \neq 0}$ can then be transformed into an integral in (5.3), which then can be finite. There is no contradiction any more: the number, or density of particles for all $\varepsilon > 0$, given by the expression (5.3), can indeed go to zero as $T \rightarrow 0$, but the *total* number of particles can still be conserved: the ‘missing’ particles are now *in the condensate*, in the state with $\mathbf{p} = 0$ and $\varepsilon = 0$.

Thus at $T < T_0$, where the chemical potential is identically zero, we have for the states with $\varepsilon > 0$,

$$dN_\varepsilon \Big|_{\varepsilon > 0} = \frac{V m^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\varepsilon/T} - 1}, \quad (5.7)$$

and the total number of particles with $\varepsilon > 0$ is

$$N_{\varepsilon > 0} = \int dN_\varepsilon = \frac{V(mT)^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\infty \frac{\sqrt{z} dz}{e^z - 1} = N \left(\frac{T}{T_0} \right)^{3/2}. \quad (5.8)$$

The remaining

$$N_{\varepsilon=0} = N - N_{\varepsilon > 0} = N \left(1 - \left(\frac{T}{T_0} \right)^{3/2} \right) \quad (5.9)$$

particles are in the state $\mathbf{p} = 0$ – in a condensate. This is the *Bose condensation* (or Bose–Einstein condensation).

Problem: Check what would be the situation with Bose condensation of an ideal Bose gas in one-dimensional and two-dimensional systems.

Solution: Why does Bose condensation occur in 3d systems? In equations (5.2), (5.3) (with the minimal possible value of the chemical potential $\mu = 0$) the integral *converges*. Then as $T \rightarrow 0$ we cannot fulfil the condition (5.3), and we have to put an infinite number of particles in one particular state – in a condensate.

It turns out that in 1d and 2d cases the corresponding integrals diverge, and there exists a solution of similar equations with $\mu \neq 0$ for all $T > 0$. As a result there occurs *no Bose condensation* at any nonzero temperature in 1d and 2d cases!

Indeed, the equation similar to (5.2) has, in general, schematically the form

$$n = \text{const.} \int_0^\infty \frac{\rho_d(\varepsilon) d\varepsilon}{e^{(\varepsilon-\mu)/T} - 1} \quad (5.10)$$

where at small ε the density of states $\rho_d(\varepsilon) \sim \sqrt{\varepsilon}$ for the 3d case ($d = 3$), $\rho_2(\varepsilon) \sim \rho_2 = \text{const.}$, and $\rho_1(\varepsilon) \sim 1/\sqrt{\varepsilon}$.¹

Let us make a change of variables, $\varepsilon/T = z$, $\mu/T = \tilde{\mu}$. We then obtain

$$n = Tc \int \frac{dz}{e^{z-\tilde{\mu}} - 1} \quad (2\text{d case}) \quad (5.11)$$

and

$$n = c T^{1/2} \int \frac{dz}{\sqrt{z}(e^{z-\tilde{\mu}} - 1)} \quad (1\text{d case}) \quad (5.12)$$

(c is a certain constant). The integral in (5.3) is finite even for $\tilde{\mu} = 0$, and when $T \rightarrow 0$ we have a contradiction: the left-hand side of equation (5.3) is finite, and the right-hand side goes to zero. The resolution of this paradox leads to Bose condensation. However, for the 2d case the integral in (5.11) is logarithmically divergent for $\tilde{\mu} = 0$. Thus when $T \rightarrow 0$ we can compensate the small factor T in (5.11) by the corresponding increase of the integral, choosing the appropriate dependence $\tilde{\mu}(T) (\neq 0)$ so that the product $Tc \int dz/(e^{z-\tilde{\mu}} - 1)$ remains finite (equal to n).

The same is true also for the 1d case: the integral in (5.12) diverges even more strongly than in the 2d case, which means that there should be no Bose condensation in one-dimensional systems either.

In an ideal Bose gas one can calculate all thermodynamic functions at the Bose condensation transition. It turns out that thermodynamic functions E , F , Φ , S , c_V are continuous, i.e. this transition is not even a second-order phase transition (at the second-order phase transition there is a jump in c). Here, not c_V but dc_V/dT has a jump, i.e. it is a ‘third-order’ phase transition.

But:

- (1) The situation would be different if we were to work not *at fixed volume* (or fixed density of particles), as we have until now, but *at fixed pressure*. In this case Bose condensation becomes a real second-order phase transition even for an ideal Bose gas.
- (2) The interaction between bosons is especially important – it will also change the order of the transition. This we will consider in the next section.

¹ Why do we have this form of the density of states $\rho_d(\varepsilon)$ at the edge of the spectrum $\varepsilon \rightarrow 0$? Say, for the 3d case we had initially $d^3 p$, with $d^3 p \sim p^2 dp$ which we transformed to $\rho(\varepsilon)d\varepsilon$. In the 3d case, with the spectrum $\varepsilon(p) = p^2/2m$, this gives

$$\rho(\varepsilon)|_{3\text{d}} \sim \frac{p^2}{d\varepsilon/dp} \sim \frac{p^2}{p} \sim p \sim \sqrt{\varepsilon} .$$

Similar considerations show that:

In the 2d case: $d^2 p \sim p dp = \rho(\varepsilon)d\varepsilon$, $\rho(\varepsilon) \sim p/(d\varepsilon/dp) \sim \text{const.}$

In the 1d case: $d^1 p \sim dp = \rho(\varepsilon)d\varepsilon$, $\rho(\varepsilon) \sim 1/(d\varepsilon/dp) \sim 1/p \sim 1/\sqrt{\varepsilon}$.

We will often use these asymptotics of the density of states later on.

5.2 Weakly interacting Bose gas

Let us include an interaction between bosons

$$v(\mathbf{r} - \mathbf{r}') n(\mathbf{r}) n(\mathbf{r}') = v(\mathbf{r} - \mathbf{r}') \Psi^*(\mathbf{r}) \Psi(\mathbf{r}) \Psi^*(\mathbf{r}') \Psi(\mathbf{r}') , \quad (5.13)$$

which we will treat as weak.

In the second quantization form it is convenient to work in the momentum representation. The Hamiltonian in this representation is

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{int} = \sum_{\mathbf{p}} \frac{\mathbf{p}^2}{2m} \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}} + \sum_{\mathbf{p}'\mathbf{q}} v(\mathbf{q}) \hat{a}_{\mathbf{p}+\mathbf{q}}^\dagger \hat{a}_{\mathbf{p}'-\mathbf{q}}^\dagger \hat{a}_{\mathbf{p}'} \hat{a}_{\mathbf{p}} \quad (5.14)$$

(or $\sum_{\mathbf{p}_1+\mathbf{p}_2=\mathbf{p}_3+\mathbf{p}_4} v \hat{a}_{\mathbf{p}_1}^\dagger \hat{a}_{\mathbf{p}_2}^\dagger \hat{a}_{\mathbf{p}_3} \hat{a}_{\mathbf{p}_4}$). Here, in the beginning, we keep the notation $\hat{\cdot}$ for operators.

For simplicity we take the interaction as constant, $v = U/2V$ (the volume V in the denominator is needed for normalization). Physically this corresponds to the assumption that the interaction is point-like, and that it does not depend on the angle, so-called *s*-wave scattering.

In the Bose condensed state there is a macroscopic occupation of the state $\mathbf{p} = 0$ by N_0 particles. This means that for the momentum $\mathbf{p} = 0$,

$$\hat{a}_0^\dagger \hat{a}_0 = N_0 \sim N , \quad (5.15)$$

i.e. $a_0 \sim \sqrt{N} \gg 1$. In this case the commutator

$$[\hat{a}_0, \hat{a}_0^\dagger] = \hat{a}_0 \hat{a}_0^\dagger - \hat{a}_0^\dagger \hat{a}_0 = 1 \quad (5.16)$$

is small compared with a_0 itself, and therefore commutation relations for the zero momentum operators a_0 are not important. This means that for this particular state we may treat a_0, a_0^\dagger as ordinary c-numbers and not as operators.

Note: a_0, a_0^\dagger are *complex numbers*, that is

$$\begin{aligned} a_0 &= \sqrt{N_0} e^{i\varphi} , \\ a_0^\dagger &= \sqrt{N_0} e^{-i\varphi} . \end{aligned} \quad (5.17)$$

The phase φ is in general very important, as we will discuss later. In our present discussion, however, we always have bilinear combinations of the type $a^\dagger a$, and at this stage we do not have to worry about the phase.

Thus we can treat a_0, a_0^\dagger as (large, $\sim \sqrt{N}$) c-numbers, and $\hat{a}_p, \hat{a}_p^\dagger$ as (small) operators. Let us make this substitution and keep the leading terms in the Hamiltonian,

of order N^2 and N :

$$\begin{aligned}\mathcal{H}_{\text{int}} &= \frac{U}{2V} \left[a_0^\dagger a_0^\dagger a_0 a_0 + \sum_{p \neq 0} (2\hat{a}_p^\dagger a_0^\dagger \hat{a}_p a_0 + 2\hat{a}_{-p}^\dagger a_0^\dagger \hat{a}_{-p} a_0 \right. \\ &\quad \left. + \hat{a}_p^\dagger \hat{a}_{-p}^\dagger a_0 a_0 + a_0^\dagger a_0^\dagger \hat{a}_p \hat{a}_{-p}) \right] \\ &= \frac{U}{2V} \left[a_0^4 + a_0^2 \sum_{p \neq 0} (4\hat{a}_p^\dagger \hat{a}_p + \hat{a}_p \hat{a}_{-p} + \hat{a}_p^\dagger \hat{a}_{-p}^\dagger) \right]. \quad (5.18)\end{aligned}$$

For noninteracting particles at $T = 0$ all particles are in the condensate, $N_0 = N$. For weakly interacting bosons *almost* all particles will be there, $N_0 \sim N$, $N - N_0 \ll (N, N_0)$. In the second term in (5.18) we can put $a_0^2 = N$ (the second term is already of first order in the small parameter, due to the presence of $a_p^\dagger a_p$). The term a_0^4 should be treated more accurately, keeping all terms of the same order. As

$$a_0^2 + \sum_{p \neq 0} \hat{a}_p^\dagger \hat{a}_p = N, \quad (5.19)$$

we should write

$$a_0^4 = \left(N - \sum_{p \neq 0} \hat{a}_p^\dagger \hat{a}_p \right)^2 = N^2 - 2N \sum_p \hat{a}_p^\dagger \hat{a}_p + \sum_{p, p' \neq 0} \hat{a}_p^\dagger \hat{a}_p \hat{a}_{p'}^\dagger \hat{a}_{p'} . \quad (5.20)$$

The last term here is only of order 1, thus it can be omitted. In effect equation (5.18) becomes

$$\mathcal{H}_{\text{int}} = \frac{U}{2V} \left[N^2 + N \sum_{p \neq 0} (2\hat{a}_p^\dagger \hat{a}_p + \hat{a}_p^\dagger \hat{a}_{-p} + \hat{a}_p \hat{a}_{-p}) \right], \quad (5.21)$$

and the full Hamiltonian (5.14) takes the form

$$\mathcal{H} = \frac{UN^2}{2V} + \frac{1}{2} \sum_{p \neq 0} \left[\left(\frac{p^2}{2m} + \frac{UN}{V} \right) (\hat{a}_p^\dagger \hat{a}_p + \hat{a}_{-p}^\dagger \hat{a}_{-p}) + \frac{UN}{V} (\hat{a}_p^\dagger \hat{a}_{-p}^\dagger + \hat{a}_p \hat{a}_{-p}) \right]. \quad (5.22)$$

The expression (5.22) is nondiagonal in the operators $\hat{a}_p^\dagger, \hat{a}_p$. But it is a quadratic form and can be easily diagonalized using the so-called *Bogolyubov canonical transformation*, or $u-v$ transformation:

$$\begin{aligned}\hat{a}_p &= u_p b_p + v_p b_{-p}^\dagger \\ \hat{a}_p^\dagger &= u_p b_p^\dagger + v_p b_{-p}\end{aligned} \quad (5.23)$$

(here we assume the coefficients u_p, v_p to be real).

Problem: Write down b^\dagger, b in terms of a^\dagger, a .

Solution: $b_p = u_p a_p - v_p a_{-p}^\dagger$ (u_p, v_p are even functions of p), and the corresponding equation for b_p^\dagger is obtained from this one by Hermitian conjugation.

We require that (we now omit the notation $\hat{\cdot}$ for operators) b^\dagger, b are bosons:

$$b_p b_{p'}^\dagger - b_{p'}^\dagger b_p = \delta_{pp'}, \quad b_p b_{p'} - b_{p'} b_p = 0. \quad (5.24)$$

In order for this to hold, the coefficients u_p, v_p should satisfy the condition

$$u_p^2 - v_p^2 = 1. \quad (5.25)$$

Thus we can write

$$\begin{aligned} a_p &= \frac{1}{\sqrt{1 - A_p^2}} (b_p + A_p b_{-p}^\dagger) \\ a_p^\dagger &= \frac{1}{\sqrt{1 - A_p^2}} (b_p^\dagger + A_p b_{-p}), \end{aligned} \quad (5.26)$$

where $u_p = 1/\sqrt{1 - A_p^2}$, $v_p = A_p/\sqrt{1 - A_p^2}$ (or, equivalently, we can write down $u_p = \cosh \alpha_p$, $v_p = \sinh \alpha_p$, and express everything through α_p). We can determine the coefficients u_p, v_p , or A_p from the condition that the nondiagonal terms in (5.22), after making the canonical transformation, drop out. This gives the equation

$$\left(\frac{p^2}{2m} + nU \right) 2A_p + nU(1 + A_p^2) = 0, \quad (5.27)$$

or

$$A_p = \frac{1}{nU} \left(-\frac{p^2}{2m} - nU + \sqrt{\left(\frac{p^2}{2m} + nU \right)^2 - (nU)^2} \right), \quad (5.28)$$

where we have introduced the density $n = N/V$. The Hamiltonian then takes the form

$$\begin{aligned} \mathcal{H} &= \frac{UN^2}{2V} - \frac{1}{2} \sum_{p \neq 0} \left[\left(\frac{p^2}{2m} + nU \right) - \sqrt{\left(\frac{p^2}{2m} + nU \right)^2 - (nU)^2} \right] \\ &\quad + \sum_{p \neq 0} \sqrt{\left(\frac{p^2}{2m} + nU \right)^2 - (nU)^2} b_p^\dagger b_p. \end{aligned} \quad (5.29)$$

The first two terms give the energy of the ground state at $T = 0$, and the third term describes *elementary excitations* (cf. phonons, (4.26)),

$$\sum_{p \neq 0} \varepsilon_p b_p^\dagger b_p, \quad (5.30)$$

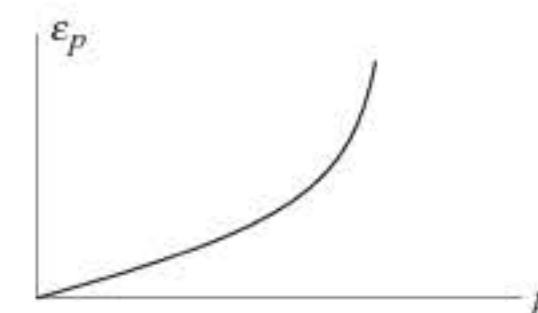


Fig. 5.2

with the spectrum

$$\varepsilon_p = \sqrt{\left(\frac{p^2}{2m} + nU\right)^2 - (nU)^2} = \begin{cases} \sqrt{\frac{nU}{m}} \cdot p & (p \rightarrow 0) \\ \frac{p^2}{2m} & (\text{large } p). \end{cases} \quad (5.31)$$

Thus the elementary excitations in a weakly interacting Bose condensed system have the character of *sound* at small momenta p (Bogolyubov sound), and they continuously go over to *free particles* with the spectrum $p^2/2m$ at large p , see Fig. 5.2.

We should make here several remarks:

- The sound velocity (5.31) coincides with the standard sound velocity of a gas with density $n = N/V$ and interaction U .
 - One can find the coefficients of the canonical transformation (5.23) or (5.26) not from the condition that nondiagonal terms in the Hamiltonian cancel, but from the condition of the *minimum* of the ground state energy.

Problem: Check this: put (5.26) in (5.22), collect the terms without operators, and minimize the resulting expression in $A_{\mu\nu}$.

- One can calculate the total energy of this weakly interacting Bose gas. Usually one expresses all the quantities through the scattering length a given by

$$U = \frac{4\pi}{m} a \quad (5.32)$$

(a is the scattering amplitude for energy tending to zero). The resulting energy is given by the expression

$$\frac{E}{V} = \frac{2\pi a}{m} n^2 \left[1 + \frac{128}{15\sqrt{\pi}} a^{3/2} n^{1/2} \right] \quad (5.33)$$

(T D Lee, C N Yang, 1957)

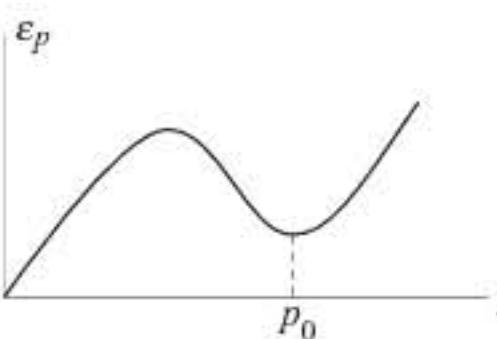


Fig. 5.3

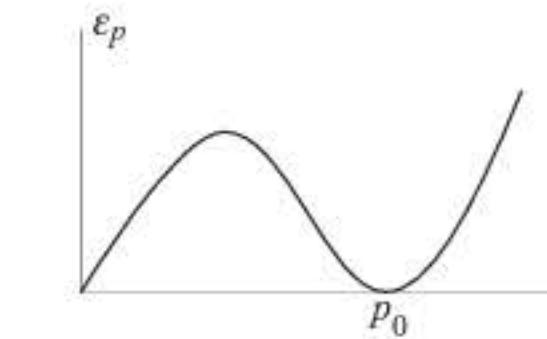


Fig. 5.4

From (5.33) one can find the sound velocity in the usual way, as we are doing in gases:

$$s = \sqrt{\frac{V^2}{mN} \frac{\partial^2 E}{\partial V^2}} = \frac{\sqrt{4\pi an}}{m}, \quad (5.34)$$

which coincides with (5.31) (taking into account (5.32)).

5.3 Bose condensation and superfluidity

The main system for which, for a long time, one applied the concept of Bose condensation (before the recently observed Bose condensation of optically trapped supercooled atoms) is superfluid ${}^4\text{He}$. ${}^4\text{He}$ atoms are *bosons*, and helium remains liquid down to $T = 0$ (see Section 4.4.3). It goes over to a superfluid state at $T_c = 2.4\text{ K}$ (P. L. Kapitza). Superfluidity in ${}^4\text{He}$ is attributed to a Bose condensation of He atoms into the state with $p = 0$.

There exists in real helium one important difference relative to the previous treatment: He atoms interact strongly, as a result of which there is a number of modifications and because of which there exists actually no microscopic theory of superfluid ${}^4\text{He}$ (there is no small parameter – weak interaction – which we have used in the theoretical treatment above). Nevertheless, the basic concepts described above apply, with some modifications, also to this case. The main modifications are:

1. The actual number of atoms in the condensate N_0 is finite, but even at $T = 0$ it is rather small, $N_0/N \sim 8\text{--}10\%$ at most.
2. The spectrum of elementary excitations (originally postulated in a slightly different form by Landau) has the form shown in Fig. 5.3. As $p \rightarrow 0$ the excitations remain phonons (spectrum linear in p). At larger p there exists an extra minimum – the so-called *rotons*. Physically the roton minimum is a consequence of *strong interaction* in the liquid; it reflects the tendency to crystallization (under pressure the roton minimum becomes deeper, and when ε_{p_0} approaches zero, Fig. 5.4, the corresponding mode becomes *unstable*, and there appears a positive increment, i.e. a large standing wave with wavevector p_0 , or with period $a = \hbar/p_0$, will develop; this signals the formation of a crystal). Cf. the discussion of the reverse process of melting in Section 4.4.3, Fig. 4.13(a).

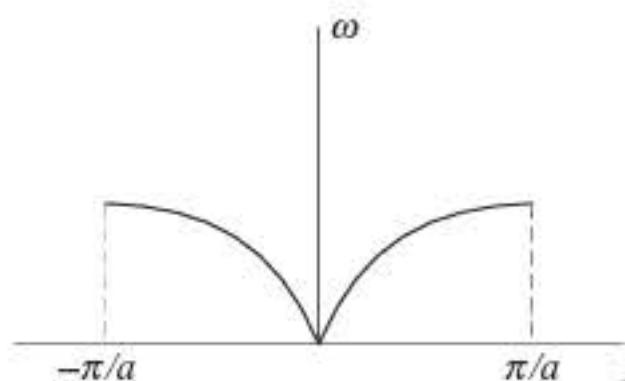


Fig. 5.5

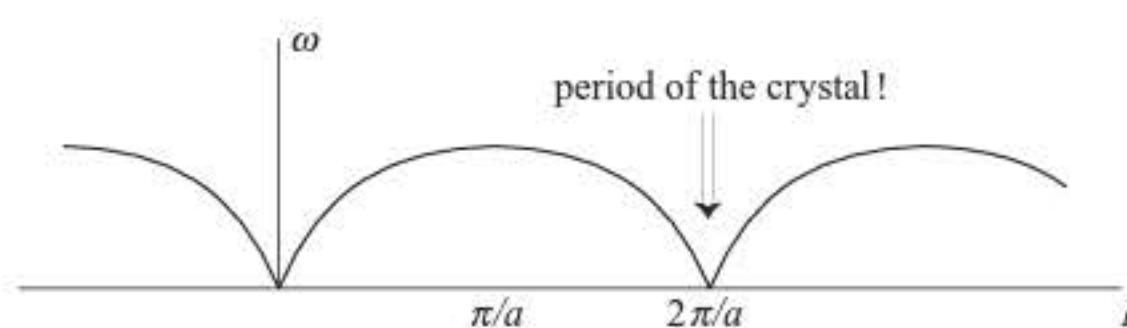


Fig. 5.6

Problem: Compare this situation with ordinary phonons in crystals.

Solution: For an ordinary crystal with period a the phonon spectrum in the first Brillouin zone has the form schematically shown in Fig. 5.5. In the extended zone scheme it may be represented as shown in Fig. 5.6, with the plot extended to larger p . If we do not have real long-range crystalline order, but only short-range order typical for liquids, the spectrum would not go to zero at $p = 2\pi/a$, but would retain a minimum at this wavevector (and of course would acquire an imaginary part, i.e. would be strongly damped). Thus there is a close analogy between this situation and that of rotons in liquid helium shown in Figs. 5.3 and 5.4; that is, the spectrum of Fig. 5.4 with the roton minimum is not something specific to liquid ^4He , but in principle such a minimum could exist in any liquid close to the melting point. An important difference is that in normal liquids these excitations with short wavelengths are usually extremely strongly damped, so that there is not much sense in speaking about them there, whereas they are well-defined excitations in the superfluid phase of ^4He .

These arguments are of course only qualitative. But one can make them more accurate. R. Feynman has shown (1954) that the spectrum of elementary excitations in ^4He can be written as

$$\varepsilon_p = \frac{p^2}{2mS(p)}, \quad (5.35)$$

where $S(p)$ is the static structure factor describing spatial correlation of atoms in a liquid. At small p $S(p) = p/2ms$, where s is the velocity of Bogolyubov sound, $s = \sqrt{nU/m}$, see (5.31), so that the spectrum (5.35) goes over to (5.31). For large p , however, $S(p)$ has a maximum at the value $p_0 \sim \hbar/d_0$ where d_0 is the typical distance between He atoms (of the order of the lattice parameter of solid ^4He at high pressures); this tells us that the probability of finding an atom at distance d from a given atom is a maximum at $d \sim d_0$. Correspondingly, the spectrum (5.35) would develop a minimum at $p \sim p_0$ which is nothing else but the roton minimum of Fig. 5.3.

3. An important point: in Bose condensation, and in superfluidity, the order parameter η (cf. (2.1)) is $\eta \sim \langle \hat{a}_0 \rangle$ (it is zero above T_c , and nonzero in the Bose condensed phase). This is a *complex* scalar (see the remark (5.17) in Section 5.2):

$$\langle \hat{a}_0 \rangle = a_0 = \sqrt{N_0} e^{i\varphi}. \quad (5.36)$$

At the phase transition, at $T < T_c$, its *phase* becomes fixed, i.e. the superfluid state is a *coherent* state (phase coherence). But the *number* of particles in the condensate N_0 fluctuates. The operators \hat{N} and $\hat{\varphi}$ are conjugate variables in quantum mechanics, like \hat{x} and \hat{p} ; they obey the uncertainty relation (Heisenberg relation)

$$\Delta N_0 \Delta \varphi \simeq \hbar. \quad (5.37)$$

Bose condensation is thus a phase transition with breaking of a continuous symmetry – gauge symmetry (fixing of the phase φ which is a continuous variable). Correspondingly, Bogolyubov sound is the *Goldstone mode* for this broken symmetry. This also gives another explanation of the absence of Bose condensation at any $T \neq 0$ in the 1d and 2d systems discussed in the Problem in Section 5.1: phase fluctuations caused by the excitation of this gapless mode are so strong that in the 1d and 2d cases they destroy the long-range order at any finite temperature. This is yet another application of the Mermin–Wagner theorem mentioned at the end of Chapter 4.

4. The fact that the order parameter in Bose condensed and superfluid systems is a complex scalar (5.36) permits one also to establish the correspondence with certain other systems with the same symmetry, notably the anisotropic spin system – the so-called *xy* model, in which spins are confined to the *xy*-plane. In this case the order parameter takes the form $s = |s|e^{i\varphi}$, where the angle φ determines the orientation of spin in the *xy*-plane (see below, Section 6.4.3). One can use this analogy by ‘borrowing’ the concepts and results from one field and applying them to the other. Thus one often speaks now about Bose condensation of magnons, although one must be careful in applying this

- concept. Also, the concept of vortices, first introduced in superfluid ^4He , is now ‘translated’ to magnetic vortices, see Section 6.4.3(b), p. 118.
5. Generalizing the description of a Bose condensed state to the case with spatial inhomogeneities (cf. Section 2.4 above), we should treat the order parameter (5.36) as a function of position. The most important is the change in space of the phase $\varphi(\mathbf{r})$. It turns out that the gradient of the phase determines the local superfluid velocity in the system:

$$\mathbf{v}_s = \frac{\hbar}{m} \nabla \varphi . \quad (5.38)$$

Actually the collective mode we have described above – Bogolyubov sound – is predominantly the oscillations of the *phase* φ and velocity \mathbf{v}_s (or local currents) in the liquid.

5.3.1 Landau criterion of superfluidity

Why is ^4He superfluid? The answer to this question is given by the *Landau criterion of superfluidity*: it turns out that for the excitation spectrum of Fig. 5.3 there is no dissipation at velocities not exceeding a certain critical value. The corresponding arguments are straightforward, but require a bit of concentration.

Suppose that a liquid flows with velocity \mathbf{v} through a capillary (thin tube). The elementary processes leading to *friction* are the creation of excitations in the liquid, one after another. These excitations should reduce the total momentum of the flowing liquid. If such processes are allowed, friction would appear, and there would be no superfluidity.

Let us first consider this situation in the system of coordinates where the liquid is at rest but the walls of the tube move with velocity $-\mathbf{v}$. Suppose that one (the first) such an excitation appears, with momentum \mathbf{p} and energy $\varepsilon(\mathbf{p})$. Now let us go back to the laboratory coordinate frame, in which the liquid moves with velocity \mathbf{v} . In this coordinate system the total energy of the liquid with one excitation is²

$$E = \frac{Mv^2}{2} + \varepsilon(\mathbf{p}) + \mathbf{p} \cdot \mathbf{v} = \frac{Mv^2}{2} + \delta E , \quad \text{where } \delta E = \varepsilon(\mathbf{p}) + \mathbf{p} \cdot \mathbf{v} . \quad (5.39)$$

Here $Mv^2/2$ is the initial kinetic energy of the moving liquid, and δE is the change in the total energy due to the creation of the excitation. For such a process to occur we need $\delta E < 0$, otherwise the excitation would cost us energy, and such

² This follows from the well-known formulae of mechanics: energy and momentum are transformed from one reference frame to another, moving with velocity \mathbf{v} , as $E = E_0 + \mathbf{p}_0 \cdot \mathbf{v} + Mv^2/2$, $\mathbf{p} = \mathbf{p}_0 + M\mathbf{v}$, where E_0 and \mathbf{p}_0 are the energy and momentum in the frame with the liquid at rest. In our case $E_0 = \varepsilon(\mathbf{p})$, $\mathbf{p}_0 = \mathbf{p}$, which gives (5.39).

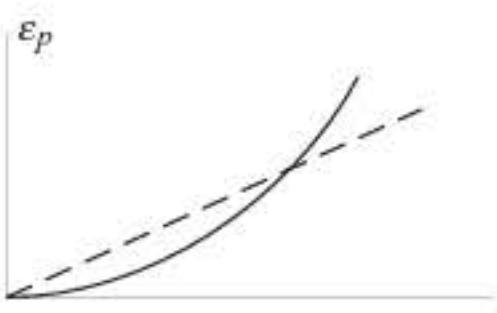


Fig. 5.7

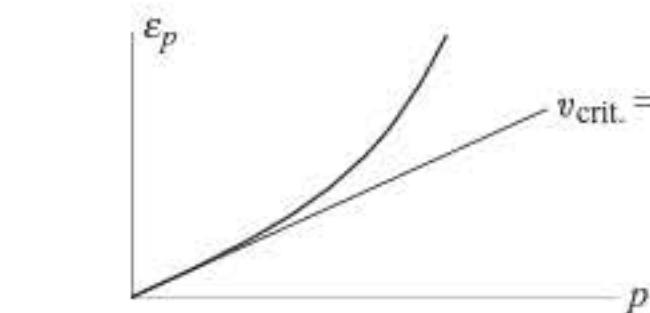


Fig. 5.8

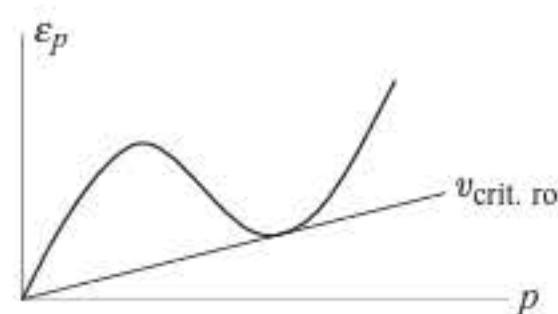


Fig. 5

an excitation would not be created spontaneously. But for that p should, first of all, be antiparallel to v , and, most important, the change of the energy δE (5.39) should be negative, i.e. $\varepsilon - pv < 0$. Thus for such a process (friction) to begin, the velocity of the liquid should satisfy the condition

$$v > \frac{\varepsilon(p)}{p} \quad (5.40)$$

(at least for some p). That is, the excitations can be created only if the velocity of the flow exceeds the *critical velocity*.

$$v \geq v_{\text{crit}} = \left(\frac{\varepsilon}{p} \right)^{1/p}, \quad (5.41)$$

starting from which the flow can slow down, and dissipation, or friction, appears.

If we have a usual liquid or gas, consisting of noninteracting particles, the excitation spectrum is $\varepsilon_p = p^2/2m$, Fig. 5.7, and there is *no* superfluidity at any velocity (the critical velocity $v_{\text{crit}} = 0$). But if the spectrum has the form shown in Fig. 5.8, see equation (5.31), then there exists a finite critical velocity $v_{\text{crit}} = s$, which in this case is equal to the sound velocity; for smaller v such excitations cannot be formed, and the motion is dissipationless, i.e. superfluid.

For real ${}^4\text{He}$ the sound velocity $s = 2.4 \times 10^4 \text{ cm/sec}$, and this condition would give the critical velocity which is too large. Experimentally dissipation starts much earlier. One of the possible explanations is that the real spectrum looks as shown in Fig. 5.9 and the critical velocity could be determined by *rotons*. Actually even

this velocity is too large, and the excitations determining the critical velocity in the bulk helium in most of the actual experiments are special topological excitations – vortices (similar to smoke rings from a pipe) – see below, Section 5.3.2. Only in cases when the formation of vortices is suppressed due to a restricted geometry, for example in thin films of ^4He or in very thin capillaries, can we reach the critical velocity determined by rotons, which is indeed much higher than in bulk ^4He .

We have seen that if the velocity is below a certain critical value, new excitations cannot be spontaneously created in the moving liquid. This conclusion is valid not only at $T = 0$ and not only for the ground state. However, at finite temperature there are always present thermally excited elementary excitations in the liquid. And when the liquid flows through a capillary, these excitations can collide with the walls and can change their momentum. Therefore these excitations, which initially ‘flow’ with the liquid, will gradually slow down, exactly like ordinary gas flowing through a tube. In effect it looks as though a part of the liquid experiences friction, whereas the remaining part moves without any resistance. In other words, it seems as though there exist two components in the liquid; a normal component and a superfluid one, with the total density $\rho = \rho_{\text{norm}} + \rho_s$. Such a two-fluid picture (L. Tisza) gives a very useful phenomenological description of many properties of superfluid helium. It is also widely used for the description of many properties of superconductors. But one has to realize that it is only a way to interpret the properties of these systems; in no way should we take this picture too literally and think that indeed some of the atoms are moving without dissipation, whereas the others experience friction. In fact, it is the same atoms which display both types of behaviour, and the real meaning of these two ‘fluids’ is the one explained above: the normal ‘fluid’ consists of elementary excitations – collective modes of the liquid as a whole.

5.3.2 Vortices in a superfluid

As mentioned in the previous section, there is yet another very important type of excitation in a superfluid liquid: topological excitations, or vortices. If one starts to rotate a vessel containing a superfluid, initially the liquid remains at rest. However, starting from a certain critical angular velocity, a vortex will be formed in the liquid: a circular motion of the superfluid around a certain line which is called the vortex core. As a result some circulation is transferred to the liquid, i.e. the liquid starts to participate in the rotation. In a cylindrical vessel vortices start at the bottom and go all the way up to the upper surface of the liquid, Fig. 5.10; they cannot be ‘interrupted’ and cannot simply end inside the liquid.

Using equation (5.38), we can show that the circulation of velocity around a vortex should be quantized. Let us integrate (5.38) over a contour c surrounding

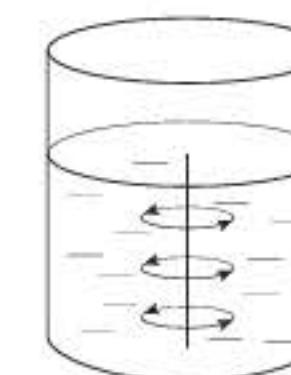


Fig. 5.10

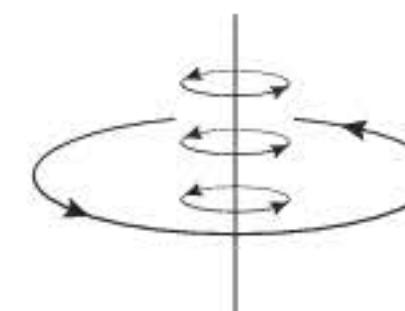


Fig. 5.11

the vortex, Fig. 5.11. The circulation is

$$\oint \mathbf{v}_s \cdot d\mathbf{l} = \frac{\hbar}{m} \Delta\varphi , \quad (5.42)$$

where $\Delta\varphi$ is the total change of phase along the contour c . However the total wavefunction of the superfluid has to be a single-valued function, which means that $\Delta\varphi = 2\pi n$, where $n = 0, \pm 1, \pm 2, \dots$. Thus the circulation is

$$\oint \mathbf{v}_s \cdot d\mathbf{l} = \frac{\hbar}{m} 2\pi n , \quad (5.43)$$

i.e. it is indeed quantized. Such quantization is a manifestation of the quantum nature of superfluidity and confirms its interpretation as a ‘macroscopic quantum phenomenon’ (the whole system is described by one quantum wavefunction $\Psi(\mathbf{r}) = \sqrt{N_0} e^{i\varphi(r)}$). The above-mentioned fact that the vortex cannot end inside the liquid is actually connected with this property: if it were to, we could continuously deform the contour c in equation (5.43) in such a way that it would be ‘above’ the end of the vortex, after which we could contract it to zero, with zero circulation – in contrast to the finite (quantized) value (5.43) we started with. This is why the vortices are actually *topological excitations*.

The situation may be much more intricate in superfluid systems with a more complicated order parameter, e.g. such as that of liquid ^3He . In these cases the space of the order parameter is different from the case of ^4He (which lives ‘on the circle’ $\eta = |\eta|e^{i\varphi}$ with $0 \leq \varphi \leq 2\pi$). Consequently the types and properties of

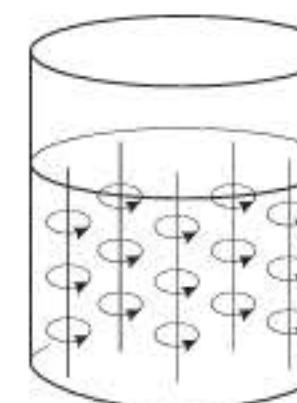


Fig. 5.12

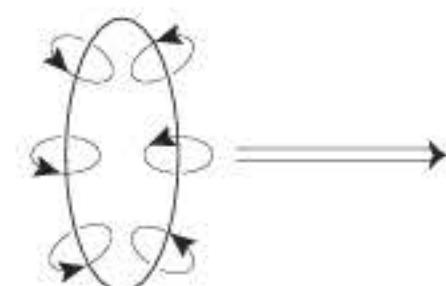


Fig. 5.13

topological excitations in such systems, including vortices, may be very different from those of ^4He .

As mentioned above, in most of the real experiments the critical velocity in liquid helium is determined not by the sound velocity and not even by rotons, but by excitation of vortices in moving liquid He. Vortices are created before the critical velocity for excitations of sound quanta or rotons is reached, and their creation and motion leads to dissipation. In a rotating cylinder vortices are parallel to the rotation axis, Fig. 5.12. In a liquid flowing through a capillary the vortices form vortex rings, Fig. 5.13, very much like smoke rings from a pipe (as we mentioned before, vortices cannot be simply interrupted inside a liquid: they either end at the surface of the liquid, or form closed loops, as in these rings).

Many features and phenomena described above are also met (and are even much better known) in superconductors. Thus, the general description of superconductivity as a macroscopic quantum phenomenon is rather similar to that given above; the Landau criterion of the existence of supercurrents without dissipation works there as well, and the notion of quantized vortices leading to dissipation plays a very important role in the physics and application of superconductivity (in the so-called type-II superconductors, to which all practically important superconducting materials, including high-temperature superconductors, belong). Theoretical work by Abrikosov and Ginzburg laying the foundations of the description of these systems earned them a Nobel Prize in 2003.

6

Magnetism

6.1 Basic notions; different types of magnetic response

I will again start by briefly recalling the basic notions from general physics and quantum mechanics about different sources and types of magnetic response, which are actually covered in most of the corresponding textbooks. For simplicity I will mostly ignore in this chapter the details of atomic structure leading to different contributions to atomic magnetic moments (e.g. orbital contributions, with the often important role of spin-orbit coupling), see e.g. Goodenough (1963) and Kugel and Khomskii (1982), and will consider only the spin contribution, mostly illustrating the results on the example of spin $\frac{1}{2}$. More detailed treatments can be found, e.g. in the books by White (2006) and Yosida (1996), and in many others.

The Hamiltonian of electrons in a magnetic field has the form

$$\mathcal{H} = \frac{1}{2m} \left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A} \right)^2 - \frac{\mu}{|\mathbf{S}|} \mathbf{S} \cdot \mathbf{H}. \quad (6.1)$$

The first term in this Hamiltonian describes the response due to the orbital motion of electrons, and the second one is due to the spin of the electron. Here μ is the magnetic moment of spin \mathbf{S} . [Often the last term in the Hamiltonian (6.1) is written as $g\mu_B \mathbf{S} \cdot \mathbf{H}$, where $\mu_B = e\hbar/2mc$ is the Bohr magneton, and g is the so-called g -factor, which for free electron spins is $g_{\text{spin}} = 2$ (and for orbital moments $g_{\text{orb}} = 1$).] In general the vector potential \mathbf{A} is a function of the coordinate, $\mathbf{A} = \mathbf{A}(\hat{\mathbf{x}})$, and it does not commute with the momentum $\hat{\mathbf{p}}$, $\hat{\mathbf{p}} \cdot \mathbf{A} - \mathbf{A} \cdot \hat{\mathbf{p}} = -i\hbar \operatorname{div} \mathbf{A}$. However, we can make a gauge transformation of \mathbf{A} , and if we choose a gauge such that $\operatorname{div} \mathbf{A} = 0$, the commutator of $\hat{\mathbf{p}}$ and \mathbf{A} will be zero. For example, we can take

$$\mathbf{A} = \frac{1}{2} [\mathbf{H} \times \mathbf{r}]. \quad (6.2)$$

Then

$$\mathcal{H} = \frac{1}{2m} \hat{\mathbf{p}}^2 - \frac{e}{mc} \hat{\mathbf{p}} \cdot \mathbf{A} + \frac{e^2}{2mc^2} \mathbf{A}^2 - \frac{\mu}{|\mathbf{S}|} \mathbf{S} \cdot \mathbf{H}. \quad (6.3)$$

As to the magnetic response of various systems, there exist different situations:

- (1) Closed shells with orbital moment $L = 0$ and spin $S = 0$. In the ground state $\langle 0 | \mathbf{p} \cdot \mathbf{A} | 0 \rangle = 0$, and here first of all the third term in (6.3) works (see also (2) below); the energy is

$$\Delta E = \langle \mathcal{H} \rangle = \frac{e^2}{2mc^2} \langle \mathbf{A} \rangle^2 = \frac{e^2}{8mc^2} \sum_a [\mathbf{H} \times \mathbf{r}_a]^2 = \frac{e^2}{12mc^2} H^2 \sum_a \bar{r}_a^2 \quad (6.4)$$

after averaging over angles, i.e. over all directions of \mathbf{r} .

The energy of a system in a magnetic field is

$$\Delta E = -\mathbf{M} \cdot \mathbf{H}, \quad \text{i.e.} \quad \mathbf{M} = -\frac{\partial \Delta E}{\partial \mathbf{H}}. \quad (6.5)$$

As the magnetic moment is $\mathbf{M} = \chi \mathbf{H}$, the susceptibility for N such atoms with charge Z is, using (6.4),

$$\chi = -\frac{e^2}{6mc^2} \sum_a \bar{r}_a^2 \quad \left(= -\frac{Ze^2 N \langle r^2 \rangle}{6mc^2} \right). \quad (6.6)$$

This is the standard *diamagnetism* – classical diamagnetic screening of the external field. Note again that it is due to the term \mathbf{A}^2 in the Hamiltonian (6.3); this is also the case in other situations, e.g. in the famous Meissner effect, the ideal diamagnetism of superconductors.

- (2) The term in (6.3) linear in \mathbf{A} can admix the excited states with $L \neq 0$ to the ground state: in second order in perturbation theory (using the second term in (6.3) as a perturbation) we then have the change of the energy in the magnetic field

$$\Delta E = -\sum_n \frac{\left| \langle 0 | \mathbf{H} \cdot \mathbf{M}_L | n \rangle \right|^2}{\varepsilon_n - \varepsilon_0} \quad (6.7)$$

(here we have used that $\mathbf{M} = \frac{e}{2mc} \hat{\mathbf{L}}$, $\hat{\mathbf{L}} = \mathbf{r} \times \mathbf{p}$, and we have used the gauge (6.2)).

This would give *positive* susceptibility, which in a first approximation does not depend on temperature. This is the temperature-independent *Van Vleck paramagnetism*.¹

The two terms described above, the usual diamagnetism and Van Vleck paramagnetism, are always present in all materials, even in those with much stronger magnetic response due to localized spins; these contributions are responsible

¹ Note that in certain cases, where there exist low-lying magnetic excited states close to the nonmagnetic ground state, the Van Vleck paramagnetism may become temperature dependent. This, for example, is the case for many compounds containing Eu^{3+} .

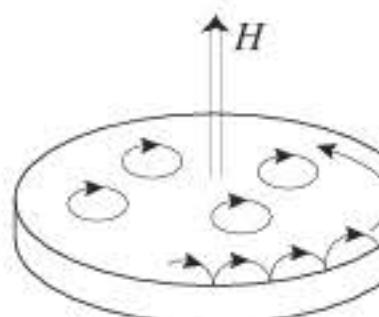


Fig. 6.1

for the temperature-independent ‘background’ in magnetic susceptibility. In metals there are two extra contributions to the magnetic response.

- (3) Free electrons in metals. There exists a diamagnetic contribution to the susceptibility due to the orbital motion of electrons, which is called *Landau diamagnetism*:

$$\chi_{\text{Landau}} = -\frac{(N/V)e^2}{4mc^2 p_F^2} = -\frac{e^2 p_F}{12\pi^2 mc^2}. \quad (6.8)$$

The calculations giving this expression are not simple; the physics is connected with the boundary effects. In *classical physics* one can show that there is no magnetism in thermodynamic equilibrium (Bohr–van Leeuwen theorem): if we apply an external field H to a metal with classical electrons, the diamagnetic currents created inside the sample will be compensated by the surface current along the boundary flowing in the opposite direction, see Fig. 6.1. In *quantum mechanics* there is no such compensation, which results in Landau diamagnetism.

The physical reasons underlying the Bohr–van Leeuwen theorem may be understood if we recall that classically the force acting on an electron in a magnetic field is the Lorentz force $\mathbf{F} \sim \mathbf{H} \times \mathbf{v}$, i.e. it is perpendicular to the velocity \mathbf{v} and consequently it does not change the energy of the electron. In effect the magnetic field does not enter the thermodynamic potentials and does not induce a magnetic response in thermodynamic equilibrium. In quantum mechanics this is no longer true.

- (4) Spins of electrons in metals give rise to *Pauli paramagnetism*. Its origin is the splitting and shift of the spin-up and spin-down subbands in a magnetic field, $\epsilon(H) = \epsilon_0 \pm \mu H$. This leads to the redistribution of electrons between these subbands, see Fig. 6.2, because the chemical potential of both these components should be the same. As a result there appears a net polarization of conduction electrons, proportional to the magnetic field, $\mathbf{M} = \chi_{\text{Pauli}} \mathbf{H}$. Straightforward calculations give for χ_{Pauli} the expression

$$\chi_{\text{Pauli}} = \mu_B^2 \rho(\epsilon_F) = \frac{e^2 p_F}{4\pi^2 mc^2}. \quad (6.9)$$

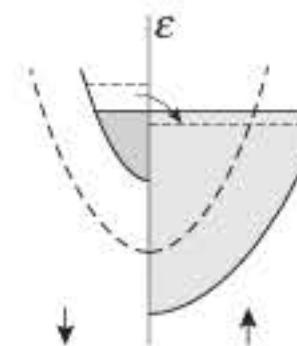


Fig. 6.2

It turns out that the Landau diamagnetism discussed above is determined by the same parameters as in equation (6.9), i.e. by the density of states at the Fermi level $\rho(\varepsilon_F)$, and is equal to

$$\chi_{\text{Landau}} = -\frac{1}{3} \chi_{\text{Pauli}} . \quad (6.10)$$

(5) Localized electrons (localized spins, localized magnetic moments). Why localized electrons exist in certain systems will be discussed later, especially in Chapters 12 and 13; briefly speaking, this is connected with the existence of partially filled inner shells and with strong electron-electron interactions. Typical systems of this type are those containing the following:

- *Transition metals with partially filled d shells.* In the 3d series (Mn, Fe, Co, Ni, ...) the d electrons are relatively strongly localized, especially in compounds such as oxides, e.g. NiO, MnO, Fe₂O₃, etc. In the 4d and 5d elements (Ru, Ir, Pd, Pt, ...) the d electrons are usually less localized than those of the 3d series.
- *Rare earth elements*, containing 4f electrons (Gd, Eu, Dy, ...). The 4f electrons are almost always very strongly localized (see, however, Section 13.3).
- *Actinides* with 5f electrons (U, Np, Am, ...). From the point of view of electron localization these are rather analogous to the 3d transition metals. However, there is one important difference here: due to the much larger atomic mass the relativistic effects in actinides, notably the spin-orbit interaction, are much stronger than in transition metals (this also applies to rare earths).

The main interaction of localized electrons with the magnetic field is the Zeeman term,

$$-\mathbf{M} \cdot \mathbf{H} = -g\mu_B \mathbf{S} \cdot \mathbf{H} . \quad (6.11)$$

This interaction gives rise to *paramagnetism of localized spins*; see the next section.

6.1.1 Susceptibility of noninteracting spins

Here we consider the susceptibility of localized magnetic moments without an exchange interaction between them. First we present the classical treatment, using Boltzmann statistics. Suppose we have a collection of atoms with magnetic moment \mathbf{M} . In the magnetic field \mathbf{H} the probability of finding the moment \mathbf{M} is

$$n(\mathbf{M}) \sim \exp\left(\frac{\mathbf{M} \cdot \mathbf{H}}{T}\right) \quad (k_B = 1) \quad (6.12)$$

(see (1.1), with the energy (6.5)). From this we find the average moment

$$\langle \mathbf{M} \rangle = \frac{\int \mathbf{M} e^{\mathbf{M} \cdot \mathbf{H}/T} d\Omega}{\int e^{\mathbf{M} \cdot \mathbf{H}/T} d\Omega}, \quad (6.13)$$

where Ω is the solid angle. From (6.13), the magnetic susceptibility is

$$\chi_0 = N \left\langle \frac{\partial \mathbf{M}}{\partial \mathbf{H}} \right\rangle = \frac{N}{T} \langle \mathbf{M}^2 \rangle = \frac{1}{3} \frac{Ng^2 \mu_B^2 S(S+1)}{T}, \quad (6.14)$$

which is the well-known Curie law; the index ‘0’ denotes the fact that we are dealing with noninteracting spins. Here we have already used the connection $\mathbf{M} = g\mu_B \mathbf{S}$, see equation (6.11), and also the fact that in quantum mechanics $\langle \mathbf{S}^2 \rangle = S(S+1)$. The factor $\frac{1}{3}$ comes from averaging over all directions, see e.g. Kittel (1987).

The susceptibility per unit volume is thus

$$\chi_0 = \frac{N g^2 \mu_B^2 S(S+1)}{V 3T} \equiv \frac{C}{T}, \quad (6.15)$$

where C is called the Curie constant.

Consider now the quantum case. Instead of the integral over all orientations of \mathbf{M} in (6.11) we have to take a *sum* over possible quantum states S^z ($M^z = g\mu_B S^z$, $-S \leq S^z \leq S$).

Thus for $S = \frac{1}{2}$ we would have (for the field in the z -direction and for the moment parallel to the field; we omit the index ‘ z ’ below):

$$M = g\mu_B \langle S \rangle, \quad \langle S \rangle = \frac{1}{2} \frac{e^{g\mu_B \frac{1}{2} H/T} - e^{-g\mu_B \frac{1}{2} H/T}}{e^{g\mu_B \frac{1}{2} H/T} + e^{-g\mu_B \frac{1}{2} H/T}} = \frac{1}{2} \tanh\left(\frac{g\mu_B H}{2T}\right). \quad (6.16)$$

Taking into account that for electrons $g = 2$, we can rewrite equation (6.16) as

$$M = \mu_B \tanh\left(\frac{\mu_B H}{T}\right). \quad (6.17)$$

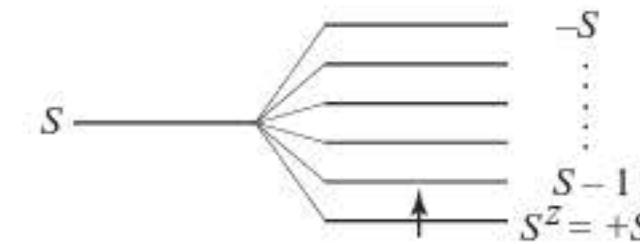


Fig. 6.3

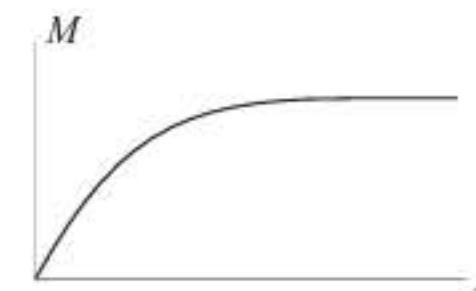


Fig. 6.4

For small H ($g\mu_B H \ll T$) the moment M is linear in the field,

$$M = \frac{N g^2 \mu_B^2 H}{V 4T},$$

and

$$\chi_0 = \frac{\partial M}{\partial H} = \frac{N g^2 \mu_B^2}{V 4T}, \quad (6.18)$$

which coincides with (6.15) for $S = \frac{1}{2}$, $S(S+1) = \frac{3}{4}$.

For the general case (arbitrary S , or total angular momentum \mathcal{J}):

$$M(H) = g\mu_B \mathcal{J} B_{\mathcal{J}}(g\mu_B \mathcal{J} H/T), \quad (6.19)$$

where

$$B_{\mathcal{J}}(x) = \left(1 + \frac{1}{2\mathcal{J}}\right) \coth \left[\left(1 + \frac{1}{2\mathcal{J}}\right)x \right] - \frac{1}{2\mathcal{J}} \coth \frac{x}{2\mathcal{J}} \quad (6.20)$$

is the so-called Brillouin function (used here instead of \tanh in equation (6.16), which was valid for $\mathcal{J} = S = \frac{1}{2}$).

The physics leading to (6.14)–(6.20) is illustrated in Fig. 6.3. In a magnetic field there occurs the Zeeman splitting of the levels, and with decreasing temperature more and more spins in our system will accumulate at the lowest level, with the spin parallel to the field, which leads to the increase of total magnetization (6.13), (6.16) and to the susceptibility (6.14).

Both equation (6.16) and equations (6.19)–(6.20) describe the *saturation* of magnetization in strong fields $g\mu_B \mathcal{J} H \gg T$, see Fig. 6.4. For very large spins the

quantum expressions go over to the classical ones, with the substitution $S(S+1) \rightarrow S^2$. This is a general property of any spin system: it becomes classical for $S \rightarrow \infty$, because for $S \rightarrow \infty$ the noncommutativity of spin operators is irrelevant, and quantum effects disappear (cf. the treatment of Bose condensation in Chapter 5).

6.2 Interacting localized moments; magnetic ordering

The main interaction between localized spins is the exchange interaction:

$$\mathcal{H} = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - g\mu_B \mathbf{H} \cdot \sum_i \mathbf{S}_i , \quad (6.21)$$

where we have introduced also the interaction with the external field \mathbf{H} . This is the Heisenberg exchange interaction, the simplest form of spin–spin interaction. In general exchange may be anisotropic, e.g. $J_{\parallel} S^z S^z + J_{\perp} (S^x S^x + S^y S^y)$; short-range ($J_{ij} = J \delta_{j,i\pm 1}$) or long-range, etc. For higher spins $S > \frac{1}{2}$ the exchange interaction may also contain higher-order terms, for example biquadratic exchange $S_i^2 S_j^2$; there may also exist other, more special terms. We will treat below predominantly the simplest interaction (6.21) or its anisotropic generalizations; the general case is considered in specialized monographs or reviews on magnetism, e.g. in White (2006) and Yosida (1996).

Note: often the exchange interaction (our equation (6.21)) is defined differently: sometimes with the opposite sign, $-\sum J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$, and sometimes as $\pm 2 \sum J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$; this corresponds to different definitions of the exchange integral J_{ij} . For example, the definitions of exchange integrals in two of the most popular textbooks, those by Kittel (1987) and by Ashcroft and Mermin (1976), differ by a factor of 2. It is also important to know whether in the summation in the Hamiltonian (6.21) each pair ij is counted only once or the summation is carried out for all i and j independently, i.e. each pair enters twice (we use the latter convention below); this is in fact the reason for the difference in the factor of 2 mentioned above. Thus you have to be careful when someone cites the value of the exchange constant for a particular system; you should always check which definition of the exchange integral is being used.

Depending on the sign and the detailed distance dependence of $J_{ij} = J(\mathbf{R}_i - \mathbf{R}_j)$ the exchange interaction can give different types of magnetic ordering:

- ferromagnetic: all spins parallel, $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$;
- antiferromagnetic: in the simplest case, alternating spins, $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$ (so-called *Néel ordering*);
- spiral, e.g. helicoidal or cycloidal state: $\uparrow \nearrow \rightarrow \nwarrow \downarrow \swarrow \leftarrow \nwarrow \uparrow$;

etc.

6.2.1 Mean field approximation

The simplest treatment of the influence of the exchange interaction (6.21) on magnetic properties of the system, in particular on magnetic ordering, is the *mean field*, or self-consistent field approximation. In this method we consider each spin as being in an average field created by other spins of the system, which has to be determined self-consistently. This is equivalent to the *decoupling*

$$J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \implies J_{ij} \left(\mathbf{S}_i \cdot \langle \mathbf{S}_j \rangle + \langle \mathbf{S}_i \rangle \cdot \mathbf{S}_j - \langle \mathbf{S}_i \rangle \cdot \langle \mathbf{S}_j \rangle \right), \quad (6.22)$$

where

$$\langle \mathbf{S}_i \rangle = \langle \mathbf{S} \rangle \quad (6.23)$$

is the average spin, in the ferromagnetic case independent of the site. The last term in equation (6.22) is necessary to avoid double counting; this is important in the calculation of the total energy. If we take z as the quantization axis, only z -components of the spin remain. Consequently, later on we will omit vector notation and denote the average spin simply as $\langle S \rangle$. This mean field approximation (the decoupling (6.22)) means that we consider each spin, say spin S_i , as being in a *molecular field* (also called the internal, or effective field) H_{intern} created by its neighbours and given by the expression

$$g\mu_B H_{\text{intern}} = -2 \sum_j J_{ij} \langle S \rangle. \quad (6.24)$$

(We have used here the standard form of the coupling (6.11); the factor of 2 comes from the fact that, according to our definition of the exchange Hamiltonian (6.21), we sum over all indices ij independently, i.e. each pair of spins is counted twice.) For the nearest-neighbour coupling $\sum_j J_{ij} = Jz$, where z is the number of nearest neighbours. Having in mind ferromagnetic interactions and introducing for convenience the notation $\tilde{J} = -J$ (so that $\tilde{J} > 0$), we get for the molecular field the expression

$$g\mu_B H_{\text{intern}} = 2\tilde{J}z\langle S \rangle. \quad (6.25)$$

Putting this expression into equation (6.16), we now obtain the *self-consistency* equation (the *mean field* equation) for the average magnetization $M = g\mu_B\langle S \rangle$, which for the case of $S = \frac{1}{2}$ ($g = 2$) with ferromagnetic interaction takes the form

$$\langle S \rangle = \frac{1}{2} \tanh \left(\frac{\tilde{J}z\langle S \rangle}{T} \right) \quad (6.26)$$

or

$$M/\mu_B = \tanh \frac{\tilde{J}z(M/\mu_B)}{2T}. \quad (6.27)$$

In the presence of an external field H that field would enter in the numerator in \tanh in (6.27) together with the molecular field (6.24).

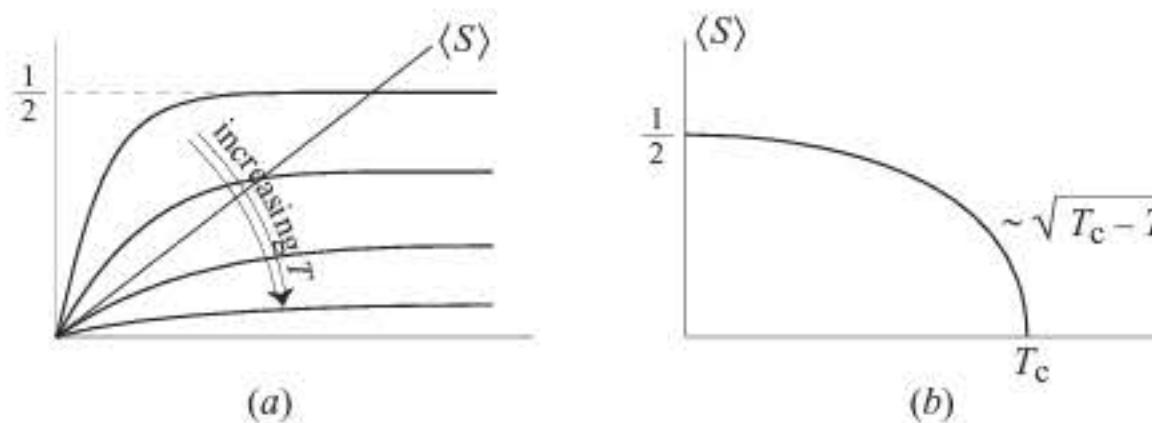


Fig. 6.5

The easiest way to analyse the mean field equations (6.26), (6.27) is the graphical solution, see Fig. 6.5(a): we plot the curves for the left- and right-hand sides of these equations and look at their crossings. As we see, for zero external field $H = 0$ there is always a zero (nonmagnetic) solution $M = 0$, or $\langle S \rangle = 0$. But for low enough temperatures there also exists a nonzero solution with finite value M (and also $-M$). One can show that these nontrivial solutions, when they exist, correspond to the minimum of the free energy, whereas the zero solution becomes the maximum. The temperature dependence of the spontaneous magnetization M , or the average spin $\langle S \rangle$, given by equation (6.27), is shown in Fig. 6.5(b). The value of the critical temperature in this case ($S = \frac{1}{2}$) is

$$T_c = \frac{1}{2} J z . \quad (6.28)$$

For an arbitrary spin S with nearest-neighbour interaction the corresponding expression is

$$T_c = \frac{2}{3} J z S(S + 1) , \quad (6.29)$$

which for $S = \frac{1}{2}$ reduces to (6.28).

Using equations (6.24)–(6.27) we can also easily obtain an expression for the magnetic susceptibility of interacting electrons. We can write the magnetic moment as

$$M = \chi_0(H + H_{\text{intern}}) , \quad (6.30)$$

where χ_0 is given by the expression (6.15). Using the expression (6.24) for H_{intern} , we finally obtain for a short-range interaction

$$M = \frac{C H}{T - T_c} , \quad (6.31)$$

where we took into account the expressions (6.15) for C and (6.29) for T_c .

The full susceptibility χ , defined by the relation $M = \chi H$, is given in this case by the expression

$$\chi = \frac{C}{T - T_c} . \quad (6.32)$$

This is the famous *Curie–Weiss* law, which is usually written as

$$\chi = \frac{C}{T - \Theta}. \quad (6.33)$$

In the mean field approximation in the case of only a nearest-neighbour interaction J , the *Weiss temperature* is

$$\Theta = T_c = \frac{2}{3}S(S+1)\tilde{J}z = -\frac{2}{3}S(S+1)Jz, \quad (6.34)$$

where $J = -\tilde{J}$ is the exchange integral as introduced in equation (6.21) for the nearest-neighbour interaction. The sign of Θ tells us whether the corresponding exchange interaction is ferromagnetic ($\Theta > 0$) or antiferromagnetic ($\Theta < 0$).

In the general case the Weiss temperature is given by the expression

$$\Theta = -\frac{2}{3}S(S+1) \sum_j J_{ij}, \quad (6.35)$$

where the summation goes over all neighbours with which a given spin interacts. This general expression (6.35) has broader applicability than the nearest-neighbour version (6.34). It can happen, for example, that for anisotropic and especially for frustrated magnets, or for systems with long-range interactions, the value of Θ is very different from T_c or even has the opposite sign. It is important to realize that the sign of Θ is determined by the *sum of all exchange interactions*, with all neighbours of a given site. If these interactions are predominantly antiferromagnetic, the sign of Θ would be negative, and the magnetic ordering would be antiferromagnetic. There may be situations, however, when the strongest interactions are ferromagnetic, e.g. a strong ferromagnetic interaction in a magnetic layer, but if the interlayer coupling is antiferromagnetic (and, e.g. weaker), the resulting state would be also antiferromagnetic (ferromagnetic planes stacked antiferromagnetically). In this case at high temperatures we would have a ‘ferromagnetic’ susceptibility ($\Theta > 0$), although the ground state is actually antiferromagnetic. On the other hand, for frustrated systems with antiferromagnetic interactions the value of the critical temperature (the Néel temperature T_N , see below) may be much smaller than the typical absolute values of the exchange interaction. In this case $|\Theta|$ may be much larger than T_N ; the small value of $T_N/|\Theta|$ (or large $|\Theta|/T_N$) is now often taken as an empirical criterion, a fingerprint of strong frustrations.

A word of caution again: for a different definition of the exchange constant, when, in contrast to our convention, each pair ij in the summation in the exchange Hamiltonian (6.21) is counted only once, one would use the exchange integral J' which is twice our J , $J' = 2J$; this is, e.g. the definition used by Ashcroft and Mermin (1976) and Ziman (1979). Then the results (6.29), (6.34) for the critical temperature T_c or for the Weiss temperature Θ , written through this J' , would contain, instead of the factor $\frac{2}{3}$, the factor $\frac{1}{3}$, and the value of the exchange constant

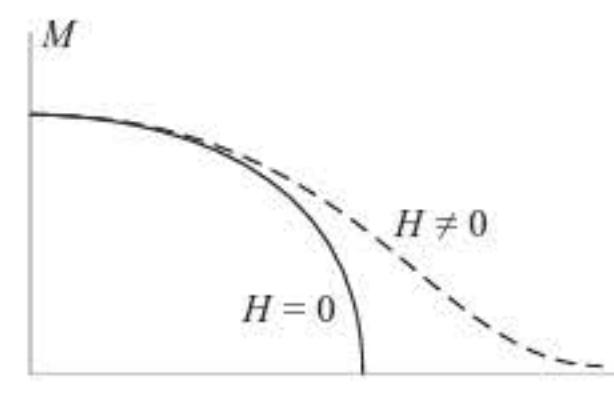


Fig. 6.6

determined, e.g. from the high-temperature susceptibility, would differ from the more conventionally determined one by a factor of 2.

6.2.2 Landau theory for ferromagnets

The mean field approximation gives results equivalent to the general Landau theory of second-order phase transitions. The Landau expansion of the free energy has here the form

$$\Phi = AM^2 + BM^4 - \mathbf{H} \cdot \mathbf{M} . \quad (6.36)$$

We have introduced in (6.36) the interaction with the external magnetic field \mathbf{H} to point out two consequences:

1. We can obtain from this approach the behaviour of the magnetic susceptibility at the phase transition, which turns out to be the same as that obtained above in the mean field approximation. The equation for \mathbf{M} is

$$\frac{\partial \Phi}{\partial \mathbf{M}} = 2AM + 4BM(\mathbf{M})^2 - \mathbf{H} = \mathbf{0} . \quad (6.37)$$

As $\mathbf{M} \parallel \mathbf{H}$, we may omit vector notation here:

$$2AM + 4BM^3 - H = 0 . \quad (6.38)$$

It is clear that, for finite H , M is always nonzero, even above T_c , Fig. 6.6. Close to T_c ($T > T_c$), where $M \ll 1$, we have (with $A = a(T - T_c)$, see (2.3))

$$M = \frac{H}{2A} = \frac{H}{2a(T - T_c)} , \quad (6.39)$$

i.e. with $M = \chi H$, we get

$$\chi = \frac{1}{2a(T - T_c)} , \quad (6.40)$$

the standard Curie–Weiss law, cf. (6.32).

The expression (6.39) is valid for $T > T_c$. Below T_c there exists spontaneous magnetization in the absence of the magnetic field H , so that one cannot define the susceptibility as $\chi = \lim_{H \rightarrow 0} M/H$, as is usually done. However one can always define the differential susceptibility dM/dH . From Fig. 6.6, where the temperature dependence of the magnetization of a ferromagnet is shown in the presence and in the absence of an external magnetic field, it is clear that in the finite external field the magnetization increases both above and below T_c . From equation (6.38) we find for $T < T_c$ (where $M_{H=0} \neq 0$):

$$\frac{d}{dH} \left(\frac{\partial \Phi}{\partial M} \right) = \frac{\partial}{\partial H} \left(\frac{\partial \Phi}{\partial M} \right) + \frac{\partial}{\partial M} \left(\frac{\partial \Phi}{\partial M} \right) \frac{dM}{dH} = 0, \quad (6.41)$$

i.e.

$$-1 + (2A + 12BM^2) \frac{dM}{dH} = 0, \quad (6.42)$$

or

$$\chi_{\text{diff}} = \frac{dM}{dH} = \frac{1}{2A + 12BM^2}. \quad (6.43)$$

For $T < T_c$ the coefficient $A = a(T - T_c) < 0$, $M^2 = -A/2B = a(T_c - T)/2B$, and

$$\chi = \frac{1}{2A - 6A} = -\frac{1}{4A} = +\frac{1}{4a(T_c - T)}. \quad (6.44)$$

Thus the differential susceptibility also diverges as $1/(T_c - T)$ from below, for $T \rightarrow T_c - 0$, but with the coefficient two times smaller than above T_c , cf. (6.44) and (6.40) – see also (2.37); as mentioned there, this is a real effect, measurable experimentally.

In obtaining equations (6.39)–(6.44) we have taken into account only terms linear in M and H . However, the full equation (6.38) contains also nonlinear terms. They become important for higher fields. One can use equation (6.38) as a very convenient way to determine experimentally the critical temperature of a ferromagnetic phase transition.

The point is that by just measuring the magnetization in weak fields it is very difficult to get an accurate value of T_c . As is well known, there always appear in such systems ferromagnetic domains with different spin orientations, which change with field and temperature and which dominate the magnetic response at small fields. One can get rid of this problem if one works at high enough fields, sufficient to orient all spins in one direction. But in this case one has to take into account nonlinear effects in the $M(H)$ dependence, described by the cubic term

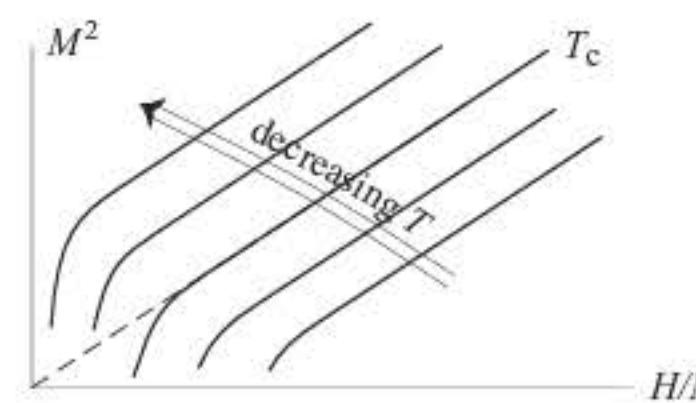


Fig. 6.7

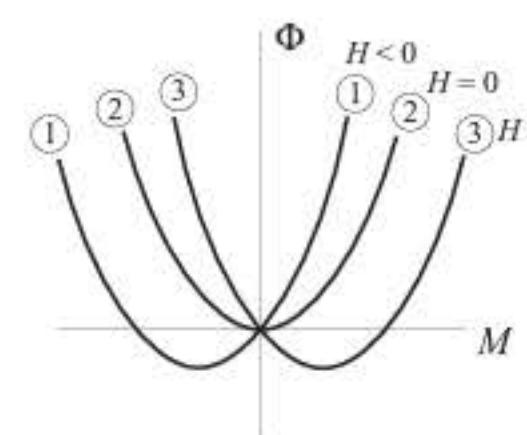


Fig. 6.8

in equation (6.38). Keeping all terms there, one can rewrite equation (6.38) in the form

$$2BM^2 = H/2M - A . \quad (6.45)$$

Thus if we plot M^2 vs. H/M at different temperatures, we should have a series of straight lines, see Fig. 6.7. The slope of these lines would give us the value of the coefficient B in the Landau expansion of the free energy, and the offset, the value at $H = 0$, would give the coefficient A . Remembering that in the Landau theory $A = a(T - T_c)$, we see that the value of the temperature at which such a straight line passes through zero would give us the value of T_c .

In real situations, due to domain effects, at small fields this dependence could strongly deviate from that of equation (6.45), but it is usually satisfied at large enough fields. Thus to determine T_c one has to use the extrapolation of the curves of Fig. 6.7 measured at high fields to $H = 0$. This method is widely used in practice. The plot (6.45), Fig. 6.7, is called the *Arrott plot* (or sometimes the Belov–Arrott plot).

2. Let us now consider the free energy (6.36) as a function of M for different temperatures *and fields*. For $T > T_c$ it has the form shown in Fig. 6.8, i.e. as a

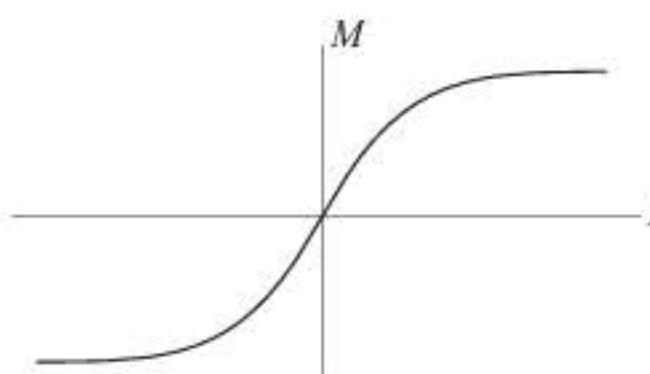


Fig. 6.9

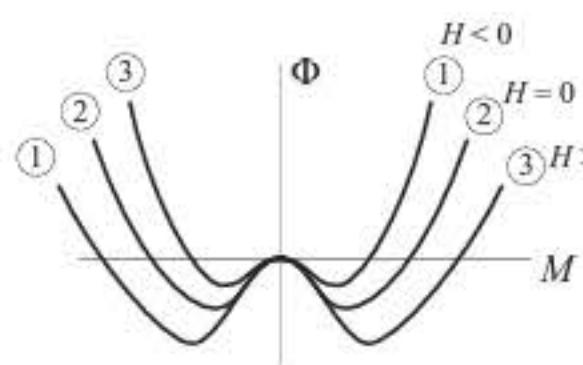


Fig. 6.10

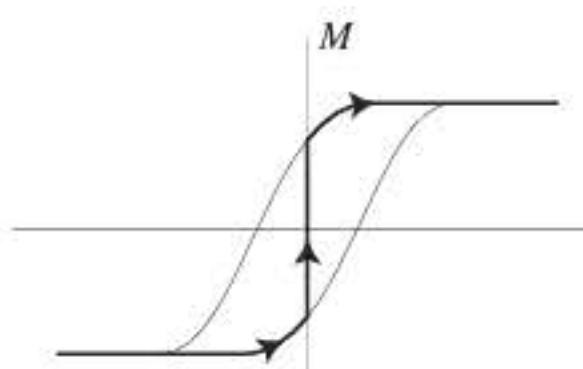


Fig. 6.11

function of H the magnetization changes continuously, Fig. 6.9. Now, consider the situation for $T < T_c$. The set of curves for $\Phi(M)$ is now given in Fig. 6.10. We see that as the field changes sign, the minima with positive and negative M change absolute values; for $H > 0$ the minimum with $M > 0$ lies deeper, and for $H < 0$ – that with $M < 0$. Thus there should be a jump of M , when H passes zero, very much like in the first-order transitions discussed in Chapter 2! (cf. Figs. 2.5, 2.8). This is nothing else but the well-known *hysteresis* of ferromagnets, Fig. 6.11. And it really *is* a first-order transition. However, not as a function of temperature, but as a function of field. Thus, the phase diagram of a ferromagnet in the (T, H) plane looks as shown in Fig. 6.12. There is indeed a first-order transition line, and the *end point* of this line (critical point,

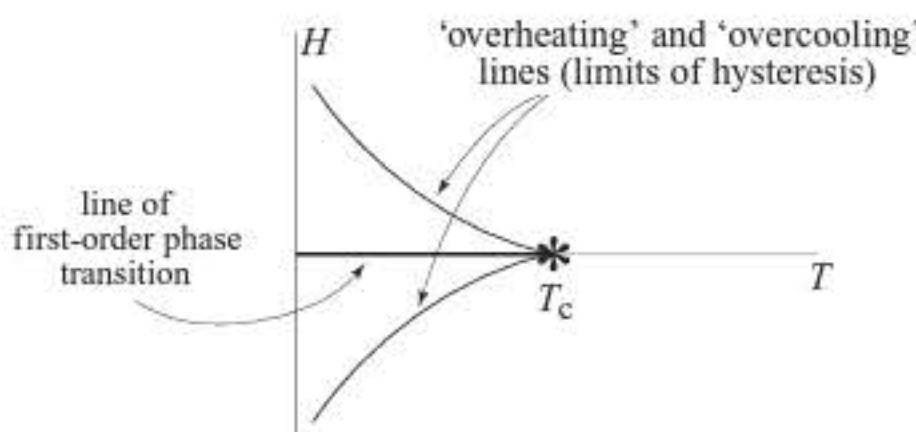


Fig. 6.12

in the terminology of first-order phase transitions) is our old familiar T_c – the critical point of the second-order phase transition. All the anomalies of different quantities at the second-order phase transition point are actually the same as in the critical point of first-order phase transitions, cf. e.g. Fig. 2.9.

6.2.3 Antiferromagnetic interactions

The mean field description of antiferromagnetic ordering coincides with that of ferromagnetic ordering, with the only difference that we change the spin direction in one of the sublattices, together with the opposite sign of the exchange interaction. The corresponding self-consistency equations, analogous to equations (6.26), (6.27), will now be written for a sublattice magnetization. Below we discuss the response of an antiferromagnet to an external field, which is different from that of a ferromagnet.

Let us write down the Landau free energy for an antiferromagnet. In an antiferromagnet in the absence of external field there are two sublattices with antiparallel spins, $\mathbf{M}_1 = -\mathbf{M}_2$. The order parameter here is

$$\mathbf{L} = \mathbf{M}_1 - \mathbf{M}_2 ; \quad (6.46)$$

it is zero above the critical temperature (usually denoted as T_N , the *Néel temperature*), and nonzero for $T < T_N$. The free energy of an antiferromagnet in the presence of an external field has the form

$$\Phi = \Phi_0 + AL^2 + BL^4 + D(\mathbf{H} \cdot \mathbf{L})^2 - \frac{1}{2}\chi_p \mathbf{H}^2 . \quad (6.47)$$

It is important that in contrast to ferromagnets the external field \mathbf{H} does not couple to the order parameter \mathbf{L} linearly (linear couplings with different sublattices cancel, because $\mathbf{M}_1 = -\mathbf{M}_2$), so that the lowest nonzero coupling allowed by symmetry is quadratic. At the same time there would definitely appear a certain magnetization in

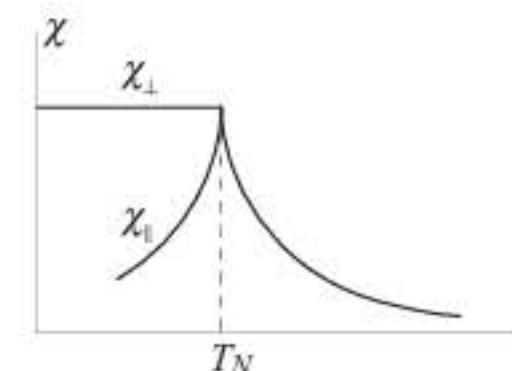


Fig. 6.12

the external field, even in the absence of antiferromagnetic ordering, e.g. above T_c . This effect is described by the last term in equation (6.47). (We recall that the magnetic moment $M = -\partial\Phi/\partial H$, i.e. here it is equal to $\chi_p H$, as it should be.) Here χ_p is the magnetic susceptibility of the sample in the paramagnetic phase, which is given by the Curie-Weiss law (6.33) with $\Theta = -\frac{2}{3}S(S+1)Jz$ (6.34).

On the other hand, the presence of antiferromagnetic order below T_N should modify the susceptibility. Let us consider the susceptibility below the Néel temperature. We have to discriminate two situations: the field parallel to \mathbf{L} (or to the sublattice magnetization) or perpendicular to it. In general the moment is

$$M = -\frac{\partial \Phi}{\partial H} = \chi_p H - 2DL(L \cdot H) . \quad (6.4)$$

(g) For the perpendicular field, $\mathbf{H} \perp \mathbf{L}$, we obtain from (6.48) that

$$\gamma_+ \equiv \gamma_{\tau_+} \quad (6.4)$$

i.e. below T_N the perpendicular susceptibility is constant, independent of temperature.

(b) For the field parallel to the sublattice magnetization, $\mathbf{H} \parallel \mathbf{L}$, the second term equation (6.48) also contributes. We then obtain

$$\chi_{\parallel} = \chi_p - 2DL^2 = \chi_{\perp} - \frac{Da}{B}(T_N - T) \quad (6)$$

(by (6.49) $\chi_p = \chi_\perp$; we also took the standard expression for the order parameter of an antiferromagnet $J_z^2 \equiv \frac{a}{\pi}(T_N - T)$, see equation (2.6)).

Thus we see that below T_N , χ_{\parallel} and χ_{\perp} are different, see Fig. 6.13. The moment in the ordered phase is smaller for the field parallel to the sublattice magnetization than for the perpendicular field. In the parallel field we have to *invert* some spins, Fig. 6.14(a), and this costs a large amount of energy, and the resulting susceptibility is small, whereas for the field *perpendicular* to the sublattice magnetization moments the sublattices can *cant*, Fig. 6.14(b), which is much easier. And

3

Bose and Fermi statistics

This chapter is a short reminder and a collection of basic formulae on Fermi and Bose statistics. For noninteracting particles with the spectrum ε_k , the energy of the quantum state, in which there are n_k particles, is $E_{k,n_k} = \varepsilon_k n_k$ (we incorporated in the index k also spin indices, and other indices if they exist). Then, according to (1.32), (1.33), the thermodynamic potential Ω for this quantum state is equal to

$$\Omega_k = -T \ln \sum_{n_k} (e^{(\mu-\varepsilon_k)/T})^{n_k}. \quad (3.1)$$

For bosons (the occupation numbers n_k can take any value, i.e. the summation in equation (3.1) goes from $n_k = 0$ to ∞), the expression (3.1) converges if $e^{(\mu-\varepsilon_k)/T} < 1$, i.e. we necessarily have $\mu < \varepsilon_k$ (or $\mu < 0$ if $\varepsilon_k \sim k^2/2m$), and after summation we obtain

$$\Omega_k^B = T \ln (1 - e^{(\mu-\varepsilon_k)/T}). \quad (3.2)$$

Then from (1.31) the average occupation of the state k is

$$\bar{n}_k^B = -\frac{\partial \Omega_k^B}{\partial \mu} = \frac{1}{e^{(\varepsilon_k-\mu)/T} - 1}. \quad (3.3)$$

For fermions, due to the Pauli principle, we can have no more than one particle in a given quantum state, i.e. $n_k = 0$ or 1. Then the thermodynamic potential (3.1) is

$$\Omega_k^F = -T \ln (1 + e^{(\mu-\varepsilon_k)/T}), \quad (3.4)$$

and

$$\bar{n}_k^F = -\frac{\partial \Omega_k^F}{\partial \mu} = \frac{1}{e^{(\varepsilon_k-\mu)/T} + 1}. \quad (3.5)$$