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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

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

where \hat{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.

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

1.2 Thermodynamic functions

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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:

$$\begin{aligned} dF &= -S dT - P dV + \mu dN \\ d\Phi &= -S dT + V dP + \mu dN \\ dE &= T dS - P dV + \mu dN. \end{aligned} \quad (1.24)$$

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

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

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.

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

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

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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

$$\Omega = -T \ln Z_{\text{Gr}} , \quad (1.32)$$

where Z_{Gr} is called *grand partition function*:

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

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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

2.1 Second-order phase transitions

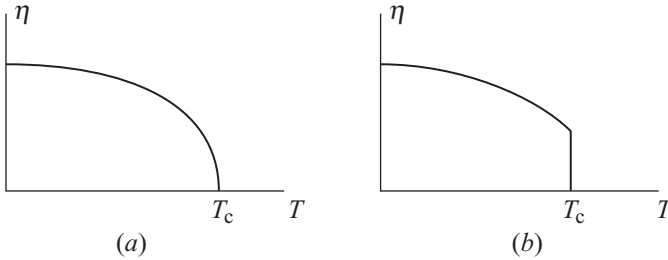


Fig. 2.1

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,

$$\Phi = \Phi_0 + \alpha\eta + A\eta^2 + C\eta^3 + B\eta^4 + \dots \tag{2.1}$$

(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

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

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 :

$$A(P, T) = a(T - T_c) , \tag{2.3}$$

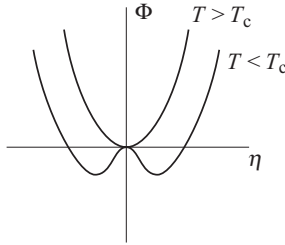


Fig. 2.2

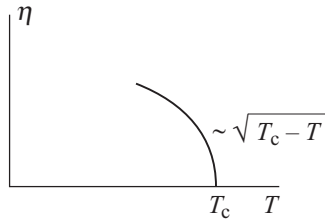


Fig. 2.3

with the coefficient $a > 0$. Then

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

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

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

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

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 ($\partial \Phi / \partial T$),

2.1 Second-order phase transitions

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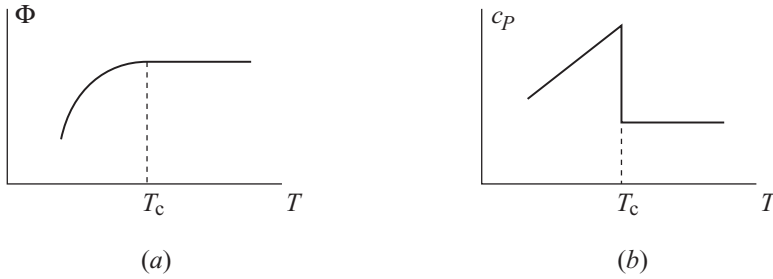


Fig. 2.4

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.

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

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

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

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

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

As

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

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