

PHASE TRANSITIONS

X.1. The ferromagnetic continuous phase transition.

The Weiss' model of the ferromagnetism. A number of physico-chemical systems, which undergo phase transitions, can be represented, to varying degrees of accuracy, by an *array of lattice sites*. For instance, a solid crystal has been discussed in some detail in §IV.4. This simple-minded model turns out to be good enough to provide a unified theoretical basis for understanding a variety of phenomena such as ferromagnetism and antiferromagnetism, gas-liquid, liquid-solid and gas-solid (see paragraph X.2. here below) transitions, order-disorder transitions in alloys, phase separation in binary solutions, *et cetera*. There is no doubt that this model considerably oversimplifies the actual physical systems it is supposed to represent: in this sense, we can look at it as an *effective model*. Nevertheless, it does retain the essential statistical features of the problem and, accordingly, it does lead to the onset of a phase transition in the given system, which appears to arise in the nature of a *cooperative* phenomenon. We find it convenient here to formulate the problem in the language of ferromagnetism. We regard each of the N lattice sites to be occupied by an *atom* possessing a magnetic dipole moment operator $\hat{\mathbf{m}}$. Quite generally, we have a direct relationship between the magnetic moment $\hat{\mathbf{m}}$ of a given dipole and its angular momentum operator: namely,

$$\hat{\mathbf{m}} = g \frac{e}{2m_e c} \hat{\mathbf{J}}, \quad (1.1)$$

where $m_e = 9.1093897(54) \times 10^{-28}$ g is the free electron mass, $e = 4.8032068(15) \times 10^{-10}$ esu is the electron charge magnitude, whereas the square of the total angular momentum operator $\hat{\mathbf{J}}^2$ of the dipole has eigenvalues $\hbar^2 J(J+1)$ with $J = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, 3, \dots$. Notice that here the magnetic moment of the dipole is supposed to be totally due to the electron

structure of the atom; in other words, the magnetic moment of the nucleus – which is three orders of magnitude smaller – is disregarded. The quantity $(eg/2m_e c)$ is referred to as the *gyromagnetic ratio* of the dipole while the number g is known as the *Landé's g -factor* [A. Landé (1923)]. On the one hand, if the total angular momentum of the dipole is due only to electron spins, then $g = 2$ from relativistic Dirac's theory; on the other hand, if it is due only to orbital motions, then $g = 1$. In general, however, its origin is mixed; g is then given by [see e.g. L. D. Landau & E. M. Lifšits (1976): *Meccanica Quantistica (Teoria non relativistica)*, Editori Riuniti, Roma, eq. (113,7) p. 543]

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} , \quad (1.2)$$

S and L being, respectively, the spin and the orbital quantum numbers of the dipole. Note that there are no upper or lower bounds for the values that g can have. As a consequence we can write

$$|\mathbf{m}| = g\mu J , \quad (1.3)$$

where $\mu = e\hbar/2m_e c = 9.273 \times 10^{-21}$ erg G⁻¹ (esu cm) is the *Bohr's magneton*.

Let us suppose that the system is under the influence of a uniform – *i.e.* static and homogeneous – applied external magnetic field along the Oz -direction $\mathbf{B} = (0, 0, B)$. The eigenvalues of the component \hat{m}_z of the magnetic moment operator in the direction of the applied field are accordingly given by

$$m_z = g\mu m , \quad (1.4)$$

where the magnetic quantum number m , in agreement with the rules of space quantization, takes the values

$$m = -J, -J+1, \dots, J-1, J . \quad (1.5)$$

We can assume that the atoms of the system are distinguishable as they are constrained to lie at the lattice sites. Furthermore, within the simple-minded model we are discussing, the atoms are supposed to interact only through a *nearest-neighbour* potential that depends upon the manner of occupation of the neighbouring sites – in other words, we completely neglect any other interaction but the nearest-neighbour dipole potential and the interaction with the applied external magnetic field. Let us first disregard the nearest-neighbour dipole potential: in such a situation, the magnetic hamiltonian operator will be simply given by

$$\hat{H}_m = - \sum_{i=1}^N \mathbf{B} \cdot \hat{\mathbf{m}}_i ,$$

where $\hat{\mathbf{m}}_i$ is the magnetic moment operator of the i -th lattice site, so that the magnetic partition function of the system becomes

$$Z_m(N, \beta; B) \equiv \text{Tr} \exp\{-\beta \hat{H}_m\} = \left[\sum_{m=-J}^J \exp\{\beta g \mu B m\} \right]^N . \quad (1.6)$$

After the introduction of the dimensionless parameter $b \equiv \beta g \mu J B \in \mathbf{R}$, from the well known sum of the geometric progression

$$\sum_{k=1}^n a^{k-1} = \frac{a^n - 1}{a - 1} , \quad a \neq 1$$

we definitely find

$$Z_m(N, \beta; B) = \sinh^N \left\{ \left(1 + \frac{1}{2J} \right) b \right\} \sinh^{-N} \left(\frac{b}{2J} \right) . \quad (1.7)$$

The *magnetization* or *magnetic polarization*, *i.e.* the mean magnetic moment of the system *per* unit volume, is then given by

$$\overline{M}_z = \frac{kT}{V} \frac{\partial}{\partial B} \ln Z_m(N, T; B) = \frac{N}{V} g \mu J \mathcal{B}_J(b) , \quad (1.8)$$

where $\mathcal{B}_J(b)$ is the *Brillouin function* [Lèon Brillouin (Sévres 1889 – New York 1969)] of order J : namely $[b \equiv \beta g \mu J B]$

$$\mathcal{B}_J(b) \equiv \left(1 + \frac{1}{2J}\right) \coth \left\{ \left(1 + \frac{1}{2J}\right) b \right\} - \frac{1}{2J} \coth \left(\frac{b}{2J} \right) . \quad (1.9)$$

It is worthwhile to recall that in the C.G.S. gaussian electromagnetic system of units the magnetization has the same dimensions of the electromagnetic field, *i.e.* Gauss or dine/esu. Let us now consider a few limiting situations. On the one hand, we note that for strong fields and low temperatures we have

$$\lim_{b \rightarrow \pm\infty} \mathcal{B}_J(b) = \pm 1 , \quad \forall J$$

which corresponds to the two states of magnetic saturation. On the other hand, for high temperatures and weak fields $b \ll 1$, the Brillouin function of order J may be written as

$$\mathcal{B}_J(b) = \frac{J+1}{3J} b + O(b^3) , \quad (1.10)$$

so that

$$\overline{M}_z \stackrel{b \ll 1}{\approx} \frac{n g^2 \mu^2 J(J+1)}{3kT} B ,$$

where $n \equiv N/V$ denotes as usual the number of dipoles *per* unit volume. The Curie's law is then obeyed with a *volume's magnetic susceptibility* χ_m , which is a temperature dependent numerical constant, given by

$$\chi_m \equiv \left(\frac{\partial \overline{M}_z}{\partial B} \right) = \frac{n g^2 \mu^2 J(J+1)}{3kT} . \quad (1.11)$$

The mean magnetic energy density of the dipole system, *i.e.* the magnetic energy *per* cm³ of the lattice, can be easily computed to be

$$u_m \equiv -\frac{1}{V} \frac{\partial}{\partial \beta} \ln Z_m(N, T; B) = - B n g \mu J \mathcal{B}_J(b) . \quad (1.12)$$

Now, in order to take the dipole nearest neighbour interaction suitably into account, let us proceed according to the original ideas firstly put forward in 1907 by *Pierre Ernest Weiss* (Mulhouse 25.3.1865 – Lion 24.10.1940): the nearest–neighbour dipole interaction does create a *molecular mean field* B_{mol} leading to a cooperative phenomenon contrasted by thermal excitation. As a consequence, each dipole is under the influence of an *effective magnetic field* B_* which equals the sum of the external applied field and the molecular mean field¹. According the Weiss’ hypothesis, the latter one can be thought to be proportional to the very same magnetization: namely,

$$B_* = B + B_{\text{mol}} = B + \lambda \overline{M}_z , \quad (1.13)$$

where λ is the phenomenological Weiss’ dimensionless constant.

The *Weiss’ mean field theory of the ferromagnetism* is obtained under the assumption that the net average effect of the dipole nearest–neighbour interaction gives rise to the self–consistent transcendental equation, which is obtained from the paramagnetic formula (1.8) under the consequent replacement $b \mapsto b_* \equiv \beta g \mu J B_* = b + \beta g \mu J \lambda \overline{M}_z$ so that we eventually find

$$\overline{M}(T; B) = n g \mu J \mathcal{B}_J(b_*) = n g \mu J \mathcal{B}_J(b + \beta g \mu J \lambda \overline{M}) , \quad (1.14)$$

where $n \equiv N/V$ and the index for the Oz –component along the direction of the applied field is understood from now on. We notice that for a vanishing external field we obtain

$$\overline{M}(T; 0) = \overline{M}(0; 0) \mathcal{B}_J\left(\frac{g \mu J}{kT} \lambda \overline{M}(T; 0)\right) , \quad (1.15)$$

¹ In magnetostatics it is customary to introduce the magnetic induction \mathbf{B} and the macroscopic magnetic field $\mathbf{H} = \mathbf{B} - 4\pi\mathbf{M}$, as well as the incremental permeability tensor $\mu_{ij} = (\partial B_i / \partial H_j)$. Here we use some slightly different notations and conventions.

where we have set $\overline{M}(0;0) \equiv ng\mu J$, which corresponds to the mean field equation for the *spontaneous or residual magnetization* $\overline{M}(T;0)$.

Now, if we introduce the so called *order parameter*

$$\overline{m}(T;0) \equiv \overline{M}(T;0)/\overline{M}(0;0) ,$$

which is dimensionless, non-trivial solutions for $T \neq 0$ can be obtained graphically on the (\overline{m}, y) -plane from the intersections of the straight line $y = \overline{m}$ with the Brillouin curve:

$$\begin{cases} y = \overline{m} , \\ y = \mathcal{B}_J(a\overline{m}) , \end{cases} \quad (1.16)$$

where we have set

$$a = \beta g\mu J \lambda \overline{M}(0;0) = \frac{n\lambda}{kT} (g\mu J)^2 \equiv \frac{3J}{\theta(J+1)} .$$

When $\lambda = 0$ the only possible solution is $\overline{M}(T;0) = 0$ but, from eq. (1.10), it is easy to see that we can obtain one and only one non-trivial solution iff the slope at the origin of the Brillouin curve is no less than one, that means

$$\theta^{-1} \equiv \lambda \frac{n(g\mu)^2}{3kT} J(J+1) \geq 1 . \quad (1.17)$$

The face value temperature, above which spontaneous magnetization is no longer possible, is called the *Curie temperature* and turns out to be, for a given total angular momentum of the atom, into a one-to-one correspondence with the Weiss' constant

$$T_c = \lambda \frac{n(g\mu)^2}{3k} J(J+1) . \quad (1.18)$$

The presence of a spontaneous magnetization $\overline{M}(T;0)$ for $T < T_c$ and its absence for $T > T_c$ will be interpreted as implying a *ferromagnetic phase transition* at the Curie temperature T_c . If we plot the order parameter \overline{m} versus the dimensionless ratio $\theta \equiv T/T_c$, for

any value of J , the corresponding graph will be a monotonically decreasing continuous convex curve ranging from $\bar{m}(0) = 1$ to $\bar{m}(1) = 0$, identically vanishing for $\theta \geq 1$ and with a discontinuous derivative at the critical point $\theta = 1$. Detailed investigations, both theoretical and experimental, unravel that for **all** ferromagnetic materials data upon the temperature dependence of the spontaneous magnetization $\bar{M}(T;0)$ the best fit occurs at the value $J = 1/2$.

The conclusion is therefore that the phenomenon of ferromagnetism is associated **only** to the spin angular momentum of the electrons of the ferromagnetic atoms and not to their orbital motion. This is further confirmed by the *gyromagnetic experiments* [S. J. Barnett: *Proc. Am. Acad. Arts & Sci.* **75**, 109 (1944); G. G. Scott: *Phys. Rev.* **82**, 542 (1951); *ibid.* **87**, 697 (1952)] in which either the magnetization of a freely suspended rod of a ferromagnetic sample is reversed and its resulting rotation is observed or a rotation is performed on the rod and its resulting magnetization is measured. The former is known as the *Einstein–de Haas* method, the latter as the *Barnett* method. From these experiments one can derive the relevant value of g which, in all cases, turns out to be very close to the value two and vindicates thereby the electron spin origin of ferromagnetism.

Accordingly, for $J = 1/2$ the basic equation (1.14) takes the form

$$\bar{m} = \tanh(b + \bar{m}/\theta) , \quad |\bar{m}| \leq 1 \quad (1.19)$$

and will be called the *Weiss' mean field equation of ferromagnetism*. Here we have set

$$\bar{m} \equiv \frac{\bar{M}}{n\mu} , \quad b \equiv \frac{\mu B}{kT} , \quad \theta \equiv \frac{T}{T_c} , \quad T_c = \lambda \frac{n\mu^2}{k} .$$

In order to set up some canonical partition function for the Weiss' mean field model, we have to take into account that, admittedly, we do not know the precise form of the microscopic magnetic hamiltonian. In such a circumstance, we have to put forward some

ansatz in terms of the effective magnetic field, the sum of the background and mean molecular field, and try to verify *a posteriori* the self-consistency of the consequent results.

It turns out that the self-consistent Weiss' mean field partition function is given by

$$\begin{aligned} Z_{\text{Weiss}}(N, T; B) &= 2^N \exp \left\{ -\frac{\lambda V}{2kT} \overline{M}^2(T; B) \right\} \cosh^N(\beta\mu B_*) \\ &= 2^N \exp \left\{ -N \frac{\overline{m}^2}{2\theta} \right\} \cosh^N \left(b + \frac{\overline{m}}{\theta} \right) . \end{aligned} \quad (1.20)$$

As a matter of fact we have

$$\overline{m} \equiv \frac{1}{N} \frac{\partial}{\partial b} \ln Z_{\text{Weiss}} = -(\overline{m}/\theta) \frac{\partial \overline{m}}{\partial b} + \left(1 + \theta^{-1} \frac{\partial \overline{m}}{\partial b} \right) \tanh \left(b + \frac{\overline{m}}{\theta} \right)$$

which turns out to be self-consistent with the Weiss' mean field equation (1.19). From the expression of the Weiss' mean field partition function (1.20) we can calculate the mean magnetic energy density of the ferromagnetic lattice model: namely,

$$\begin{aligned} u_{\text{m}}(\theta; b) &\equiv -\frac{1}{V} \frac{\partial}{\partial \beta} \ln Z_{\text{Weiss}}(N, T; B) \\ &= \frac{1}{2} nkT_c \overline{m}^2 - nkT_c (\overline{m} + \theta b) \tanh(b + \overline{m}/\theta) \\ &\quad + \frac{n}{\theta} [\overline{m} - \tanh(b + \overline{m}/\theta)] \frac{\partial \overline{m}}{\partial \beta} . \end{aligned}$$

Now, taking the Weiss' mean field equation (1.19) into account, we come to the result

$$u_{\text{m}}(\theta; b) = -\frac{1}{2} nkT_c \overline{m} (2\theta b + \overline{m}) . \quad (1.21)$$

As a consequence, it turns out that the explicit form (1.20) of the canonical partition function of the Weiss' mean field model is uniquely fixed by the requirements that the magnetic polarizability and the magnetic mean energy density did indeed fulfill eq.s (1.19) and (1.21) respectively.

It is worthwhile to remark that, for a vanishing applied field and below the Curie temperature, *i.e.* $b = 0$, $\theta < 1$, the absolute minimum of the mean magnetic energy

density becomes $u_0 = -(n/2)kT_c$, which occurs at the saturation values $|\bar{m}| = 1$. This is consistent with the fact that in the ferromagnetic materials the spin alignment (exchange interaction) is favoured with respect to the spin anti-alignment (direct interaction).

The hysteresis cycle. In order to find a graphical solution of the Weiss' mean field equation (1.19) below the Curie point it is expedient to introduce the auxiliary dimensionless variable $b_* \equiv \beta\mu B_* = b + \bar{m}/\theta$, so that the definition (1.13) of the effective magnetic field can be rewritten as

$$\bar{m} = \theta b_* - \theta b, \quad 0 < \theta < 1, \quad (1.22)$$

which represents, for given values of B and T , a straight line in the (b_*, \bar{m}) -plane with a slope $\tan \gamma = \theta < 1$, that cuts the vertical axis at the intercept of coordinate $-\theta b$. The applied external magnetic field intensity B can take positive and negative values, *i.e.* it can be reversed. It is worthwhile to notice that the slope of the straight line is proportional to the parameter $\theta := \tan \gamma$. At the room temperature, as the Weiss' constant is very large and the Curie's temperature is pretty high ², the angle γ turns out to be relatively small.

Now, if we adiabatically increase the applied magnetic field from zero to large positive values, the intercept runs along the negative vertical axis; conversely, for negative values of the external magnetic field, the intercept will move along the positive vertical axis. If we rewrite eq. (1.19) in terms of the auxiliary variable b_* : namely,

$$\begin{cases} \bar{m} = \tanh b_* , \\ \bar{m} = \theta b_* - \theta b , \end{cases} \quad 0 < \theta < 1 \quad (1.23)$$

we can easily recognize that for each value B of the applied magnetic field, a straight line exists in the (b_*, \bar{m}) -plane that crosses the curve of the hyperbolic tangent at some

² As a matter of fact, we have e.g. $\lambda_{\text{Fe}} \simeq 2.8 \times 10^6$, $T_{\text{Fe}} = 1047$ °K, $\lambda_{\text{Ni}} \simeq 11.1 \times 10^6$, $T_{\text{Ni}} = 645$ °K, $T_{\text{Co}} = 1022$ °K.

points which just represent the values of magnetic polarizability $\overline{M}(T; B)$ corresponding to the given value of B . Empirically, by varying the applied field B , we can build up the isothermal magnetization function $\overline{M}(T; B)$ of a ferromagnetic material. Let us first describe what we find out experimentally.

When we start from a sufficiently large negative intercept, in such a way that the transcendental system (1.23) has one single root, and increase the positive applied magnetic field, then the intercept will move towards the right and the magnetization will grow very slowly approaching asymptotically the saturation value $N\mu$, *i.e.* the ferromagnetic sample becomes *magnetically saturated*. If we now decrease the external field down to zero the magnetization will be equal to its spontaneous positive value $|\overline{M}(T; 0)|$ which, usually, is still very close to the saturation large value.

Let us now invert the applied field and increase it to larger and larger negative values: the magnetization will smoothly decrease and stays positive until the straight line (1.22) becomes tangent to the positive branch of the magnetization curve (1.23), in such a way that the magnetization achieves the positive value $\overline{M}_c = n\mu^2 H_c/k$, where $-H_c$ is the corresponding negative value of the applied magnetic field. At that point, if we increase a little bit more the absolute value of the applied field, then the magnetization will suddenly jump from the positive value $+\overline{M}_c$ to the negative value $-\overline{M}' = -|\overline{M}(T, B = -H_c)|$. The negative field intensity leading to the inversion of the magnetic polarizability is called the *coercive magnetic field* and it is usually denoted by $-H_c$. If we drive the negative applied magnetic field back to zero and further to positive values until $B = +H_c$, then the magnetization stays negative, it passes through the spontaneous value $-|\overline{M}(T; 0)|$ and further increases until the border value $-\overline{M}_c$, where another sudden inversion takes place, as the magnetization jumps to the positive value $+\overline{M}' = |\overline{M}(T, B = +H_c)|$. This is what

we find out empirically.

It follows that for a ferromagnetic material the isothermal magnetization $\overline{M}(T; B)$ is not a single-valued function of the applied external magnetic field.

As we have seen, the actual amount of the magnetization for a given value of the applied magnetic field depends upon the *history* of the above described magnetization–demagnetization process, its graph being represented by a closed path called the *hysteresis cycle*. It is now our purpose to try to understand the above described behaviour of a ferromagnetic sample in terms of the Weiss’ mean field theory. To this concern, it is very important to make the following remark.

The straight line (1.22) cuts the magnetization curve at one single point iff the applied field is sufficiently strong, *i.e.*, for $B < -H_c$ on the positive branch of the magnetization as well as for $B > H_c$ on the negative branch of the magnetization. At the coercive value $B = -H_c$ the magnetization achieves two possible values $+\overline{M}_c$ and $-\overline{M}' = -|\overline{M}(T, B = -H_c)|$ leading to the discontinuous jump in the left hand side of the hysteresis cycle. Similarly, at the coercive value $B = +H_c$ the magnetization achieves the two possible values $-\overline{M}_c$ and $+\overline{M}' = |\overline{M}(T, B = +H_c)|$ leading to the discontinuous jump in the right hand side of the hysteresis cycle. Finally, for sufficiently weak applied magnetic fields such that $|B| < H_c$ the straight line (1.22) cuts three times the magnetization curve. In particular, for a vanishing applied magnetic field we have three possible values of the spontaneous magnetization, namely $\overline{M}(T, 0) = 0$, $\overline{M}(T, 0) = \pm\overline{M}_0(T)$.

The very fact that for weak applied magnetic fields B the isothermal magnetization $\overline{M}(T, B)$ below the Curie’s temperature is not uniquely determined is a peculiar feature of the Weiss’ mean field approximation. Particularly noticeable is the fact that the *S*–like shaped magnetization curve $\overline{M}(T \leq T_c; B)$, as a function of the applied magnetic field B ,

does contain a portion with a negative slope, *i.e.* a *negative magnetic susceptibility* which clearly corresponds to the presence of *unphysical thermodynamical states*.

Actually, one can immediately obtain analytically the inverse function $b(\bar{m})$ from the Weiss' mean field equation (1.19). As a matter of fact, from the identity

$$b + \frac{\bar{m}}{\theta} = \text{Arth}(\bar{m}) \equiv \frac{1}{2} \ln \frac{1 + \bar{m}}{1 - \bar{m}}$$

we readily obtain the equation of state

$$b = -\frac{\bar{m}}{\theta} + \frac{1}{2} \ln \frac{1 + \bar{m}}{1 - \bar{m}}. \quad (1.24)$$

As mentioned above, for a given field b the value of the magnetization for $\theta < 1$ is not everywhere unique: e.g. for $b = 0$, the three values occur $\bar{m} = 0$, $\bar{m} = \pm\bar{m}_0$. Furthermore, the condition $db/d\bar{m} = 0$ leads to $\pm\bar{m}_c = \pm\sqrt{1-\theta}$ and in turn to the symmetric values of the coercive fields: namely,

$$b(\pm\bar{m}_c) := \pm h_c = \pm \frac{\sqrt{1-\theta}}{\theta} + \frac{1}{2} \ln \frac{1 \pm \sqrt{1-\theta}}{1 \mp \sqrt{1-\theta}}, \quad 0 < \theta < 1. \quad (1.25)$$

Again, when the applied fields achieves the negative coercive value $H_c = -kTh_c/\mu$ the magnetization jumps from the positive value $\bar{M}_c = n\mu\sqrt{1-\theta}$ to the negative value $-\bar{M}' = -n\mu\bar{m}'$, where $-\bar{m}'$ is the other negative solution of the equation of state

$$-h_c = \frac{\bar{m}'}{\theta} - \frac{1}{2} \ln \frac{1 + \bar{m}'}{1 - \bar{m}'} \quad (1.26)$$

with $\bar{m}' > \bar{m}_c$. Accordingly, the vertical jump in left hand side of the hysteresis cycle is recovered in such a way that the magnetic susceptibility is never negative – a specular behaviour occurs in the right hand side of the hysteresis cycle.

Chemical potential and domain walls energy. In order to find out which parts of the equation of state are physically meaningful and stable, we can also investigate the structure

of the thermodynamic potentials. The Helmholtz free energy in the molecular mean field approximation can be readily obtained from the partition function (1.21) and reads

$$F(N, T; B) = -kT \ln Z_{\text{Weiss}}(N, T; B) = NkT \left\{ \frac{\bar{m}^2}{2\theta} - \ln 2 - \ln \cosh \left(b + \frac{\bar{m}}{\theta} \right) \right\} . \quad (1.27)$$

From the hyperbolic trigonometric identity

$$\cosh x = \{1 - \tanh^2 x\}^{-1/2}$$

taking the Weiss' mean field equation (1.19) into account, we readily obtain

$$\ln \cosh \left(b + \frac{\bar{m}}{\theta} \right) = -\frac{1}{2} \ln(1 - \bar{m}^2)$$

and consequently

$$F(N, T; B) = NkT \left\{ \frac{\bar{m}^2}{2\theta} - \ln 2 + \frac{1}{2} \ln(1 - \bar{m}^2) \right\} , \quad (1.28)$$

where \bar{m} has to be expressed in terms of b as a solution of the Weiss' mean field equation.

It is also useful to introduce the Helmholtz free energy *per atom* in units of the so called critical energy kT_c that reads

$$f(\theta; b) \equiv \frac{F(N, T; B)}{NkT_c} = \frac{1}{2} \bar{m}^2 - \theta \ln 2 + \frac{\theta}{2} \ln(1 - \bar{m}^2) . \quad (1.29)$$

Now, taking into account that

$$V\bar{M} = - \left(\frac{\partial F}{\partial B} \right)_{N, T} \quad (1.30)$$

we can easily obtain the Gibbs free enthalpy under the Legendre transform

$$G(N, T; \bar{M}) = F(N, T; B) + V\bar{M}B = NkT_c g(\theta; \bar{m}) , \quad (1.31)$$

where the chemical potential in units of the critical energy turns out to be

$$g(\theta; \bar{m}) = \frac{1}{2} \bar{m}^2 - \theta \ln 2 + \frac{\theta}{2} \ln(1 - \bar{m}^2) + \bar{m} \theta b , \quad (1.32)$$

in such a way that

$$b \equiv \frac{1}{\theta} \left(\frac{\partial g}{\partial \bar{m}} \right)_{\theta}. \quad (1.33)$$

Now, taking the equation of state (1.24) into account we eventually come to the chemical potential of the Weiss' mean field theory of the ferromagnetism, in units of the critical energy³, that we shall call the *effective potential*: namely,

$$g(\theta; \bar{m}) = -\frac{1}{2} \bar{m}^2 - \theta \ln 2 + \frac{\theta}{2} \ln(1 - \bar{m}^2) + \frac{\theta}{2} \bar{m} \ln \frac{1 + \bar{m}}{1 - \bar{m}}. \quad (1.34)$$

The local minima of the effective potential are the solutions of the transcendental equation

$$\frac{\bar{m}}{\theta} = \frac{1}{2} \ln \frac{1 + \bar{m}}{1 - \bar{m}}$$

that is the equation of state (1.24) with vanishing applied magnetic field. Now, for $\theta \geq 1$, *i.e.* above the Curie temperature, we have the minimum at $\bar{m} = 0$ corresponding to the paramagnetic phase, whereas for $\theta < 1$ we find two symmetric minima in the ferromagnetic phase. From eq. (1.33) it is clear that the positions of the minima of the effective potential just correspond to the spontaneous or residual magnetization $\pm \bar{m}_0(\theta)$.

The vanishing of the second derivative of the effective potential leads to the symmetric values of the backbending positions

$$\pm \bar{m}_c = \pm \sqrt{1 - \theta}, \quad 0 < \theta < 1,$$

so that we recover the result of eq. (1.25) that the backbendings of the effective potential correspond to the coercive fields. Furthermore, it is also apparent that, for $0 < \theta < 1$, the part of the effective potential between the backbendings is never attained by the system, as it involves unphysical states with negative susceptibilities.

³ Notice that *e.g.* for iron we have $kT_c \simeq 9.013 \times 10^{-2}$ eV.

Let us go back to the residual magnetization in the absence of the applied magnetic field. As the values $\pm\bar{m}_0$ ($\theta < 1$) do rely to the same horizontal tangent to the effective potential, it is clear that, *a priori*, regions of magnetization $+\bar{m}_0$ and $-\bar{m}_0$ might therefore be present in equilibrium with each other. When some fraction q of a ferromagnetic sample has the magnetization $-\bar{m}_0$ and the complementary fraction $1 - q$ has the magnetization $+\bar{m}_0$, then for $0 \leq q \leq 1$ the average magnetization of the body would be

$$\bar{m}_q = -q\bar{m}_0 + (1 - q)\bar{m}_0 = (1 - 2q)\bar{m}_0 \quad (1.35)$$

in the interval between $-\bar{m}_0$ and $+\bar{m}_0$. In such a situation, the effective potential of this highly inhomogeneously magnetized sample would still attain the minimum value

$$g[\pm\bar{m}_0(\theta), \theta] := g_0(\theta)$$

and would be thus lower than the part of the Weiss' mean field effective potential (1.34) which corresponds instead to homogeneous equilibrium states in the coexistence region of the two states $+\bar{m}_0$ and $-\bar{m}_0$. As a consequence, within the interval $[-\bar{m}_0, +\bar{m}_0]$, the system should not enter the homogeneous state with its higher effective potential, but instead would break up into the so called *Weiss' domains*⁴ which, according to eq. (1.35), yield altogether the magnetization \bar{m}_q . If this were true, the hysteresis cycle would be hardly understood on the ground of the Weiss' mean field molecular model.

The pitfall in the above argument, as clearly and beautifully explained in the Lecture Notes by R. P. Feynman, R. B. Leighton & M. Sands (1993): *The Feynman Lectures on Physics*, Volume II Part 2, Masson (Milano) pp. 37–8/37–20, is as follows. Consider the layer between two domains, one having up-spinning electrons adjacent to the other one

⁴ A region of a ferromagnetic sample having only one direction of magnetization is called a *Weiss' domain* or simply a domain.

with down-spinning electrons, in a real ferromagnetic sample. But ferromagnetism appears only in those materials for which the energy is *reduced* if the electrons are parallel rather than opposite. So, we have added some extra energy in the layer between the two domains; this energy is sometimes called the *domain walls energy*.

Now it becomes evident that the residual magnetization can not move spontaneously from, say, $+\bar{m}_0$ to $-\bar{m}_0$ passing through the inhomogeneous states \bar{m}_q of eq. (1.35), because some extra domain walls energy in the intermediate states is necessary to create two or more domains with opposite magnetizations. In other words, it is not true that all the inhomogeneous states \bar{m}_q have the same value $g_0(\theta)$ of the effective potential, just because of the presence of the domain walls energy that acts just like a true potential barrier: namely,

$$g(\bar{m}_q, \theta) > g_0(\theta) , \quad 0 < q < 1 , \quad 0 < \theta < 1 . \quad (1.36)$$

The very same argument allows to explain the nature of the hysteresis curve for sufficiently weak applied magnetic fields. As a matter of fact, let us compare the effective potentials of the magnetization homogeneous states belonging to a small but nonzero applied field b [see e.g. Franz Schwabl (2002): *Statistical Mechanics*, Springer–Verlag, Berlin, pp. 283–297]. Suppose that b is sufficiently small and positive: then, along with the positive magnetization, there are also two more solutions of eq. (1.33) with negative magnetization. It is not difficult to verify, graphically or numerically, that the latter two have higher effective potential than the positive solution. Consequently, for a positive applied magnetic field, the state with positive magnetization is thermodynamically stable and this explains why any ferromagnetic sample keeps its positive magnetization as long as the applied magnetic field runs from large positive values to zero, where the residual value \bar{m}_0 is reached.

Now, suppose that we invert the applied magnetic field: accordingly, for weak enough negative b , it is easy to verify that the solution with negative magnetization has a lower effective potential than the two other solutions with positive magnetization. In particular, the up-spinning homogeneous solution which is continuously connected with \bar{m}_0 seems to be thermodynamically unstable and likely to decay into the down-spinning solution with the lowest value of the effective potential. However, in order to reach the latter solution the system should pass through inhomogeneous states involving many domains and a considerable domain walls energy. But this transition is not allowed until the applied field does not attain the coercive value $-H_c$, in such a way that the variation of the magnetic free enthalpy provided by the applied coercive field $|\Delta G_c(N, T; \bar{M})| \simeq V^2 H_c (\bar{M}' + \bar{M}_c)$, where V is the volume of the ferromagnetic sample under consideration, is enough to supply the domain walls free enthalpy ΔG_{dw} necessary to realize the sudden inversion of the magnetization. As a matter of fact, for a weak positive coercive field, we can write approximatively

$$\begin{aligned} \Delta G_{dw} &= |\Delta G_c| \\ &= \left| G(N, T; \bar{M}_c) - G(N, T; -\bar{M}') \right| \\ &\simeq V^2 H_c (\bar{M}' + \bar{M}_c) = \frac{V}{\lambda} H_c \Delta B_* \end{aligned}$$

where the very last expression just corresponds approximately to half of the area of the hysteresis cycle, as expected. This completes the discussion of the physical mechanism that allows to understand the hysteresis cycle on the ground of the Weiss' molecular field model of the ferromagnetism.

The critical indices of the Weiss' model. Let us now go back to the Weiss' mean field

equation (1.19): from the well known elementary hyperbolic trigonometric identity

$$\tanh(x + y) = \frac{\tanh x + \tanh y}{1 + \tanh x \tanh y} ,$$

it follows that

$$\tanh b = \bar{m} + \bar{m} \tanh b \tanh(\bar{m}/\theta) - \tanh(\bar{m}/\theta) . \quad (1.37)$$

In the neighbourhood of the critical point $\theta = 1$, $b = \bar{m} = 0$ all the arguments of the hyperbolic functions are small. Consequently, from the expansion

$$\tanh x = x - \frac{x^3}{3} + \frac{2x^5}{15} + \dots ,$$

we can easily derive

$$\tanh b = \bar{m} + \bar{m} \tanh b \left[\frac{\bar{m}}{\theta} - \frac{1}{3} \left(\frac{\bar{m}}{\theta} \right)^3 \right] - \frac{\bar{m}}{\theta} + \frac{1}{3} \left(\frac{\bar{m}}{\theta} \right)^3 + O(\bar{m}^5) , \quad (1.38)$$

whence we readily obtain

$$\left(1 - \frac{\bar{m}^2}{\theta} + \frac{\bar{m}^4}{3\theta^3} \right) \tanh b = \bar{m} \left(1 - \frac{1}{\theta} \right) + \frac{1}{3} \left(\frac{\bar{m}}{\theta} \right)^3 + O(\bar{m}^5) . \quad (1.39)$$

Finally, after setting

$$\tau := (T_c - T)/T_c$$

and keeping only the dominant contributions near the critical point, we can write

$$b \approx \frac{\bar{m}^3}{3} - \bar{m} \tau , \quad (1.40)$$

which is called the *Weiss' critical equation*. From this basic relationship we can extract the so called *critical indices* which fully characterize the behaviour of a ferromagnetic crystal near its critical Curie point $T \sim T_c$.

(i) Order parameter exponent β : when $b = 0$ and $0 \leq \tau \ll 1$ eq. (1.40) gives

$$\bar{m}^2 \approx 3\tau ,$$

whence the power like behaviour

$$|\bar{m}| \stackrel{T \sim T_c}{\sim} \sqrt{3} \vartheta(T_c - T) \left(\frac{T_c - T}{T_c} \right)^{1/2}, \quad (1.41)$$

where $\vartheta(x)$ denotes the Heaviside's step distribution, leading to the identification of the *order parameter critical exponent* $\beta = 1/2$.

(ii) Susceptibility exponents γ, γ' : from the definition

$$\chi_m \equiv \left\{ \frac{\partial \bar{M}(T; B)}{\partial B} \right\}_{B=0} = \frac{n\mu^2}{kT} \left(\frac{\partial \bar{m}}{\partial b} \right)_{b=0} \quad (1.42)$$

taking eq. (1.40) into account when $\tau \sim 0$ we obtain

$$1 \approx \left(\frac{\partial \bar{m}}{\partial b} \right)_{b=0} (\bar{m}^2 - \tau) \quad (1.43)$$

and consequently

$$\chi_m \stackrel{T \sim T_c}{\sim} \frac{n\mu^2}{kT} \{\bar{m}^2 - \tau\}^{-1}. \quad (1.44)$$

In the paramagnetic phase for $T \geq T_c$ we have that $b = 0 \Rightarrow \bar{m} = 0$ whence

$$\chi_m \stackrel{T \sim T_c}{\sim} \frac{n\mu^2}{k(T - T_c)}, \quad T \geq T_c, \quad (1.45)$$

that corresponds to a power like divergence of the magnetic susceptibility above the Curie temperature, *i.e.* to the *susceptibility critical exponent* $\gamma = 1$. Notice that the above approximate relationship is nothing but the Curie law (1.11), with $J = 1/2$ and $g = 2$, in which T is replaced by $T - T_c$. In the ferromagnetic phase for $T \leq T_c$, taking into account eq. (1.41) which defines the critical index β , we find $[\bar{m}^2 \approx 3\tau]$

$$\chi_m \stackrel{T \sim T_c}{\sim} \frac{n\mu^2}{2k(T_c - T)}, \quad T \leq T_c, \quad (1.46)$$

which leads again to a power-like divergent volume magnetic susceptibility below the Curie temperature, *i.e.* to the *susceptibility critical exponent* $\gamma' = 1$. Notice again

that even below the Curie temperature we still have the same Curie-like behaviour of the magnetic susceptibility *per* unit volume, albeit its coefficient is one-half the corresponding value above T_c .

- (iii) Critical isothermal exponent δ : if we consider the critical Weiss' equation along the critical isothermal $\tau = 0$ we obtain

$$b \approx \frac{\bar{m}^3}{3} \quad (1.47)$$

leading to *critical isothermal exponent* $\delta = 3$.

- (iv) Heat capacity at zero field exponent α : according to the Weiss' hypothesis, taking eq.(1.21) suitably into account, we can safely define the magnetic energy density, *i.e.* the magnetic energy *per* unit volume, of the dipole lattice model in the Weiss' approximation to be

$$u_m \approx -\frac{n}{2} kT_c \bar{m}(\theta, b) \{2\theta b + \bar{m}(\theta, b)\} . \quad (1.48)$$

For a vanishing applied external magnetic field $B = 0$ we get

$$u_m \approx -\frac{n}{2} kT_c \bar{m}^2(\theta, 0) , \quad (1.49)$$

and taking eq. (1.41) into account we find

$$u_m \approx -\frac{3}{2} nk(T_c - T) \vartheta(T_c - T) , \quad (1.50)$$

where, as usual, $\vartheta(x)$ denotes the Heaviside's step distribution. As a consequence, the *molar magnetic heat capacity* of a ferromagnetic sample in the Weiss' mean field approximation turns out to be a discontinuous function around the Curie point:

$$C_m \stackrel{T \sim T_c}{\sim} \frac{3R}{2} \vartheta(T_c - T) . \quad (1.51)$$

Such a finite jump of the molar magnetic heat capacity at the Curie temperature entails, by definition, the vanishing of the *heat capacity at zero field critical exponent* $\alpha = 0$.

To summarize, the Weiss' mean field theory of the ferromagnetic phase transition leads to the following set of critical exponents:

$$\alpha = 0 , \quad \beta = 1/2 , \quad \gamma = \gamma' = 1 , \quad \delta = 3 . \quad (1.52)$$

Experimental analysis leads to the following values for Iron and Nickel real samples:

$$\begin{aligned} \alpha_{\text{Fe}} &= -0.03 \pm 0.12 , & \alpha_{\text{Ni}} &= 0.04 \pm 0.12 , \\ \beta_{\text{Fe}} &= 0.37 \pm 0.01 , & \beta_{\text{Ni}} &= 0.358 \pm 0.003 , \\ \gamma_{\text{Fe}} = \gamma'_{\text{Fe}} &= 1.33 \pm 0.015 , & \gamma_{\text{Ni}} = \gamma'_{\text{Ni}} &= 1.33 \pm 0.02 , \\ \delta_{\text{Fe}} &= 4.3 \pm 0.1 ; & \delta_{\text{Ni}} &= 4.29 \pm 0.05 . \end{aligned}$$

The above values show that the Weiss' mean field theory, in spite of its simplicity, does represent a reasonable *zeroth-order* approximation to the ferromagnetic phase transition near the Curie point. Furthermore, it turns out to be quite reliable below the Curie temperature, as described above, iff $J = 1/2$.

We close by noticing that the Gibbs free enthalpy near the critical point can be obtained from eq.s (1.31) and (1.34): it reads, up to the fourth power of the magnetization,

$$G(N, T; \overline{M}) \approx NkT_c \left\{ -\theta \ln 2 - \frac{\tau}{2} \overline{m}^2 + \frac{\overline{m}^4}{12} \right\} . \quad (1.53)$$

It turns out, as firstly shown by Lev Davidovic Landau (1937): *Phys. Zs. Sowjet* **11**, 545, that a general mathematical theory of the second order phase transitions can be given, *mutatis mutandis*, by the very same general form of the Gibbs free enthalpy. This is the so called *Landau's theory of second order phase transitions*, as described in the book by

L. D. Landau & E. M. Lifchitz (1967): *Physique Statistique*, MIR, Moscow, pp. 517–522, see in particular eq. (138,4) p. 519. The main remarkable result of the Landau's theory is that the *classical values* (1.52) of the critical exponents turn out to be *universal*: within the range of validity of the approximation (1.53), the critical exponents are the same for all the second order phase transitions, provided the number d of the dimensions as well as the number D of the components of the order parameters of the physical systems are the same. In particular, the critical exponents do not depend upon the details of the microscopic molecular interactions, a key feature that holds true even beyond the Landau's approximation. In this sense, the ferromagnetism does represent the paradigm of all the second order phase transitions with the same $d = 3$ and $D = 1$.

The reason of the denomination *second order* for the phase transitions described by the Gibbs free enthalpy (1.53) in the vicinity of the critical point is as follows. The Gibbs potential (1.53) turns out to be a polynomial function of its arguments and is thereby continuous across the critical point. Let us now consider the first partial derivatives of the Gibbs free enthalpy (1.53) in the vicinity of the transition point: we find out

$$S \equiv - \left(\frac{\partial G}{\partial T} \right)_{N, \bar{M}} \approx Nk \ln 2 - \frac{3}{2} Nk\tau, \quad (1.54a)$$

$$B \equiv \frac{1}{V} \left(\frac{\partial G}{\partial \bar{M}} \right)_{N, T} \approx \lambda n \mu \bar{m} \left\{ -\tau + \frac{\bar{m}^2}{3} \right\}. \quad (1.54b)$$

We see that also the entropy and the applied magnetic field are continuous across the transition point. Moreover, the magnetic heat capacity – see eq. (1.51) – and the inverse of the magnetic susceptibility – see eq.s (1.45) and (1.46) – are respectively given by

$$C_m = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_{N, \bar{M}} \approx (3/2) Nk \vartheta(T_c - T), \quad (1.55a)$$

$$\chi_m^{-1} = \frac{1}{V} \left(\frac{\partial^2 G}{\partial \bar{M}^2} \right)_{N, T} \approx \frac{2k}{n\mu^2} |T_c - T| - \frac{k}{n\mu^2} (T - T_c) \vartheta(T - T_c). \quad (1.55b)$$

It turns out that the Gibbs free enthalpy and its first partial derivatives are *continuous* at the transition point, whereas its second partial derivative (1.55a) is discontinuous, *i.e.*, the heat capacity exhibits a finite jump at the transition point.

This is the reason for the denomination *continuous or second order* phase transitions, as described by the Landau's theory in the vicinity of the critical point, to be contrasted by the so called *discontinuous or first order* phase transitions, in which the first derivatives of the thermodynamic potential are discontinuous and a finite non-vanishing latent heat is involved, as we shall discuss in the next paragraph.

As a final remark, we recall that the magnetic susceptibility is directly related to the magnetization variance. In fact we have

$$(\Delta\bar{M})^2 := \left(\frac{kT}{V}\right)^2 \frac{\partial^2}{\partial B^2} \ln Z_{\text{Weiss}} = \frac{kT}{V} \chi_m , \quad (1.56)$$

so that the critical indices $\gamma = \gamma' = 1$ do indicate the presence of very large anomalous fluctuations of the magnetization near the Curie temperature. As already discussed in §V.4, this is a general feature known as the fluctuation–dissipation theorem. Going back to eq.s (4.21) and (4.22) we have

$$c_v = \frac{k}{M} \beta^2 (\Delta H)^2 ; \quad (1.57a)$$

$$\kappa_T = \frac{kT}{V} (\Delta N)^2 ; \quad (1.57b)$$

$$\chi_m = \beta V (\Delta\bar{M})^2 , \quad (1.57c)$$

which show that very large fluctuations of extensive quantities like average energy, density and magnetization are signalled by divergencies of corresponding intensive parameters such as specific heat, isothermal compressibility and magnetic susceptibility.

X.2. The sublimation discontinuous phase transition.

Here we want to discuss a specific example of *discontinuous or first order phase transition*, *i.e.*, a phase change in which a non-vanishing absorption or emission of thermal energy is involved. To this aim, we shall consider some portion of a crystal solid in thermal equilibrium with its own saturated vapour at a given temperature T . In such a condition, the pressure exerted by the saturated vapour on the walls of the container is fixed by the temperature and it does not change until the solid sample is fully sublimated or, *vice versa*, until the saturated vapour is fully frozen.

It is not difficult to calculate the saturated vapour tension $p(T)$ of a solid crystal, as a function of the absolute thermodynamic temperature T , under the assumption that the saturated vapour could be treated as a perfect ideal gas of N identical monoatomic molecules of mass m , whereas the solid sample is described by a crystal lattice with N cells and A point-like atoms, of the same mass m , per unit cell. The solid sample and its saturated vapour are enclosed in a large vessel of volume V in thermal equilibrium with a large heat reservoir at the absolute temperature T .

The thermodynamic equilibrium between the solid crystal and its saturated vapour can be expressed as [see E. Fermi (1972): *Termodinamica*, Boringhieri, Torino, p. 97]

$$\varphi_{\text{crystal}} = \varphi_{\text{vapour}} , \quad (2.1)$$

where $\varphi(p, T)$ indicates the specific Gibbs potential, *i.e.* the Gibbs free enthalpy *per* unit of mass, which is also called *chemical potential*. As a matter of fact, consider the vapour-solid mixture in equilibrium at temperature T and vapour tension $p(T)$. The mass of the solid is $M_{\text{crystal}} = ANm$ and the mass of the vapour is $M_{\text{vapour}} = Nm$. If the system is in equilibrium with the given T and $p(T)$, the Gibbs potential Φ of this state must be

at a minimum. That is, if any parameters other than T and $p(T)$ are varied slightly, we must have $\delta\Phi = 0$. Let us vary the composition of the mixture by converting an amount $\delta M_{\text{crystal}}$ of solid into vapour, so that $-\delta M_{\text{crystal}} = \delta M_{\text{vapour}} = \delta M > 0$.

The total Gibbs free enthalpy of the solid-vapour mixture may be represented, if we neglect surface effects, as $\Phi = M_{\text{crystal}}\varphi_{\text{crystal}} + M_{\text{vapour}}\varphi_{\text{vapour}}$. Now, owing to the fact that the mass transfer takes place at a given T and $p(T)$, it immediately follows that

$$\delta\Phi = 0 = \delta M(\varphi_{\text{vapour}} - \varphi_{\text{crystal}}) ,$$

whence the equilibrium condition of eq. (2.1). This means in turn that

$$\frac{F_{\text{crystal}}}{ANm} - \frac{F_{\text{vapour}}}{Nm} = p \left(\frac{V_{\text{vapour}}}{Nm} - \frac{V_{\text{crystal}}}{ANm} \right) \simeq pv \simeq \frac{kT}{m} , \quad (2.2)$$

where $F(T, V)$ denotes the Helmholtz free energy and where we have taken into account that the specific volume v_{crystal} of the crystal sample is much smaller than the specific volume v_{vapour} of the vapour, namely:

$$v_{\text{crystal}} \ll v_{\text{vapour}} \simeq v \quad (2.3)$$

and we have supposed to treat the saturated vapour as a perfect gas with N monoatomic molecules of mass m .

The Helmholtz free energy is obtained from the partition function according to

$$F(T, V) = -kT \ln Z(T, V) , \quad (2.4)$$

the partition functions of a perfect gas and of a solid sample in the Debye's approximation being respectively given by

$$\ln Z_N(T, V) = N \left(1 + \ln \frac{V}{N} \right) + \frac{3N}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) , \quad (2.5)$$

$$\begin{aligned} \ln Z_{\Theta}(T, V_{\text{crystal}}) = \\ -\beta U_0 - V_{\text{crystal}} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \int_0^{k\Theta/\hbar} \frac{d\omega}{2\pi^2} \omega^2 \ln(1 - e^{-\beta\hbar\omega}) . \end{aligned} \quad (2.6)$$

Here we have denoted by Θ the Debye's temperature, v_l and v_t are the longitudinal and transversal sound velocities in the crystal solid respectively, whilst U_0 does represent the non-vanishing internal energy of the crystal solid at zero temperature. Notice that the Debye's temperature and the total number of the crystal lattice degrees of freedom are related by

$$\begin{aligned} 3AN &= \frac{1}{2\pi^2} V_{\text{crystal}} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \int_0^{k\Theta/\hbar} d\omega \omega^2 \\ &= \frac{1}{2\pi^2} V_{\text{crystal}} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \frac{k^3 \Theta^3}{3\hbar^3} . \end{aligned} \quad (2.7)$$

The zero-point internal energy U_0 can be also expressed in terms of the Debye's temperature and the minimum $\mathcal{V}_0 < 0$ of the interatomic potential according to

$$\begin{aligned} U_0 &= \mathcal{V}_0 + \frac{1}{2\pi^2} V_{\text{crystal}} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \int_0^{k\Theta/\hbar} d\omega \omega^2 \frac{\hbar\omega}{2} \\ &= \mathcal{V}_0 + V_{\text{crystal}} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \frac{k^4 \Theta^4}{16\pi^2 \hbar^3} \\ &= \mathcal{V}_0 + \frac{9}{8} ANk\Theta . \end{aligned} \quad (2.8)$$

Taking eq.s (2.4)-(2.8) into account, we can rewrite the equilibrium condition (2.2) in the form

$$1 = N^{-1} \ln Z_N(T, V) - (AN)^{-1} \ln Z_\Theta(T, V_{\text{crystal}}) , \quad (2.9)$$

namely:

$$\begin{aligned} \ln \frac{N}{V} &= \ln \frac{p}{kT} = \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{\mathcal{V}_0}{ANkT} + \frac{9\Theta}{8T} \\ &+ \frac{9\hbar^3}{k^3 \Theta^3} \int_0^{k\Theta/\hbar} d\omega \omega^2 \ln(1 - e^{-\beta\hbar\omega}) . \end{aligned} \quad (2.10)$$

Now, it is convenient to rewrite the very last term of the RHS of the above equation as follows: after the change of variable $x \equiv \beta\hbar\omega$ and an integration by parts, we eventually

obtain

$$\begin{aligned} \ln p = & \frac{5}{2} \ln(kT) + \frac{3}{2} \ln\left(\frac{2\pi m}{h^2}\right) + \frac{\mathcal{V}_0}{ANkT} + \frac{9\Theta}{8T} \\ & + 3 \left\{ \ln\left(1 - e^{-\Theta/T}\right) - \left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} dx \frac{x^3}{e^x - 1} \right\}. \end{aligned} \quad (2.11)$$

Now, if we set

$$\Delta(\xi) \equiv \xi^3 \int_0^{1/\xi} dx \frac{x^3}{e^x - 1}, \quad \xi \equiv (T/\Theta), \quad (2.12)$$

the saturated vapour tension can be recast in the form

$$\begin{aligned} p(T) = & \frac{kT}{\lambda_T^3} \left(1 - e^{-\Theta/T}\right)^3 \\ & \times \exp\left\{ \frac{\mathcal{V}_0}{ANkT} + \frac{9\Theta}{8T} - 3\Delta(T/\Theta) \right\}, \end{aligned} \quad (2.13)$$

where $\lambda_T \equiv h/\sqrt{2\pi mkT}$ is the thermal wavelength. Notice that $\lim_{T \downarrow 0} \Delta(T/\Theta) = 0$, whereas $\lim_{T \rightarrow \infty} 3\Delta(T/\Theta) = 1$.

In order to better understand the physical meaning of eq. (2.13), let us first consider the low temperature regime $T \ll \Theta$, in which the quantum behaviour of the crystal is important whilst the saturated vapour is always treated like a perfect gas⁵. In this limit one can readily obtain the leading behaviour

$$p(T) \simeq \frac{kT}{\lambda_T^3} \exp\left\{ -\frac{|\mathcal{V}_0|}{ANkT} + \frac{9\Theta}{8T} \right\}, \quad T \ll \Theta. \quad (2.14)$$

It is worthwhile to stress the following fact: when $T \downarrow 0$, no vapour is present anymore, all the matter being frozen into the crystal, so that

$$\lim_{T \downarrow 0} N(T) = 0, \quad \lim_{T \downarrow 0} p(T) = 0. \quad (2.15)$$

This entails, taking eq. (2.14) into account, that

$$\mathcal{V}_0 < 0, \quad |\mathcal{V}_0| > (9/8)NAk\Theta. \quad (2.16)$$

⁵ It turns out that this assumption is truly realistic in dealing with most of the common crystals, as the Debye's temperatures range from ~ 215 °K (Ag) to ~ 1850 °K (C).

Conversely, in the high temperature regime $T \gg \Theta$, which corresponds to the classical limit, we find instead the dominant contribution to be

$$p(T) \simeq \frac{kT}{e\lambda_T^3} \left(\frac{\Theta}{T}\right)^3 \exp\left\{-\frac{|\mathcal{V}_0|}{ANkT}\right\}, \quad T \gg \Theta. \quad (2.17)$$

As required by general arguments that we shall discuss here below, the saturated vapour tension of eq. (2.17) must be a monotonically increasing function of the temperature: it follows therefrom that

$$\Theta \ll T < T_* \equiv (2|\mathcal{V}_0|/ANk) \simeq T_{\text{fusion}}$$

which represents an upper bound for the validity of the present approximations.

As a matter of fact, it is instructive to compare the approximate formulae (2.14) and (2.17) for the saturated vapour tension of a crystal solid with the approximate solution of the Clapeyron's equation [see *e.g.* Enrico Fermi (1972): *Termodinamica*, Boringhieri, Torino, pp. 73–79; L. D. Landau & E. M. Lifchitz (1967): *Physique Statistique*, MIR, Moscou, pp. 318–320]

$$\frac{dp}{dT} = \frac{s_{\text{vapour}} - s_{\text{crystal}}}{v_{\text{vapour}} - v_{\text{crystal}}} = \frac{q(T)}{T(v_{\text{vapour}} - v_{\text{crystal}})}, \quad (2.18)$$

where $q(T)$ is the *latent heat* of sublimation at the temperature T , *i.e.*, the heat quantity necessary to transform into vapour 1 g of crystal at the temperature T . Notice that

$$q(T) = T(s_{\text{vapour}} - s_{\text{crystal}}), \quad (2.19)$$

in which s_{vapour} and s_{crystal} just denote the specific entropies of the vapour and of the crystal respectively. Now, under the previously assumed conditions

$$v_{\text{crystal}} \ll v_{\text{vapour}} \simeq kT/mp,$$

if we suppose the latent heat of sublimation to be independent of the temperature within a suitable range of values $T_i \leq T \leq T_f$, then the integration of eq. (2.18) yields

$$p(T) \simeq p_{i,f} \exp \left\{ \frac{mq}{kT_{i,f}} \right\} \exp \left\{ -\frac{mq}{kT} \right\} = \bar{p} \exp \left\{ -\frac{mq}{kT} \right\}, \quad (2.20)$$

where \bar{p} is a suitably chosen constant pressure. It follows that we can read off the constant pressure and the latent heat of sublimation in the low (\downarrow) and high (\uparrow) temperature regimes, up to the above mentioned approximations: namely,

$$p_{\uparrow} = \frac{kT_*}{e\lambda_{T_*}^3} \left(\frac{\Theta}{T_*} \right)^3, \quad q_{\uparrow} \simeq \frac{|\mathcal{V}_0|}{M_{\text{crystal}}}, \quad \Theta \ll T \leq T_*; \quad (2.21)$$

$$p_{\downarrow} = \frac{k\Theta}{\lambda_{\Theta}^3}, \quad q_{\downarrow} \simeq \frac{|\mathcal{V}_0|}{M_{\text{crystal}}} - \frac{9k}{8m}\Theta > 0, \quad T \ll \Theta. \quad (2.22)$$

It follows therefrom that eq.s (2.21) and (2.22) may allow an experimental determination of the minimum \mathcal{V}_0 of the interatomic potential, as well as of the Debye's temperature Θ , from the measure of the latent heat of sublimation q .

As a final remark, we stress that the equilibrium curve of the phases $p = p(T)$ is derived from the equilibrium condition $\varphi_1(p, T) = \varphi_2(p, T)$, where the indices $i = 1, 2$ refer to the two phases. Actually, eq. (2.23) just represents a curve in the (T, p) -plane. Now, since we have

$$\left(\frac{\partial \varphi_i}{\partial T} \right)_p = -s_i, \quad \left(\frac{\partial \varphi_i}{\partial p} \right)_T = v_i, \quad (2.24)$$

it follows from the Clapeyron's equation (2.18) that the chemical potential is continuous across the equilibrium curve of the two phases, whilst the first partial derivatives appear to be discontinuous, the discontinuity being proportional to the latent heat of transition. This is just the reason for the terminology *first order discontinuos phase transitions* in which a non-vanishing latent heat of transition is always involved.

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