
Pure Crystalline Solids

Crystalline solids are characterized by the regular and periodic spatial arrangement of entities at the nodes of a lattice. The nature of the entities thus arranged defines the nature of the solid. There are four distinct classes:

- atomic solids, comprising a lattice of atoms, such as solid argon, for example;
- molecular solids, where the entities arranged at the nodes of the lattice are molecules, as is the case in solid benzene;
- ionic crystals. In this case, the entities are ions, and they are arranged into two sublattices: one of cations and the other of anions. The proportions of sites occupied by these two sublattices are obviously such that the whole solid is electrically neutral, overall. The ions thus arranged could either be simple ions, as is the case with sodium chloride, or complex ions such as in ammonium carbonate;
- metals, in which ions are arranged at the nodes of the lattice. To ensure electrical neutrality, more-or-less mobile electrons are distributed around these ions.

1.1. Characteristic values of a solid

Solids are incompressible, which means that their derivative $(\partial V / \partial P)_T$ is practically zero, so they do not have an equation of state such as $F(P, V, T) = 0$.

However, solids do experience changes in volume, under the influence of temperature, which is characterized by its cubic expansion coefficient or its linear expansion coefficient.

Similarly, when heat is applied to it, solids heat up. The extent of that rise in temperature is characterized by the solid's specific heat capacity.

When a solid is subjected to a stress (or load) – i.e. a certain amount of force per unit surface area or a moment per unit length, such as axial traction (Figure 1.1(a)) or axial compression (Figure 1.1(b)), for example – it normally deforms. This deformation is also known as “strain”.

Other values pertaining to the dielectric and magnetic properties are also available.

In the next section, we will examine the first three effects, starting with the effect of a stress. Then we will develop models of solids which we can go on to use in dealing with the questions of specific heat capacities and thermal expansion.

1.2. Effect of stress and Young's modulus

When a solid is subjected to a stress, it generally experiences a strain which, if pursued, could cause the material to fracture. The applied stress is measured in newtons per square meter.



Figure 1.1. *Cylindrical test tube a) under traction; b) under compression*

Take the example of traction applied to a cylinder whose initial length is l_0 and cross-section area is s (Figure 1.1(a)). If we begin with zero stress, and very gradually increase the stress (i.e. the traction

force) at a constant temperature, the relative strain $\Delta l/l_0$ increases, obeying a law which is often identical to its tangent to the origin – that is, a practically linear law (the part “OA” of the curve shown in Figure 1.2) – which is known as Hooke’s law, and is written as follows for a given temperature:

$$\frac{F}{s} = E \frac{\Delta l}{l_0} \quad [1.1]$$

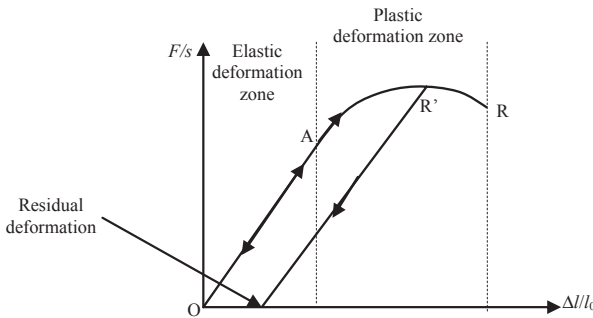


Figure 1.2. Strain/stress curve under traction

A solid, therefore, is characterized by its modulus of longitudinal elasticity, known as Young’s modulus, defined by:

$$E = \frac{l_0 s}{1 \left(\frac{\partial l}{\partial F} \right)} \quad [1.2]$$

If we start at O and arrive at a point between O and A (a point marking the start of a lesser increase of the curve), and we slowly decrease the stress, the strain decreases in accordance with the same Hooke curve. We then say that we are in the domain of elastic deformation. When the stress returns to zero, the sample returns to its initial length. The load at point A is called the elastic limit.

After point A in Figure 1.2, the curve changes direction, and Hooke’s law is no longer obeyed. If we stop at a point R’ between A

and R, and decrease the stress, the curve then follows a straight line which is practically parallel to Hooke's straight line. The result of this is that when the stress returns to zero, there is a remaining deformation which is known as the residual deformation. We say that between points A and R, the solid undergoes a plastic deformation.

When we reach a point R, the test-tube breaks. The corresponding stress is called the fracture limit.

The different characteristics of the curves in Figure 1.2 vary greatly from one material to another. Hence, for example, the fracture load is much greater for steel than for concrete, which has pitiful traction resistance – this is why steel rods are used in reinforced concrete.

NOTE.– We have pointed out that the stress variations must, during increase and decrease, take place very slowly, because strictly speaking, the Young's modulus depends not only on the temperature but also on the rate at which the load changes.

The Young's modulus obviously depends on the temperature, but these data can sometimes be replaced by a state equation in the form $F(F,l,T) = 0$, such as that given for rubber, which links the temperature T , the length l of a cylinder of rubber with section s , to the force of traction F exerted upon it in the elastic domain by way of two constants, B and its cubic expansion coefficient β which is of the form:

$$F = BT \left\{ \frac{l}{l_0} - [1 + \beta(T - T_0)] \left(\frac{l_0}{l} \right)^2 \right\} \quad [1.3]$$

We can obtain very similar results by imposing other types of stresses such as compression or shear. Of course, the corresponding moduli have completely different values from those encountered in the case of traction.

1.3. Microscopic description of crystalline solids

From a microscopic point of view, we find the four classes of solids introduced at the start of this chapter.

Based on each of these models, we will establish canonical partition functions which define the microscopic system, followed by the Helmholtz energy, which links the microscopic point of view to the macroscopic system, and finally the internal energy, which will be useful for us later on to establish the specific heat capacities.

1.4. Partition function of vibration of a solid

Irrespective of the nature of the solid, there are always species (atoms, ions and molecules) placed at the nodes of the lattice, and are animated with a motion of vibration around their equilibrium positions. Thus, the partition function will include a contribution due to these vibrations. On the statistical level, the entities in question (atoms, ions or molecules) are considered to be localized particles and, in general, to describe the vibrations of the solid, it is sufficient to place ourselves in the context of the conventional limit case of statistics. It results from this that the contribution Z_C of the vibrations to the canonical partition function can be calculated on the basis of the atomic partition functions z by the relation:

$$Z_C = z^N \quad [1.4]$$

We will calculate this contribution by first considering a solid as a macromolecule with N vibrating entities, having $3N$ independent vibrational degrees of freedom: phonons. Two models can be used to express a contribution of these vibrations to the canonical partition function: Einstein's model and Debye's, which is more general. Let us look at each of these two models in turn.

1.4.1. Einstein's single-frequency model

In this model, the crystalline solid is a system of $3N$ oscillators, in which all have the same fundamental frequency ν_E . The corresponding characteristic temperature of vibration, defined on the basis of the relation:

$$\Theta_E = \frac{h\nu}{k_B} \quad [1.5]$$

is called the *Einstein temperature* Θ_E . By applying equation [1.4] and the expression of the vibrational partition function, written as:

$$z_v = \frac{\exp\left[-\frac{\Theta_E}{2T}\right]}{1 - \exp\left[-\frac{\Theta_E}{T}\right]} \quad [1.6]$$

we can write the canonical partition function of vibration in the form:

$$Z_{C(v)} = (z_v)^{3N} = \exp\left(-\frac{3N\Theta_E}{2T}\right) \left[1 - \exp\left(-\frac{\Theta_E}{T}\right)\right]^{-3N} \quad [1.7]$$

or if we switch to the logarithm, the previous equation becomes:

$$\ln Z_{C(v)} = -\frac{3N\Theta_E}{2T} - 3N \ln \left[1 - \exp\left(-\frac{\Theta_E}{T}\right)\right] \quad [1.8]$$

1.4.2. Debye's frequency distribution model

In the case of Debye's model, the $3N$ oscillators no longer have the same fundamental frequency. By applying the equation:

$$z_v \cong \prod_E \frac{\exp\left(-\frac{\Theta_E}{2T}\right)}{1 - \exp\left(-\frac{\Theta_E}{T}\right)} \quad [1.9]$$

we are able to write the following for the canonical partition function of vibration:

$$Z_{C(v)} = \prod_{i=1}^{3N} \frac{\exp\left(-\frac{h\nu_i}{2k_B T}\right)}{1 - \exp\left(-\frac{h\nu_i}{k_B T}\right)} \quad [1.10]$$

However, if we reformulate in logarithmic terms, we find:

$$\ln Z_{C(\nu)} = \frac{\sum_{i=1}^{3N} h\nu_i}{2k_B T} - \sum_{i=1}^{3N} \ln \left[1 - \exp \left(-\frac{h\nu_i}{k_B T} \right) \right] \quad [1.11]$$

Debye supposes that the frequencies are sufficiently similar so that the distribution can be supposed to be continuous, which enables us to replace the sum of equation [1.11] by an integral, which is written as follows for a frequency distribution $g(\nu)$:

$$\ln Z_{C(\nu)} = -\frac{\int_0^{\nu_D} h\nu g(\nu) d\nu}{2k_B T} - \int_0^{\nu_D} \ln \left[1 - \exp \left(-\frac{h\nu}{k_B T} \right) \right] g(\nu) d\nu \quad [1.12]$$

Debye also supposes that this frequency distribution is of the same form as the elastic frequency distribution of the solid, supposed to be a continuum. Those frequencies themselves are linked to the propagation of sound in that solid. These frequencies range from the value 0 to a maximum frequency ν_D defined by equation [1.13], where c is the celerity of sound in the solid.

$$\nu_D = c \left(\frac{3N}{4\pi V} \right)^{1/2} \quad [1.13]$$

The corresponding frequency temperature – defined, as for Einstein's temperature, using relation [1.5] – which is called the *Debye temperature* Θ_D , is thus defined by:

$$\Theta_D = \frac{h\nu_D}{k_B} \quad [1.14]$$

Table 1.1 shows a selection of values of the Debye temperature which can, as we can see, be very different depending on the solid.

Solid	$\Theta_D(\text{K})$
Pb	88
Ag	220
Al	396
KCl	227
C (diamond)	2067

Table 1.1. The Debye temperature of various solids (data taken from [INF 06])

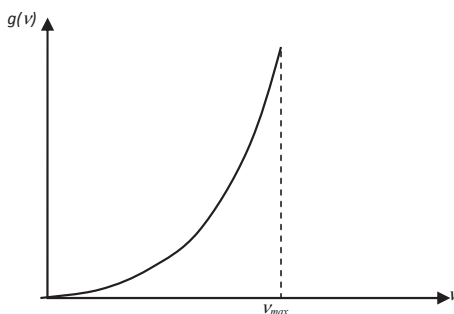


Figure 1.3. Frequency distribution according to Debye

The frequency distribution $g(\nu)$ is of the form (see Figure 1.3):

$$\left\{ \begin{array}{l} \text{For } \nu \leq \nu_D : g(\nu) = \frac{9N\nu^2}{\nu_D^3} \\ \text{For } \nu > \nu_D : g(\nu) = 0 \end{array} \right. \quad [1.15]$$

obviously, with the standardization condition:

$$\int_0^{\nu_D} g(\nu) d\nu = 3N \quad [1.16]$$

Relation [1.12] then takes the form:

$$\ln Z_{C(\nu)} = -\frac{9N\Theta_D}{8T} - \frac{9N}{\nu_D^3} \int_0^{\nu_D} \nu^2 \ln \left[1 - \exp\left(-\frac{h\nu}{k_B T}\right) \right] d\nu \quad [1.17]$$

If we set:

$$x = \frac{h\nu}{k_B T} \quad [1.18]$$

relation [1.17] can also be written:

$$\ln Z_{C(v)} = -\frac{9N\Theta_D}{8T} - \frac{9NT^3}{\Theta_D^3} \int_0^{\Theta_D/T} x^2 \ln[1 - \exp(-x)] dx \quad [1.19]$$

The integral appearing in this formula cannot be expressed by a simple algebraic sum. However, if we integrate by parts, we find:

$$\begin{aligned} \ln Z_{C(v)} = & -\frac{9N\Theta_D}{8T} - 3N \ln \left[1 - \exp\left(-\frac{\Theta_D}{T}\right) \right] \\ & + \frac{3NT^3}{\Theta_D^3} \int_0^{\Theta_D/T} \frac{x^3 \exp(-x)}{1 - \exp(-x)} dx \end{aligned} \quad [1.20]$$

1.4.3. Models with more complex frequency distributions

Debye's model, which allows for a frequency distribution given by relation [1.9], has only yielded correct values of the specific heat capacity at constant volume (see section 1.8) for fairly low temperatures. Other authors have improved the model by modifying that frequency distribution. For example, Born and Karman took a new approach to the establishment of the frequency distribution, this time supposing that the solid was no longer a continuum, but instead was represented by a periodic lattice of particles, which led them to the distribution function as shown in Figure 1.4(a). The distribution function reaches its peak very near to the limit frequency.

Blackman, for his part, determined the vibration spectrum for simple cubic lattices. The frequency distribution which it achieves exhibits two maximum points (see Figure 1.4(b)). One point of these is always situated in the vicinity of the limit frequency; the other point, which is less clear, is at a lower frequency.

In fact in this types of models, with a frequency distribution modified compared to Debye's, we can keep the developments obtained using Debye's model, but as if the Debye temperature varied with temperature.

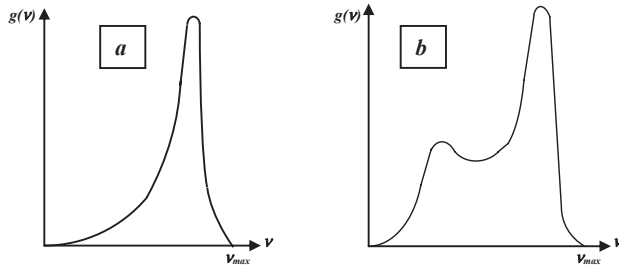


Figure 1.4. Frequency distributions: a) Born and Karman; b) Blackman

Variations in the Debye temperature with the temperature have, indeed, been observed by Mott and Jones.

1.5. Description of atomic solids

In an atomic solid, each node of the lattice is occupied by an atom, e.g. in the case of a solid rare gas, but also chlorine, fluorine, etc. For a pure solid, there is only one sort of atom.

1.5.1. Canonical partition function of an atomic solid

Besides the vibrating motion of the atoms which we have discussed above, the solid is home to electron motion and nuclear spin, each of which makes a contribution to the canonical partition function.

With regard to the motion of the electrons, we choose as energy origin the fundamental level in the atom, and these electrons are not excited, so that the contribution to the atomic partition function of electrons is reduced to its statistical weight, according to the equation $z = g_0$, and therefore the electron contribution to the canonical partition function will be:

$$\ln Z_{C(e)} = N \ln g_{0(e)} \quad [1.21]$$

For the contribution of nucleus spin, we see the same situation as for the electrons, so their contribution will be:

$$\ln Z_{C(n)} = N \ln g_{0(n)} \quad [1.22]$$

The overall canonical partition function for the solid will be:

$$\ln Z_C = \ln Z_{C(v)} + \ln Z_{C(e)} + \ln Z_{C(n)} \quad [1.23]$$

However, it is helpful, in studying solids, to choose as the energy origin the atoms which are infinitely far apart, instead of the fundamental level of vibration. Therefore, for each atom, we need to involve the crosslink energy u_R , which is the energy needed to send that atom to infinity. This introduces a new term, known as crosslinking – a relative distribution function of the atoms – into the canonical partition function, and gives us a term in the following form:

$$\ln Z_{C(v)} = \frac{Nu_R}{k_B T} = \frac{U_R}{k_B T} \quad [1.24]$$

In light of relations [1.21], [1.22] and [1.24], expression [1.23] becomes:

$$\begin{aligned} \ln Z_{C(v)} = & \frac{U_R}{k_B T} - \frac{9N\Theta_D}{8T} - 3N \ln \left[1 - \exp\left(-\frac{\Theta_D}{T}\right) \right] \\ & + \frac{3NT^3}{\Theta_D^3} \int_0^{\Theta_D/T} \frac{x^3 \exp(-x)}{1 - \exp(-x)} dx + N \ln g_e g_n \end{aligned} \quad [1.25]$$

1.5.2. Helmholtz energy and internal energy of an atomic solid

The Helmholtz energy F of a solid, comprising N atoms, can be calculated using the relation that links Helmholtz energy to the canonical partition function:

$$F = -k_B T \ln Z_C \quad [1.26]$$

In view of the canonical partition function, given by relation [1.25], the molar Helmholtz energy F_m is obtained by applying the two relations $N = N_a$ and $k_B N_a = R$ in expression [1.26]. From this, we can easily deduce the molar internal energy using the relation:

$$U_m - U_0 = -\frac{1}{RT^2} \frac{d\left(\frac{F_m}{T}\right)}{dT} \quad [1.27]$$

In fact, that internal energy is the sum of the four contributions: crosslink (independent of temperature), vibration (a function of the temperature), electron and nuclear activity (practically independent of temperature), which is written as:

$$U_m - U_0 = U_{m(R)} + U_{m(v)}(T) + U_{m(e)} + U_{m(n)} \quad [1.28]$$

For the contribution of vibration, we can either use Einstein's model, which yields:

$$U_{m(v)} = \frac{3R\Theta_E}{\left[\exp\left(-\frac{\Theta_E}{T}\right) - 1\right]} \quad [1.29]$$

or Debye's model, which gives us:

$$U_{m(v)} = \frac{9RT^4}{\Theta_D^3} \int_0^{\Theta_D/T} \frac{x^3}{[\exp(x) - 1]} dx \quad [1.30]$$

We cannot analytically calculate the integral appearing in relation [1.30], but we can give two approximate values for it depending on whether the temperature is high or low in relation to the Debye temperature.

For the high temperatures ($T \gg \Theta_D$), we develop the function to be integrated into a Maclaurin series and integrate, we find:

$$U_{m(v)} = -\frac{9R\Theta_D}{8} + 3RT \left[1 + \frac{1}{20} \left(\frac{\Theta_D}{T}\right)^2 + O\left(\frac{\Theta_D}{T}\right)^4 \right] \quad [1.31]$$

The term $O\left(\frac{\Theta_D}{T}\right)^4$ indicates the rest of the series development.

For low temperatures ($T \ll \Theta_D$), we replace the integral with the difference of two integrals – the first between 0 and infinity and the second between Θ_D/T and infinity. We can show that we obtain:

$$U_{m(v)} = 3RT \left[\frac{\pi^4 T^3}{5\Theta_D^3} - 3 \exp\left(-\frac{\Theta_D}{T}\right) + O\left(\frac{\Theta_D}{T} \exp\left(-\frac{\Theta_D}{T}\right)\right) \right] \quad [1.32]$$

1.6. Description of molecular solids

If, instead of one atom per crystalline site, a solid contains a group of atoms (ions or molecules) at each site, if the crystal contains N molecules, the lattice will always have $3N$ degrees of vibrational freedom, but there will still be $3(s^{-1})$ internal degrees of freedom per molecule if the molecule contains s atoms.

1.6.1. Partition function of molecular crystals

The new “internal” degrees of freedom will generally tend to be vibrational degrees of freedom, and if the corresponding fundamental frequencies are $\nu_1, \nu_2, \dots, \nu_i, \dots$, the contribution corresponding to the canonical partition function is:

$$\ln Z_{C(\text{int})} = N \sum_{i=4}^{3s} \ln \left[1 - \exp\left(-\frac{\Theta_i}{T}\right) \right] \quad [1.33]$$

In Einstein’s model, in view of the new electronic and nuclear contributions, this would give us:

$$\begin{aligned} \ln Z_C = & -\frac{U_0}{k_B T} - \frac{3N\Theta_E}{2T} - 3N \ln \left[1 - \exp\left(-\frac{\Theta_E}{T}\right) \right] \\ & - N \sum_{i=4}^{3s} \ln \left[1 - \exp\left(-\frac{\Theta_i}{T}\right) \right] + N \sum_{i=1}^s \ln g_{s(e)} + N \sum_{i=1}^s \ln g_{s(n)} \end{aligned} \quad [1.34]$$

and in Debye's model, we would have:

$$\begin{aligned} \ln Z_C = & -\frac{9N\Theta_D}{8T} - 3N \ln \left[1 - \exp\left(-\frac{\Theta_D}{T}\right) \right] \\ & + \frac{3NT^3}{\Theta_D^3} \int_0^{\Theta_D/T} \frac{x^3 \exp(-x)}{1 - \exp(-x)} dx - N \sum_{i=4}^{3s} \ln \left[1 - \exp\left(-\frac{\Theta_i}{T}\right) \right] \\ & + N \sum_{i=1}^s \ln g_{i(e)} + N \sum_{i=1}^s \ln g_{i(n)} \end{aligned} \quad [1.35]$$

It is possible that two or three of these degrees of freedom internal to the molecule may be better described as rotations than as vibrations. Such would be the case, for example, with the H_2 molecule. For molecules containing only one atom other than hydrogen atoms – e.g. ClH , CH_4 , NH_4^+ – we obtain better results when we consider that a movement is indeed a high-temperature rotation, but also a low-temperature vibration. There would be a rather sharp transition within a certain temperature range. In the case of a rotation, a rotational partition function term replaces a vibrational term in equation [1.30] and the corresponding terms in relations [1.30] and [1.32].

1.6.2. Thermodynamic functions of molecular solids

As is the case with atomic solids, we can calculate the Helmholtz energy F of a solid containing N molecules by applying equation [1.26] using the canonical partition function given by equation [1.34] or [1.35]. The molar Helmholtz energy F_m is deduced in the same manner by applying the two relations $N=N_a$ and $k_B N_a = R$ in the expressions thus obtained. We can easily deduce the molar internal energy from relation [1.26]. In fact, this internal energy is the sum of five terms:

$$U_m - U_0 = U_{m(R)} + U_{m(v)}(T) + U_{m(e)} + U_{m(n)} + U_{m(int)} \quad [1.36]$$

The contributions $U_{m(R)}$ and $U_{m(v)}$ are the same as with an atomic solid. Thus the contribution of the internal movements in the molecule is expressed as:

$$U_{m(\text{int})} = \frac{R}{T^4} \sum_{i=4}^s \frac{\Theta_i \exp\left(-\frac{\Theta_i}{T}\right)}{1 - \exp\left(-\frac{\Theta_i}{T}\right)} \quad [1.37]$$

The electron and nuclear contributions are also sums on the number of atoms contained in the molecule:

$$U_{m(e)} = \frac{R}{T^2} \sum_{i=1}^s \frac{d \ln g_{i(e)}}{dT} = 0 \quad [1.38]$$

$$U_{m(n)} = \frac{R}{T^2} \sum_{i=1}^s \frac{d \ln g_{i(n)}}{dT} = 0 \quad [1.39]$$

1.7. Description of an ionic solid

An ionic solid is made up of two kinds of ions: anions and cations. These ions are located at the nodes of two interlocking periodic lattices: the anionic sublattice and the cationic sublattice.

There are two distinct types of ionic solid:

- simple ionic solids, where the ions contain only one atom;
- complex ionic solids, containing at least one type of ion. Usually, the anion is a complex ion, which means that it is a molecule made up of several atoms, which carries an electrical charge.

1.7.1. Crosslink energy of an ionic solid

We model the energy of an ionic crystal limiting us to the case of a diatomic crystal with the formula A_aB_b linking a cation A with electrovalence z_A and an anion B with electrovalence z_B . We assume that these ions are comparable to spheres on which the charges are uniformly distributed. The overall cohesion of the crystal is provided by the Coulombian field at $1/r^2$ created by each ion, plus a repulsive potential

especially sensitive over a short distance, but which cannot be overlooked if we want to give an account of an equilibrium state of the crystal.

1.7.1.1. Attraction energy

Let us consider an ion i in the lattice, bearing the charge q_i . At that point, there is an electrostatic potential Φ_i , created by all the other ions, and the energy of interaction between that ion i and the rest of the lattice is:

$$U_i = q_i \Phi_i \quad [1.40]$$

In order to find the total attraction energy, we only need to add the above expression for all the ions, taking care only to count the interaction between each pair of ions once (which we do by using the coefficient $\frac{1}{2}$), as follows:

$$U_i = \frac{1}{2} \sum_i q_i \Phi_i \quad [1.41]$$

In a large crystal, it can be assumed that at each node A of the lattice, the potential is identical – i.e. Φ_A – and at each node B, the potential will be Φ_B (so we overlook any possible edge effects). Thus, if we compare the electrostatic energy to a mole, where e is the elementary charge, we find the following for the molar attraction term:

$$U_{attr} = \frac{N_a}{2} (az_A e\Phi_A + bz_B e\Phi_B) \quad [1.42]$$

As a unit of length, let us choose a distance d which is characteristic of the lattice. An ion i will be at distance $d(\rho_i)_A$ from an arbitrary origin, chosen in place of an ion A and at distance $d(\rho_i)_B$ from another arbitrary origin, chosen in place of an ion B. The potentials Φ_A and Φ_B at those origins are, respectively:

$$\Phi_A = \frac{1}{\epsilon_0 d} \sum_i \frac{z_i e}{(p_i)_a} \quad [1.43]$$

and

$$\Phi_B = \frac{1}{\epsilon_0 d} \sum_i \frac{z_i e}{(p_i)_a} \quad [1.44]$$

Because of the principle of electrical neutrality of the crystal, we must have:

$$az_A + bz_B = 0$$

Thus:

$$\frac{z_A}{b} = \left| \frac{z_B}{a} \right| = \varpi \quad [1.45]$$

The attraction energy per mole becomes:

$$U_{attr} = \frac{N_a e^2 \varpi^2 ab}{2\epsilon_0 d} \left(\sum_i \frac{\theta_i}{(p_i)} - \sum_i \frac{\theta_i}{(p_B)} \right) \quad [1.46]$$

θ_i is equal to b if the ion i is of type A, and to $(-a)$ if the ion i is of type B. This energy can be written in the form:

$$U_{attr} = \frac{N_a e^2 \varpi^2}{\epsilon_0 d} M \quad [1.47]$$

including a value M , known as the Madelung constant, which depends solely on the nature of the lattice and is defined by:

$$M = \frac{ab}{2} \left(\sum_i \frac{\theta_i}{(p_i)} - \sum_i \frac{\theta_i}{(p_B)} \right) \quad [1.48]$$

There are various algorithms which can be used to calculate the Madelung constant. Table 1.2 shows the values obtained for cubic lattices.

Type of lattice	Madelung constant
Sodium chloride	1.74756
Cesium chloride	1.76267
Blende	1.63806
Wurtzite	1.641

Table 1.2. Values of the Madelung constant in different cubic lattices

1.7.1.2. Repulsion energy

The previous expression of electrostatic energy gives an energy that can only grow in absolute value if the crystalline lattice parameter d of the crystalline lattice decreases. No equilibrium state can be achieved. To explain this, we must introduce a repulsion term, whose intensity will decrease as the distance d increases. Born and Mayer put forward an expression for this repulsion energy arising from the repulsion of the electron clouds if they intermingle. This energy has an exponential form that seems consistent with quantum mechanics. For the interaction of an ion pair i and j located a distance $d\rho_{ij}$ apart, we set:

$$U_{rep(i,j)} = mc_{i,j} \exp\left(-\frac{d\rho_{i,j}}{\rho}\right) \quad [1.49]$$

In this expression, $c_{i,j}$ and ρ are constants. Authors have shown that we can take the value 0.345×10^{-10} m for ρ for all ions, and that the constant $c_{i,j}$ is given by:

$$c_{i,j} = \left(1 + \frac{z_i}{n_i} + \frac{z_j}{n_j}\right) \exp\left(\frac{r_i + r_j}{\rho}\right) \quad [1.50]$$

In this expression, z_i and z_j are the electrovalences of the ions i and j , n_i and n_j are the numbers of electrons on the outermost layer, r_i and r_j are the ionic radii and m is a new constant, which we will discuss later on.

Looking again at the case of a biatomic solid: we still need to consider the repulsion energy associated with an ion A taken as the origin of the system, and with an ion B taken as the origin. However, in the case of repulsion, the potential decreases very quickly as the distance between the ions increases, and the only way to simplify the calculation is to consider the nearest neighbors to a given ion, with opposite signs.

Let us first examine an ion A as the origin. All its near neighbors will be ions B, and there will be a number β of them. The repulsion energy attached to that ion A will be:

$$U_{rep(A,B)} = m \sum_{i=1}^{\beta} c_{A,B} \exp\left(\frac{d\rho_{A,B_i}}{\rho}\right) \quad [1.51]$$

where:

$$c_{A,B} = \left(1 + \frac{z_A}{n_A} + \frac{z_B}{n_B}\right) \exp\left(\frac{r_A + r_B}{\rho}\right) \quad [1.52]$$

If we now take an ion B as the origin, its nearest neighbors will be α ions A, and its contribution to the repulsion will be:

$$U_{rep(B,A)} = m \sum_{j=1}^{\alpha} c_{B,A} \exp\left(-\frac{d\rho_{B,A_j}}{\rho}\right) \quad [1.53]$$

where, clearly:

$$c_{A,B} = c_{B,A} \quad [1.54]$$

Hence, the repulsion energy per mole can be written as follows, by adding together the two contributions:

$$U_{rep} = \frac{N_a m}{2} c_{A,B} \exp\left(-\frac{d}{\rho}\right) \left[a \sum_{i=1}^{\beta} \exp \rho_{A,B_i} + b \sum_{j=1}^{\alpha} \exp \rho_{B,A_j} \right] \quad [1.55]$$

1.7.1.3. Crosslink energy

The crystal's total crosslink energy is given by the sum of the terms of attraction and repulsion, which (in light of expressions [1.47] and [1.55] given above) gives:

$$U_{m(R)} = \frac{N_a e^2 \overline{\omega}^2}{\epsilon_0 d} \mathfrak{N} + \frac{N_a m}{2} c_{A,B} \exp\left(-\frac{d}{\rho}\right) \left[a \sum_{i=1}^{\beta} \exp(\rho_{A,B_i}) + b \sum_{j=1}^{\alpha} \exp(\rho_{B,A_j}) \right] \quad [1.56]$$

Thus, in the expression of the crosslink energy, there is a constant m which needs to be determined. We can find its value by looking at the compressibility coefficient. Imagine that we compress a crystal at the temperature of absolute zero. The variation in internal energy will be:

$$dU = -P dV \quad [1.57]$$

This variation is due only to the change in the crosslink energy. By taking account of the definition of the compressibility coefficient, which is:

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad [1.58]$$

we find:

$$\chi_T V \left(\frac{d^2 U_{(R)}}{dV^2} \right) = 1 \quad [1.59]$$

By applying the derivation of a function of function, we can write:

$$\left(\frac{d^2 U_{(R)}}{d d^2} \right) = \frac{d^2 U_{(R)}}{dV^2} \left(\frac{dV}{d d} \right)^2 + \frac{dU_{(R)}}{dV} \frac{d^2 V}{d d^2} \quad [1.60]$$

For the equilibrium position $d = d_0$, the crosslink energy is minimal, so:

$$\left(\frac{dU_{(R)}}{dd}\right)_{d=d_0} = 0 \text{ which gives us } \left(\frac{dU_{(R)}}{dV}\right)_{d=d_0} = 0 \quad [1.61]$$

and therefore, equation [1.53] becomes:

$$\left(\frac{d^2U_{(R)}}{dd^2}\right)_{d=d_0} = \left[\frac{d^2U_{(R)}}{dV^2}\left(\frac{dV}{dd}\right)^2\right]_{d=d_0} \quad [1.62]$$

The molar volume can always be written in the form:

$$v^0 = \lambda d_0^3 \quad [1.63]$$

with λ being a constant that depends only on the type of lattice. Thus, in view of expression [1.59], relation [1.62] gives us:

$$\left(\frac{d^2U_{m(R)}}{dd^2}\right)_{d=d_0} = \frac{4\lambda^2 d_0^4}{\chi v^0} \quad [1.64]$$

For simplicity's sake, let us write expression [1.56], of the crosslink energy, in the form:

$$U_{m(R)} = -\frac{A}{d} + B \frac{m}{\rho} \exp\left(-\frac{d}{\rho}\right) \quad [1.65]$$

where:

$$A = \frac{N_a e^2 \bar{\omega}^2 M}{\epsilon_0} \quad [1.66]$$

and:

$$B = \frac{N_a}{2} c_{A,B} \left[a \sum_{i=1}^{\beta} \exp(\rho_{A,B_i}) + b \sum_{j=1}^{\alpha} \exp(\rho_{B,A_j}) \right] \quad [1.67]$$

By twice deriving the function [1.65], we find:

$$\left(\frac{d^2 U_{m(R)}}{d d^2} \right)_{d=d_0} = 2 \frac{A}{d_0^3} + \frac{Bm}{\rho^3} \exp\left(-\frac{d_0}{\rho}\right) \quad [1.68]$$

By equaling the two expressions [1.64] and [1.68] for the second derivative, we obtain:

$$m = \frac{\rho^3}{B} \left[\frac{4\lambda^2 d_0^4}{\chi v^0} + \frac{2A}{d_0^3} \right] \exp\left(\frac{d_0}{\rho}\right) \quad [1.69]$$

In view of equations [1.61] and [1.65], the equilibrium condition is expressed as:

$$\frac{A}{d_0^2} + \frac{Bm}{\rho^2} \exp\left(-\frac{d_0}{\rho}\right) = 0 \quad [1.70]$$

Hence, expressions [1.69] and [1.70] constitute a system of two equations where the unknowns are the constants m and d_0 , which we can calculate numerically.

1.7.2. Born/Haber cycle

Born and Haber envisaged a thermodynamic cycle that can be used to calculate the crosslink energy on the basis of independently-measured data. They begin with the observation that the crosslink energy is the energy that is released if the lattice is formed of gaseous ions which are infinitely immobile in relation to one another. Figure 1.5 shows the cycle for a crystal $A_a B_b$ based on solid metal and a gaseous molecular non-metal, with the symbols having the following meanings:

- S : sublimation heat for a gram atom of metal A;
- D : dissociation heat for the non-metal B expressed in relation to a gram atom of that substance;
- I : ionization energy for a gram atom of metal;
- A : electron affinity of a gram atom of non-metal;

– $\Delta_f H$: enthalpy of formation of the solid crystallized from its elements.

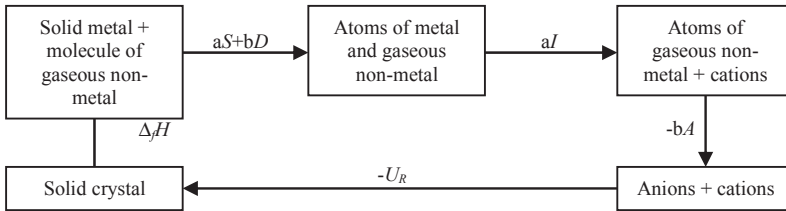


Figure 1.5. Born–Haber cycle for a compound $A_a B_b$

From the cycle shown in Figure 1.5, we deduce the relation:

$$\Delta_f H = aS + bD + aI - bA - U_{m(R)} \quad [1.71]$$

If the other values are known, this expression can be used to calculate the crosslink energy $U_{m(R)}$.

Comparison of the direct calculation on the basis of the microscopic model and the result given by the Born–Haber cycle shows that the values overlap at less than 5%. This result is entirely acceptable when we remember the relatively-simple hypotheses of the model, and in particular the assimilation of the ions to non-deformable hard spheres. We can refine the model by introducing deformability of the ions by their polarizability, which leads us to take account of the ion–dipole and dipole–dipole electrostatic interactions.

1.7.3. Vibrational partition function and internal energy of an ionic solid

Earlier, when we were looking at molecular solids (see section 1.5.1), we saw the mixture of Debye and Einsteinian terms in the partition function of the same solid with degrees of vibration of the lattice and degrees of vibration within the molecule. We will now make broader use of this concept, which was developed by Born and Blackman, on the subject of ionic compounds.

To begin with, in the ionic solid, we will construct neutral subsets by associating the minimum number of ions of opposite signs, such as a potassium ion and a chlorine ion to create potassium chloride, a calcium ion and two chlorine ions to make calcium chloride, or a calcium ion and a carbonate ion for calcium carbonate. Such a subset contains s atoms and therefore has $3s$ degrees of freedom – all of them vibrational. The whole of the solid contains N subsets and will therefore have $3Ns$ vibrational degrees of freedom.

Born divides the $3s$ degrees of freedom into two categories, acoustic vibrations and optical vibrations (infrared):

– acoustic vibrations (or phonons), throughout the crystal, have a frequency distribution with a limit frequency. This distribution could be that chosen by Debye (see equation [1.9]) or those proposed by Born or Blackman (Figures 1.4(a) and (b)). These acoustic vibrations give us vibrational terms for the partition function and then for the internal energy, which will be of the same type as those proposed by Debye, in accordance with equations [1.24] for the vibrational partition function and [1.29] for the internal energy;

– optical vibrations, each with its own frequency, which, for the partition function, has a sum of Einsteinian terms such as that given by equation [1.3] and for the internal energy a sum of terms such as those in equation [1.28].

However, in order to express these vibrational partition functions and the corresponding internal energies, for a given solid, we need to know the number of vibrations in each group: how many acoustic vibrations will there be, and then how many optical vibrations?

This distribution depends on a number of factors.

Let us first envisage ionic compounds with simple ions – i.e. one anionic atom and one cationic atom, as is the case in potassium chloride.

If the bond is markedly ionic in nature (say, over 50% ionic), we choose six acoustic vibrations. We then need to ask ourselves whether the two groups of three acoustic vibrations have the same value of the

Debye temperature. If the atoms have similar dimensions, as is the case with potassium chloride, we choose a single Debye temperature; if, however, the ions have very different dimensions – as is the case, for instance, with cesium fluoride or lithium iodide – we choose two values of the Debye temperature. The partition function and the internal energy then contain either one or two Debye terms, depending on the case.

If the bond is mainly covalent, we choose three acoustic vibrations with a Debye temperature and three optical vibrations with three Einsteinian temperatures. The partition function and the internal energy therefore include a Debye term and the sum of three Einsteinian terms.

If we now look at more complex ionic compounds, such as calcium fluoride or calcium carbonate, we group together species that are linked by a covalent bond, such as the two fluorine atoms in calcium fluoride, or of the carbonate ion in calcium carbonate. With regard to this latter bond between fluorine and calcium or between carbonate and calcium, we refer to the previous case depending on the covalent nature of the bond. Hence, for calcium fluoride which has nine degrees of freedom, six will be acoustic, with the same Debye temperature for the di-fluorine molecules and calcium, and three will be optical vibrations with three corresponding Einsteinian terms. The partition function (and the internal energy which arises from it) contains a Debye term and three Einsteinian terms.

For calcium carbonate, which has 15 degrees of freedom, six will be acoustic vibrations with two Debye temperatures and nine degrees of freedom will be optical vibrations, with an Einstein temperature for each one. The partition function (and the resulting internal energy) contains two Debye terms and nine Einsteinian terms.

In fact, that distribution between acoustic vibrations and optical vibrations is only significant at temperatures close to the Debye temperature. If the temperature is very low (much lower than the lowest Debye temperature), only the corresponding Debye term is predominant; the other terms are negligible. This explains why all the internal energies (and, as we will see in section 1.8.1) all the specific

heat capacities at constant volume, tend toward zero, with a T^3 law for the latter.

However, at high temperatures, if the temperature is much higher than the highest of the Debye temperatures, only Einsteinian terms are significant: those for which the Einstein temperature is not too low.

1.8. Description of a metallic solid

Over the course of history, pure metal has been described by a variety of models. The initial model, attributable to Drude, considered the metal to comprise a gas of electrons enveloping positive ions in a constant potential. Drude applies Maxwell–Boltzmann statistics to that electron gas. In fact, as the electrons are fermions, it is most appropriate to apply Fermi–Dirac statistics to them, as Sommerfeld did in his model, still using a constant potential. Unlike with molecules, though, because of their low mass, the electrons cannot be used for the approximation of the classic limit statistics given by:

$$n_i = g_i \exp(-\alpha - \beta \epsilon_i) \quad [1.72]$$

However, we will see that it is helpful to apply to them the opposite hypothesis to that condition, i.e.:

$$\exp(-\alpha) \gg 1 \quad [1.73]$$

Sommerfeld's model is perfectly well suited for chemical applications – particularly for determining specific heat capacities – but it is totally unsuited for explaining the electrical properties and the experimental fact that not all energy levels are acceptable in the metal. It was the band theory, developed by Brillouin, which was first able to explain these properties and also the nature of the bond between the metal atoms with the introduction of a periodic field.

We will begin by discussing Sommerfeld's constant-field theory, and then go on to show the modifications made by the periodic field and the grouping of electrons in the metal.

1.8.1. Sommerfeld's electron perfect gas model

Thus, we consider that a metal whose volume is V contains a certain N number of electrons that are free to move around. The ratio of the number of free electrons to the number of metal atoms contained in the volume V , for the time being, will be taken as being close to 1 (or perhaps 2 or 3). Only with the band model we will be able to actually calculate that ratio, later on. That gas cloud is comparable to perfect gas made up of electrons placed in a constant average potential, so that they are contained within the volume V . We will apply Fermi–Dirac statistics to that perfect gas, accepting condition [1.73] for now, and verifying it at the end of section 1.8.1.1.

1.8.1.1. Determination of the coefficient α

To begin with, we will calculate the coefficient α , which is the Lagrange multiplier relative to the numbers of electrons N . In the knowledge that the other multiplier β always has the same value ($1/k_B T$) irrespective of the molecular statistics, we can calculate α by using the first method described in section A.1.3 of Appendix 1.

Because the electrons obey Fermi–Dirac statistics, the total number thereof obeys the following law:

$$N = \sum_i n_i \quad [1.74]$$

and their distribution between the different energy levels obeys:

$$(n_i)_{FD} = \frac{g_i \exp(-\alpha - \beta \varepsilon_i)}{1 + \exp(-\alpha - \beta \varepsilon_i)} \quad [1.75]$$

Hence, the number of free electrons is given by:

$$N = \sum_i \frac{g_i}{1 + \exp\left(\alpha + \frac{\varepsilon_i}{k_B T}\right)} \quad [1.76]$$

We have chosen $\varepsilon_0 = 0$ as the origin of the energies for the electrons at rest within the metal.

Consider that the electrons, whose mass is m_e , are contained in a cubic box with side length a and volume $V = a^3$. The kinetic energy, which depends on three quantum numbers (l , m and n) is given by:

$$\varepsilon_i = \frac{h^2}{8m_e a^2} (l^2 + m^2 + n^2) \quad [1.77]$$

For each energy level, there are two corresponding electrons with opposite spin, so the degeneration coefficient is $g_i = 2$. If we consider all the states with the same energy ε_i , the quantum numbers l , m and n have values arranged over the surface of the positive quarter of the sphere defined by:

$$\frac{8m_e \varepsilon_i}{h^2} = \frac{1}{a^2} (l^2 + m^2 + n^2) \quad [1.78]$$

Thus, all the states whose energy is less than or equal to ε_i have the values of their quantum numbers located within the positive quarter of the sphere. The number of points with integer coordinates l , m and n within that positive quarter-sphere is equal to the volume of that quarter-sphere, so:

$$\frac{\pi}{6} \left(\frac{8m_e \varepsilon_i}{h^2} \right)^{3/2} a^3 = \frac{\pi}{6} \left(\frac{8m_e \varepsilon_i}{h^2} \right)^{3/2} V \quad [1.79]$$

V is the volume of the space containing the electrons.

NOTE.— We have chosen to use a cubic sample volume, but it is possible to demonstrate that relation [1.79] applies no matter what the shape of that space.

After the degeneration of two of the electrons, the number of electron states with energy less than ε_i is, clearly, double the number of points within the quarter-sphere, so:

$$n_{\varepsilon \leq \varepsilon_i} = \frac{\pi}{3} \left(\frac{8m_e \varepsilon_i}{h^2} \right)^{3/2} V \quad [1.80]$$

By deriving the above relation, we obtain the number of electron states for which the energy level is between ε and $\varepsilon + d\varepsilon$.

$$g(\varepsilon) = \frac{\pi}{2} \left(\frac{8m_e}{h^2} \right)^{3/2} V \varepsilon^{1/2} d\varepsilon \quad [1.81]$$

We will consider all these states to be the degeneration of a single energy state ε , so that:

$$g_i = g(\varepsilon) = \frac{\pi}{2} \left(\frac{8m_e}{h^2} \right)^{3/2} V \varepsilon^{1/2} d\varepsilon \quad [1.82]$$

By substituting this value of g_i back into relation [1.76] and replacing the sum with an integral, as the states are very close to one another, we obtain the following for the number of free electrons:

$$N = \frac{\pi}{2} \left(\frac{8m_e}{h^2} \right)^{3/2} V \int_0^{\infty} \frac{\varepsilon^{1/2} d\varepsilon}{1 + \exp\left(\frac{\varepsilon}{k_B T} + \alpha\right)} \quad [1.83]$$

For simplicity's sake, we set the new integration variable x such that:

$$\frac{\varepsilon}{k_B T} = x \quad [1.84]$$

Relation [1.83] is then written as:

$$N = \frac{\pi}{2} \left(\frac{8m_e k_B T}{h^2} \right)^{3/2} V \int_0^{\infty} \frac{x^{1/2} dx}{1 + \exp(x + \alpha)} \quad [1.85]$$

To simplify our expressions, we will introduce an energy level that is characteristic of the solid, known as the *Fermi energy* (or *Fermi-level*)

energy) as being the maximum value reached by the energy of an electron if the N electrons, two by two, fill all the lower energy levels; thus, according to relation [1.80], this energy must satisfy the condition:

$$\frac{N}{V} = \frac{\pi}{3} \left(\frac{8m_e \varepsilon_F}{h^2} \right)^{3/2} \quad [1.86]$$

Therefore, by definition, the Fermi energy is:

$$\varepsilon_F = \frac{h^2}{8m_e} \left(\frac{3N}{\pi V} \right)^{2/3} \quad [1.87]$$

By taking account of relation [1.85], we find that the value of this Fermi level is:

$$\left(\frac{\varepsilon_F}{k_B T} \right)^{3/2} = \frac{3}{2} \int_0^\infty \frac{x^{1/2} dx}{1 + \exp(x + \alpha)} \quad [1.88]$$

Therefore, it is helpful to evaluate the integral I defined by:

$$I = \int_0^\infty \frac{x^{1/2} dx}{1 + \exp(x + \alpha)} \quad [1.89]$$

There is no exact analytical solution for this integral, but we can show that a good approximation is given by a limited expansion:

$$I = - \left(\frac{2\alpha^{1/2}}{3} + \frac{\pi^2 \alpha^{-1/2}}{12} \right) \quad [1.90]$$

Thus, if we substitute the value back into relation [1.88], the Fermi energy becomes:

$$\left(\frac{\varepsilon_F}{k_B T} \right)^{3/2} \approx - \left(\alpha^{3/2} + \frac{\pi^2 \alpha^{1/2}}{8} \right) \quad [1.91]$$

We can see that, if we focus on the first term in this expansion, an approximation of the Fermi level is given by:

$$\varepsilon_F \approx -\alpha k_B T \quad [1.92]$$

Based on this last approximation, which we can put back into equation [1.91] in place of the first term on the right-hand side, we obtain an approximate value of α :

$$\alpha = -\frac{\varepsilon_F}{k_B T} \left(1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 \right) \quad [1.93]$$

We are going to evaluate an order of magnitude for the coefficient α . In order to do so, we choose one electron per atom of the metal, with these atoms being a few angstroms apart from each other, so the ratio N/V is approximately:

$$\frac{N}{V} \approx 10^{29} \text{ m}^{-3} \quad [1.94]$$

Thus, using relation [1.88], we find the following for the Fermi level:

$$\frac{\varepsilon_F}{k_B T} \approx 1.25 \times 10^{-18} \text{ joules} \quad [1.95]$$

Thus, at a temperature of around 1000 K, using relation [1.83], we obtain the following value for the coefficient α :

$$\alpha \approx -90 \quad [1.96]$$

Hence, we can verify that the condition [1.73], which we have simply accepted for simplicity's sake up until now, is indeed respected.

Moreover, we can see that the second term in expression [1.93] has a value of approximately $1/90^2 \approx 10^{-4}$, which is much less than 1, which means that approximation [1.92] is also very appropriate.

1.8.1.2. Kinetic energy of electrons in the metal

In order to calculate the kinetic energy of the mobile electrons, we use the relation:

$$E = \sum_i n_i \varepsilon_i \quad [1.97]$$

To do so, we merely need to introduce the term ε into the integral given in relation [1.83]. Thus, we obtain:

$$E_{kin} = \frac{\pi}{2} \left(\frac{8m_e}{h^2} \right)^{3/2} V \int_0^{\infty} \frac{\varepsilon^{3/2} d\varepsilon}{1 + \exp\left(\frac{\varepsilon}{k_B T} + \alpha\right)} \quad [1.98]$$

Using the same change of variables as above (see equation [1.84]), and if we introduce the definition [1.87] of the Fermi energy, we find that:

$$E_{kin} = \frac{3}{2} N k_B T \left(\frac{k_B T}{\varepsilon_F} \right)^{3/2} V \int_0^{\infty} \frac{x^{3/2} dx}{1 + \exp(x + \alpha)} \quad [1.99]$$

Just like the integral I in relation [1.89], the integral in terms of x that appears in equation [1.99] has no analytical solution. We can show, however, that its approximate value can be found by the expansion [1.100]:

$$I' = \int_0^{\infty} \frac{x^{3/2} dx}{1 + \exp(x + \alpha)} \approx -\frac{2}{5} \alpha^{3/2} + \frac{\pi^2}{4} \alpha^{1/2} \quad [1.100]$$

Taking account of the value of α given by equation [1.96], we find:

$$E_{kin} \approx \frac{3}{5} N \varepsilon_F \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 \right] \quad [1.101]$$

Similarly as for relation [1.91], we can content ourselves with the following relation, with a fairly high degree of accuracy:

$$E_{kin} \approx \frac{3}{5} N_a \varepsilon_F \quad [1.102]$$

Thus, we obtain an absolute error of around 0.05 J at 1000 K.

Hence, we can see that for the free electrons in a metal, the kinetic energy is non-null at the temperature of 0 K; this is the consequence of the application of the Fermi–Dirac statistics. Thus, we can no longer define a temperature scale on the basis of the kinetic energy of the free electrons in a metal.

1.8.1.3. *Electrochemical potential of the electrons in the metal and the Fermi energy*

Regardless of the type of statistics used, we can show that the two coefficients α and β , relative to the stresses, respectively, linked to the number of moles and to the energy, are connected to one another by the expression:

$$\mu_A = -\frac{\alpha_A}{\beta} \quad [1.103]$$

Applied to the electrochemical potential of the electron, this gives us:

$$\tilde{\mu}_{el} = -k_B T \alpha \quad [1.104]$$

Thus, by using relation [1.93], the electrochemical potential, still using the electrons at rest as the origin of the energies, is given by:

$$\tilde{\mu}_{el} = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 \right] \quad [1.105]$$

The application of expression [1.92] gives us the approximate value:

$$\tilde{\mu}_{el} = \varepsilon_F \quad [1.106]$$

Thus, the electrochemical potential of the free electrons, at the temperature of 0 K, is equal to the Fermi energy of the metal. As approximation [1.92] is very accurate, we can say that this electrochemical potential practically does not vary with temperature.

On the basis of the Fermi energy, we define a temperature known as the *Fermi temperature*, as:

$$T_F = \frac{\mathcal{E}_F}{k_B} \quad [1.107]$$

Let us evaluate an order of magnitude for that Fermi temperature. In view of relation [1.95], we have:

$$\mathcal{E}_F \cong 1.25 \times 10^{-18} \text{ joules} \quad [1.108]$$

Thus, by applying definition [1.107], we find the value:

$$T_F \cong 9.10^4 \text{ K} \quad [1.109]$$

Hence, in general, the temperature of the metal for which it remains solid is much lower than the Fermi temperature. Therefore, we can consider that the metal always behaves as though the temperature was 0 K, and we can content ourselves with approximation [1.106]. The Fermi temperature defines the temperature beyond which the effects of Fermi–Dirac statistics begin to manifest themselves. We can write that:

$$\text{If } T \ll T_F, \text{ then } k_B T \ll \tilde{\mu}_{el} \quad [1.110]$$

NOTE.— We sometimes come across the term *Fermi impulsion*, which is the maximum value of the impulsion of the free electrons at the temperature of absolute zero. To find the expression of it, we only need to write:

$$p_F = \sqrt{2m_e \mathcal{E}_F} = \left(\frac{3h^3 N}{8\pi V} \right)^{1/3} \quad [1.111]$$

1.8.1.4. Energy distribution of the free electrons

Based on the distribution function, which is written as follows:

$$\langle dn \rangle = \frac{N}{V} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \exp \left(-\frac{p_{x_1}^2 + p_{x_2}^2 + p_{x_3}^2}{2m k_B T} \right) dp_{x_1} \cdot dp_{x_2} \cdot dp_{x_3} \quad [1.112]$$

$$\cdot dx_1 \cdot dx_2 \cdot dx_3$$

we calculate the average number of free electrons which have the energy ε . It is given at 0 K, in light of expressions [1.92] and [1.106], by one of the following relations:

$$\langle n_\varepsilon \rangle = \frac{1}{1 + \exp \left(\frac{\varepsilon}{k_B T} + \alpha \right)} = \frac{1}{1 + \exp \left(\frac{\varepsilon - \varepsilon_F}{k_B T} \right)} = \frac{1}{1 + \exp \left(\frac{\varepsilon - \tilde{\mu}_{el}}{k_B T} \right)} \quad [1.113]$$

Figure 1.6 shows this distribution at the temperature 0 K. Beyond the Fermi level, there are no more electrons.

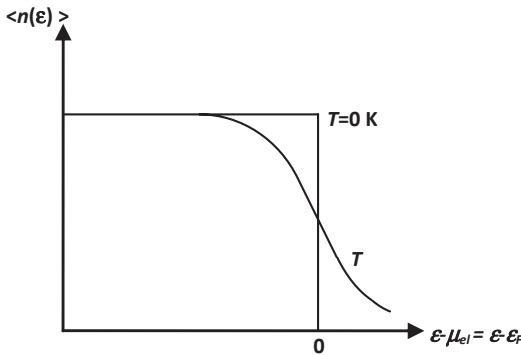


Figure 1.6. Energy distribution of the free electrons in a metal at 0 K

At a temperature T , the curve differs only very little from the curve at 0 K, because of the excellent approximation offered by relation [1.92] in respect to the expansion [1.91] and by relation [1.106] in respect to the expansion [1.105], because the temperature of the solid metal is generally far lower than the Fermi temperature.

1.8.1.5. Contribution of the free electrons to the internal energy of a metal

On the basis of the electrochemical potential, we can express the function of the electrochemical Helmholtz energy by integrating at constant volume and temperature:

$$\tilde{F}_{el} = \int_0^N \tilde{\mu}_{el} dN \quad [1.114]$$

By introducing, into that integral, the expression of the electrochemical potential given by relation [1.105], we find:

$$\tilde{F}_{el} = \int_0^N \mathcal{E}_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B t}{\mathcal{E}_f} \right)^2 \right] dN \quad [1.115]$$

We know, from relation [1.87], that the Fermi energy is proportional to $(N/V)^{2/3}$. Thus, for the electrochemical Helmholtz energy, we calculate:

$$\tilde{F}_{el} = N \left[\frac{3}{5} \mathcal{E}_F - \frac{\pi^2}{4 \mathcal{E}_F} (k_B T)^2 \right] \quad [1.116]$$

This expression gives us the electrochemical Helmholtz energy, having chosen $\varepsilon_0 = 0$ as the origin of the energies, for the electrons at rest within the metal, in section 1.8.1.1. In order to compare the energies of the electrons with the contributions of the other terms for the solid, it is helpful to change the origin of that energy by taking as the origin the electrons at rest very far from the metal and very far removed from one another. This introduces a term E_p at a given temperature and volume. This energy represents an average potential energy of the free electrons obtained by averaging the attractions of the positive ions and the other electrons. We suppose that this energy, which is electrostatic in origin, is independent of the temperature but does depend on the volume of the solid, which alters the distances between the ions. If we change the temperature, this energy

will only vary by way of the variation in volume – i.e. the thermal expansion.

For a mole of metal, if we let n_{el} denote the number of free electrons per atom of metal, we can rewrite relation [1.116] in the form:

$$\tilde{F}_{el} = n_{el} N_a \left[-E_p(V) + \frac{3}{5} \varepsilon_F(V) - \frac{\pi^2}{4\varepsilon_F(V)} (k_B T)^2 \right] \quad [1.117]$$

Based on this expression [1.117] of the Helmholtz energy, which is a characteristic function in our choice of variables, we have access to all the thermodynamic properties, and in particular, we can calculate the contribution of the free electrons to the (electrochemical) internal energy of the metal by using the relation:

$$\tilde{U}_{el} = -T^2 \frac{\partial (F_{el} / T)}{\partial T} \quad [1.118]$$

This gives us:

$$\tilde{U}_{el} = \frac{n_{el} N_a}{T} \left[-E_p(V) + \frac{3}{5} \varepsilon_F(V) + \frac{\pi^2}{4\varepsilon_F(V)} (k_B T)^2 \right] \quad [1.119]$$

This expression will be used later on when we are calculating the contribution of the free electrons to the molar specific heat capacity of the metal at constant volume (see section 1.8.2.1). However, in order to do that, we need to know the term n_{el} , which is the number of free electrons per atom of the metal. Sommerfeld's model does not provide us with this number, but Brillouin's band theory, or zone theory, can be used to evaluate it.

1.8.2. The metallic bond and band theory

As we have just seen, the average potential theory cannot be used to determine the number of free electrons per atom of metal. In order to find it, we need to return to the average potential hypothesis and

take account of a periodic potential. To do so, we will recap a few details about metallic bonds.

1.8.2.1. *Origin of energy bands*

In the metal, each of the electrons is subject to the influence of all the nuclei and all the other electrons. In view of the periodic arrangement of the atoms, that potential is periodic, becoming infinite at each nucleus and minimal at the points furthest from the nuclei. We cannot hope to solve the Schrödinger equation for so complex a system. Certain calculations have been performed in specific cases – in particular, by Bloch, Brillouin, Wigner, Seitz and Slater, among others.

In order to gain an understanding of the formation of the bands, we will greatly simplify the system, by considering a one-dimensional solid formed of an infinitely-long line of ions, along which, atomic nuclei are arranged at an equal distance from one another (Figure 1.7). To simplify the problem of quantum mechanics, we suppose that the electrons are classified into two categories;

- the electrons in the outer layer, which are usually the bonding electrons, and are shared in overall orbitals created by the overlapping of the individual orbitals;

- the electrons in the inner layers, which we can assume are not highly affected by the neighboring ions or by the electrons in the bond. Hence, these electrons remain in the vicinity of their respective nuclei.

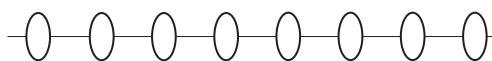


Figure 1.7. *Diagrammatic representation of a one-dimensional metal*

We suppose that the wave function of the bond electrons is independent of the wave function of the ions comprising nuclei and inner-layer electrons.

Thus, it is useful to solve the Schrödinger equation for the valence electrons, which is written as:

$$\frac{\hbar^2}{8\pi^2 m_e} \Delta \Phi + (E_p - \epsilon) \Phi = 0 \quad [1.120]$$

We construct the wave function of the valence electrons by linear combination of the atomic orbitals by adding the atoms in the line one after another, reasoning on the example of the s orbitals.

The first atom has an s orbital with a certain level of energy. When a second atom is added, its s orbital overlaps with that of the previous atom, and forms two molecular orbitals – one bonding and the other antibonding. If we add a third atom, its s orbital overlaps with the previous two molecular orbitals to form three new molecular orbitals, and so on. Hence, by adding n atoms, we form s molecular orbitals, which, as new atoms are added, extends the available energy domain covered by molecular orbitals.

We will solve the Schrödinger equation [1.120] by using the method of addition of the states in the Hückel approximation (see Appendix 2). The secular determinant is written as:

$$\begin{vmatrix} H_{i,i} - \epsilon & H_{i,j} & 0 & 0 & \dots & 0 \\ H_i & H_{i,i} - \epsilon & H_i & 0 & \dots & 0 \\ 0 & H_i & H_{i,i} - \epsilon & H_i & \dots & 0 \\ 0 & 0 & H_i & H_{i,i} - \epsilon & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \dots & \vdots \\ 0 & 0 & 0 & 0 & \dots & H_{i,i} - \epsilon \end{vmatrix} = 0 \quad [1.121]$$

$H_{i,i}$ and H_i , respectively, denote the Coulomb integral and the resonance integral between two adjacent atoms.

The determinant theory applied to this triangular determinant yields the solution:

$$\varepsilon_k = H_{i,i} + 2H_i \cos \frac{k\pi}{n+1}, \text{ where } k = 1, 2, \dots, n \quad [1.122]$$

When the number n of nuclei is very large, the difference between two energy levels, corresponding to two successive values k and $k + 1$, is very slight, so that we can consider that the levels are continuous, but relation [1.122] gives a solution that is acceptable only if the cosine is between -1 and $+1$:

$$-1 \leq \cos \frac{k\pi}{n+1} \leq 1 \quad [1.123]$$

In view of relation [1.122], this gives us the twofold inequality at the conditions on the energy:

$$H_{i,i} - 2H_i \leq \varepsilon_k \leq H_{i,i} + 2H_i \quad [1.124]$$

This means that only one energy band is allowed, and that the breadth of that band, therefore, is:

$$\Delta\varepsilon_k = 4H_i \quad [1.125]$$

The energy band thus permitted will be known as an s band (Figure 1.8).

Similarly, if the atoms used have available p orbitals, they will form a p band (Figure 1.8). If the energies in the p band are greater than those of the s band, the p band will be situated above the s band, and between the two, there may be an energy band that is “prohibited” to electrons.

Depending on the case, the bands formed may be spaced a long way apart, close together or even overlapping. Hence, the bands $2s$ and $2p$ overlap partially (we will see later on that this overlap accounts for the conductive behavior of alkaline earth metals). Similarly, the bands $3d$ and $4s$ overlap, and this explains the conductive properties of the transition metals.

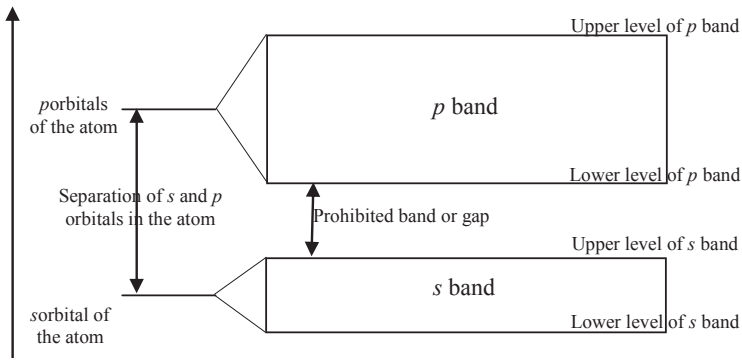


Figure 1.8. *Combination of levels into bands*

1.8.2.2. *Conductors, insulators and semiconductors*

If we look at the Fermi level in the conduction band, we encounter two possible cases:

- in the first case, the Fermi level is included in the conduction band (Figure 1.9, left-hand diagram). A temperature rise enables electrons to pass to a higher level in that band which is still available. Those electrons facilitate conduction, and the solid is cataloged as a conductor. Such is the case, in particular, with metals. The number of excited electrons will be greater when the temperature is higher, but with this rise in temperature, the vibrations of the atoms become more intense, which decreases the electrons' mobility. On balance, the second effect wins out over the first, and the conductivity of metals decreases at higher temperatures;

- in the second case, the Fermi level is identical to the upper level of the conduction band (Figure 1.9, right-hand diagrams). Thus, there are no more levels available in the conduction band to accommodate electrons. The solid is then said to be non-conductive of electricity. In order for a substance to be able to conduct electricity, the electrons must be capable of crossing over a prohibited band and reaching a level in a new authorized band. Thus, two scenarios may arise:

- either the energy jump required to cross the gap is too great in comparison to $k_B T$, and so the gap cannot be crossed. In this case, we say that the non-conductor is an insulator,

- or the gap is sufficiently narrow, and electrons can cross it, thus freeing up places in the conduction band and facilitating the passage of electrical current. We then say that the non-conductor is a semiconductor. When the temperature increases, the effect due to the increased number of electrons jumping to the highest level prevails over the effect due to the most intense vibrations of the atoms, and the conductivity of semiconductors increases with temperature.

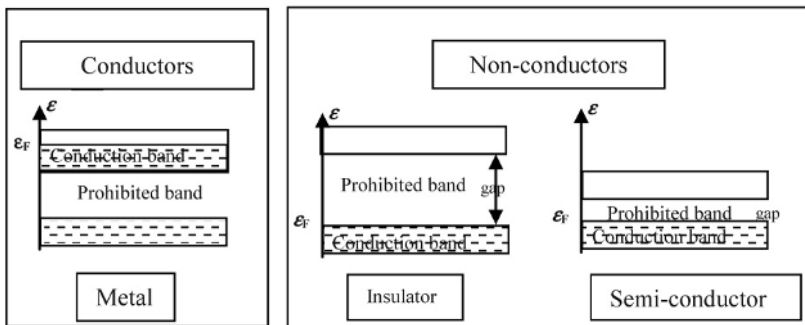


Figure 1.9. Diagram of bands for metals, insulators and semi-conductors

1.8.2.3. Determination of the number N of free electrons

We will say that the free electrons are the electrons contained in the band with highest energy, which may be completely or partially filled (see Figure 1.10). Hence, the number of free electrons is N and n_e is the ratio of that number N to the number of metal atoms n contained in the volume in question.

The band contains the electrons that are furthest away from the nuclei, and thus we can consider that the amplitude of the periodic potential created by those electrons is slight. Therefore, we can make the approximation that, in the conduction band, the potential is essentially constant. Thus, all the calculations performed in section 1.8.1 are valid within that band, if we take the bottom of the band as the origin of the energies. Thus, the Fermi energy is given by relation [1.87], which is the height, in that band, occupied by electrons at absolute zero.

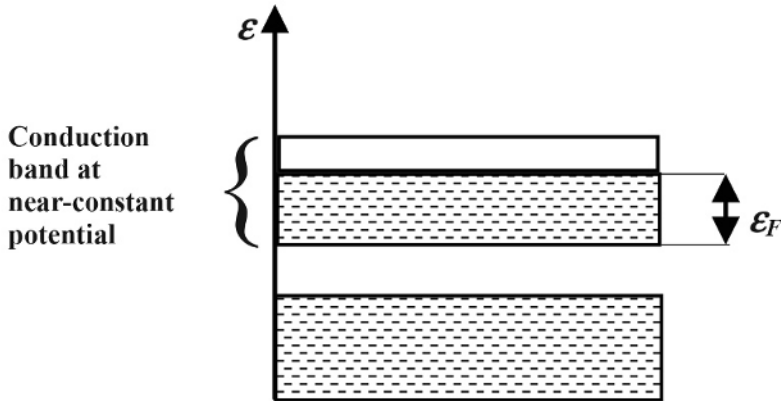


Figure 1.10. Energy band structure in a metal

Using this reasoning, it is easy to calculate N . We will now take a look at a few examples.

Let us choose an alkali metal (such as Li, Na, etc.). These atoms have a final electron layer which has one free electron on an s orbital. If the metal contains n atoms, their overlapping will give us $n \times s$ orbitals, and therefore n energy levels in the s band, which can thus accept $2n$ electrons. As there are fewer than $2n$ of them, the conduction band is incomplete, and the Fermi level is within that band. Thus, the ratio n_e is equal to 1, so there is one free electron per metal atom.

Let us now consider an alkaline earth metal (Mg, Ca, etc.). These atoms have a final electron layer containing two electrons on an s orbital. If the metal contains n atoms, then their overlap will give $n \times s$ orbitals, so n energy levels in the s band, which can therefore accommodate $2n$ electrons. Hence, the s band is complete and the Fermi level is at the upper level of that band. Alkaline earth metals should not exhibit metallic behavior; however, experience proves that they are, indeed, metals. This arises from the fact that, in these elements, the s band partially overlaps the p band immediately above it, to form one conduction band, so that the Fermi level actually lies somewhere within

that conduction band, because the new band can accommodate more than two electrons per atom (with a maximum of eight if the s and p bands were precisely tangential to one another). Hence, the ratio n_e is equal to 2, meaning that there are two free electrons per atom of metal. These metals, which have two free electrons per atom, should conduct electricity better than alkali metals. However, this is absolutely not the case, because, at a temperature higher than absolute zero, the number of single electrons, which are responsible for conduction, is lesser in alkaline earth metals than in alkali metals.

We now look at the example of solid fluorine (or any other halogen). Its atoms have a last electron layer comprising two electrons on an s orbital and 5 electrons on three equivalent p orbitals. If the solid contains n atoms, then their overlap will give us $n \times s$ orbitals and $3n \times p$ orbitals, and therefore a total of $4n$ energy levels which can accommodate $8n$ electrons, so the band ($s + p$) is incomplete, and the Fermi level is included in that band. Halogens should behave like metals, but experience tells us that they are not conductive. This arises from the fact that it is not atoms of fluorine which make up the solid, but rather diatomic F_2 molecules. The combination of those $n/2$ molecules of di-fluorine gives us $n \times s$ orbitals, $2n \times p$ orbitals and $n/2$ orbitals linking two fluorines, and all of those levels, of where there are $7n/2$, can accept up to $7n$ electrons, which means that the Fermi level is at the highest part of the sp band thus constructed, and therefore fluorine is an insulator.

1.8.2.4. *Distribution of energy states and of free electrons at absolute zero*

In order to find the distribution of the electrons, it is important to know the distribution function $g(\epsilon)$ which, in a solid with volume V , gives us the number $g(\epsilon)$ of states whose energy is between ϵ and $\epsilon+d\epsilon$. Each state is capable of accommodating two electrons. It is complicated to calculate this distribution. Figure 1.11 shows the distribution calculated by Jones and Mott for the band created by the s and p bands in a centered cubic crystal.

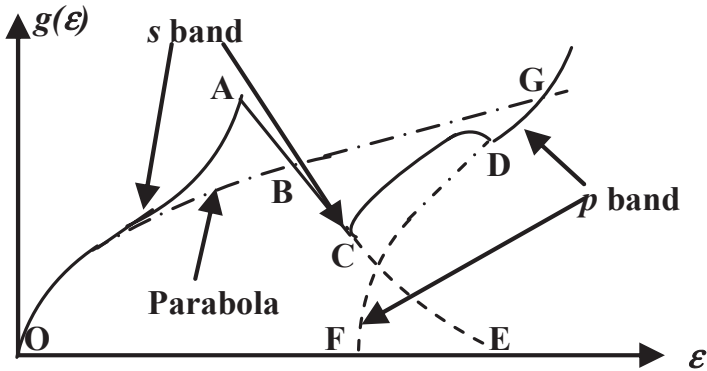


Figure 1.11. Distribution of states of s and p bands, with overlap, for a centered cubic crystal (data from [FOW 49])

The curve OABCE represents the distribution in the s band, which has the lowest energy (the curve OBG is a parabola). The curve FDG represents the distribution in the start of the p band, which is highest. The plot OABCDG shows the distribution resulting from the partial overlap of the s and p bands.

Figure 1.12 shows the distribution of the energy levels and electron filling in four cases at the temperature of absolute zero. Cases (a) and (b) correspond respectively to mono- and divalent metals (alkali metals and alkaline earth metals found in section 1.8.2.3). These are conductive metals, in which the s and p bands partly overlap. In case (a), the electrons do not completely fill the s band; in case (b), they completely fill the s band, but the p band is available because of the partial overlap. Case (c) corresponds to the case of a non-insulating semiconductor, wherein the bands do not overlap. The lower band is full but the upper band is very close to the former. Case (d) corresponds to an insulator, where the bands do not overlap. The lower band is full, and the upper band is very far removed and is empty.

Thus, we find (a), (b) and (c) – the three cases of conduction illustrated in Figure 1.9.

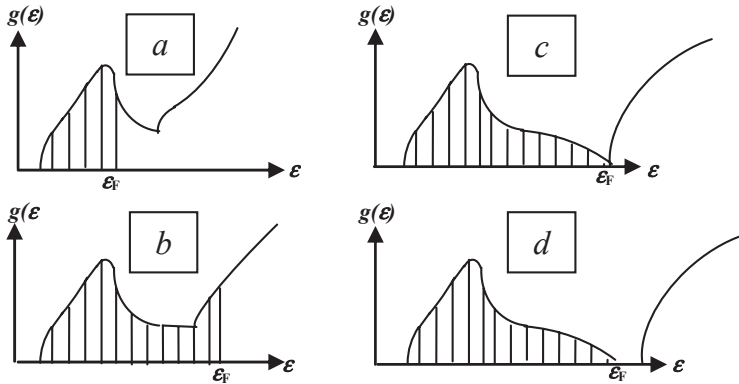


Figure 1.12. Occupation of states in a) a monovalent metal; b) a divalent metal; c) a semi-conductor; d) an insulator

1.9. Molar specific heat capacities of crystalline solids

We can determine the molar specific heat capacities at constant volume by derivation of the molar internal energy, using the relation:

$$C_V = \left(\frac{\partial U_m}{\partial T} \right)_V \quad [1.126]$$

We know that depending on the solids, the molar internal energy is the sum of several contributions – e.g. the sum shown in relation [1.35]. By application of relation [1.126], we find that the overall specific heat capacity will also be the sum of various contributions, but only the contributions of the internal energy, which are temperature-dependent, give us a term for the contribution to the overall specific heat capacity.

1.9.1. Contribution of the vibrational energy to the specific heat capacity at constant volume

The contribution of the vibrational motions to the internal energy is found in all crystalline solids, and is always temperature-dependent. We have found two types of contributions:

- the so-called Einsteinian contribution, with a unique vibration, mainly applicable to an optical vibration;
- the distribution of $3N$ acoustic vibrations in Debye's model and its derivatives.

We will now calculate the contribution corresponding to each of these models to the specific heat capacity at constant volume.

1.9.1.1. Case of a unique vibration in Einstein's model

By combining expressions [1.29] and [1.126], we obtain the contribution of a unique vibration to the specific heat capacity at constant volume:

$$C_{V(v)} = 3R \left(\frac{\Theta_E}{T} \right)^2 \frac{\exp\left(\frac{\Theta_E}{T}\right)}{\left[\exp\left(\frac{\Theta_E}{T}\right) - 1 \right]^2} \quad [1.127]$$

We often adopt the function $E(T/\Theta_E)$, known as *Einstein's function*, which is defined by:

$$E\left(\frac{T}{\Theta_E}\right) = \left(\frac{\Theta_E}{T}\right)^2 \frac{\exp\left(\frac{\Theta_E}{T}\right)}{\left[\exp\left(\frac{\Theta_E}{T}\right) - 1 \right]^2} \quad [1.128]$$

The corresponding specific heat capacity will thus be written:

$$C_{V(v)} = 3RE\left(\frac{T}{\Theta_E}\right) \quad [1.129]$$

At high temperature, the molar specific heat capacity is reduced to:

$$C_{V(v)} \cong 3R \quad [1.130]$$

This is the Dulong and Petit law, which we can deduce from the kinetic theory of gases, noting that $3N$ vibrational degrees of freedom correspond to $6N$ quadratic terms.

At low temperature, the molar specific heat capacity tends toward zero.

The Einstein temperature is obtained on the basis of the infrared spectra which enable us to determine the vibration frequencies of the links and then apply the expression $\Theta_E = \frac{h\nu}{k_B}$.

1.9.1.2. Case of Debye's acoustic vibration distribution

By combining relations [1.30] and [1.126], we obtain the contribution of an acoustic vibration distribution, according to Debye, to the specific heat capacity at constant volume, so:

$$C_{V(v)} = 12R \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3}{\exp(x)-1} dx \quad [1.131]$$

We often posit the function $D(T/\Theta_D)$, known as *Debye's function*, defined by:

$$D(T/\Theta_D) = 4 \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3}{\exp(x)-1} dx \quad [1.132]$$

The corresponding specific heat capacity is then written:

$$C_{V(v)} = 3R D \left(\frac{T}{\Theta_D} \right) \quad [1.133]$$

At high temperature, the molar specific heat capacity is reduced to:

$$C_{V(v)} \cong 3R \quad [1.134]$$

We see the Dulong–Petit law.

At low temperature ($T \ll \Theta_D$), relation [1.26] gives the so-called “ T^3 ” law, for the specific heat capacity:

$$C_{V(v)} = \frac{12}{5} R \pi^4 \left(\frac{T}{\Theta_D} \right)^3 \quad [1.135]$$

Figure 1.13 compares the curve given by the Einsteinian relation [1.129] and that given by Debye’s law [1.133]. We can see a difference between the two curves – particularly at low temperature.

The Debye temperature can be measured in a variety of ways. The most common are:

- evaluation on the basis of the whole curve $C_V(T)$;
- evaluation on the basis of the values of the specific heat capacities obtained at low temperature (less than $\Theta_D/12$), and application of the T^3 law [1.135];
- the Debye temperature can also be deduced from elastic data in the vicinity of 200 K.

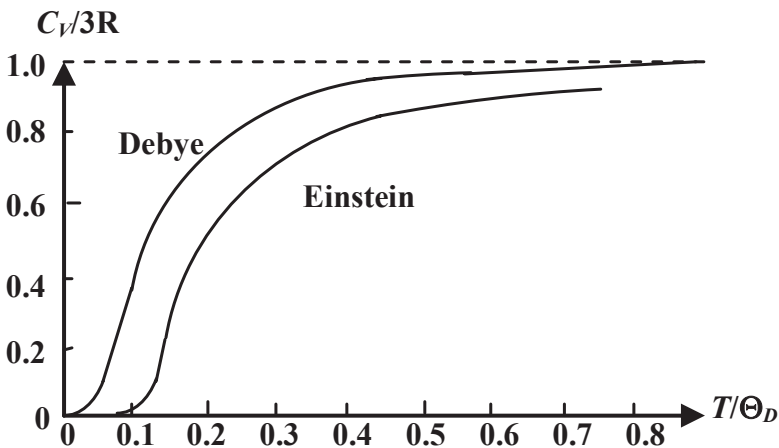


Figure 1.13. Comparison of the curves of the Einstein and Debye contributions for the specific heat capacity

Figure 1.14 gives a few of the values that are used. For example, for copper, the values obtained by the different methods all fall within the range 310–340 K.

If we choose a wavelength distribution other than Debye's, then the laws are obviously changed. For example, the Born–von Karmann distribution (Figure 1.4(a)) gives us a law combining the Einsteinian and Debye terms, as follows:

$$C_{V(v)} = \frac{3}{2} R \left[E \left(\frac{\gamma T}{\Theta_m} \right) + D \left(\frac{0,8T}{\Theta_m} \right) \right] \quad [1.136]$$

where γ and Θ_m being two constants, which we adjust in relation to the experimental data.

Choosing to use Blackman's distribution (Figure 1.4(b)), Nernst and Lindemann put forward the following law:

$$C_{V(v)} = \frac{3}{2} R \left[E \left(\frac{T}{\Theta} \right) + E \left(\frac{2T}{\Theta} \right) \right] \quad [1.137]$$

We are going to make use of these contributions of the vibrations to the construction of the specific heat capacity at constant volume for different types of solids.

1.9.2. Specific heat capacity of an atomic solid at constant volume

An atomic solid has an energy given by a relation similar in form to equation [1.28], which involves a temperature-dependent vibrational term, which gives us a vibrational contribution to the specific heat capacity of the form:

$$C_{V(v)} = 3R D \left(\frac{T}{\Theta_D} \right) \quad [1.138]$$

A priori, the vibrational term is the only one in equation [1.28] which is temperature-dependent. However, we need to take a slightly

closer look at the electron contribution – particularly in the wake of our study of section 1.7, and distinguish conductive atomic solids from non-conductive solids.

1.9.2.1. Case of conductors

Conductive solids have free levels for the electrons above the Fermi level in the conduction band. Thus, we distinguish between:

– electrons in the lower bands, which are not excited, whose internal energy does not depend on the temperature (as envisaged in relation [1.28]) and which make no contribution to the specific heat capacity;

– electrons which can be described as “free”, located at the temperature 0 K in the conduction band below the Fermi level. At temperature T , the internal energy of these free electrons is given by relation [1.119], which is a function of the temperature. By applying expression [1.126], we can deduce a contribution of the free electrons to the specific heat capacity, given by:

$$C_{V^{(el)}} = \frac{4\chi}{3^{2/3}} \frac{R\pi^{8/3}V^{2/3}}{h^2 N_a^{2/3}} T \quad [1.139]$$

Thus, strictly speaking, the specific heat capacity of a metal at constant volume will be the sum of two contributions: one from the vibration of the ions and the other from the free electrons, so by applying the contributions [1.138] and [1.139]:

$$C_V = \frac{4\chi}{3^{2/3}} \frac{R\pi^{8/3}V^{2/3}}{h^2 N_a^{2/3}} T + 3R D\left(\frac{T}{\Theta_D}\right) \quad [1.140]$$

Based on this general relation, we can formulate two observations:

1) The first deals with the relative orders of magnitude of the two terms in addition [1.140]. The electronic term would be order of $5 \times 10^{-4} T/\text{mole.K}^{-1}$, which means it is negligible at normal temperatures. It only becomes significant at around 1 K. This was confirmed by Keesom and Kok, who measured such a contribution of $2.5 \times 10^{-4} T$ for copper, which corresponds to a contribution of

0.033 J/mole.K⁻¹ at 133 K, as compared to a vibrational contribution of 16.2 J/mole.K⁻¹.

2) The second observation pertains to the influence of the temperature. The same two authors observed that in the vicinity of absolute zero, the value of the specific heat capacity is greater than that given by the extrapolation of the T^3 law given by equation [1.135]. The capacity is thus written as:

$$C_V = \frac{4\chi}{3^{2/3}} \frac{R\pi^{8/3}V^{2/3}}{h^2N_a^{2/3}}T + \frac{12}{5}R\pi^4 \left(\frac{T}{\Theta_D} \right)^3 \quad [1.141]$$

At the temperature of 1 K, the T term could even become predominant.

1.9.2.2. Case of insulating materials

In the case of insulating materials, the electrons in the conduction band do not have the opportunity to gain energy by an increase in temperature, as the gap to be crossed is very large indeed, so the electron contribution will be null. However, as we noted in the case of fluorine, the crystal must be considered to be a crystal of diatomic molecules. This being the case, each molecule F₂ has six degrees of freedom. Three will be degrees of acoustic vibrations, arising from the Debye term, and three will be optical vibrations, each arising from an Einsteinian term. Thus, the specific heat capacity contains only a vibrational contribution, formed of four terms in accordance with the following (for a mole of fluorine or 1/2 a mole of difluorine):

$$C_V = \frac{3R}{2}D\left(\frac{T}{\Theta_D}\right) + \frac{R}{2}\sum_{s=4}^{s=6}E_s\left(\frac{T}{\Theta_{E(s)}}\right) \quad [1.142]$$

If the three Einsteinian terms have very similar frequencies, then the relation can be simplified to:

$$C_V = \frac{3R}{2}\left[D\left(\frac{T}{\Theta_D}\right) + E\left(\frac{T}{\Theta_E}\right)\right] \quad [1.143]$$

In fact, in general, the Debye temperature is much lower than the Einstein temperature, so we can divide the temperature scale into three regions:

– if $T \ll \Theta_D$, the Debye term is predominant, the Einstein term can be ignored and we find the T^3 law around the temperature of absolute zero;

– if $T \gg \Theta_D$, the Einstein term is predominant, and Debye's can be ignored.

Only if the temperature lies between those two characteristic temperatures we do need to apply relation [1.143].

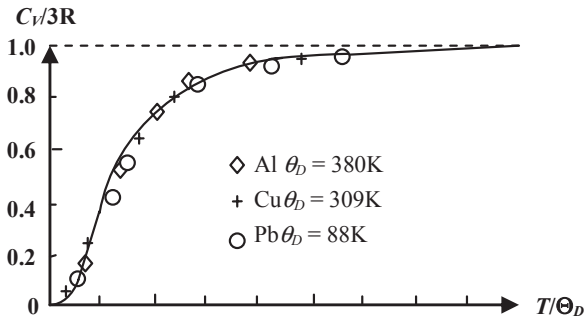


Figure 1.14. Debye curve and specific heat capacities at constant volume for a number of atomic solids

NOTE.— In the case of semiconductors, the situation is the same as for insulators, but there is the possibility of populating the band above the Fermi level by increasing the temperature, which would introduce an electron term, as a function of the temperature in the internal energy and therefore an electron contribution to the specific heat capacity. However, the breadth of the gap to be crossed is such that few electrons can make that jump at low temperature, and therefore the corresponding term will always be negligible in comparison to the vibrational term.

Figure 1.14 shows that Debye's curve corresponds closely with the variations in the $C_V/3R$ ratio for a number of metals. Note that the

curve is only plotted above a certain temperature, above the temperature where the electronic term becomes significant.

1.9.3. Specific heat capacity of a molecular or ionic solid at constant volume

For molecules, as for ionic solids after grouping into neutral entities (see section 1.7.3), the internal energy is given by the sum such as [1.35], wherein only the vibrational term varies with temperature.

However, as we have seen in section 1.7.3, the vibrations are divided into acoustic vibrations by multiples of three and arising from the Debye terms and optical vibrations, whose number is complementary to the former and which all result from an Einsteinian term. Hence, the specific heat capacity takes the following form:

$$C_V = 3R \left[\sum_{\text{ac}} D \left(\frac{T}{\Theta_D} \right) + \sum_{\text{opt}} E \left(\frac{T}{\Theta_E} \right) \right] \quad [1.144]$$

In general, at low temperatures, only the Debye terms need to be taken into account, whereas at high temperatures, the Einstein terms are largely predominant. This means that the T^3 extrapolation to absolute zero is correctly observed, because only the Debye term remains.

1.9.4. Conclusion as to the specific heat capacity of a crystalline solid

In conclusion, it can very often be admitted that, outside of metals, the specific heat capacity varies with temperature like Debye's law at low temperatures, with a law proportional to T^3 at very low temperatures (below 40 K), while Einstein's law performs better at higher temperatures. For metals, caution needs to be exercised when we come very close to absolute zero: a law proportional to T is better than the T^3 law.

At very high temperatures, all laws tend toward the Dulong–Petit law, meaning that the specific heat capacity at constant volume becomes temperature-independent, obeying relation [1.130].

Macroscopic modeling always gives us the specific heat capacity at constant volume. We can switch to the specific heat capacity at constant pressure by using the relation:

$$C_p - C_v = T \left(\frac{\partial P}{\partial T} \right)_v \left(\frac{\partial V}{\partial T} \right)_p \quad [1.145]$$

Using the thermomechanical coefficients (see section 1.9.1), we construct expression [1.146], which links the difference between the specific heat capacities at constant pressure and volume to the expansion coefficient β , and to the compressibility coefficient χ_T :

$$C_p - C_v = \frac{V\beta^2}{\chi_T} \quad [1.146]$$

This very general relation for solids is the equivalent of relation [1.145], but is easier to use for gases on the basis of the state equation.

1.10. Thermal expansion of solids

The thermal expansion of a solid is the variation in that solid's dimensions when its temperature is changed. A few exceptions aside, dimensions generally increase when the temperature rises. This expansion is due to the anharmonicity of the molecules' vibrations.

1.10.1. Expansion coefficients

On the macroscopic level, the expansion is characterized by the linear and cubic expansion coefficients.

1.10.1.1. Linear expansion coefficient

In a direction in space, the increase of a length under the influence of temperature is defined at a given pressure by the linear expansion coefficient at constant pressure α :

$$\alpha = \frac{1}{l} \left(\frac{\partial l}{\partial T} \right)_p \quad [1.147]$$

We often express that coefficient in relation to the l_0 at the temperature of 0°C , defining a standard linear expansion coefficient α_0 as:

$$\alpha_0 = \frac{1}{l_0} \left(\frac{\partial l}{\partial T} \right)_p \quad [1.148]$$

Table 1.3 gives the value of the linear expansion coefficient for a number of substances at standard temperature.

This linear expansion coefficient can be measured either by using a dilatometer or by shift in X-ray diffraction lines as a function of the temperature.

Substance	α (10^{-6} C^{-1})	Substance	α (10^{-6} C^{-1})
Aluminum	22.38	Brass	18.5
Copper	16.70	Invar	1
Iron	11.70	Glass	7
Lead	27.26	Pyrex glass	3
Tantalum	6.46	Quartz	0.55
Tungsten	4.28	Porcelain	3
Zinc	35.40		

Table 1.3. Linear expansion coefficients of a number of substances

1.10.1.2. Thermal expansion tensor

In anisotropic solids, the expansion coefficient depends on the direction, so to describe the expansion we use a second-order symmetrical tensor, which, in the case of a triclinic solid, has six expansion coefficients:

$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix}$$

Because this tensor must be symmetrical, we have:

$$\alpha_{12} = \alpha_{21}; \alpha_{13} = \alpha_{31} \text{ and } \alpha_{23} = \alpha_{32}$$

With an orthorhombic solid, the tensor is diagonal, the three terms α_{12} , α_{12} and α_{12} have a value of zero, and the three diagonal terms α_{11} , α_{22} and α_{33} give the expansion along the three axes a , b and c of the material.

The eigenvalues of that tensor are the three primary expansion coefficients α_1 , α_2 and α_3 .

1.10.1.3. Cubic expansion coefficient (or coefficient of relative volume increase)

To characterize changes in volume under the influence of temperature, we define a volume expansion coefficient for a level of pressure maintained as constant, thus:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad [1.149]$$

Sometimes that coefficient is expressed in relation to the volume V_0 occupied at the temperature of 0°C :

$$\beta_0 = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_p \quad [1.150]$$

The volume expansion coefficient is obtained by “plotting” the expansion tensor – i.e. by the sum of the three primary coefficients – but also, because the plot of a square matrix is invariant in a changed system of coordinates, by the sum of the three diagonal terms in the thermal expansion tensor, which gives us the relations:

$$\beta = \alpha_1 + \alpha_2 + \alpha_3 = \alpha_{11} + \alpha_{22} + \alpha_{33} \quad [1.151]$$

NOTE.– In isotropic media, the linear expansion coefficient is the same in all three directions in space, so:

$$\alpha_1 = \alpha_2 = \alpha_3 = \alpha$$

Thus:

$$\beta = 3\alpha \quad [1.152]$$

1.10.1.4. Relation between the thermomechanical coefficients

We define the isothermal compressibility coefficient at constant temperature T by the relation:

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad [1.153]$$

The minus sign is introduced because the true intensive variable, conjugate to the volume, is the opposite of the pressure: $-P$.

We also define the coefficient of pressure increase at constant volume by the relation:

$$\delta = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_V \quad [1.154]$$

If, for the phase in question, there is an equation of state such as $f(P, V, T) = 0$, we have the relation:

$$\beta = \delta \chi_T P \quad [1.155]$$

Indeed, for that state function, we can write:

$$\delta \chi_T P = -\frac{1}{P} \frac{\frac{\partial f}{\partial P}}{\frac{\partial f}{\partial T}} \cdot \frac{1}{V} \frac{\frac{\partial f}{\partial V}}{\frac{\partial f}{\partial P}} P = -\frac{1}{V} \frac{\frac{\partial f}{\partial V}}{\frac{\partial f}{\partial T}} = \frac{1}{V} \frac{\partial V}{\partial T} = \beta$$

1.10.2. Origin of thermal expansion in solids

We will now show that the thermal expansion can be attributed to the vibrations of the atoms at the nodes of the crystalline lattice.

For this purpose, we will use the following values for the definite integrals:

$$\int_{-\infty}^{+\infty} \exp -x^2 dx = \sqrt{\pi} \quad [1.156]$$

$$\int_{-\infty}^{+\infty} x \exp -x^2 dx = 0 \quad [1.157]$$

$$\int_{-\infty}^{+\infty} x^3 \exp -x^2 dx = 0 \quad [1.158]$$

$$\int_{-\infty}^{+\infty} x^4 \exp -x^2 dx = \frac{3\sqrt{\pi}}{4} \quad [1.159]$$

To begin with, we will consider a harmonic vibration. In conventional mechanics, the curve that gives the potential energy of the harmonic oscillator as a function of the length of the spring is a parabola (Figure 1.15(a)). On that parabola, an increase in temperature results in a rise of the potential energy, at various temperatures T_1 , T_2 , T_3 and T_4 shown in the figure. When the temperature is raised, we can clearly see from the figure that the average position of the end of the spring does not change, and therefore this average position follows a vertical line. This means that no expansion is observed with this increase in temperature. This can be demonstrated numerically.

The equation for the curve of the parabola is written as:

$$\varepsilon - \varepsilon_0 = a(r - r_0)^2 = ax^2 \quad [1.160]$$

Let us calculate the average stretching of the spring $\langle r - r_0 \rangle$ by applying the definition of the average of a value Q :

$$\langle Q \rangle = \frac{\sum_{\text{Accessible states}} Q}{\sum_{\text{Accessible states}} 1} \quad [1.161]$$

When we apply this formula to the average stretching, by using Boltzmann statistics, we find:

$$\langle r - r_0 \rangle = \frac{\int_{-\infty}^{+\infty} x \exp\left(-\frac{\varepsilon - \varepsilon_0}{k_B T}\right) dx}{\int_{-\infty}^{+\infty} \exp\left(-\frac{\varepsilon - \varepsilon_0}{k_B T}\right) dx} = \frac{\int_{-\infty}^{+\infty} x \exp\left(-\frac{ax^2}{k_B T}\right) dx}{\int_{-\infty}^{+\infty} \exp\left(-\frac{ax^2}{k_B T}\right) dx} = 0 \quad [1.162]$$

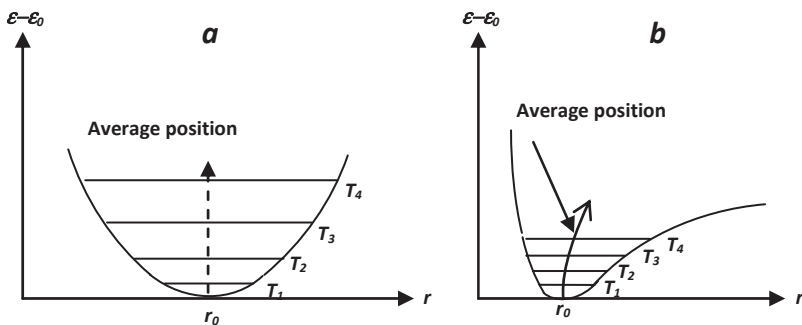


Figure 1.15. Potential energy curves for a) the harmonic oscillator, and b) an anharmonic oscillator

We can see from the value of the integral [1.157] that the stretching is zero. Thus, we confirm the approximation of a harmonic oscillator which does not allow for thermal expansion.

Now let us consider an anharmonic oscillator, the potential energy for which is plotted by the curve in Figure 1.15(b). We can clearly see that this shape of curve allows for the breaking of the link. However, we can also see that if the temperature increases, the average position of the end of the spring follows a curve that inclines to the right, thus showing an expansion. We can demonstrate this numerically.

To the equation for the parabola, we add a cubic term to express the anharmonicity of the potential energy curve. Thus, we adopt a

position that is fairly close to the minimum – i.e. at low temperatures. Hence, the energy can be written as:

$$\varepsilon - \varepsilon_0 = a(r - r_0)^2 + b(r - r_0)^3 = ax^2 + bx^3 \quad [1.163]$$

Using Boltzmann statistics like in equation [1.162] but with the new formula for the energy given by relation [1.163], we obtain:

$$\langle r - r_0 \rangle = \frac{\int_{-\infty}^{+\infty} x \exp\left(-\frac{ax^2}{k_B T} - \frac{bx^3}{k_B T}\right) dx}{\int_{-\infty}^{+\infty} \exp\left(-\frac{ax^2}{k_B T} - \frac{bx^3}{k_B T}\right) dx} \quad [1.164]$$

The exponential term of anharmonicity, which is deemed to be low, is replaced by the development limited to the first two terms:

$$\exp\left(-\frac{bx^3}{k_B T}\right) \approx 1 - \frac{bx^3}{k_B T} \quad [1.165]$$

By substituting this value back into equation [1.164], we find:

$$\langle r - r_0 \rangle = \frac{\int_{-\infty}^{+\infty} x \exp\left(-\frac{ax^2}{k_B T} \left(1 - \frac{bx^3}{k_B T}\right)\right) dx}{\int_{-\infty}^{+\infty} \exp\left(-\frac{ax^2}{k_B T} \left(1 - \frac{bx^3}{k_B T}\right)\right) dx} \quad [1.166]$$

The numerator and the denominator in this fraction can both be expanded, giving us:

$$\langle r - r_0 \rangle = \frac{\int_{-\infty}^{+\infty} x \exp\left(-\frac{ax^2}{k_B T} - \frac{bx^4}{k_B T}\right) dx - \int_{-\infty}^{+\infty} \frac{bx^3}{k_B T} \exp\left(-\frac{ax^2}{k_B T}\right) dx}{\int_{-\infty}^{+\infty} \exp\left(-\frac{ax^2}{k_B T} - \frac{bx^3}{k_B T}\right) dx - \int_{-\infty}^{+\infty} \frac{bx^3}{k_B T} \exp\left(-\frac{ax^2}{k_B T}\right) dx} \quad [1.167]$$

We recognize the different definite integrals whose values are given in equations [1.156], [1.157], [1.158] and [1.159]. If we substitute in those values, the stretching becomes:

$$\langle r - r_0 \rangle = -\frac{3b}{4a^2} k_B T \quad [1.168]$$

The expansion coefficient can thus be obtained on the basis of its definition:

$$\alpha = \frac{1}{r_0} \frac{d\langle r - r_0 \rangle}{dT} = -\frac{3b}{4a^2 r_0} k_B \quad [1.169]$$

We can see that simply introducing an anharmonic term into the equation for the potential energy curve is sufficient to take account of the existence of linear expansion.

Unfortunately, our model gives us a linear expansion coefficient that is temperature-independent. This result would be kept if a larger number of terms were added to the potential energy equation in relation [1.163]. However, experience tells us that α is dependent on the temperature.

In order to achieve a correct representation of the expansion, we will approach the problem using quantum mechanics.

1.10.3. Quantum treatment of thermal expansion. Grüneisen parameter

To begin with, note that by using relations [1.152], [1.154] and [1.155], we can write:

$$\alpha = \frac{\chi_T}{3} \left(\frac{\partial P}{\partial T} \right)_V \quad [1.170]$$

In order to calculate the linear expansion coefficient, we first need to calculate the thermodynamic coefficient $(\partial P / \partial T)_V$. For this purpose, we will work with the variables V and T .

We will consider our solid to be a collection of quantum oscillators, phonons, each of which has its own natural frequency of vibration ν_i .

The partition function relative to such an oscillator is:

$$z_i = \frac{\exp\left(-\frac{h\nu_i}{2k_B T}\right)}{1 - \exp\left(-\frac{h\nu_i}{k_B T}\right)} \quad [1.171]$$

The characteristic function with variables T, V is the Helmholtz energy. Thus, for each phonon, we can write its contribution to the Helmholtz energy in the form:

$$F_i = -k_B T \ln z_i = \frac{h\nu_i}{2} + k_B T \ln \left[1 - \exp\left(-\frac{h\nu_i}{k_B T}\right) \right] \quad [1.172]$$

Similarly, the contribution of that phonon to the internal energy will be:

$$U_i = -\frac{\partial \ln z_i}{\partial \left(\frac{1}{k_B T}\right)} = \frac{h\nu_i}{2} + \frac{h\nu_i}{\exp\left(\frac{h\nu_i}{k_B T}\right) - 1} \quad [1.173]$$

The anharmonic effect of the oscillations will be taken into account by considering that the vibration frequency of the phonon is a function of the volume.

As the pressure is the derivative of the Helmholtz energy in relation to the volume, the contribution of our phonon to that pressure will be:

$$P_i = -\left(\frac{\partial F_i}{\partial V}\right)_T = -\left[\frac{h\partial v_i}{2\partial V} + \frac{\frac{\partial v_i}{\partial V} h \exp\left(-\frac{h v_i}{k_B T}\right)}{1 - \exp\left(-\frac{h v_i}{k_B T}\right)}\right] \quad [1.174]$$

From this, we deduce:

$$P_i = -\frac{\partial v_i}{\partial V} \left[\frac{h}{2} + \frac{h}{\exp\left(\frac{h v_i}{k_B T}\right) - 1} \right] = -\frac{U_i}{v_i} \frac{\partial v_i}{\partial V} \quad [1.175]$$

Additionally, we can always write:

$$\frac{\partial v_i}{\partial V} = \frac{v_i}{V} \cdot \frac{V}{v_i} \cdot \frac{\partial v_i}{\partial V} = \frac{v_i}{V} \cdot \frac{\partial \ln v_i}{\partial \ln V} \quad [1.176]$$

We define a value γ_i by the expression:

$$\gamma_i = -\frac{\partial \ln v_i}{\partial \ln V} \quad [1.177]$$

This value is called the *Grüneisen factor* of the phonon i .

The pressure due to all the phonons, in view of relations [1.176] and [1.177], and by adding relation [1.175] for all the phonons, will be written as:

$$P = \sum_i P_i = \sum_i \gamma_i \frac{U_i}{V} \quad [1.178]$$

We derive this pressure in relation to temperature, at constant volume. In view of expression [1.126], we obtain:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{V} \sum_i \gamma_i \left(\frac{\partial U_i}{\partial T}\right)_T = \frac{1}{V} \sum_i \gamma_i C_{Vi} \quad [1.179]$$

By substituting that derivative back into equation [1.170], the expansion coefficient is written as:

$$\alpha = \frac{\chi_T}{3V} \sum_i \gamma_i C_{Vi} = \frac{\chi_T}{3V} \frac{\sum_i \gamma_i C_{Vi}}{\sum_i C_{Vi}} \sum_i C_{Vi} \quad [1.180]$$

We define the value $\gamma(T, V)$, called the *Grüneisen parameter*, by the expression:

$$\gamma(T, V) = \frac{\sum_i \gamma_i C_{Vi}}{\sum_i C_{Vi}} \quad [1.181]$$

NOTE.— It is important not to confuse the Grüneisen factor γ_i with the Grüneisen parameter $\gamma(T, V)$.

Thus, the expansion coefficient will be:

$$\alpha = \frac{\chi_T}{3} \gamma(T, V) C_V \quad [1.182]$$

As the isothermal compressibility χ_T and the specific heat capacity at constant volume C_V are both values which are always positive, the Grüneisen parameter has the same sign as the expansion coefficient – i.e. positive in the majority of cases and negative in the few cases of contraction with increased temperature.

Experience tells us that the product $\chi_T \gamma(T, V) / V$ is essentially constant as the temperature varies, which means that, in practice, the linear expansion coefficient is practically proportional to the specific heat capacity at constant volume, i.e.:

$$\alpha \propto C_V \quad [1.183]$$

Thus, the variation of the expansion coefficient with temperature will be the same in form as that of the specific heat capacity at

constant volume, so we obtain the curve shown in Figure 1.16, which has the same shape as Figure 1.14.

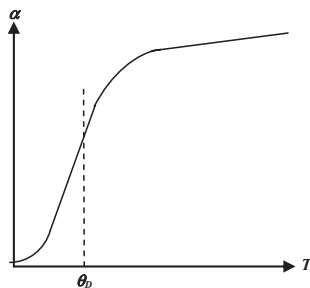


Figure 1.16. Shape of the curve of the expansion coefficient with temperature in the context of the Debye approximation

In view of expression [1.183], we can reach the same conclusions as those about the specific heat capacity at constant volume in section 1.9.1.2 (see relations [1.134] and [1.135]):

$$\begin{aligned} T \ll \Theta_D & \quad \alpha \propto T^3 \\ T \gg \Theta_D & \quad \alpha \text{ essentially constant} \end{aligned} \quad [1.184]$$

Experimentally, the Grüneisen parameter is determined at zero pressure or atmospheric pressure, on the basis of measurements of the volume expansion coefficient β , the adiabatic compressibility (constant entropy) χ_S and the specific heat capacity at constant pressure C_p because we have:

$$\gamma(T, V) = \frac{3\alpha}{\chi_T C_V} = \frac{\beta V}{\chi_S C_p} \quad [1.185]$$

Relation [1.177] shows that the Grüneisen parameter for the phonon i is dimensionless, and therefore the parameter $\gamma(T, V)$, defined by relation [1.181], is also dimensionless.

In the majority of cases, the Grüneisen parameter is of the order of magnitude of a few units at all temperatures, as is demonstrated by the

curves in Figure 1.17, which give the variations of that parameter for several alkali halides.

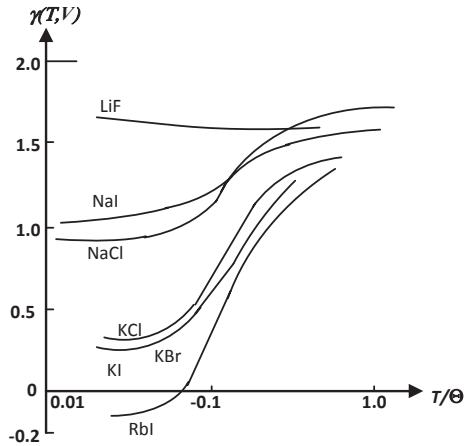


Figure 1.17. Grüneisen parameter for a few alkali halides (data from [WHI 65])

However, we note a few cases of values that are far greater – either positive or negative.

The Grüneisen parameter also varies with the volume, as is shown by the example of copper illustrated in Figure 1.18.

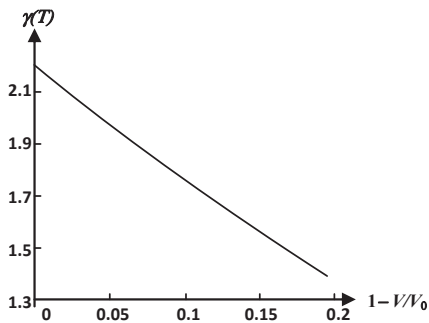


Figure 1.18. Variation of the Grüneisen parameter for copper with the volume (data taken from [GIR 00])

1.10.4. Expansion coefficient of metals

The reasoning we employed in the previous section is valid for insulating solids. Indeed, for metals, we know that a contribution is made by the free electrons to the partition function and therefore to the specific heat capacity at constant volume. We will now look at the situation for the expansion.

We can think in the case of the electron gas subject to Fermi–Dirac statistics, but calculation shows that we obtain an identical result by using the simple model of the gas of electrons subject to three degrees of freedom of translation, in the case of the equal energy distribution model. If the metal includes n_e electrons per atom, its molar internal energy will be:

$$U_{el} = \frac{3n_e N_a k_B T}{2} \quad [1.186]$$

By application of the ideal gas law, we deduce the electron pressure:

$$P_{el} = \frac{n_e N_a k_B T}{V} = \frac{2U_{el}}{3V} \quad [1.187]$$

By deriving this pressure in relation to the temperature, we find:

$$\left(\frac{\partial P_{el}}{\partial T} \right)_V = \frac{2}{3V} \left(\frac{\partial U_{el}}{\partial T} \right)_V = \frac{2}{3V} C_{vel} \quad [1.188]$$

If we substitute this back into equation [1.170], we find an electron parameter of the Grüneisen constant: $\gamma_{el}(T, V) = 2/3$

Thus, the linear expansion coefficient of the metal will be the sum of two terms: the contribution of the lattice $\gamma_r(T, V)C_{vr}$ and the contribution of the free electrons $\gamma_{el}(T, V)C_{vel}$. Hence, we can write:

$$\alpha = \frac{1}{3} \chi_T (\gamma_e(T, V)C_{ve} + \gamma_r(T, V)C_{vr}) \quad [1.189]$$

At low temperature, we know that the contribution of the lattice varies as the cube of the temperature. By keeping the product $\chi_T \gamma_e(T, V)$ practically constant, the electron contribution also varies as the electron contribution to the specific heat capacity at constant volume. However, as we have seen (relation [1.139]), that contribution varies with T , so, at low temperature, the linear expansion coefficient of a metal will be of the form:

$$\alpha \cong aT + bT^3 \quad [1.190]$$

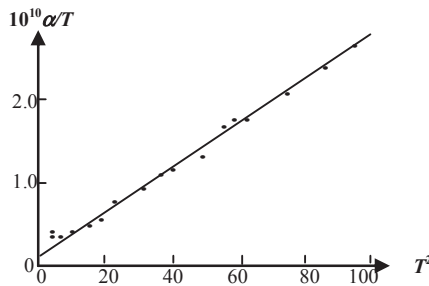


Figure 1.19. Expansion of copper at low temperature, according to [PER 70]

Figure 1.19 shows a good example of the application of this law. For copper, it represents the curve showing the α/T ratio as a function of the square of the temperature. This curve is, indeed, a straight line with the equation:

$$\frac{\alpha}{T} \cong 1.3 \times 10^{-10} + 2.7 \times 10^{-11} T^2$$

On the basis of this expression, authors have determined the value $\gamma_e(T, V) = 0.57$ for the electron Grüneisen parameter, which is near to the theoretical value of $2/1$.

As previously stressed, other properties characterize solids – electrical properties, magnetic properties and other mechanical properties such as resilience, resistance to hardness, etc. All of these properties are not studied here because they are beyond the remit of this book.

