Chapter 14
Vibrational Motions of the Ions and Thermal Effects

## Topics

Elastic Waves in Crystals
Acoustic and Optical Branches
Debye and Einstein Models
Phonons
The Melting Temperature
Mössbauer Effect

14.1 Motions of the Ions in the Harmonic Approximation

Hereafter we shall afford the problem of the motions of the ions around their equilibrium positions in an ideal (disorder- and defect-free) crystal. The motions are called *lattice vibrations*. The Born-Oppenheimer separation and the adiabatic approximation (Sect. 7.1) will be implicit and the concepts involved in the description of the normal modes (Sect. 10.6) in the harmonic approximation will be used. In fact, the crystal cell will be considered as a molecular unit: its normal modes propagate along the crystal with a phase factor, in view of the spatial periodicity.

According to the definitions sketched below,

atom at site s in the cell at l
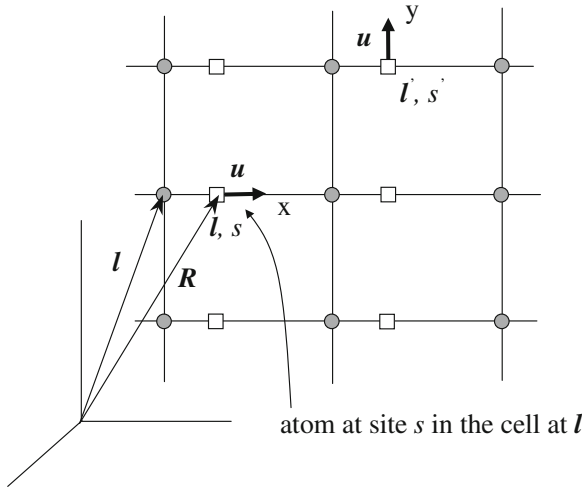
within the harmonic approximation the potential energy will be written

$$V_2 = \frac{1}{2} \sum_{\mathbf{l},s,\alpha} \sum_{\mathbf{l}',s',\beta} \left(\frac{\partial^2 V}{\partial \alpha(\mathbf{l}, s)\partial \beta(\mathbf{l}', s')} \right)_o \mathbf{u}_\alpha(\mathbf{l}, s)\mathbf{u}_\beta(\mathbf{l}', s')$$

$$\equiv \sum_{\mathbf{l},s,\alpha} \sum_{\mathbf{l}',s',\beta} \Phi^{(\alpha,\beta)}_{\mathbf{l},s,\mathbf{l}',s'} \mathbf{u}_\alpha(\mathbf{l}, s)\mathbf{u}_\beta(\mathbf{l}', s'), \qquad (14.1)$$

where $\Phi^{(x,y)}_{\mathbf{l},s,\mathbf{l}',s'}$ involves the force along the x direction on the ion at site s of the lth cell when the ion at site s' in the l' cell is displaced by the unit length along the y direction. From Eq. (14.1) the equations of motion turn out

$$m_s \frac{d^2\mathbf{u}_{l,s}}{dt^2} = -\frac{\partial V_2}{\partial \mathbf{u}_{l,s}} = -\sum_{\mathbf{l}',s'} \Phi_{\mathbf{l},s,\mathbf{l}',s'}\mathbf{u}_{l',s'}, \qquad (14.2)$$

namely $3SN$ coupled equations (S number of atoms in each cell).

Recalling the normal modes in the molecules (Sect. 10.6) it is conceivable that due to the translational invariance, the motion of the atom at site s in a given cell differs only by a phase factor with respect to the one in another cell (this is the analogous of the Bloch orbital condition for the electron states). Therefore the displacement of the $(\mathbf{l}, s)$ atom along a given direction is written in terms of plane waves propagating the normal coordinates within a cell:

$$u^{(\mathbf{q})}_\alpha(\mathbf{l}, s) = U_\alpha(s, \mathbf{q})e^{i\mathbf{q} \cdot \mathbf{R}(\mathbf{l},s)}e^{-i\omega_\mathbf{q}t}, \qquad (14.3)$$

where $\mathbf{q}$ are the wavevectors defined by the boundary conditions (the analogous of the electron wavevector $\mathbf{k}$, Sect. 12.4).

From Eqs. (14.2) and (14.3) for each $\mathbf{q}$, by taking $\mathbf{h} = \mathbf{l}_s - \mathbf{l}'_{s'}$, one has

$$m_s \omega_{\mathbf{q}}^2 U_\alpha(s, \mathbf{q}) = \sum_{\beta, s'} U_\beta(s', \mathbf{q}) M_{\alpha, \beta}(s, s', \mathbf{q}), \tag{14.4}$$

where

$$M_{\alpha, \beta}(s, s', \mathbf{q}) \equiv \sum_{\mathbf{h}} \Phi_{\mathbf{l}, s, \mathbf{l}', s'}^{(\alpha, \beta)} e^{i \mathbf{q} \cdot \mathbf{h}} \tag{14.5}$$

is the *dynamical matrix*, namely the Fourier transform of the elastic constants.

14.2 Branches and Dispersion Relations

For a given wave-vector Eq. (14.4) can be rewritten in the compact form

$$\omega^2 m \mathbf{U} = \mathbf{M} \mathbf{U} \tag{14.6}$$

where $\mathbf{M}$ is a square matrix of $3S$ degree, m is a diagonal matrix and $\mathbf{U}$ is a column vector. As for the normal modes in molecules (see Eq. (10.53)) the condition for the existence of the normal coordinates is

$$|\mathbf{M} - \omega^2 m| = 0. \tag{14.7}$$

For each wavevector $\mathbf{q}$ Eq. (14.7) yields $3S$ angular frequencies $\omega_{\mathbf{q}, j}^2$. Here j is a *branch index*. $3S - 3$ branches are called *optical* since, as it will appear at Sect. 14.3.2, they can be active in infrared spectroscopy, while 3 branches are called *acoustic*, since in the limit $\mathbf{q} \to 0$ the crystal must behave like an *elastic continuum*, where $\omega_{\mathbf{q}} = v_{sound} \mathbf{q}$. At variance, for the optical branches (see Sect. 14.3.2) for $q = 0$ one has $\omega_{\mathbf{q}, j} \neq 0$.

The $\mathbf{q}$-dependence of $\omega_{\mathbf{q}, j}$ is called *dispersion relation*. In analogy to the density of $\mathbf{k}$-states for the electrons (Sect. 12.5), one can define a density of $\mathbf{q}$ values in the reciprocal space: $D(\mathbf{q}) = N v_c / 8\pi^3$. One also defines the *vibrational spectrum* $D_j(\omega)$ for each branch, with the sum rule $\sum_{j=1}^{3S} \int D_j(\omega) d\omega = 3NS$.

In the next section illustrative examples of vibrational spectra will be given.

14.3 Models of Lattice Vibrations

In this section the classical vibrational motions of the ions within the harmonic approximation will be addressed for some model systems.

14.3.1 Monoatomic One-Dimensional Crystal

Let us refer to a linear chain of identical atoms, for simplicity by considering only the longitudinal motions along the chain direction:
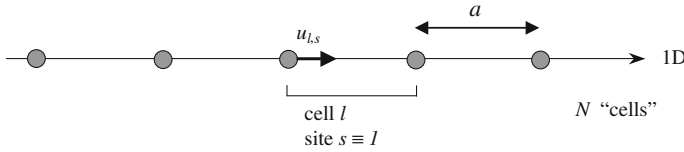
The equations of motions are of the form Eq. (14.2), the index s being redundant. One first selects in the reciprocal space a wavevector $q = n_1 2\pi / Na$, with $-N/2 \leq n_1 \leq N/2$. Then one writes the $u_{l,s}$ displacement as due to the superposition of the ones caused by the waves propagating along the chain, for each q (correspondent to Eq. (14.3)). From Eqs. (14.2) and (14.4) one writes
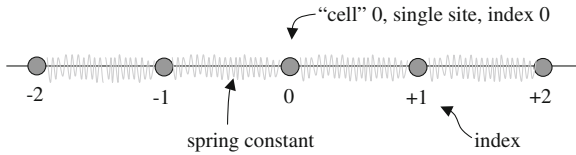
$$m_s \omega_{\mathbf{q}}^2 U(s, \mathbf{q}) = \sum_{s'} U(s', \mathbf{q}) M(s, s', \mathbf{q}), \tag{14.8}$$

where

$$M(s, s', \mathbf{q}) \equiv \sum_{\mathbf{h}} \Phi_{l,s,l',s'} e^{i\mathbf{q} \cdot \mathbf{h}} \tag{14.9}$$

is the *collective force constant*, representing the Fourier transform of the elastic constants. Equations (14.8) and (14.9) describe the propagation of the normal modes of the "cell" along the chain.

By limiting the interaction to the nearest neighbors,

the equation of motion for the atom in the cell at the origin ($l = 0$) turns out

$$m \frac{d^2 u_0}{dt^2} = -2k u_0 + k u_1 + k u_{-1} \tag{14.10}$$

implying $\Phi(0, 0) = 2k$ and $\Phi(\pm 1, 0) = -k$.

The dynamical matrix (Eq. (14.5)) is reduced to

$$M = \Phi(0,0) + \sum_{n=\pm 1} \Phi(n,0)e^{iqna}$$

and Eq. (14.8) takes the form

$$m\omega_q^2 U_q = (2k - 2k\cos(qa))U_q, \tag{14.11}$$

namely the one for a single *normal oscillator*, with an effective elastic constant taking into account the coupling to the nearest neighbors.
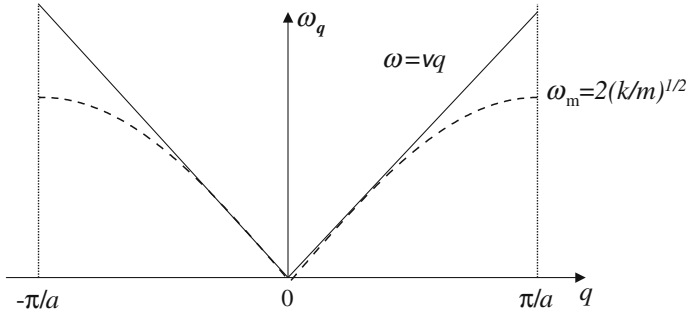
The solubility condition (Eq. (14.7)) corresponds to

$$\omega_q^2 = \frac{2k}{m}(1 - \cos(qa)), \tag{14.12}$$

yielding the dispersion relation

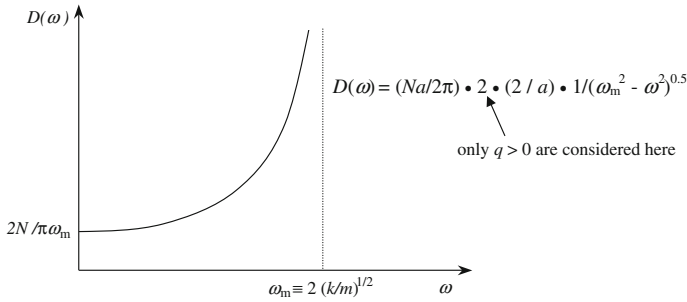$$\omega_q = 2\sqrt{\frac{k}{m}}\sin(qa/2) \tag{14.13}$$

sketched below:

The vibrational spectrum, or density of states $D(\omega) = D(q)dq/d\omega$, with $D(q) = Na/2\pi$, turns out

$$D(\omega) = \left(2N/\pi\sqrt{\omega_m^2 - \omega^2}\right), \tag{14.14}$$

reported below

$$D(\omega) = (Na/2\pi) \cdot 2 \cdot (2/a) \cdot 1/(\omega_m^2 - \omega^2)^{0.5}$$

only $q > 0$ are considered here

$$\omega_m \equiv 2 \, (k/m)^{1/2}$$

The situation arising at the zone boundary, where $\omega_{q=\pi/a} \equiv \omega_m$, is equivalent to the one encountered at the critical points of the electronic states (see Sect. 12.5).

14.3.2 Diatomic One-Dimensional Crystal

For a chain with two atoms per unit cell, with mass m_1 and m_2 ($m_1 > m_2$), again considering the longitudinal modes and assuming a single elastic constant and nearest neighbour interactions,
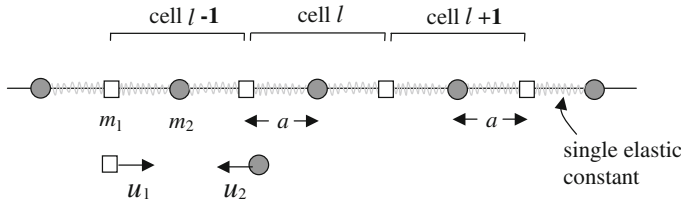
the equations of motions for the atoms at sites $s = 1$ and $s = 2$, within the lth cell, are

$$m_1 \frac{d^2 u_{l,1}}{dt^2} = -2k u_{l,1} + k u_{l,2} + k u_{l-1,2}$$

$$m_2 \frac{d^2 u_{l,2}}{dt^2} = -2k u_{l,2} + k u_{l,1} + k u_{l+1,1} \qquad (14.15)$$

Again resorting to solutions of the form

$$u(l, 1) = U_1 e^{iq2la} e^{-i\omega_q t}$$

and

$$u(l, 2) = U_2 e^{iq(a+2la)} e^{-i\omega_q t}$$

(the index q in $U_{1,2}$ is dropped here), one has

$$\left(\frac{2k}{m_1} - \omega^2\right) U_1 - \frac{k}{m_1}(e^{iqa} + e^{-iqa})U_2 = 0$$

$$-\frac{k}{m_2}(e^{iqa} + e^{-iqa})U_1 + \left(\frac{2k}{m_2} - \omega^2\right) U_2 = 0. \qquad (14.16)$$

The dynamical matrix is

$$M = \begin{pmatrix} 2k & -k(e^{iqa} + e^{-iqa}) \\ -k(e^{-iqa} + e^{iqa}) & 2k \end{pmatrix}$$

and the solubility condition

$$\begin{pmatrix} 2k - m_1\omega^2 & -2k\cos(qa) \\ -2k\cos(qa) & 2k - m_2\omega^2 \end{pmatrix} = 0$$

leads to

$$\omega_q^2 = k\left(\frac{1}{m_2} + \frac{1}{m_1}\right) \pm k\left[\left(\frac{1}{m_2} + \frac{1}{m_1}\right)^2 - \frac{4}{m_1 m_2}\sin^2(qa)\right]^{\frac{1}{2}}. \qquad (14.17)$$

The dispersion relations are shown in Fig. 14.1, with μ reduced mass.

At the boundaries of the Brillouin zone ($q = \pm\pi/2a$) the frequencies of the acoustic and optical modes are $\omega^A = \sqrt{2k/m_1}$ and $\omega^O = \sqrt{2k/m_2}$, respectively.

It is noted that when $m_1 = m_2$ the two frequencies coincide, the gap at the zone boundary vanishes: the situation of the monoatomic chain is restored, once that the length of the lattice cell becomes a instead of $2a$.

For a given wavevector one can obtain the atomic displacements induced by each normal mode. For instance, by choosing $q = 0$ for the acoustic branch one derives $U_A(0, 1) = U_A(0, 2)$, the same displacement for the two atoms, corresponding to

Fig. 14.1 Frequencies of the acoustic (A) and optical (O) longitudinal modes in one-dimensional diatomic crystal, according to Eq. (14.17)
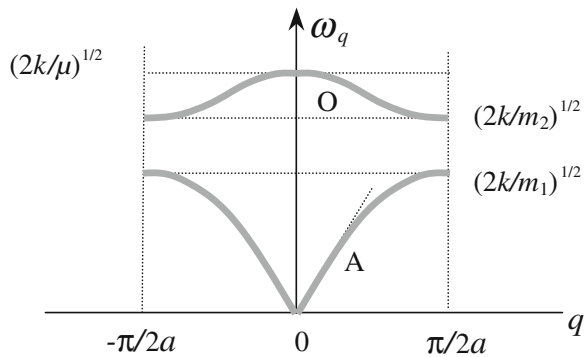
the translation of all the crystal. For the optical mode, again for $q = 0$ one has $m_1 U_O(0, 1) = -m_2 U_O(0, 2)$, keeping fixed the center of mass. As for the diatomic molecule (see Sect. 10.6) the difference of the two displacements corresponds to the normal coordinate.

In a similar way one can derive the displacements associated with the zone boundary wavevectors (Fig. 14.2, where also the transverse modes are schematized).

From the dispersion relations (Eq. (14.17)) the vibrational spectra reported in Fig. 14.3 are derived.

Up to now only longitudinal modes have been considered. To describe the transverse vibrations the elastic constants for the displacements perpendicular to the chain should be considered. In this way, for a given wave-vector, 3 vibrational branches would be obtained for the monoatomic chain and 6 branches for the diatomic one, at longitudinal (L) and transverse (T) optical and acoustic characters (see Fig. 14.2).

Finally one should observe that the interaction with electromagnetic waves requires the presence of *oscillating electric dipole* within the cell. To grant energy and momentum conservation, the absorption process should occur in correspondence to the *photon momentum* $q = \hbar\omega/c$, which for typical values of the frequencies
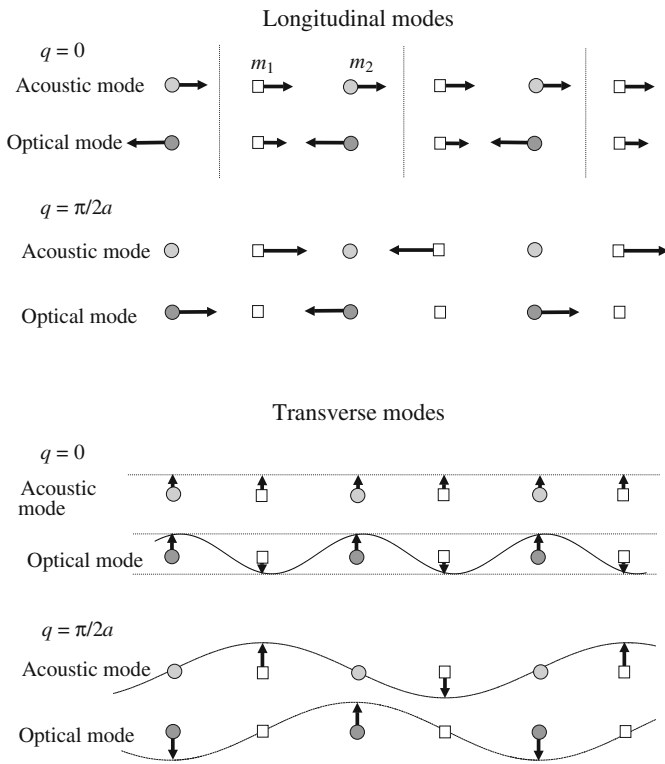
Fig. 14.2 Atomic displacements associated with the $q = 0$ and the $q = \pi/2a$ acoustic (A) and optical (O) modes, for one-dimensional diatomic crystal

Fig. 14.3 Vibrational spectra for the longitudinal acoustic (A) and optical (O) branches in one-dimensional diatomic crystal
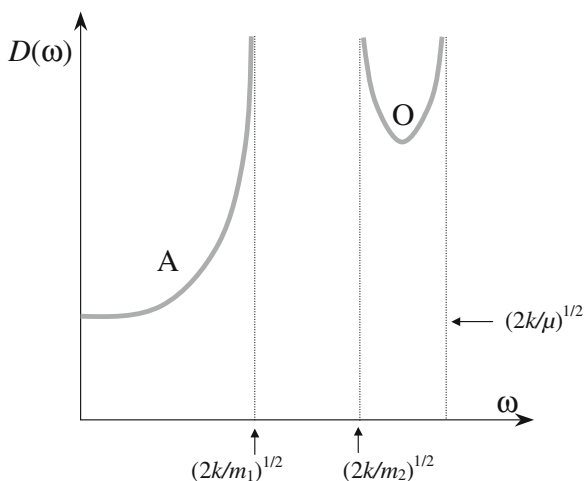

$(\omega \sim 10^{13} - 10^{14} \text{ rad s}^{-1})$ is much smaller than $h/2a$. For $q \to 0$, at the center of the Brillouin zone, the acoustic modes do not yield any dipole moment. Therefore only the optical branches, implying in general oscillating dipoles (as schematized in Fig. 14.2), can be active for the absorption of the electromagnetic radiation, similarly to the case described for the molecules.

14.3.3 Einstein and Debye Crystals

The phenomenological models due to Einstein and to Debye are rather well suited for the approximate description of specific properties related to the lattice vibrations in real crystals.

The *Einstein crystal* is assumed as an ensemble of independent atoms elastically connected to equilibrium positions. The interactions are somewhat reflected in a vibrational constant common to each oscillator, yielding a characteristic frequency ω_E. As regards the dispersion curves, one can think that for each **q** there is a threefold degenerate mode at frequency ω_E. Thus, the vibrational spectrum could be schematized as below:
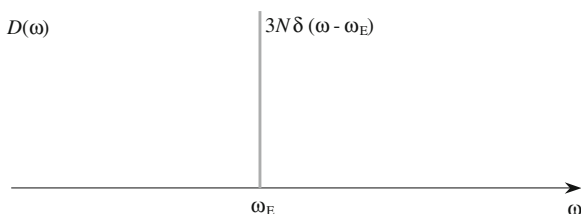
Although introduced to justify the low-temperature behavior of the specific heat (see Sect. 14.5), the Einstein model is often applied in order to describe the properties of the optical modes in real crystals, at least at qualitative level. In fact, the optical modes are often characterized by weakly q-dependent dispersion curves with a narrow $D(\omega)$, not too different from the delta-like vibrational spectrum of the Einstein model heuristically broadened, as sketched below:
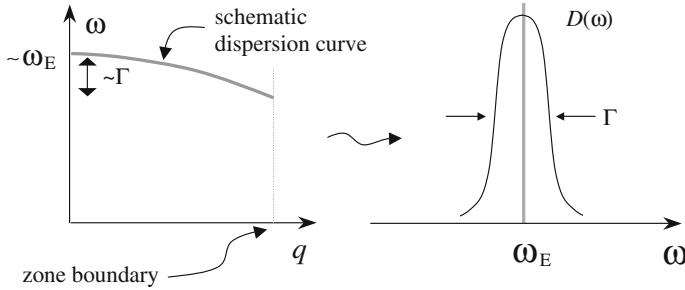
In the *Debye model* it is assumed that the vibrational properties are basically the ones of the *elastic* (and sometimes isotropic) *continuum*, with *ad hoc* conditions in order to take into account the discrete nature of any real crystal. In particular:

(i)   the Debye model describes rather well the acoustic modes of any crystal, since for $\mathbf{q} \to 0$ the dispersion curves of the acoustic branches practically coincide with the ones of the continuum solid, the wavelength of the vibration being much larger than the lattice step.

(ii) the model cannot describe the vibrational contribution from optical modes.

(iii) one has to introduce a cutoff frequency ω_D in the spectrum in order to keep the number of modes limited to $3N$ (for N atoms).

(iv) only 3 branches have to be expected, with dispersion relations of the form $\omega_q^j = \mathbf{v}_{sound}^j \mathbf{q}$, where the sound velocity can refer to transverse or to longitudinal modes.

For a given branch, in the assumption of isotropy, the vibrational spectrum turns out

$$D_j(\omega) = \frac{N v_c}{8\pi^3} d\mathbf{q} = \frac{N v_c}{8\pi^3} 4\pi q^2 dq = \frac{N v_c}{8\pi^3} \frac{4\pi \omega^2}{v_j^3}. \tag{14.18}$$

One can introduce an average velocity v and again in the isotropic case, $3/v^3 = 2/v_T^3 + 1/v_L^3$. Therefore

$$D(\omega) = \frac{N v_c}{8\pi^3} \frac{12\pi \omega^2}{v^3} = \frac{N v_c}{v^3} \frac{3}{2\pi^2} \omega^2, \tag{14.19}$$

the typical vibrational spectrum characteristic of the continuum.

Now a cutoff frequency ω_D (known as *Debye frequency*) has to be introduced. The role of ω_D in the dispersion relation and in the vibrational spectrum $D(\omega)$ is illustrated below:
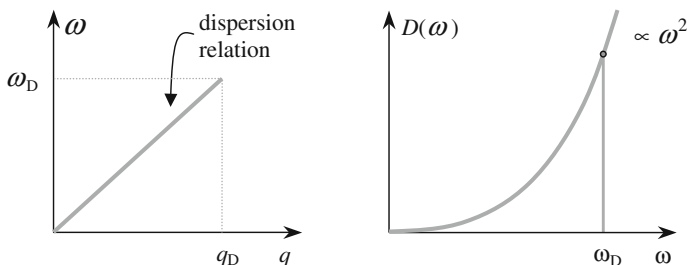
ω_D can be derived from the condition $\int D(\omega)d\omega = 3N$ or, equivalently, by evaluating the Debye radius q_D of the sphere in the reciprocal space which includes the N allowed wavevectors.

Thus $(Nv_c/8\pi^3)(4\pi q_D^3/3) = N$ and then

$$q_D = \left(\frac{6\pi^2}{v_c}\right)^{\frac{1}{3}} \tag{14.20}$$

and

$$\omega_D = vq_D = v\left(\frac{6\pi^2}{v_c}\right)^{\frac{1}{3}}. \tag{14.21}$$

In real crystals detailed descriptions of the vibrational modes are often difficult. One can recall the following. In the $\mathbf{q} \to 0$ limit one can refer to the conditions of the continuum and the acoustic branches along certain symmetry directions can be discussed in terms of effective elastic constants. These constants are usually derived from *ultrasound propagation* measurements.

The frequencies of the various branches can become equal in correspondence to certain wavevectors, implying *degeneracy*. Although the optical branches have non-zero frequency even for $q = 0$ they are not always optically active, since do not always imply oscillating electric dipoles. For instance, in diamond, although the optical modes cause the vibration of the two sublattices (see Sect. 11.3) against each other, no electric dipole is induced and no interaction with the electromagnetic waves can occur.

The dispersion curves are usually obtained by inelastic *neutron spectroscopy*. The schematic structure of a triple axes neutron spectrometer is reported below:
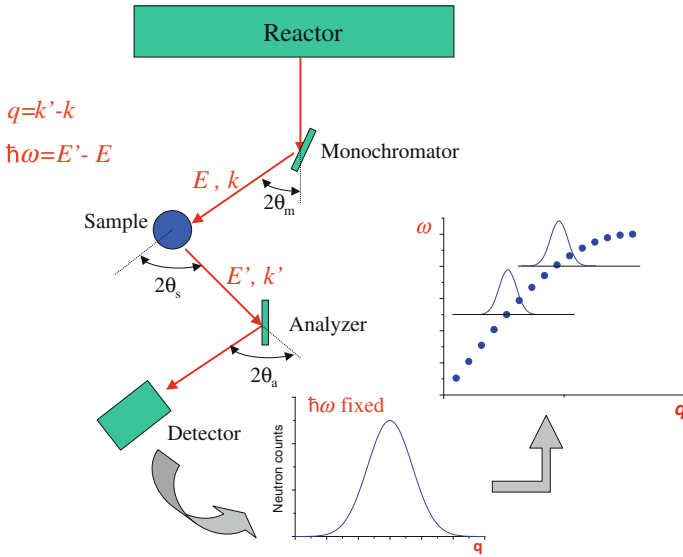
A suited description of the lattice vibrations, with theory and basic aspects of neutron spectroscopy, can be found in the report by *Cochran*.

14.4 Phonons

While discussing the normal modes in molecules (Sect. 10.6) it was shown how a non-normal Hamiltonian (in terms of local coordinates) could be transformed into a normal one by writing the local displacements as a superposition of excitations, each one associated to a normal oscillator. The collective normal coordinate was shown to be a linear combination of the local ones. The treatment given at Sect. 10.6 can be extended to the displacements of the atoms around their equilibrium positions in a crystal. Thus, returning to Eq. (14.3), for each branch (j) we write the displacement in the form

$$\mathbf{u} = \sum_{\mathbf{q}} \mathbf{U}_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{R}} e^{-i\omega_{\mathbf{q}} t} \tag{14.22}$$

Therefore the problem is reduced to the evaluation of the normal coordinates $\mathbf{Q}_{\mathbf{q}}^{(j)}$ of the crystal cell, that one can build up from the amplitudes $\mathbf{U}_{\mathbf{q}}$ by including the masses and the normalization factors. The translational invariance of the crystal implies the propagation of the normal excitations of the cell with phase factor $e^{i\mathbf{q} \cdot \mathbf{R}}$.

Hence, one can start from Hamiltonians of the form $\mathcal{H} = \sum_{j} \mathcal{H}_{j}[Q^{j}(\mathbf{q})]$, for each wavevector $\mathbf{q}$ of a given branch j. By indicating with $\mathbf{Q}$ the group of the normal coordinates and with $\phi(\mathbf{Q})$ the related wavefunction, one expects

$$\phi(\mathbf{Q}) = \prod_{\mathbf{q},j} \phi_{\mathbf{q}}^{(j)}(Q^j(\mathbf{q})). \qquad (14.23)$$

In the harmonic approximation $\phi_{\mathbf{q}}^{(j)}$ is the eigenfunction of single normal oscillator, characterized by quantum number $n_j(\mathbf{q})$ and eigenvalues

$$E_{\mathbf{q}}^{(j)} = \hbar\omega_{\mathbf{q}}^{(j)} \left[1/2 + n_j(\mathbf{q})\right].$$

The total energy is

$$E_T = \sum_j \sum_{\mathbf{q}} \left(n_j(\mathbf{q}) + \frac{1}{2}\right) \hbar\omega_{\mathbf{q}}^{(j)}. \qquad (14.24)$$

Therefore the vibrational state of the crystal is defined by the set of $3SN$ numbers $|\ldots, \ldots, n_j(\mathbf{q}), \ldots >$ that classify the eigenfunctions of the normal oscillators. At $T = 0$, the ground-state is labelled $|0, 0, 0 \ldots >$ and the wavefunction is the product of Gaussian functions (see Sect. 10.3.1).

At finite temperature one has to take into account the thermal excitations to excited states, for each normal oscillator. Two different approaches can be followed:

(A)—the *normal oscillators* are *distinguishable* and the numbers $n_j(\mathbf{q})$ select the stationary states for each of them. Then the Boltzmann statistics holds and for a given oscillator with characteristic frequency ν the average energy is

$$\overline{E} = \sum_v p_v E_v, \qquad (14.25)$$

with

$$p_v = \frac{e^{-E_v/k_B T}}{\sum_v e^{-E_v/k_B T}}$$

and

$$E_v = (v + 1/2)h\nu \quad v = 0, 1, 2, \ldots$$

For each normal mode the average energy $\overline{E}$ is found as shown at Problem 1.25 for photons (Planck derivation), here having to include the zero-point energy:

$$\overline{E} = h\nu \left(\frac{1}{2} + \frac{1}{e^{h\nu/k_B T} - 1}\right) \qquad (14.26)$$

The energy turns out the one for the quantum oscillator, provided that an *average excitation number*

$$< v > = \frac{1}{e^{\frac{h\nu}{k_B T}} - 1} \tag{14.27}$$

is introduced.

The total thermal energy of the crystal is obtained by summing Eq. (14.26) over the various modes, for each branch.

(B)—the crystal is considered as an assembly of *indistinguishable pseudo-particles*, each of energy $\hbar\omega_{\mathbf{q},j}$ and momentum $\hbar\mathbf{q} = (\hbar\omega_{\mathbf{q},j}/v_{j,\mathbf{q}})\hat{q}$. These quasi-particles are the quanta of the elastic field and are called *phonons* in analogy with the photons for the electromagnetic field.

Then the total energy has to be written

$$< \overline{E} > = \sum_{\mathbf{q},j} \left(\overline{n}_{\mathbf{q},j} + \frac{1}{2} \right) \hbar\omega_{\mathbf{q},j}, \tag{14.28}$$

where the average number of pseudo-particles is given by the Bose-Einstein statistics, i.e.

$$\overline{n}_{\mathbf{q},j} = \frac{1}{e^{\frac{\hbar\omega_{\mathbf{q},j}}{k_B T}} - 1}, \tag{14.29}$$

for a given branch j.

The two ways A and B to conceive the aspects of the lattice vibrations give equivalent final results, as it can be seen by comparing Eq. (14.26) (summed up to all the single oscillators) and Eq. (14.28). The derivation of some thermal properties (Sect. 14.5) will emphasize the equivalence of the two ways to describe the quantum aspects of the vibrational motions of the ions.

14.5   Thermal Properties Related to Lattice Vibrations

All the thermodynamical properties related to the vibrational motions can be derived from the total partition function $Z_{TOT} = \prod_{\mathbf{q},j} Z_{\mathbf{q},j}$, with

$$Z_{\mathbf{q},j} = \sum e^{\frac{-E(\mathbf{q},j)}{k_B T}} \tag{14.30}$$

where the sum is over all the energy levels, for each $\mathbf{q}$-dependent oscillator of each branch.

The thermal energy can be directly evaluated by resorting to the vibrational spectra $D(\omega)$, in the light of Eqs. (14.28) and (14.29), by writing

$$U = \int \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \right) D(\omega) d\omega. \qquad (14.31)$$

For instance, for Einstein crystals where $D(\omega) = 3N\delta(\omega - \omega_E)$ one derives

$$U = 3N\hbar\omega_E \left[1/2 + 1/\left(e^{\frac{\hbar\omega_E}{k_B T}} - 1 \right) \right].$$

The molar ($N = N_A$) specific heat for $T \gg \Theta_E \equiv \hbar\omega_E/k_B$ (Θ_E often defined *Einstein temperature*) turns out $C_V \simeq 3R$. At variance with the classical results, for $T \ll \Theta_E$ one has

$$C_V \simeq 3R \left(\frac{\Theta_E}{T} \right)^2 e^{\frac{-\Theta_E}{T}} \qquad (14.32)$$

For Debye crystals, from Eq. (14.31) by resorting to Eq. (14.19), one writes

$$C_V = \frac{\partial}{\partial T} \left\{ \int_0^{\omega_D} D(\omega)\hbar\omega \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} d\omega \right\}$$

and then, for $N = N_A$

$$C_V = 9R \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{z^4 e^z}{(e^z - 1)^2} dz, \qquad (14.33)$$

with $z = \hbar\omega/k_B T$.

For $T \gg \Theta_D$, with $\Theta_D \equiv \hbar\omega_D/k_B$ (known as *Debye temperature*), one again finds the classical result $C_V \to 3R$.

In the low temperature range ($\Theta_D/T \to \infty$) Eq. (14.33) yields $C_V \simeq (12\pi^4/5) R(T/\Theta_D)^3$. Equation (14.33) points out that the vibrational specific heat of Debye crystals is a universal function of the variable T/Θ_D. From Eq. (14.21) Θ_D can be written $\Theta_D = (\hbar v/k_B)(6\pi^2/v_c)^{1/3}$.

The temperature dependences of the molar specific heat in the framework of Einstein and Debye models are sketched below:
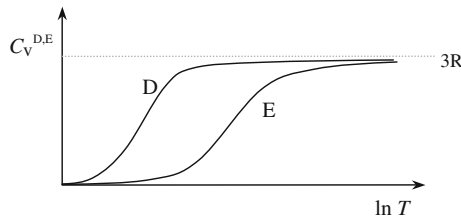
For $T \to 0$ the Debye specific heat C_V^D vanishes less rapidly than the Einstein C_V^E. The different behavior of C_V^D for $T \to 0$ originates from the fact that the vibrational spectrum in the Debye model includes oscillatory modes with energy separation of the order of $k_B T$, even at low temperature. On the contrary in the Einstein crystal in the low-temperature range one has $\hbar \omega_E \gg k_B T$.

In the Table below the Debye temperatures of some elements are reported.

		Debye Temperature θ_D (K) estimated from low-temperature $(T \ll \theta_D)$ specific heat measurements												C diamond 2230			Ne 75
Li 344	Be 1440																
Na 158	Mg 400									Al 428		Si 645					Ar 92
K 91	Ca 230	Sc 360	Ti 420	V 380	Cr 630	Mn 410	Fe 470	Co 445	Ni 450	Cu 343	Zn 327	Ga 320	Ge 374	As 282	Se 90		Kr 72
Rb 56	Sr 147	Y 280	Zr 291	Nb 275	Mo 450		Ru 600	Rh 480	Pd 274	Ag 225	Cd 209	In 108	Sn 200	Sb 211	Te 153		Xe 64
Cs 38	Ba 110	La 142	Hf 252	Ta 240	W 400	Re 430	Os 500	Ir 420	Pt 240	Au 165	Hg 72	Tl 78.5	Pb 105	Bi 119			Rn 64

By resorting to the expression for the thermal energy in terms of the vibrational spectra, the mean square displacement of a given ion as a function of temperature can be directly derived. According to the extension of Eq. (14.3) to include all the normal excitations, the mean square vibrational amplitude of each atom around its equilibrium position is written

$$< |\mathbf{u}|^2 > = \sum_{\mathbf{q}, j} |\mathbf{U}_{\mathbf{q}, j}|^2. \tag{14.34}$$

By recalling that for each oscillator the mean square displacement can be related to the average energy, $< u^2 > = < E > /(m\omega^2)$, then for a given branch j one can write $|\mathbf{U}_{\mathbf{q}}|^2 = < E_{\mathbf{q}} > /Nm\omega_{\mathbf{q}}^2$. Hence,

$$< u^2 > = \frac{1}{mN} \sum_{\mathbf{q}, j} \frac{< E_{\mathbf{q}, j} >}{\omega_{\mathbf{q}, j}^2} = \frac{\hbar}{mN} \int \left[\frac{1}{2} + \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \right] \frac{D(\omega)}{\omega} d\omega. \tag{14.35}$$

For Debye crystals, at temperatures $T \gg \Theta_D$, from Eq. (14.19) one obtains

$$< u^2 > \simeq \frac{9 k_B T}{m \omega_D^2} \tag{14.36}$$

and at low temperature $< u^2 > \simeq 9\hbar/4m\omega_D$.

It should be remarked that $< u^2 >$ controls the temperature dependence of the strength of the elastic component in scattering processes, through the *Debye-Waller* factor $e^{-4\pi <u^2>/\lambda^2}$, with λ wavelength of the radiation (see Sect. 14.6 for the derivation of this result).

According to the *Lindemann criterium* the crystal melts when the mean square displacement $< u^2 >$ reaches a certain fraction ξ of the square of the nearest neighbor distance R, $< u^2 > = \xi R^2$.

Empirically it can be devised that ξ is around 1.5×10^{-2} ($\sqrt{< u^2 >} \simeq 0.12R$). This criterium allows one to relate the melting temperature T_m to the Debye temperature. From Eq. (14.36)

$$T_m = \xi \Theta_D^2 \frac{m k_B R^2}{\hbar^2}. \tag{14.37}$$

Problems

Problem 14.1 Derive the vibrational entropy of a crystal in the low temperature range ($T \ll \Theta_D$).

Solution: From C_V^D (Eq. (14.33)) in the low temperature limit, by recalling that

$$S = \int_0^T \frac{C_V^D}{T} dT$$

the molar entropy is $S(T) = [12R\pi^4/(15\Theta_D^3)]T^3$. This result justifies the assumption for the lattice entropy used at Sect. 6.4. The contribution from optical modes can often be neglected.

Problem 14.2 Derive the vibrational contribution to the Helmoltz free energy and to the entropy in Einstein crystals.

Solution: For N oscillators the total partition function is $Z_T = Z^N$, with

$$Z = e^{-\hbar\omega_E/2k_BT} \sum_v e^{-\hbar\omega_E v/k_BT} = \frac{e^{-\hbar\omega_E/2k_BT}}{1 - e^{-\hbar\omega_E/k_BT}}$$

(remind that $\sum x^n = 1/(1-x)$, for $x < 1$).

Then the total free energy turns out

$$F = -Nk_BT \ln Z = N \left\{ \frac{\hbar\omega_E}{2} + k_BT \ln \left(1 - e^{-\hbar\omega_E/k_BT}\right) \right\}$$

and the entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -Nk_B \left\{ \ln \left(1 - e^{-\hbar\omega_E/k_BT}\right) - \frac{\hbar\omega_E}{k_BT} \frac{1}{e^{\hbar\omega_E/k_BT} - 1} \right\}.$$

Problem 14.3 Evaluate the specific heat per unit volume for Ag crystal (fcc cell, lattice step $a = 4.07$ Å) at $T = 10$ K, within the Einstein model (the elastic constant can be taken $k = 10^5$ dyne/cm) and within the Debye model, assuming for the sound velocity $v \simeq 2 \times 10^5$ cm/s.

Solution: The Einstein frequency $\omega_E \simeq \sqrt{k/M_{Ag}}$, corresponds to the temperature $\Theta_E \simeq 170$ K. In the unit volume there are $n = 1/(N_A v_c)$ moles, with $v_c = a^3/4$ the volume of the primitive cell. Then, since $T = 10$ K $\ll \Theta_E$, from Eq. (14.32) one derives $C_V^E \simeq 280$ erg/K cm^3.

The Debye frequency can be estimated from Eq. (14.21) and the corresponding Debye temperature turns out $\Theta_D \simeq 220$ K $\gg 10$ K. Then

$$C_V^D \simeq \frac{12\pi^4 k_B}{5 v_c} \left(\frac{T}{\Theta_D}\right)^3 \simeq 1.72 \times 10^5 \text{ erg/Kcm}^3.$$

Problem 14.4 Specific heat measurements in copper (fcc cell, lattice step $a = 3.6$ Å, sound velocity $v = 2.6 \times 10^5$ cm/s) show that C_V/T (in 10^{-4} Joule/mole K^2) is linear when reported as a function of T^2, with extrapolated value (C_V/T) for $T \to 0$ given by about 7 and slope about 0.6. Estimate the Fermi temperature and the Debye temperature and the temperature at which the electronic and vibrational contributions to the specific heat are about the same (from the equations at Sects. 12.7.1 and 14.5) and compare the estimates with the experimental findings.

Solution: From the specific mass $\rho = 9.018$ g/cm^3 the number of electrons per cm^3 is found $n = 8.54 \cdot 10^{22}$ cm^{-3}. From Eq. (12.28) $T_F = 7.8 \cdot 10^4$ K.

The Debye temperature, for the primitive cell of volume $v_c = a^3/4$, is
$\theta_D = (\hbar v/k_B)\left(6\pi^2/v_c\right)^{1/3} = 323$ K.

From

$$\frac{\pi^2}{2} n k_B \frac{T^*}{T_F} = \frac{1}{v_c} k_B \frac{12\pi^4}{5} \left(\frac{T^*}{\theta_D}\right)^3,$$

(per unit volume) the temperature T^* at which the electronic and vibrational contributions are the same is obtained:

$$T^* = \sqrt{5 v_c n}(\Theta_D)^{3/2} / \left(\pi\sqrt{24 T_F}\right) \simeq 3 \text{ K}.$$

From the experimental data according to Eq. (12.31) for $NZ = N_A$
$\gamma = \pi^2 R/(2T_F) = 7 \times 10^3$ erg/ mole K^2, one finds $T_F \simeq 5.8 \cdot 10^4$ K and from

$$C_V^D \simeq \frac{12\pi^4 R}{5} \left(\frac{T}{\Theta_D}\right)^3,$$

one derives $\theta_D \simeq 343$ K.

Problem 14.5 Write the zero-point vibrational energy of a crystal in the Debye model and derive the bulk modulus for $T \to 0$.

Solution: The zero-point energy is $E_0 = \frac{1}{2} \int_0^{\omega_D} \hbar \omega D(\omega) d\omega$ (Eq. (14.31)). From Eq. (14.19) one derives $E_0 = 9N\hbar\omega_D/8$.

At low temperature the bulk modulus is ($B \simeq V\partial^2 E_0/\partial V^2$). Then, by writing ω_D in terms of the volume $V = N v_c$ one finds

$$B = \frac{1}{2}\frac{N}{V}\hbar\omega_D \equiv \frac{1}{2}\frac{1}{v_c}k_B\Theta_D.$$

14.6 The Mössbauer Effect

The recoil-free emission or absorption of γ-ray (for the first time experimentally noticed by Mössbauer in 1958) is strictly related to the vibrational properties of the crystals. Meantime it allows one to recall some aspects involving the interaction of radiation with matter.

Let us consider an atom, or a nucleus, ideally at rest, emitting a photon due to the transition between two electronic or nucleonic levels. At the photon energy $h\nu$ is associated the momentum $(h\nu/c)$. Then in order to grant the momentum conservation the atom has to recoil during the emission with kinetic energy $E_R = (h\nu/c)^2/2M$, with M the atomic mass. Because of the energy conservation the emission spectrum (from an assembly of many atoms) displays a Lorentzian shape,
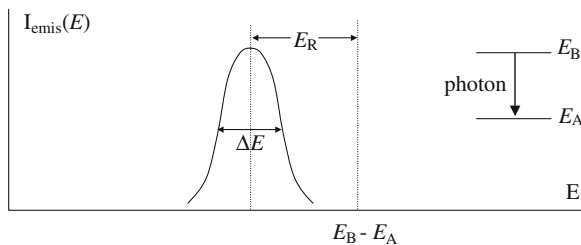
at least with the line broadening ΔE related to the *life-time* of the level (the inverse of the spontaneous emission probability, see Problem 1.24). Another source of broadening arises from the thermal motions of the atoms and the emission line usually takes a Gaussian shape, with width related to the distribution of the Doppler modulation in the emitted radiation (see Problem 1.30).

Let us suppose to try the *resonance absorption* of the same emitted photon from an equivalent atom (or nucleus). Again, by taking into account the energy and momentum conservation in the absorption process, the related spectrum must have an energy distribution of Gaussian shape, centered at $E = (E_B - E_A) + E_R$:
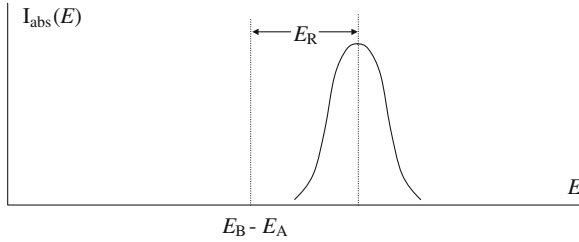
From the comparison of the emission and absorption spectra one realizes that the fraction of events that grant the resonance absorption is only the one corresponding to the energy range underlying the emission and absorption lines.

In atomic spectroscopy, where energy separations of the order of the eV are involved, the condition of resonant absorption is well verified. In fact, the recoil energy is $E_R \sim 10^{-8}$ eV, below the broadening $\Delta E \sim 10^{-7}$ eV typically associated with the life time of the excited state. At variance, when the emission and the absorption processes involve the γ-rays region, with energies around 100 keV, the recoil energy increase by a factor of the order of 10^{10}. Since the lifetime of the excited nuclear levels is of the same order of the one for electronic levels, only a limited number of resonance absorption processes can take place, for free nuclei.

In crystals, in principle, one could expect a *decrease* in the fraction of resonantly absorbed γ-rays upon cooling the source (or the absorber), due to the decrease of the broadening induced by thermal motions. Instead, an *increase* of such a fraction was actually detected by Mössbauer at low temperature. This phenomenon is due to the fact that in solids a certain fraction f of emission and absorption processes occurs *without recoil*. Thus the spectrum schematically reported below
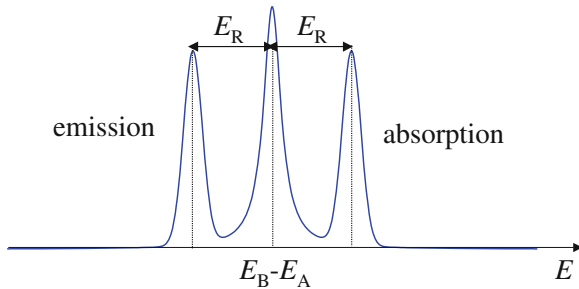
can be conceived, with a sizeable superposition of events around the energy difference $(E_B - E_A)$.

The momentum conservation is anyway granted, since the recoil energy goes to the whole crystal, with negligible subtraction of energy to the emitted or absorbed photons. The reason for the recoilless processes can be grasped by referring to the Einstein crystal, with energy $\hbar\omega_E$ larger than E_R. It is conceivable that when the quantum of elastic energy cannot be generated, then the crystal behaves *as rigid*.

Another interpretation (not involving the quantum character of the vibrational motions) is based on the classical consideration of the spectrum emitted by a source in motion. For a sinusoidal motion with frequency ω_S, the emitted spectrum has Fourier components at ω_i, $\omega_i \pm \omega_S$, ..., so that a component at the intrinsic frequency ω_i should remain.

The fraction f of recoilless processes can be evaluated by considering, in the framework of the time dependent perturbation theory used in Appendix 1.3, the emitting system as one nucleus imbedded in the crystal, looking for the transition probability between states having the same vibrational quantum numbers, while the nuclear state is changed. Since the long wave-length approximation cannot be retained, the perturbation operator reads $\sum_i \mathbf{A}_i \cdot \nabla_i$ (the sum is over all nucleons) (see Eq. (A.1.3.3)).

Let us refer to an initial state corresponding to the vibrational ground-state $|0, 0, 0, \ldots >$, by writing the amplitude of the time-dependent perturbative Hamiltonian $\sum_i e^{i\mathbf{k} \cdot \mathbf{R}_i}$. Expressing $\mathbf{R}_i$ in terms of the nucleon coordinates with respect to the center of mass, the effective perturbation term entering the probability amplitude $f^{1/2}$ is of the form $e^{i\mathbf{k} \cdot \mathbf{u}}$, with $\mathbf{u}$ the displacement of the atom from its lattice equilibrium position: $f^{1/2} \propto < 0, 0, 0 \ldots |e^{i\mathbf{k} \cdot \mathbf{u}}|0, 0, 0 \ldots >$.

The proportionality factor includes the matrix element of the variables and spins of the nucleons as well as the mechanism of the transition.

The vibrational ground-state (see Eq. (14.23)) for a given branch is $||0, 0, 0 \ldots > = \prod_{\mathbf{q}} e^{-\mathbf{Q}_{\mathbf{q}}^2/4\Delta_{\mathbf{q}}^2}$. The displacement $\mathbf{u}$ can be written as a superposition of the normal modes coordinates: $\mathbf{u} = \sum_{\mathbf{q}} \alpha_{\mathbf{q}} \mathbf{Q}_{\mathbf{q}}$ ($\alpha_{\mathbf{q}}$ normalizing factors which include the masses). Then, by referring to the component along the direction of the γ-rays, one writes

$$f^{1/2} \propto \int_{-\infty}^{+\infty} \prod_{\mathbf{q}} e^{\frac{-Q_{\mathbf{q}}^2}{2\Delta_{\mathbf{q}}^2}} e^{ik\alpha_{\mathbf{q}} Q_{\mathbf{q}}} dQ_{\mathbf{q}} \propto \prod_{\mathbf{q}} e^{\frac{-\alpha_{\mathbf{q}}^2 \Delta_{\mathbf{q}}^2 k^2}{2}} = e^{-\frac{1}{2} \sum_{\mathbf{q}} \alpha_{\mathbf{q}}^2 \Delta_{\mathbf{q}}^2 k^2}$$

The mean square displacement turns out

$$< 0, 0 \ldots |u_x^2|0, 0 \ldots > \equiv < 0, 0 \ldots | \sum_{\mathbf{q}, \mathbf{q}'} \alpha_{\mathbf{q}} Q_{\mathbf{q}} \alpha_{\mathbf{q}'} Q_{\mathbf{q}'} |0, 0 \ldots > =$$

$$= \sum_{\mathbf{q}} \alpha_{\mathbf{q}}^2 < 0, 0 \ldots |Q_{\mathbf{q}}^2|0, 0 \ldots > = \sum_{\mathbf{q}} \alpha_{\mathbf{q}}^2 \Delta_{\mathbf{q}}^2$$

and then

$$f \propto e^{-k^2 <u_x^2>} = e^{-k^2 <\mathbf{u}^2>/3}.$$

Since for $k = 0$ one can set $f = 1$, one has

$$f = e^{-k^2 <\mathbf{u}^2>/3}. \tag{14.38}$$

For $T \rightarrow 0$ f depends from the particular transition involved in the emission process (through k^2) and from the spectrum of the crystal through the zero-point vibrational amplitude $< u^2(T = 0) >$.

The temperature dependence of f originates from the one for $< u^2 >$. f is also known as the *Debye-Waller* factor, since it controls the intensity of X-ray and neutron diffraction peaks. The Bragg reflections, in fact, do require elastic scattering and therefore recoilless absorption and re-emission.

By evaluating $< |\mathbf{u}|^2 >$ for the Debye crystal, for instance, (see Eq. (14.36)) for $T \ll \Theta_D$ one has

$$f = e^{-(3E_R/2k_B\Theta_D)}. \tag{14.39}$$

The typical experimental setup for Mössbauer absorption spectroscopy is sketched below
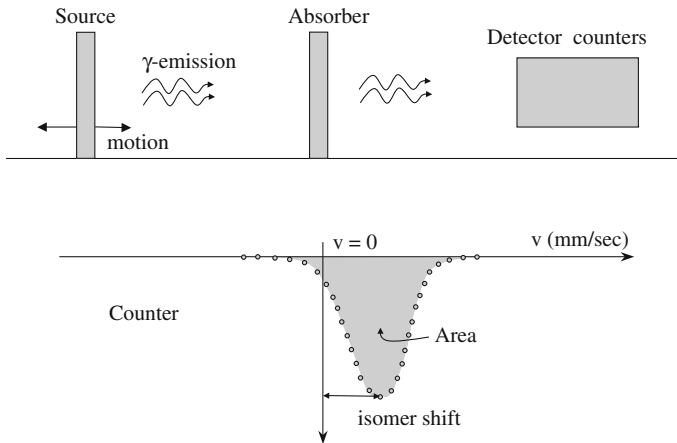
The source (or the absorber) is moved at the velocity v in order to sweep through the resonance condition. As a function of the velocity, one observes the Mössbauer absorption line, the area being proportional to the recoilless fraction f.

The shift with respect to the zero-velocity condition, *isomer shift*, is related to the finite volume of the emitting and absorbing nuclei (try to understand the shift by returning to Problems 1.6 and 5.23).

Since the motions do not affect the linewidth, the resolution of the Mössbauer line in principle depends only on the intrinsic lifetime of the level. Typically, for ~ 100 keV γ-rays, a resolution around 10^{-14} can be achieved. Therefore, the Mössbauer spectroscopy can be used in solid state physics to investigate the magnetic and electric hyperfine splitting of the nuclear levels. It has been used also in order to detect subtle relativistic effects (see Problem 14.13).

Problems

Problem 14.6 Show that an approximate estimate of the Debye temperature in a monoatomic crystal can be obtained from the specific heat, by looking at the temperature at which $C_V \simeq 23 \cdot 10^7$ erg/mole K.

Solution: From Eqs. (14.19) and (14.31)

$$U = \int_0^{\omega_D} \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} D(\omega) d\omega = \frac{3}{2\pi^2} \frac{N v_c}{v^3} \int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\frac{\hbar\omega}{k_B T}} - 1} d\omega,$$

(having neglected the zero-point energy which does not contribute to the thermal derivatives). v is the sound velocity (an average of the ones for longitudinal and transverse branches). From Eq. (14.33) the specific heat can be written

$$C_V = 9R \left[4 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \frac{z^3}{e^z - 1} dz - \frac{\theta_D}{T} \frac{1}{e^{\frac{\theta_D}{T}} - 1} \right].$$

For $T = \theta_D$

$$C_V(T = \theta_D) \simeq 36R \left[\int_0^1 \frac{z^3}{e^z - 1} dz - \frac{1}{1.72} \right]$$

and then $C_V(T = \theta_D) \simeq 2.856R \simeq 23.74 \cdot 10^7$ erg/mole K.

Problem 14.7 In a 1D linear diatomic crystal of alternating Br^- and Li^+ ions and lattice step $a = 2$ Å, the sound velocity is $v = 2.7 \cdot 10^5$ cm/s. Derive the effective elastic constant for the sound propagation under the assumption used at Sect. 14.3.2. Estimate the gap between the acoustic and optical branches.

Solution: From Eq. (14.17), in the $q \to 0$ limit, the sound velocity turns out

$$v = \sqrt{\frac{2k}{m_1 + m_2}} a.$$

Then the elastic constant is

$$k = \frac{1}{2}(m_1 + m_2) \left(\frac{v}{a} \right)^2 \simeq 1.32 \times 10^4 \text{ dyne/cm}.$$

The gap covers the frequency range from $\omega_{min} = (2k/m_1)^{1/2}$ to $\omega_{max} = (2k/m_2)^{1/2}$, with

$$\omega_{min} = 0.14 \cdot 10^{14} \text{rad s}^{-1} \quad \text{and} \quad \omega_{max} = 0.47 \cdot 10^{14} \text{rad s}^{-1}.$$

Problem 14.8 For a cubic crystal, with lattice step a, show that within the Debye model and for $T \ll \Theta_D$, the most probable phonon energy is $\hbar\omega_p \simeq 1.6k_BT$ and that the wavelength of the corresponding excitation is $\lambda_p \simeq a\Theta_D/T$.

Solution: In view of the analogy with photons (see Problem 1.25) the number of phonons with energy $\hbar\omega$ is given by

$$n(\omega) = D(\omega)/(e^{\hbar\omega/k_BT} - 1).$$

From Eq. (14.19) and from $dn(\omega)/d\omega = 0$, one finds

$$\frac{\hbar\omega_p}{k_BT}e^{\hbar\omega/k_BT} = 2(e^{\hbar\omega/k_BT} - 1)$$

and then $\hbar\omega_p/k_BT \simeq 1.6$.

Since $\lambda_p(\omega_p/2\pi) = v$, the average sound velocity, one has $\lambda_p \simeq 2\pi v\hbar/1.6k_BT$. For cubic crystal $\Theta_D = (v\hbar/k_Ba)(6\pi^2)^{1/3}$, and then $\lambda_p \simeq a\Theta_D/T$.

Problem 14.9 Show that in a Debye crystal at high temperature the thermal energy is larger than the classical one by a factor going as $1/T^2$.

Solution: From Eqs. (14.19), (14.21) and (14.31) the thermal energy is

$$U = 9Nk_BT\left(\frac{T}{\Theta_D}\right)^3\int_0^{x_D}\left(\frac{x^3}{e^x-1} + \frac{x^3}{2}\right)dx$$

with $x_D = \Theta_D/T$ and $x = \hbar\omega/k_BT$. For $x \to 0$, after series expansion of the integrand

$$\int_0^{x_D}\left(\frac{x^3}{e^x-1} + \frac{x^3}{2}\right)dx \simeq \int_0^{x_D}\left(\frac{x^3}{x + \frac{x^2}{2} + \frac{x^3}{6} + \cdots} + \frac{x^3}{2}\right)dx \simeq$$

$$\simeq \int_0^{x_D}\left[x^2\left(1 - \frac{x}{2} + \frac{x^2}{12} - \cdots\right) + \frac{x^3}{2}\right]dx \simeq \int_0^{x_D}x^2\left(1 + \frac{x^2}{12} - \cdots\right)dx.$$

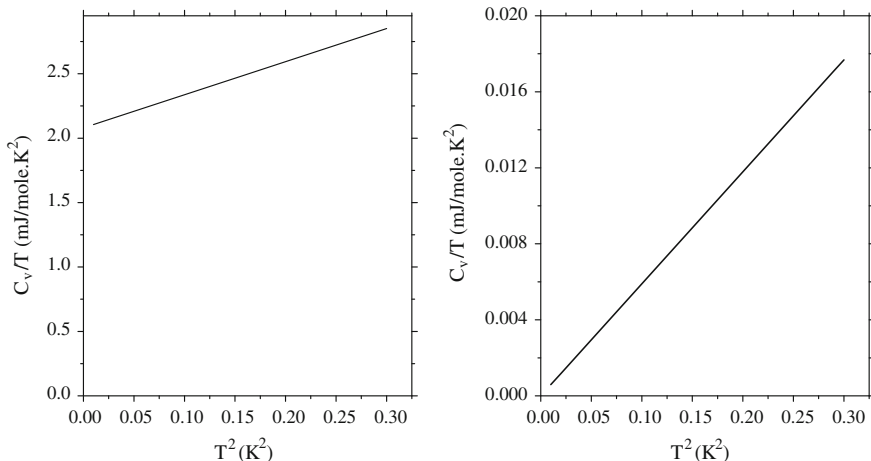Note that the second term of the expansion cancels out the zero-point energy. Then one can write

$$U = 9Nk_BT\left(\frac{T}{\Theta_D}\right)^3\left(\frac{1}{3}\left(\frac{\Theta_D}{T}\right)^3 + \frac{1}{60}\left(\frac{\Theta_D}{T}\right)^5 + \cdots\right).$$

The molar specific heat turns out

$$C_V \simeq 3R\left(1 - \frac{1}{20}\left(\frac{\Theta_D}{T}\right)^2 - \cdots\right).$$

Problem 14.10 In the figures below

the low temperature specific heats of two crystals are reported. Are they metals or insulators? Estimate the Debye temperatures and the Fermi energy.

Solution: From $C_V/T = A + BT^2$, $A = R(\pi^2/3)D(E_F)k_B$ is the term associated with the free-electron contribution (see Problem 12.14 for N_A electrons), while $B = (12\pi^4/5)(R/\Theta_D^3)$ originates from the phonon contribution. Hence the figure on the left refers to a metal while the one on the right to an insulator ($A = 0$).

From the data on the left $A \simeq 2.1 \times 10^4$ erg/K^{2}mole one finds $E_F \simeq 1.7$ eV. From $B \simeq 2.6 \times 10^4$ erg/K^{4}mole, then $\Theta_D \simeq 90$ K. From the data on the right $B \simeq 590$ erg/K^{4}mole, yielding $\Theta_D \simeq 320$ K.

Problem 14.11 Derive the vibrational contribution to the specific heat for a monoatomic 1D crystal, at high and low temperatures, within the Debye and the Einstein approximations. Compare the results with the exact estimates obtained in the harmonic approximation and nearest-neighbor interactions (Sect. 14.3.1).

Solution: Within the Debye model the vibrational spectrum is $D(\omega) = Na/(\pi v)$ and then according to Eq. (14.31)

$$U_D = \frac{N}{2}\hbar\omega_D + \frac{N}{\omega_D}\int_0^{\omega_D}\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}d\omega.$$

The molar specific heat turns out $C_V \simeq R$ for $T \gg \Theta_D = \hbar\omega_D/k_B$ and $C_V \simeq 2IR(T/\Theta_D)$ for $T \ll \Theta_D$, with $I = \int_0^\infty x/(e^x - 1)dx$.

Within the Einstein model $D(\omega) = N\delta(\omega - \omega_E)$ and results independent from the dimensionality are obtained (see Eq. (14.32)). One has $C_V \simeq R(\Theta_E/T)^2 exp(-\Theta_E/T)$ for $T \ll \Theta_E$ and $C_V \simeq R$ for $T \gg \Theta_E$.

In the harmonic approximation with nearest neighbors interactions the density of vibrational states is $D(\omega) = (2N/\pi)(1/\sqrt{\omega_m^2 - \omega^2})$ for $\omega \leq \omega_m$, while it is zero for $\omega > \omega_m$ (see Eq. (14.14)). Then

$$U = \frac{N}{2}\hbar\omega + \frac{2Nk_BT}{\pi}\int_0^{x_m}\frac{1}{\sqrt{x_m^2 - x^2}}\frac{x}{e^x - 1}dx$$

with $x = \beta\hbar\omega$ and $x_m = \beta\hbar\omega_m$. For $T \gg \Theta_m = \hbar\omega_m/k_B$ one has

$$U \simeq \frac{N}{2}\hbar\omega + \frac{2Nk_BT}{\pi}\left(\frac{\pi}{2} - \frac{x_m}{2} + \cdots\right)$$

and the molar specific heat is $C_V \simeq R$. For $T \ll \hbar\omega_m/k_B \equiv \Theta_m$

$$U \simeq \frac{N}{2}\hbar\omega + \frac{2N(k_BT)^2}{\pi\hbar\omega_m}I$$

so that

$$C_V \simeq \frac{4I}{\pi}R\frac{T}{\Theta_m}$$

showing that the Debye approximation yields the same low temperature behavior.

Problem 14.12 A diatomic crystal has two types of ions, one at spin $S = 1/2$ and $g = 2$ and one at $S = 0$. The Debye temperature is $\Theta_D = 200\,K$. Evaluate the entropy (per ion) at $T = 20\,K$ in zero external magnetic field and for magnetic field $H = 1\,$kGauss, for no interaction among the magnetic moments.

Solution: The vibrational entropy is

$$S_{vib} = \int_0^T \frac{C_V(T')}{T'}dT'$$

where for $T \ll \Theta_D$, neglecting the optical modes (see Problem 14.1)

$$C_V(T') = \frac{12\pi^4}{5}k_B\left(\frac{T'}{\theta_D}\right)^3.$$

Then at $T' = 20$ K

$$S_{vib} = k_B\frac{12\pi^4}{15}\left(\frac{T'}{\theta_D}\right)^3 = 0.078\,k_B.$$

The magnetic partition function is

$$Z_{mag} = \exp\left(-\frac{1}{2}y\right) + \exp\left(\frac{1}{2}y\right) \simeq 2 + \frac{y^2}{4}$$

with

$$y = \frac{\mu_B g H}{k_B T} \simeq \frac{0.9 \cdot 10^{-20}}{1.38 \cdot 10^{-16}} g\frac{H}{T} = 6.72 \cdot g\frac{H}{T} \cdot 10^{-5} \ll 1.$$

From

$$F = -k_B T \ln Z \quad \text{and} \quad S = -\frac{\partial F}{\partial T}$$

with

$$S_{mag}(T') \simeq k_B \left[\ln 2 - \frac{y^2}{4}\right] \simeq k_B ln2$$

one has

$$S = S_{vib} + \frac{1}{2}S_{mag} = k_B[0.078 + 0.34] = 0.42k_B/\text{ion}.$$

Problem 14.13 The life time of the ^{57}Fe excited state decaying through γ emission at 14.4 keV is $\tau \simeq 1.4 \times 10^{-7}$ s (see Problems 1.24, 1.30 and 3.13). Estimate the height at which the γ-source should be placed with respect to an absorber at the ground level, in order to evidence the gravitational shift expected on the basis of Einstein theory.

Assume that a shift of 5 % of the natural linewidth of Mössbauer resonant absorption can be detected [in the real experiment by *Pound* and *Rebka* (Phys. Rev. Lett. 4, 337 (1960)) by using a particular experimental setup resolution of the order of $10^{-14} - 10^{-15}$ could be achieved, with a fractional full-width at half-height of the resonant Lorentzian absorption line of 1.13×10^{-12}]. Try to figure out why the source-absorber system has to be placed in a liquid He bath.

Solution: On falling from the height L the energy of the γ photon becomes

$$h\nu(0) = h\nu(L)\left[1 + \frac{gL}{c^2}\right]$$

where mgL/mc^2 can be read as the ratio of a gravitational potential energy mgL to the intrinsic energy mc^2 (mass independent and therefore valid also for photons).

The natural linewidth of the Mössbauer line is $2\hbar/\tau$. Therefore, to observe a 5 % variation

$$\frac{2\hbar}{20\tau} = h\nu(L)\frac{gL}{c^2}$$

and then

$$L = \frac{\hbar c^2}{10\,g\tau\,14.4\,\text{keV}} = 284\,\text{m}$$

(in the real experiment the height of the tower was about 10 times smaller!). Note that the natural linewidth, when sweeping with velocity v the absorber (or the source) corresponds to a velocity width

$$\Delta v = \frac{2\hbar c}{h\nu\tau} \simeq 0.2\,\text{mm/s}$$

(the actual full-width at half height in the experiment by Pound and Rebka was 0.43 mm/s).

A difference in the temperatures of the source and the absorber of 1 K could prevent the observation of the gravitational shift because of the temperature-dependent *second-order* Doppler shift resulting from lattice vibrations, since $< v^2 > \sim k_B T/M$. Low temperature increases the γ-recoilless fraction f.

Specific References and Further Reading

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