The currents and the potentials in the transistor are thus approximately connected with one another through Eqs.(11.104) and (11.105). The parameters I_0 and ξ, which is a small number, thus characterize its behaviour in a circuit. The remarkable phenomenon is that small changes in V_b or in I_b produce large changes in I_c or $I_e = (1 + \xi)I_c$: the transistor is an *amplifier*. Moreover, we get a *linear* amplification of the current, since I_c is proportional to I_b, with an amplification ratio $1/\xi$. Finally, it can also operate as a *gate*, since I_e varies, according to (11.104), abruptly with V_b, which enables us to control the current $I_c \simeq I_c$ by means of the base potential.

Many other devices based upon the p-n junction are used in electronics. Depending on the potential V applied between n and p, the thickness of the charged region varies. We have seen that the conductivity is weaker in that region where the free-carrier density is reduced. One can therefore operate upon a current flowing in one of the semiconductors along the junction by simply controlling V. This idea gives the principle of the *field effect transistor* which is a device where the resistance along the junction is governed by a transverse voltage between n and p (Prob.18). The most often used type is the MOSFET – from Metal Oxide Semiconductor Field Effect Transistor; a layer of oxide (dielectric) and a layer of metal, put on one of the semiconductors of the junction, together with it form a condenser which provides the controlling voltage.

We may also mention the *variable-capacitance diode*, or *varactor*, used, for instance, to control the frequency of a radio receiver. Here also the potential V applied to the p-n junction changes the way it is charged and thus controls its capacity.

Let us finally remark that the semiconductor properties described here are not limited to the perfect crystals which we have considered. It is true that the simplifications produced by the geometry, the existence of a quasi-momentum and Bloch waves, do not exist for amorphous substances; however, the analysis of the tight binding theory shows that the electron structure of an amorphous substance retains a certain memory of the discrete nature of the levels of its atoms. In particular, the single-electron density of states retains a shape which is similar to that of an insulator: there is no longer a forbidden band, but it is replaced by a region which contains few levels and this plays an analogous rôle. The manufacture of badly crystallized or amorphous semiconductors is relatively cheap: for this reason the use of amorphous silicon is likely to develop rapidly, for applications where a completely forbidden band is not required.

11.4 Phonons

So far we have firstly studied the properties of solids which are connected with the average positions of the atomic nuclei. After that we considered their electronic properties, and there now remains for us to investigate the rôle of the nuclear displacements. Motions with relatively large amplitudes do not occur until the solid melts (Probs.8 and 10). Otherwise, the nuclei in the solid state move, in general, only slightly from their equilibrium positions and the harmonic approximation is already sufficient for describing their vibrations. These vibrations are responsible for the heat capacity of the solid. However, it is essential to treat them *quantum mechanically*. This fact was realized in 1907 by A. Einstein (Exerc.11d) even though quantum mechanics of the simplest systems (Bohr's atom model of 1913, the de Broglie relations of 1926, or the Schrödinger equation of 1926) had not been worked out at that time. A major step in the quantum theory of solid vibrations was the work by Petrus Debye (Maastricht 1884–Ithaca, NY 1966) who in 1912 gave a quantitative explanation of the specific heats and in 1914 introduced the concept of phonons, applying it to heat conduction in insulators.

11.4.1 Lattice Vibrations

As we mentioned in § 11.1.1, the last stage in the Born-Oppenheimer method (§ 8.4.1) consists in treating the eigenvalue $W(\{\boldsymbol{R}_n\})$ of Eq.(11.7) as an interaction potential for the nuclei in the effective Schrödinger equation (8.40). Eliminating the electron degrees of freedom leads thus to an effective Hamiltonian,

$$\widehat{H}_{\rm n} = \widehat{T}_{\rm n} + W(\{\widehat{\boldsymbol{R}}_n\}), \tag{11.106}$$

where the coordinates $\boldsymbol{R}_n$ of each nucleus n, which so far had been considered to be parameters, are replaced by operators. It is difficult, if not impossible, to calculate the potential $W(\{\boldsymbol{R}_n\})$ explicitly, as this would require that we had solved the electronic problem (11.7) not only when the nuclei are fixed to their equilibrium positions in the lattice as in § 11.3, but also when they are displaced from those positions. However, it will be sufficient to be aware of two essential properties of W. Firstly, $W(\{\boldsymbol{R}_n\})$ is a *minimum* when the nuclei occupy their average positions $\overline{\boldsymbol{R}_n}$ which form the lattice; as the nuclei do not move far from these positions, one can expand W around that minimum. Secondly, the periodicity of the lattice implies that W is *invariant under displacements* of the crystal group, such as translations, rotations, symmetries, and their combinations.

The energy W defined by Eq.(11.7) depends, in fact, not only on the nuclear coordinates, but also on the state λ of the electrons. Those remain practically frozen in into their ground state for an insulator, as for a molecule. We have seen that this is not the case for a metal. To be more rigorous, we must then take for the potential $W(\{\boldsymbol{R}_n\})$ which occurs in (11.106) the average, at the temperature considered, over the electron microstates λ, of $W(\{\boldsymbol{R}_n\},\lambda)$ so that this effective potential depends on T and μ. This dependence is, however, weak and can be neglected. Moreover, the fact that W depends both on the coordinates $\{\boldsymbol{R}_n\}$ and on the state λ generates an effective interaction between the nuclear and electron degrees of freedom, an interaction which we shall neglect (§ 11.4.2).

For molecules, the search for the eigenstates of the effective nuclear Hamiltonian (8.40) consisted of a study of global rotations and of internal motions, which for the simple molecules considered reduced to vibrations. Among the various possible motions of the nuclei in a crystal, the global rotations and translations, which are macroscopic displacements, are not thermally excited: in contrast to the molecules in a gas which can be rotated by thermal excitation, a crystal retains its fixed orientation and its fixed position in space when it is heated. Hence, we must only consider from amongst the nuclear motions those which correspond to *vibrations*, excluding the global rotations and translations. We remind ourselves that for a diatomic molecule there was a single vibrational mode, associated with changes in the interatomic distance, with an angular frequency ω which could be calculated by expanding the potential around its minimum reached at the equilibrium position. The *number of modes* of the lattice vibrations is $3N - 6$, where N is the number of nuclei: we have to subtract from the total number of coordinates the 3 translations and the 3 rotations of the whole system. As N is large, we shall in what follows replace $3N - 6$ by $3N$.

As in any *small vibrations* problem, we look for the *normal modes* of the vibrations of the crystal nuclei, replacing in (11.106) the potential $W(\{\boldsymbol{R}_n\})$ by its *quadratic approximation* around the average values $\overline{\boldsymbol{R}_n}$, and then *diagonalizing* the quadratic form in $\{\delta\boldsymbol{R}_n\} = \{\boldsymbol{R}_n\} - \{\overline{\boldsymbol{R}_n}\}$ which we have thus obtained. To simplify the discussion, let us assume henceforth that we have only *one atom per cell* and let its mass be M. The expression

$$W(\{\boldsymbol{R}_n\}) - W(\{\overline{\boldsymbol{R}_n}\}) \tag{11.107}$$

is a quadratic form of the $3N$ variables $\{\delta\boldsymbol{R}_n\}$, $1 \le n \le N$. We write the eigenvalues of the corresponding matrix as $\frac{1}{2}M\omega_q^2$; they are all positive as we have a stable equilibrium. Let ξ_q be the eigenvectors, which are linear functions of the displacements $\{\delta\boldsymbol{R}_n\}$; their number is $3N$. Finally, the momenta π_q, conjugate to the variables ξ_q, are the corresponding linear combinations of the nuclear momenta $\boldsymbol{P}_n$. The effective nuclear Hamiltonian (11.106) can thus be written in the small vibration approximation as

$$\begin{aligned}\widehat{H}_{\mathrm{n}} &= W(\{\overline{\boldsymbol{R}_n}\}) + \sum_{n=1}^{N} \frac{\widehat{\boldsymbol{P}}_n^2}{2M} + \left[\widehat{W}(\{\widehat{\boldsymbol{R}}_n\}) - W(\{\overline{\boldsymbol{R}_n}\})\right] \\ &= W(\{\overline{\boldsymbol{R}_n}\}) + \sum_q \left(\frac{\widehat{\pi}_q^2}{2M} + \frac{1}{2}M\omega_q^2\,\widehat{\xi}_q^2\right),\end{aligned} \tag{11.108}$$

where there are $3N$ terms in the sum over q. In fact, (11.108) includes 6 terms associated with the translations and rotations of the crystal, for which $\omega_q = 0$ since W remains constant under those displacements.

In terms of the normal coordinates ξ_q and their conjugate momenta, the nuclear small vibration Schrödinger equation can thus be split into a set of $3N$ equations for one-dimensional *independent harmonic oscillators* with angular frequencies ω_q. (Strictly speaking the frequency is $\nu = \omega/2\pi$ but ω itself is often simply called frequency.) The lattice vibrations are *quantized*; the *energy levels* of $\widehat{H}_\mathrm{n}$ are given by

$$W(\{\overline{R_n}\}) + \sum_q \hbar\omega_q \left(n_q + \frac{1}{2}\right) = b + \sum_q n_q \hbar\omega_q, \tag{11.109}$$

and characterized by $3N$ independent quantum numbers $n_q = 0, 1, 2, \ldots$. The thermodynamic properties will mainly depend on the frequency spectrum ω_q of the various vibrational modes for small ω_q and we must thus determine it by explicitly diagonalizing the quadratic form (11.107).

We solve this problem for a one-dimensional model of a crystal, containing only one kind of atoms which can oscillate around their equilibrium positions $\overline{R_j} = ja$. To simplify the calculations we assume that the effective potential W only includes interactions w between *nearest neighbour nuclei*. It is therefore expanded in powers of $\delta R_j \equiv R_j - ja$ as

$$\begin{aligned} W &= \sum_{j=1}^{N-1} w(R_{j+1} - R_j) \\ &= \sum_{j=1}^{N-1} \Big[w(a) + w'(a)\big(\delta R_{j+1} - \delta R_j\big) \\ &\qquad + \tfrac{1}{2} w''(a)\big(\delta R_{j+1} - \delta R_j\big)^2 + \cdots \Big], \end{aligned}$$

and the conditions that it is a minimum for $R_j = ja$ are $w'(a) = 0$ and $w''(a) \equiv C > 0$. In the harmonic approximation the Hamiltonian (11.106) thus reduces to

$$\widehat{H}_\mathrm{n} = \sum_{j=1}^{N} \left[\frac{\widehat{P}_j^2}{2M} + \frac{1}{2} C \big(\delta\widehat{R}_{j+1} - \delta\widehat{R}_j\big)^2 \right], \tag{11.110}$$

where we have dropped the additive constant $W(\{\overline{R_n}\})$.

As in band theory (§ 11.2.2), we wish to take advantage of the invariance group associated with the periodicity of the crystal structure. Since the number of nuclei, N, is large, the boundary effects due to the fact that the crystal is finite must play a negligible rôle. We can therefore slightly change our model and introduce periodic boundary conditions (§ 10.2.1), that is, assume that the crystal ends are joined together. We therefore identify $N+1$ with 1 in the last term in (11.110). An important simplification when we look for the normal modes is now introduced by the fact that (11.110) is *invariant under a lattice translation* over a distance a. We use that property by carrying out the same discrete Fourier transformation as the one which enabled us to connect the localized Wannier orbitals to the Bloch waves for the electrons through (11.35) and (11.36). Through this transformation we change from the lattice sites j to the wavenumbers k or the quasi-momenta $\hbar k$. One should take care to distinguish between these quasi-momenta, which are associated with the translational invariance of the lattice, and the nuclear momenta P_j. In this way we introduce the normal coordinates

$$\xi_k = \frac{1}{\sqrt{N}} \sum_j \delta R_j \, \mathrm{e}^{-\mathrm{i}k\overline{R_j}}, \qquad \delta R_j = \frac{1}{\sqrt{N}} \sum_k \xi_k \, \mathrm{e}^{\mathrm{i}k\overline{R_j}}, \tag{11.111a}$$

and their conjugate momenta

$$\pi_k = \frac{1}{\sqrt{N}} \sum_j P_j \, \mathrm{e}^{-\mathrm{i}k\overline{R_j}}, \qquad P_j = \frac{1}{\sqrt{N}} \sum_k \pi_k \, \mathrm{e}^{\mathrm{i}k\overline{R_j}}, \tag{11.111b}$$

where the indices k take on the N values

$$k = m\frac{2\pi}{L}, \qquad -\frac{\pi}{a} < k \leq \frac{\pi}{a}. \tag{11.112}$$

In terms of these new variables the Hamiltonian (11.110) has the form

$$\widehat{H} = \sum_k \left(\frac{\widehat{\pi}_k^\dagger \widehat{\pi}_k}{2M} + C(1 - \cos ka)\widehat{\xi}_k^\dagger \widehat{\xi}_k \right). \tag{11.113}$$

Although the operators $\widehat{\xi}$ and $\widehat{\pi}$ are not independent and non-Hermitean, since we have $\widehat{\xi}_k^\dagger = \widehat{\xi}_{-k}$, $\widehat{\pi}_k^\dagger = \widehat{\pi}_{-k}$, they satisfy the same commutation relations as pairs of conjugated variables, namely $\left[\widehat{\xi}_k, \widehat{\pi}_{k'}^\dagger\right] = \mathrm{i}\hbar\delta_{kk'}$, a property which one can check by using their definitions (11.111). The Hamiltonian (11.112) thus looks, for each value of $k \neq 0$, like that of a harmonic oscillator of frequency

$$\omega_k = \sqrt{\frac{2C}{M}(1 - \cos ka)} = 2\sqrt{\frac{C}{M}} \left| \sin \frac{1}{2}ka \right|. \tag{11.114}$$

To achieve its diagonalisation, we introduce, as for the ordinary harmonic oscillator, the operators

$$\widehat{c}_k = \frac{1}{\sqrt{2\hbar}} \left(\widehat{\xi}_k \sqrt{M\omega_k} + \frac{\mathrm{i}\widehat{\pi}_k}{\sqrt{M\omega_k}} \right) \tag{11.115}$$

and their conjugates, which satisfy the commutation relations

$$\left[\widehat{c}_k, \widehat{c}_{k'}\right] = 0, \qquad \left[\widehat{c}_k, \widehat{c}_{k'}^\dagger\right] = \delta_{kk'}. \tag{11.116}$$

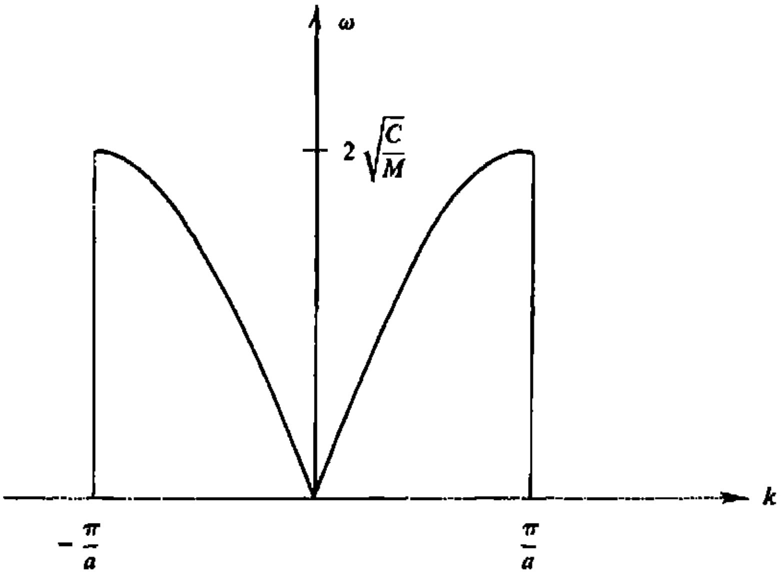

Fig. 11.19. The frequency spectrum of a one-dimensional lattice

We thus get for the Hamiltonian (11.113)

$$\widehat{H}_{\text{n}} = \sum \hbar\omega_k\left(\widehat{c}_k^\dagger \widehat{c}_k + \tfrac{1}{2}\right) = \sum \hbar\omega_k\left(\widehat{n}_k + \tfrac{1}{2}\right), \tag{11.117}$$

and its eigenvalues follow from those of $\widehat{n}_k = \widehat{c}_k^\dagger \widehat{c}_k$, which are $n_k = 0, 1, \ldots$. We show in Fig.11.19 the frequency spectrum ω_k given by (11.114); we bear in mind that the possible values of k are given by (11.112).

The term with $k = 0$ in (11.113) does not contain the operator $\widehat{\xi}_0$, which is associated with the global translations $\delta R_j = \xi_0/\sqrt{N}$. It does not describe a vibrational mode, but represents simply the global kinetic energy of the crystal. It needs only weak pinning forces to prevent the crystal from moving as a whole; if there were no such forces, the mean square thermal equilibrium velocity would be of order $\sqrt{kT/m}$, or 2×10^{-9} m s^{-1} for a 1 g crystal at room temperature.

In three dimensions, for example in the case of a cubic lattice with cell size a and one atom per cell, each *mode* occurs as a *vibrational wave* with the displacement $\delta \boldsymbol{R}_n$ of a nucleus situated at the site $\overline{\boldsymbol{R}_n}$ being, as in (11.111a), proportional to the real or the imaginary part of

$$\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\overline{\boldsymbol{R}_n}}.$$

A mode q is characterized by the *wavenumbers*

$$k_x = m_x \frac{2\pi}{L}, \qquad k_y = m_y \frac{2\pi}{L}, \qquad k_z = m_z \frac{2\pi}{L}, \tag{11.118}$$

for a crystal of size L, where the (integer) values of the m are *bounded* by

$$-\frac{L}{2a} < m \le \frac{L}{2a}. \tag{11.119}$$

Moreover, for each direction of propagation there are 3 vibrational modes, associated with the displacements of atoms in particular directions, depending on the direction of the wavevector, and being mutually orthogonal. We thus recover the $3N$ modes which we expected from the counting of degrees of freedom. If the medium were isotropic – were an amorphous solid – one of the modes would be *longitudinal* with the atoms vibrating parallel to $\boldsymbol{k}$ and the other two modes would be *transverse* for symmetry reasons. The same property holds for a cubic cystal, in the special case when $\boldsymbol{k}$ is parallel either to the edges or to the diagonals of the cell; however, in general, the direction of the vibrations of the atoms in an eigenmode is not oriented in a simple way relative to the wavevector, due to the anisotropy of the crystal.

The mode frequencies are functions of the wavenumber. As the one-dimensional model we have just studied suggests, and as more detailed theories show, the frequencies $\omega_{\boldsymbol{k}}$ of the three modes tend *linearly* to zero when k decreases. In the isotropic approximation ω/k is independent of the direction of $\boldsymbol{k}$ so that for the longitudinal and the two transverse modes we have

$$\omega \sim u_{\mathrm{l}}k, \qquad \omega \sim u_{\mathrm{t}}k. \tag{11.120}$$

Small values of k correspond to macroscopic wavelengths $\lambda = 2\pi/k$, and the lattice vibrations thus propagate the *acoustic waves* in the solid. The velocity $\nabla_{\boldsymbol{k}}\omega$ of the displacement of a wavepacket is just the *sound velocity*. It is independent of the frequency when $ka \ll 1$, but it may take on three different values, depending on the direction of the oscillations of the atoms, and it may also be not parallel to $\boldsymbol{k}$. A typical value is 5000 m s^{-1} in metals, with the longitudinal velocity u_{l} being larger than the transverse velocity u_{t}, as compared to the sound velocity of 300 m s^{-1} in air. The mechanisms for sound propagation in solids and in fluids are quite different. In the first case, we are dealing with coherent displacements of the atoms in the lattice over wavelengths which are large compared to the crystal cell size, a microscopic mechanical effect governed by the effective forces $W(\{\boldsymbol{R}_n\})$; in the second case, we are dealing with the propagation of a pressure oscillation, a macroscopic thermodynamic effect governed by the hydrodynamic equations of § 14.4.6.

For a solid with an arbitrary crystal structure the wavevectors $\boldsymbol{k}$ of the eigenmodes are restricted to the Brillouin zone which generalizes (11.119), and they continue to take on N values, where N is the number of cells in the lattice. If there are s atoms per cell, the $3Ns$ vibrational modes split into $3s$ branches, which generalize the 3 branches of a simple cubic lattice. Nevertheless, in the limit as $k \to 0$, these $3s$ branches can be classified as 3 so-called "acoustic" branches for which ω decreases linearly with k, and $3s - 3$ so-called "optical" branches for which ω remains finite. The latter correspond to oscillations for which different kinds of atoms in the same cell oscillate with opposite phases. On the contrary, for the acoustic branches all atoms oscillate in phase; the lattice is thus locally very little distorted, and this is the reason why for those modes the energy $\hbar\omega_{\boldsymbol{k}}$ tends to 0 with k.

The acoustic modes show up directly as mechanical vibrations of solids with long wavelengths and low frequencies. The optical modes, which hardly propagate, as their propagation velocity $d\omega/dk$ tends to 0 with k, play a rôle in the interaction between the crystal and electromagnetic radiation, because of the order of magnitude of their energy $\hbar\omega_k$. For instance, in NaCl, with 2 atoms per cell, apart from the three acoustic modes, there are three optical modes, two transverse and one longitudinal, with frequencies which are, respectively, equal to $3.09 \times 10^{13}\,\mathrm{s}^{-1}$ and $4.87 \times 10^{13}\,\mathrm{s}^{-1}$ in the $k = 0$ limit. Infrared waves which have frequencies of that order of magnitude interact strongly with these *optical modes* and this explains their name. A photon can be transformed into an optical phonon, that is, it can be absorbed, while exciting lattice vibrations; the conservation of energy $\hbar\omega$ and of momentum $\hbar k = \hbar\omega/c$ can here be satisfied, thanks to the large value of the light velocity c.

The calculation of the eigenfrequencies, starting from the effective interactions W between the atoms, can be done as in one dimension, using the transformation (11.111) which will for each k produce $3s$ pairs of ξ, π variables. One must thus eventually diagonalize a $3s \times 3s$ matrix (Exerc.11e).

The masses of the nuclei are sufficiently large that their average displacements in a solid remain practically always small compared to the cell size (Prob.10). Even at the melting temperature the mean square displacement rarely exceeds $\frac{1}{8}$ of the cell size (*Lindemann's criterion*). This justifies an approximation which we have made implicitly and which consists in neglecting the Pauli principle for the atomic nuclei. Their fermion or boson nature plays, in general, no rôle whatever in their vibrations – although those are quantized – as the wavefunctions remain localized round each lattice site. Under those conditions, the symmetrization or antisymmetrization of the wavefunction of the N indistinguishable nuclei will not change anything. The indistinguishability only plays a rôle in solid helium where the nuclei, bosons for ^{4}He and fermions for ^{3}He, are sufficiently light and sufficently weakly bound that the states of neighbouring nuclei overlap.

11.4.2 Interpretation of a Mode as a Boson State

Expression (11.109) for the eigenenergies of the Hamiltonian of the lattice vibrations shows a large similarity with the expression $\sum_q \varepsilon_q n_q$ of the *energy levels of a gas with an arbitrary number of bosons* (§ 10.5.2). It is therefore natural to talk about the system of *quantized lattice vibration modes* as being a gas of particles, the "*phonons*", which satisfy Bose-Einstein statistics. We shall see in § 11.4.4 and in § 13.1, where we shall study the quantized oscillation modes of the electromagnetic field, that this is more than just a simple analogy, and that the photons and phonons show all the characteristics of elementary particles. We shall restrict ourselves here to pointing out the correspondence between the two languages describing the same reality, that of the quantized vibrations and that of the phonons.

Each *oscillation mode* q corresponds to a *single-phonon state*, that is, a *plane wave* as for a particle in a box (§ 10.2.1). The *wavevector* $\boldsymbol{k}$ corresponds to the *quasi-momentum* $\boldsymbol{p} = \hbar\boldsymbol{k}$ given by the de Broglie relation and, according to (11.118) and (11.119), taking on the same values (11.30) and (11.32) as the quasi-momentum of an electron in the same crystal. Moreover, the vibrational modes are characterized by an index which can take on three values for crystals with one atom per cell, and which describes the (in the simplest cases longitudinal or transverse) *polarization* of the vibrational wave; this index plays the same rôle as an *internal quantum number* – like the spin – of the phonon. The energy (11.109) of a *vibrational micro-state* corresponds, apart from an additive constant, to that of a *system of bosons*, (10.16), provided one associates the *frequency* ω_q with the *phonon energy* $\varepsilon_q = \hbar\omega_q$ and interprets the quantum number n_q of each harmonic oscillator as the *occupation number* of the state q. A vibrational micro-state corresponds to a micro-state (10.14) of Fock space, and a change in the vibrational state is described as the *creation or annihilation* of phonons. In the harmonic oscillation approximation considered here, the phonons *do not interact*, as is shown by Eq.(11.109) for the energy. Their total *number* is not a *constant of the motion*. As a result (§ 10.5.2), their *chemical potential is zero*.

The phonons, like the conduction electrons and the holes in an insulator, are a characteristic example of *quasi-particles*. Instead of describing the crystal lattice and its motion as a system of nuclei, interacting strongly with one another, we have been led to introduce the phonons, fictitious bosons with practically *no interactions*, which enables us to describe the same physical situation, but much more simply. Even though the quasi-particles have the same properties as real particles, they are only distantly related to the true particles which make up the crystal, the electrons and the nuclei. They represent, in fact, *collective aspects*. For instance, in an insulator, a hole or a conduction electron describes how the whole of the electron cloud is changed when one takes away or adds an electron. The collective nature of phonons is even more pronounced, as the creation of a phonon amounts to changing the vibrational state of the *system* of nuclei; the quasi-momentum $\hbar \boldsymbol{k}$ of the phonon is related to the wavevector $\boldsymbol{k}$ of this vibrational state, but has nothing to do with the momenta of the nuclei.

The correspondence between the quantized vibrations of the lattice and bosons is completed by identifying the operators (11.115), which through (11.117) diagonalize the harmonic oscillators associated with each mode, with the annihilation and creation operators (10.20) of the phonons. The algebra (10.21) and (11.116) of these operators is, indeed, exactly the same. According to the general properties of § 10.2.3, each observable can be expressed as a function of the operators $\widehat{c}$ and $\widehat{c}^\dagger$. In particular, the *displacement of each nucleus* occurs as a *linear combination of phonon annihilation and creation operators*. For example, for the one-dimensional crystal model studied in § 11.4.1, we find from (11.111) and (11.115) that

$$\delta\widehat{R}_j = \sqrt{\frac{\hbar}{2N}} \sum_k \mathrm{e}^{\mathrm{i}k\overline{R_j}} \, \frac{\widehat{c}_k + \widehat{c}^\dagger_{-k}}{\sqrt{M\omega_k}}. \tag{11.121a}$$

Similarly, the momentum P_j of a nucleus is given by

$$\widehat{P}_j = \sqrt{\frac{\hbar}{2N}} \sum_k \mathrm{e}^{\mathrm{i}k\overline{R_j}} \, \left(\widehat{c}_k - \widehat{c}^\dagger_{-k}\right) \frac{\sqrt{M\omega_k}}{\mathrm{i}}, \tag{11.121b}$$

which is another combination of the annihilation and creation operators. Equations (11.121) enable us to translate all physical quantities from one representation to another, for example, to find from the average number of phonons $\langle \hat{c}_k^\dagger \hat{c}_k \rangle = f_k$ in each mode the statistical fluctuations in the position of each nucleus in thermal equilibrium.

The existence of *anharmonicity* is in the phonon language translated into the addition of extra terms to the Hamiltonian (11.117). For instance, a term with δR^4 or with δR^3 in the potential W produces, if we use (11.121), terms like $\hat{c}_{k_1}^\dagger \hat{c}_{k_2}^\dagger \hat{c}_{k_3} \hat{c}_{k_4}$ describing the scattering of two phonons with quasi-momenta k_3 and k_4 into the modes k_1 and k_2 (with conservation of total quasi-momentum), like $\hat{c}_{k_1} \hat{c}_{k_2} \hat{c}_{k_3}$ describing the annihilation of 3 phonons ($k_1+k_2+k_3 = 0$), or like $\hat{c}_{k_1}^\dagger \hat{c}_{k_2}^\dagger \hat{c}_{k_3}$ describing the transformation of one phonon into two others. Even though they are small, those terms contribute to the establishment of equilibrium in the phonon gas, where the number of phonons is not conserved ($\mu = 0$). When they are significant, we treat them using perturbative expansions similar to those used in particle physics; the phonon language is then eminently suitable.

We have similarly treated the electrons in § 11.2 in the approximation where the nuclei were fixed at their average position. A displacement $\delta \boldsymbol{R}_n$ of the nuclei adds to (11.8) a perturbation

$$-\frac{e^2}{4\pi\varepsilon_0} \sum_{i,n} \delta\hat{\boldsymbol{R}}_n \cdot \left(\hat{\boldsymbol{r}}_i - \boldsymbol{R}_n\right) \frac{Z_n}{\left|\hat{\boldsymbol{r}}_i - \boldsymbol{R}_n\right|^3},$$

which can be interpreted, if we take (11.121) into account, as an *electron-phonon interaction* describing the scattering of an electron, with the creation or annihilation of a phonon. This interaction is responsible for numerous physical phenomena, such as the Joule effect – the transfer of electron energy to the lattice, thus heating it. It also enables two electrons to exchange a phonon; this gives rise to an effective attraction between them. This attraction is enhanced by the sudden jump in $f(\varepsilon)$ at the Fermi surface, to such an extent that it is possible for two electrons with energy ε_F and with opposite momenta and spins to form a bound pair in spite of their Coulomb repulsion. The resulting pairs, the so-called Cooper pairs, resemble bosons and can condense; this is the mechanism for superconductivity in metals at low temperatures (§ 12.3.3).

The phonons are a prototype of "*Goldstone bosons*", which are quasi-particles, or particles, associated with a continuous invariance property of the system. Here we are concerned with the *translational invariance* which the Hamiltonian satisfies, but which is *spontaneously broken* (§ 9.3.3) at thermal equilibrium where the atoms occupy well-defined equilibrium positions. An arbitrary translation transforms this equilibrium state into *another* equivalent equilibrium state, with the same energy. Let us assume that we excite a vibrational mode, in the long wavelength limit. Locally this (non-equilibrium) state is obtained by a translation with an amplitude which varies slowly in space. We understand thus why the energy of this mode tends to 0 as k decreases, since for $k = 0$ we would have just a global translation. This property holds generally (Goldstone's theorem) for any long wavelength excitation of a system, occurring because a continuous invariance is broken. The linear behaviour of ω_k for small k is a specific property of the phonons, but the existence of 3 acoustic branches, for which the energy vanishes with k, is itself a mere consequence of the breaking of the translational invariance in the crystal.

Another example of a Goldstone boson is provided by the elementary excitations, called "*magnons*", of a *ferromagnetic* solid (Exerc.9a). In the Heisenberg model where the spins $\boldsymbol{\sigma}_i$ interact through an effective potential $-J(\widehat{\boldsymbol{\sigma}}_i \cdot \widehat{\boldsymbol{\sigma}}_j)$, the Hamiltonian is invariant under a *rotation* of the spins. This continuous invariance is spontaneously broken in the ground state and, more generally, in any equilibrium state at a temperature below the Curie temperature (Exerc.9a), as the spins are in that case all oriented along a privileged direction. A global rotation of the spins does not change the energy. A magnon, or spin wave, describes an oscillation of the spins around their equilibrium orientation which propagates from one spin to another. It is the Goldstone mode associated with the spin rotations, and its energy vanishes with k. The same concept exists in *particle physics* where the ground (or equilibrium) state is replaced by the *vacuum* and where an elementary excitation with momentum p and energy $\varepsilon = \sqrt{m^2c^4 + p^2c^2}$ represents a particle with a rest mass m. The Goldstone bosons have an energy which vanishes with k, so that their *mass is zero*. An example is the *photon*; one can show that this is the Goldstone boson associated with *gauge invariance*, which is broken because one must choose a particular gauge to write down the potentials occurring in the Hamiltonian of charged particles.

11.4.3 Specific Heats of Solids

The statistical mechanics of quantized lattice vibrations can be studied in either one of the two equivalent descriptions: the canonical partition function (11.117) for the independent oscillation modes, calculated by using its factorization (§ 4.2.5), is the same as the grand canonical partition function for non-interacting phonons with $\mu = 0$, written down in §§ 10.3.1 and 10.5.2. Thus, the thermodynamic functions associated with the vibrational modes of the lattice, that is, with the phonon gas in the crystal, are given by the formulæ of § 10.3 with $\mu = 0$. In particular, apart from an additive constant, the *internal energy* (10.42) of the phonons, which is the average of (11.109), equals

$$U_{\text{ph}} = \sum_q \varepsilon_q f_q = \int d\varepsilon\, \mathcal{D}(\varepsilon) \frac{\varepsilon}{e^{\beta\varepsilon} - 1}, \tag{11.122}$$

where $\mathcal{D}(\varepsilon)$ is the density of the modes,

$$\mathcal{D}(\varepsilon) = \sum_q \delta(\hbar\omega_q - \varepsilon). \tag{11.123}$$

At low temperatures the important modes in the integral in (11.122) are those with *low energies*. They have a linear spectrum so that in three dimensions the mode density (11.123) behaves as ε^2 for small ε, since $\sum_q$ introduces an integral $\int d^3k$. As a result, if we take $\beta\varepsilon$ as the variable in (11.122), we find an internal energy which is proportional to T^4 as $T \to 0$, which means a specific heat proportional to T^3. We shall determine its coefficient in what follows, in (11.129).

At high temperatures (11.122) reduces to

$$U_{\text{ph}} \sim kT \int d\varepsilon\, \mathcal{D}(\varepsilon) = 3NkT, \tag{11.124}$$

where $3N$ is the total number of modes. More exactly, in a solid with several atoms per cell and N cells, the $3N$ acoustic modes contribute to (11.124) while the optical modes do not contribute, provided kT lies between the maximum energy of the acoustic modes and the minimum energy of the optical modes. The specific heat is therefore nearly constant and equal to $3Nk$.

The *Debye model* bridges these results. It is based upon the use of the isotropic approximation (11.120) for the phonon spectrum, which in the large volume limit (§ 10.3.3) and for small ε gives

$$\begin{aligned} \mathcal{D}(\varepsilon) &= \sum_{p} \left[\delta(u_{\text{l}}p-\varepsilon)+2\delta(u_{\text{t}}p-\varepsilon)\right] \\ &= \frac{\Omega}{h^3}\int d^3p \left[\delta(u_{\text{l}}p-\varepsilon)+2\delta(u_{\text{t}}p-\varepsilon)\right] \\ &= \frac{\Omega}{2\pi^2\hbar^3}\left(\frac{1}{u_{\text{l}}^3}+\frac{2}{u_{\text{t}}^3}\right)\varepsilon^2. \end{aligned} \tag{11.125}$$

Nevertheless, $\mathcal{D}(\varepsilon)$ must vanish when ε becomes large as the total number of modes, $3N$, is finite; it must satisfy the *normalization* condition (11.124). The Debye approximation, which enables us to avoid the detailed determination of $\mathcal{D}(\varepsilon)$, consists in extrapolating (11.125) up to a certain maximum value after which one takes $\mathcal{D}$ to vanish. This value $k\Theta_{\text{D}}$ is determined by the normalization condition, which determines the only parameter of the theory, the *Debye temperature* of the crystal,

$$\Theta_{\text{D}} = \frac{\hbar}{k}\left[\frac{18\pi^2 N}{\Omega\left(u_{\text{l}}^{-3}+2u_{\text{t}}^{-3}\right)}\right]^{1/3}. \tag{11.126}$$

One can determine it from measurements of the longitudinal and transverse sound velocities. Typical values are 90 K for Pb, 400 K for Al, and 3000 K for diamond. One can therefore rewrite the mode density (11.125) in the approximate form

$$\mathcal{D}(\varepsilon) = \frac{9N\varepsilon^2}{(k\Theta_{\text{D}})^3}\,\theta(k\Theta_{\text{D}}-\varepsilon). \tag{11.125'}$$

The resulting internal energy (11.122) equals

$$U_{\text{ph}} = \frac{9NkT^4}{\Theta_{\text{D}}^3}\int_0^{\Theta_{\text{D}}/T}\frac{x^3\,dx}{e^x-1}, \tag{11.127}$$

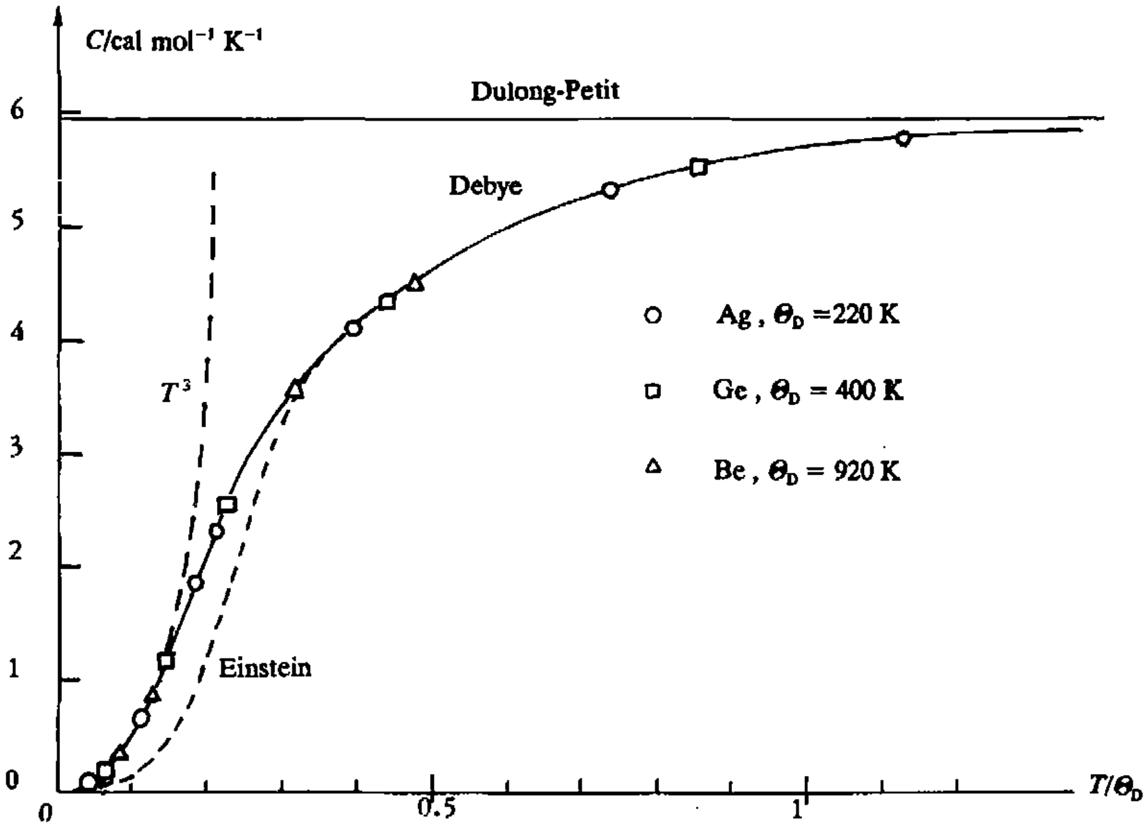

Fig. 11.20. The specific heat of some solids

where we have taken $x \equiv \beta\varepsilon$ as variable. Hence we get for the *phonon contribution to the specific heat of the crystal*

$$C_{\mathrm{ph}} = \frac{dU_{\mathrm{ph}}}{dT} = \frac{9NkT^3}{\Theta_{\mathrm{D}}^3} \int_0^{\Theta_{\mathrm{D}}/T} \frac{x^4 \mathrm{e}^x \, dx}{(\mathrm{e}^x - 1)^2}, \tag{11.128}$$

which we show in Fig.11.20. The dashed curve corresponds to the Einstein model (Exerc.10d).

The experimental results are also shown in Fig.11.20 for a few substances which have a sufficiently simple crystal structure for the phonon spectrum to be well represented by the Debye approximation. The agreement with the theoretical curve is remarkable: the Debye temperatures which produce the best agreement between theory and experiment are, up to a few %, equal to those which one evaluates from (11.126), using the sound velocities.

We find, as predicted, the T^3 *dependence at low temperatures* if in (11.128) we replace the upper integration limit by ∞, which for $T \ll \Theta_{\mathrm{D}}$ gives (see formulae section at the end of the book)

$$C_{\mathrm{ph}} \simeq \frac{9NkT^3}{\Theta_{\mathrm{D}}^3} \int_0^{\infty} \frac{x^4 \mathrm{e}^x \, dx}{(\mathrm{e}^x - 1)^2} = \frac{12\pi^4}{5} Nk \frac{T^3}{\Theta_{\mathrm{D}}^3}. \tag{11.129}$$

Figures 11.20 and 11.21 illustrate that experiments check the T^3 law very satisfactorily for most solids, and even with a remarkable accuracy for *insulators* at low temperatures (solid argon for $T < 2$ K). A notable exception

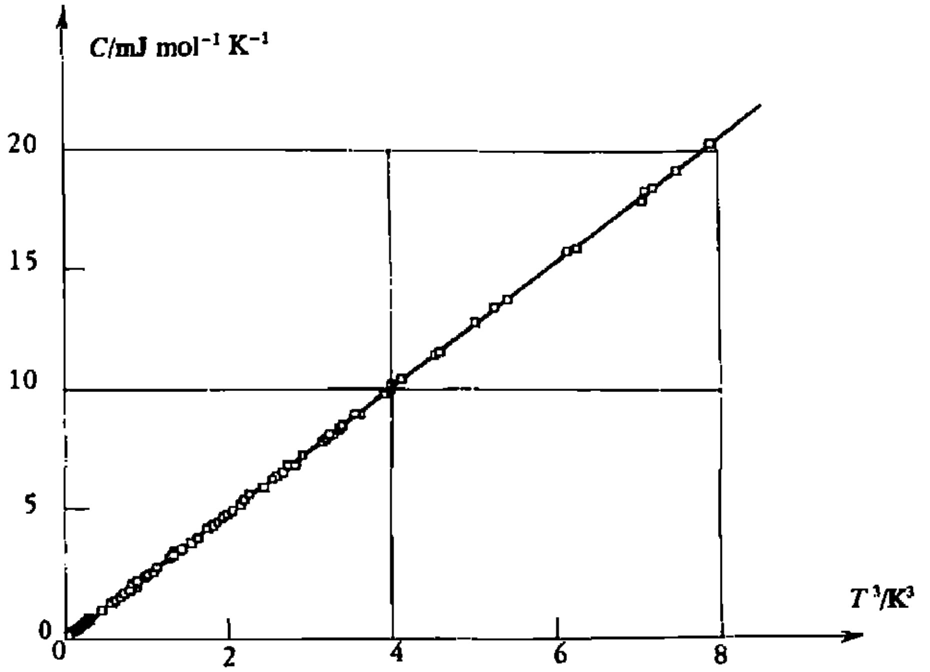

Fig. 11.21. Specific heat of solid argon. The solid line represents the theoretical curve for $\Theta_D = 92$ K

is graphite, the specific heat of which varies rather like T^2. This can be explained by the practically two-dimensional structure of this substance, which changes the mode density (11.125) and produces a behaviour $\mathcal{D}(\varepsilon) \propto \varepsilon$ instead of $\propto \varepsilon^2$ in a sufficiently large region. Nevertheless for *metals* at very low temperatures the specific heat is dominated by the *electron contribution* (11.52) which is *linear in T*, and which tends to zero less rapidly than the contribution (11.129) from the lattice vibrations. One can distinguish these two contributions easily by plotting C/T as function of T^2, as the experimental results for potassium below 0.5 K show (Fig.11.22).

When the temperature increases, the crystal vibrations become more and more unfrozen and C_{ph} increases. When $T \gg \Theta_D$, we expect to find the result of *classical* statistical mechanics, predicted by the equipartition theorem (§ 8.4.2): the number of degrees of freedom is $6N$ so that C_{ph} should tend to $3Nk$. One can check this result by expanding the integrand in (11.128) in the vicinity of $x = 0$, which yields

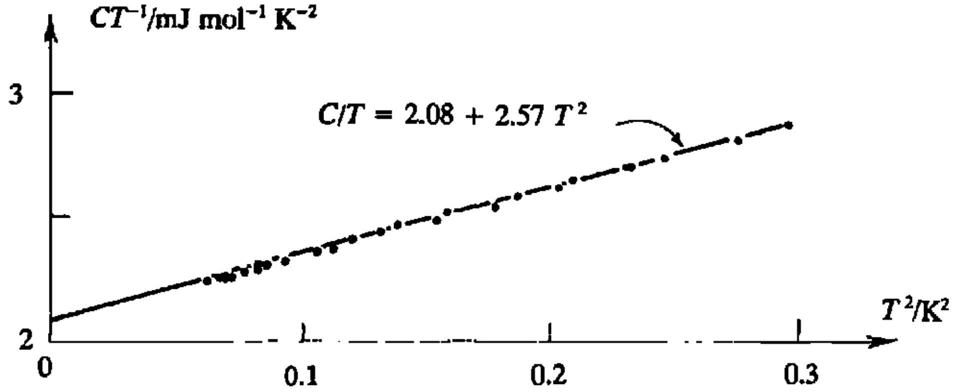

Fig. 11.22. Specific heat of metallic potassium

$$C_{\text{ph}} \sim 3Nk\left(1-\frac{\Theta_{\text{D}}^2}{20T^2}\cdots\right). \tag{11.130}$$

The value $3Nk \simeq 25\,\text{J mole}^{-1}\,\text{K}^{-1}$ for the specific heat of solids had been observed experimentally for number of them at the beginning of the nineteenth century (*Dulong and Petit law*). We see that this concerns solids with a Debye temperature which is rather low, below room temperature. We also note that the electron contribution is negligible compared to $3Nk$: for potassium, an extrapolation to $T = 300\,\text{K}$ of the linear law only gives $C_{\text{el}} \simeq 0.6\,\text{J mole}^{-1}\,K^{-1}$.

The Debye approximation thus enables us to connect the *specific heats* of solids with a simple structure to their *sound velocities*. For crystals with a less simple structure, or in order to obtain a greater accuracy, we must use (11.122) and (11.123) which connect the *thermodynamic* properties with the properties of the *vibrations*: another example of the unifying power of statistical physics. For many substances one has checked the agreement between the measured specific heat and its value calculated starting from the $\omega(\boldsymbol{k})$ spectrum, which itself is determined in experiments, for instance, on inelastic scattering of neutrons or photons by phonons.

11.4.4 Thermal Equilibrium of a Vibrating String

As an introduction to quantum field theory and as an exercise we shall study a model describing the vibrations of a *continuous* medium, rather than of a discrete system of atoms as in § 11.4.1. This will help us to deepen the equivalence which we have established between quantized oscillators and quasiparticles such as phonons (§ 11.4.2); the discrete nature of a substance should not play any role when $ka \ll 1$. This will help us also to introduce in § 13.1 the photon concept. In fact, the dynamical variables describing the deformations of a continuous medium constitute a *field* and the quantization of the electromagnetic field will follow the same stages as the present quantization of the deformation field, the eigenmodes of which are mechanical oscillations.

To simplify matters we shall restrict ourselves to a one-dimensional system, that is, to an elastic string. We assume that this string, which is fixed at its ends, $x = 0$ and $x = L$, can only be deformed in one, transverse, direction. Moreover, we limit ourselves to small displacements and we assume that the tension τ and the linear mass density ϱ are given. In *classical mechanics* the displacement $\varphi(x,t)$ of the string at the point x, which is the solution of the equations of motion (11.134) and which depends on the initial conditions $\varphi(x,0)$ and $\partial\varphi(x,0)/\partial t$, must be considered to be a *classical field*, that is, a continuum of dynamic variables φ each of which is associated with a point x of the string. The oscillation *eigenmodes* are particular solutions, forming a base. They are characterized by their wavenumber

$$k = \frac{m\pi}{L}, \qquad m = 1,\ 2,\ \ldots\ , \tag{11.131}$$