

II

CRYSTAL LATTICES. APPLICATIONS

2.1. Specific heat

If the crystal is in thermal equilibrium at temperature T , it is well known that the probability of a quantum state of energy E is $e^{-\beta E}$, where

$$\beta = \frac{1}{kT}, \quad (2.1)$$

k being Boltzmann's constant. With the result (1.65) it follows then that the mean energy of each oscillator is (using a bar over a quantity to indicate a statistical average)

$$\begin{aligned} \overline{E(\mathbf{f}, s)} &= \hbar\omega(\mathbf{f}, s) \left\{ \overline{N(\mathbf{f}, s)} + \frac{1}{2} \right\} = \frac{\sum_{N=0}^{\infty} (N + \frac{1}{2}) \hbar\omega e^{-\beta\hbar\omega(N+\frac{1}{2})}}{\sum_{N=0}^{\infty} e^{-\beta\hbar\omega(N+\frac{1}{2})}} \\ &= -\frac{\partial}{\partial\beta} \log \sum e^{-\beta\hbar\omega(N+\frac{1}{2})} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} = \frac{1}{2}\hbar\omega \coth(\frac{1}{2}\beta\hbar\omega). \end{aligned} \quad (2.2)$$

The energy of the whole crystal is

$$E = U_0 + E_Z + E_T,$$

where E_Z is the zero-point energy

$$E_Z = \sum_{\mathbf{f}, s} \frac{1}{2} \hbar\omega(\mathbf{f}, s), \quad (2.3)$$

and E_T is the thermal energy

$$E_T = \sum_{\mathbf{f}, s} \overline{N(\mathbf{f}, s)} \hbar\omega(\mathbf{f}, s) = \sum_{\mathbf{f}, s} \frac{\hbar\omega(\mathbf{f}, s)}{e^{\beta\hbar\omega(\mathbf{f}, s)} - 1}. \quad (2.4)$$

The evaluation of the sum (2.4) is, in general, very difficult, and it requires a knowledge of the frequency as a function of \mathbf{f} and s .

However, the calculation can be carried further in the two limits of high and low temperatures. Consider first a temperature so high that for all vibrations

$$\hbar\omega(\mathbf{f}, s) \ll kT.$$

This means that the summand in (2.4) can be expanded in a power series, and the three leading terms give

$$\begin{aligned} E_T &= \sum_{\mathbf{f}, s} \frac{1}{\beta} [1 - \frac{1}{2}\beta\hbar\omega(\mathbf{f}, s) + \frac{1}{12}\{\beta\hbar\omega(\mathbf{f}, s)\}^2 - \dots] \\ &= \sum_{\mathbf{f}, s} \left[kT - \frac{1}{2}\hbar\omega(\mathbf{f}, s) + \frac{1}{12} \frac{1}{kT} \{\hbar\omega(\mathbf{f}, s)\}^2 - \dots \right]. \end{aligned} \quad (2.5)$$

The first term amounts to $3rNkT$, which is precisely the classical result for a system of $3rN$ vibrational degrees of freedom. The second term just cancels the zero-point energy, so that at high temperatures not merely the specific heat, but also the energy content approaches asymptotically the classical result. The third term, which vanishes at infinite T , and which measures the deviation from the classical result, is seen to be of the second order in the quantum constant \hbar . This is a very common feature of quantum statistics. For estimating this term one must know something of the vibration spectrum. However, it is not necessary to solve the equations (1.25) for this purpose, since the sum of the squares of the frequencies can be obtained directly in terms of the coefficients of the equation.

One can, indeed, prove easily from the orthogonality relations of § 1.7 and from (1.25) that

$$\sum_{f,s} \{\omega(f, s)\}^2 = N \sum_f \frac{1}{M_f} \langle \mathbf{G}_{ff} \rangle = N \sum_f \frac{1}{M_f} \langle \mathbf{A}_{ff}(0) \rangle, \quad (2.6)$$

where the symbol $\langle \dots \rangle$ indicates the diagonal sum or 'trace' of the tensor. The last sum has a fairly direct interpretation: it represents the sum of the potential energies obtained by displacing in turn each atom of the crystal in each coordinate direction by an infinitesimal amount, dividing by the square of the displacement and half the mass of the atom.

The series (2.5) could be continued, and one would find that it contains only sums of even powers of the frequencies which can all be expressed similarly to (2.6) in terms of the force constants. However, from the last form of (2.2) it is evident that the series in powers of β will cease to converge when for some frequencies $\hbar\omega > \pi kT$.

In the opposite limit of low temperatures, it would not be right to approximate to (2.4) by assuming $\hbar\omega$ to be large compared with kT , since at no reasonable temperatures is this true for all frequencies. However, one sees that the only frequencies which will give appreciable contributions to (2.4) are those for which $\beta\hbar\omega$ is not large, and, if the temperature is low, this will be true only for the lowest part of the frequency spectrum. Now we have found earlier that the lowest frequencies belong to small values of f , and, if $r > 1$, only to three out of the $3r$ possible frequencies for each f . We also saw that for these vibrations the frequency is proportional to the magnitude of f , the factor of proportionality depending on the direction of f , and on the polarization of the wave.

Hence we may replace the frequency spectrum in (2.4) by

$$\omega(f, s) = c_s(\theta, \phi)f, \quad s = 1, 2, 3. \quad (2.7)$$

Here θ, ϕ indicate the direction of \mathbf{f} , and c_s is a velocity of sound. We may also replace the summation over \mathbf{f} by an integration, noting that the density of permitted values in \mathbf{f} space is $V/(2\pi)^3$. In polar coordinates the integral becomes

$$E_T = \frac{V}{(2\pi)^3} \sum_{s=1}^3 \int_0^\infty f^3 df \iint d\Omega \frac{\hbar c_s(\theta, \phi)}{e^{\beta \hbar c_s f} - 1}, \quad (2.8)$$

where $d\Omega$ is the element of solid angle. The integration over f may be extended to infinity, since large values do not contribute to the integral. We now introduce a new variable of integration

$$x = \beta \hbar c_s(\theta, \phi) f \quad (2.9)$$

in place of f .

$$E_T = \frac{V(kT)^4}{(2\pi\hbar)^3} \sum_s \iint \frac{d\Omega}{c_s^3} \int_0^\infty \frac{x^3}{e^x - 1} dx. \quad (2.10)$$

The last integral can be evaluated and is $\pi^4/15$. The summation over s and integration over angles can be carried out in principle if the elastic constants of the crystal are known. If we put

$$\sum_s \iint \frac{d\Omega}{\{c_s(\theta, \phi)\}^3} = \frac{12\pi}{c_{\text{eff}}^3}, \quad (2.11)$$

then c_{eff} represents a kind of mean value of the sound velocity. With this, finally,

$$E_T = \frac{\pi^2(kT)^4 V}{10\hbar^3 c_{\text{eff}}^3}. \quad (2.12)$$

This T^4 law for the thermal energy, corresponding to a T^3 law for the specific heat at low temperatures, is well confirmed by experiment. It was first derived by Debye, who also gave an interpolation formula which combines the high-temperature law with the low-temperature expression, by using a simplified vibration spectrum. He assumed that the sound velocity is constant for all wavelengths, and independent of direction or polarization, so that the law (2.7) is always true, with constant c_s . Instead of integrating \mathbf{f} over the basic cell of the reciprocal lattice and adding the other types of wave (if $r > 1$), Debye extends the integration over a sphere in \mathbf{f} space, which is chosen in such a way that it gives the right number of degrees of freedom. This means that its radius f_0 is given by

$$\frac{4\pi}{3} f_0^3 \frac{V}{(2\pi)^3} = Nr,$$

or

$$f_0^3 = \frac{6\pi^2 Nr}{V}. \quad (2.13)$$

The maximum frequency of this model is then

$$\omega_0 = cf_0, \quad (2.14)$$

c being a constant.

With these assumptions, (2.8) follows at all temperatures, provided the integration over \mathbf{f} is taken only to the upper limit f_0 . Then we obtain in place of (2.10)

$$E_T = \frac{V(kT)^4}{(2\pi\hbar)^3} \frac{12\pi}{c^3} \int_0^{x_0} \frac{x^3}{e^x - 1} dx, \quad (2.15)$$

where $x_0 = \beta\hbar\omega_0 = \hbar\omega_0/kT$. If we introduce a characteristic temperature

$$\Theta = \frac{\hbar\omega_0}{k},$$

the upper limit of the integral in (2.15) is Θ/T . We can also eliminate c by means of (2.13), (2.14):

$$E_T = 9N\tau kT \left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^3}{e^x - 1} dx. \quad (2.16)$$

This is the Debye formula for the thermal energy of a crystal. From its derivation it is clear that it can only serve as a qualitative result, and as an interpolation formula linking the high- and low-temperature data. The characteristic temperature Θ is treated as an empirical parameter. The law (2.16) is of the right form at low temperatures, where it correctly gives the variation of E_T as T^4 , and at very high temperatures, where it gives the Dulong-Petit value of the specific heat, $3k$ per atom. However, it will not in general give the right value of the constant term in (2.5), which is identical with the zero-point energy, nor the coefficient of the T^{-1} term which gives the first deviation of the specific heat from the Dulong-Petit value.

In a modified version of the Debye model, one applies the assumption of constant sound velocity only for the three lowest normal frequencies belonging to each \mathbf{f} , which form the so-called 'acoustical branch' of the vibration spectrum. The rest form what are sometimes called the 'optical' branches, since for ionic crystals they contain the frequencies which appear in the infra-red absorption spectrum, as we shall see. Since these may be pictured as vibrations of the different parts of the unit cell relative to each other, they are somewhat less dependent on whether adjacent unit cells vibrate with the same or with different phases. Hence these frequencies vary somewhat less strongly with \mathbf{f} than those in the acoustical branch. For this reason a model is sometimes used in

which one replaces the optical branches by $r-1$ frequencies, each belonging to $3N$ different normal modes. For certain cases, e.g. a molecular lattice with weak forces between the molecules as in H_2 , this is a more reasonable picture than the simple Debye formula. On the other hand, for an ionic lattice like KCl, in which the mass difference between the two ions is small, it is probably more reasonable to regard the optical branch as a continuation of the acoustic branch than as having constant frequency.

In the older literature one often finds the Debye law in one or the other form taken much more seriously than the derivation justifies, and therefore surprise was caused when precise low-temperature measurements showed considerable deviations from this simple theory. Careful discussion of the vibration spectra of crystals by Blackman and others† showed that the observed deviations were no greater than should be expected.

Nevertheless, the Debye model serves a useful purpose in summarizing the behaviour of E_T qualitatively, and in defining the characteristic temperature which also gives a measure where, for each substance, quantum corrections begin to be important.

2.2. Anharmonic terms. Thermal expansion

We now turn to the discussion of those phenomena for which the cubic terms in (1.20) are no longer negligible. The most important problems of this type concern (a) thermal expansion, (b) specific heat at high temperatures, and (c) thermal conductivity.

For the thermal expansion the most obvious definition of the problem would be in terms of boundary conditions which specify the forces on the surface of the crystal (or the absence of such forces) but allow its dimensions to adjust themselves. In terms of the variables which we have used, this would be very inconvenient, but it is sufficient to calculate the properties of the crystal as a function of temperature and volume, keeping the volume as one of the independent variables.

We may then consider the (Helmholtz) free energy of a crystal of volume $(1+\epsilon)$ times its equilibrium volume at temperature T as a function $F(T, \epsilon)$. For small ϵ we expand:

$$F(T, \epsilon) = F_0(T) + \epsilon F_1(T) + \frac{1}{2} \epsilon^2 F_2(T) \quad (2.17)$$

to second order. Now $\partial F / \partial \epsilon$ is proportional to the pressure and therefore the volume for which the pressure vanishes is given by

$$\frac{\partial F}{\partial \epsilon} = F_1(T) + \epsilon F_2(T) = 0; \quad (2.18)$$

† Blackman (1935), Kellerman (1940).

hence the actual volume exceeds that for which the potential energy is least by the relative amount

$$\epsilon(T) = -\frac{F_1(T)}{F_2(T)}. \quad (2.19)$$

Hence the numerator F_1 is small at low temperatures, and would, in fact, be zero if the potential were harmonic. On the other hand, the denominator F_2 , which, according to (2.17), represents the bulk modulus at temperature T , is finite at $T = 0$ and in the absence of anharmonic forces. It is clear that F_2 will differ only little from its value at low temperatures, and usually we may regard it as constant.

We must now discuss F_1 , i.e. consider the behaviour of a crystal if its volume differs from the normal volume, retaining only first-order terms in the expansion.

Since in the series (1.20) for the potential energy the displacements were counted from the sites of the equilibrium lattice, we now introduce new displacements \mathbf{u}' which refer to a similar lattice of a slightly increased lattice constant:

$$\mathbf{u}_{j,n} = \frac{1}{2}\epsilon(\mathbf{d}_j + \mathbf{a}_n) + \mathbf{u}'_{j,n}. \quad (2.20)$$

In a general lattice, the uniform expansion will not leave the atoms in an equilibrium position, since for equilibrium the relative positions of different atoms in the unit cell would have to change. We can, however, assert that each atom will still be in equilibrium either if there is only one atom in the unit cell ($r = 1$), or if the relative positions of all atoms in the unit cell are determined by the crystal symmetry, as in the case of the NaCl structure or the hexagonal close-packed lattice. We therefore restrict the discussion to lattices which satisfy this condition. We then know that, if we put all the \mathbf{u}' equal to zero, every atom is in equilibrium, so that the potential energy as a function of the \mathbf{u}' must again be of the form (1.20).

Imagine now (2.20) inserted in (1.20), and the result sorted according to powers of the \mathbf{u}' . The terms independent of \mathbf{u}' represent the equilibrium energy of the new lattice. The 'A' terms will contribute to this a term proportional to ϵ^2 , which is the elastic energy discussed in (1.57) and contained in the F_2 term of (2.17). Similarly, the 'B' terms contribute a term proportional to ϵ^3 , which we may neglect.

The terms linear in the \mathbf{u}' must vanish, since we know the atoms are in equilibrium when $\mathbf{u}' = 0$. We are therefore, to this order, left with an expansion of the form (1.20)

$$U - U_0 - \frac{1}{2}k\epsilon^2 = \sum_{j,j'} \sum_{n,n'} \frac{1}{2} \mathbf{A}'_{j,n;j',n'} \mathbf{u}_{j,n} \mathbf{u}'_{j',n'} + \sum_{j,j'} \sum_{n,n'} \sum_{n',n''} \frac{1}{6} \mathbf{B}'_{j,n;j',n';j'',n''} \mathbf{u}_{j,n} \mathbf{u}'_{j',n'} \mathbf{u}'_{j'',n''}, \quad (2.21)$$

where the cubic term is still negligible, but the coefficients of the quadratic term are modified:

$$\mathbf{A}'_{j,n;j',n'} = \mathbf{A}_{j,n;j',n'} + \frac{1}{3}\epsilon \sum_{j'',n''} \mathbf{B}_{j,n;j',n';j'',n''}(\mathbf{a}_{j,n''} + \mathbf{d}_{j''}). \quad (2.22)$$

The occurrence of $\mathbf{a}_{n''}$ would seem to introduce a dependence on the choice of that unit cell which we label $n = 0$. Since the uniform expansion does not destroy the translation symmetry of the crystal, this dependence cannot be real; if we change the origin by any lattice vector, the result must remain the same. This requires the condition

$$\sum_{j'',n''} \mathbf{B}_{j,n;j',n';j'',n''} = 0, \quad (2.23)$$

which is similar to (1.22).

We see, then, that the dynamical problem defined by the potential (2.19) is quite similar to the original one, except that, because of the anharmonic terms, all constants defining the vibration spectrum will be changed by corrections of first order in ϵ . The consequences of this are particularly evident if the vibration spectrum can be expressed in terms of a single parameter, Θ , as in the Debye model.

In that case we can write

$$F(T) = -Tg(T/\Theta), \quad (2.24)$$

where g is a universal function. Indeed, because of the thermodynamic identity

$$E = -T^2 \frac{d}{dT} \left(\frac{F}{T} \right), \quad (2.25)$$

this leads to

$$E = T \frac{T}{\Theta} g' \left(\frac{T}{\Theta} \right), \quad (2.26)$$

where g' is the derivative of g with respect to its argument. In other words, E/T is again a universal function of the ratio T/Θ , and this agrees with (2.16). In this case, the dependence on volume is contained in the parameter Θ , and so

$$F_1 = \frac{\partial F}{\partial \epsilon} = T \frac{T}{\Theta} g' \left(\frac{T}{\Theta} \right) \frac{1}{\Theta} \frac{\partial \Theta}{\partial \epsilon}. \quad (2.27)$$

By comparison with (2.26),

$$F_1(T) = E(T) \frac{1}{\Theta} \frac{\partial \Theta}{\partial \epsilon}. \quad (2.28)$$

Since we have seen that the temperature dependence of the denominator of (2.19) is negligible, we see that in the Debye model the thermal expansion is proportional to the thermal energy. This law, which was formulated by Grüneisen, is based on an idealized model. Its range

of validity is somewhat more general than that of Debye's law, since it holds for a more complicated spectrum provided that, if the body is expanded, all frequencies are changed by the same factor.

We have seen before (cf. (2.10), (2.11), and (2.16)) that at very low temperatures the Debye law becomes exact if we define Θ by

$$(k\Theta)^3 = \frac{3Nr}{V} 2\pi^2 \hbar^3 c_{\text{eff}}^3, \quad (2.29)$$

where c_{eff} is defined in (2.11). In that case (2.28) becomes

$$F_1(T) = E(T) \left(-\frac{1}{3} + \frac{\partial}{\partial \epsilon} \log c_{\text{eff}} \right). \quad (2.30)$$

It therefore follows that the thermal expansion at low temperatures is proportional to T^4 . It is also easy to see that at high temperatures ($T \gg \Theta$) the expansion becomes linear in T , i.e. the expansion coefficient becomes constant as the Grüneisen formula (2.28) predicts. This, of course, holds only apart from higher-order corrections, such as cubic and higher-order terms in the expansion (2.17), and the variation of the denominator of (2.19).

Lastly, it should be mentioned that the method used here will, in non-cubic crystals, still give the variation of free energy with volume, but will not give the thermal expansion correctly, since in general the shape of the crystal also changes with temperature. In such cases (2.17) has to be replaced by a function of several strain components, and (2.18) is replaced by several simultaneous equations. The Grüneisen law remains valid for the expansion in each direction if the vibration spectrum retains its shape under an arbitrary shear strain.

2.3. Linear term in specific heat

A second phenomenon entirely dependent on the anharmonic nature of the forces is the deviation of the specific heat from the Dulong-Petit value at high temperatures. The anharmonic terms will also cause a small correction to the specific heat at lower temperatures, but, since we have seen that the theoretical law cannot in practice be found to high accuracy, small corrections are of no practical interest there. On the other hand, at high temperatures where quantum effects are negligible, the theory with harmonic forces gives a simple answer, and small deviations from this can be compared with experiment.

For this purpose it is evidently sufficient to give only a classical treatment. Before writing down the general equations, it may help to discuss

the corresponding problem for a single particle oscillating in a potential field. Here the Hamiltonian form of the energy is

$$H = \frac{1}{2m} p^2 + V(x), \quad (2.31)$$

and the partition function is therefore

$$Z(\beta) = \int dp \int dx e^{-\beta p^2/2m - \beta V(x)}. \quad (2.32)$$

As usual, the integration over p can be carried out immediately, leaving

$$Z(\beta) = \left(\frac{2\pi m}{\beta} \right)^{\frac{1}{2}} \int dx e^{-\beta V(x)}. \quad (2.33)$$

Now let the potential be approximately that of a harmonic oscillator, with small anharmonic terms,

$$V(x) = \frac{1}{2}ax^2 + bx^3 + cx^4. \quad (2.34)$$

Then, if we expand the integral in (2.33) in powers of b and c , retaining the first-order term in c and the second-order term in b ,

$$Z(\beta) = \left(\frac{2\pi m}{\beta} \right)^{\frac{1}{2}} \int dx e^{-\frac{1}{2}\beta ax^2} (1 - \beta bx^3 + \frac{1}{2}\beta^2 b^2 x^6 - \beta cx^4). \quad (2.35)$$

Here the integral over the cubic term evidently vanishes by symmetry. The remaining integrations are elementary, and the result is

$$Z(\beta) = 2\pi \sqrt{\left(\frac{m}{a} \right) \frac{1}{\beta} \left(1 - \frac{3c}{a^2\beta} + \frac{15b^2}{2a^3\beta} \right)}. \quad (2.36)$$

Now we obtain the mean thermal energy from the partition function by using the relation

$$E = - \frac{\partial \log Z}{\partial \beta} \quad (2.37)$$

which gives, neglecting again higher-order terms,

$$E = kT - \frac{3c}{a^2} (kT)^2 + \frac{15b^2}{2a^3} (kT)^2. \quad (2.38)$$

To retain the analogy with the forces in a crystal we assume that each derivative of the potential differs from the next higher one by a factor of the order of the atomic distance, and this means that in order of magnitude a/b is comparable to b/c . In that case the last two terms of (2.38) are of comparable magnitude. Both give corrections to the energy proportional to T^2 , hence linear terms in the specific heat. If in order of

magnitude $a/b \sim b/c \sim d$, then both the second and the third term are of order $(kT)^2/ad^2$. In other words, they are small compared with the first, as long as the temperature is small compared with that temperature for which the mean square amplitude is d^2 . One easily verifies that the terms of higher order which we have neglected, i.e. higher-order terms in the potential (2.34), higher terms in the expansion (2.35) of the exponential and in the expansion of the logarithm in (2.37), contain higher powers of kT/ad^2 , so that (2.38) is a consistent approximation.

After this preparation we turn to the general case. It is clear that we must again include the fourth-order terms not explicitly shown in (1.20). Just as in (2.35) we shall again expand the Boltzmann factor in powers of the cubic and quartic terms, retaining the part proportional to the square of the cubic and that proportional to the quartic terms.

Since, however, the exponential contains the quadratic (harmonic) terms, we must use variables in terms of which the quadratic terms separate. In other words, we must use normal coordinates. We therefore substitute in the \mathbf{B} term of (1.20) the expression (1.30) for the u :

$$U_c = \frac{1}{8} \sum_{\mathbf{f}, \mathbf{f}'} \sum_{s, s'} b(\mathbf{f}, s; \mathbf{f}', s'; \mathbf{f}'', s'') q_{\mathbf{f}, s} q_{\mathbf{f}', s'} q_{\mathbf{f}'', s''}, \quad (2.39)$$

where

$$b(\mathbf{f}, s; \mathbf{f}', s'; \mathbf{f}'', s'') = \sum_{j, j'} \sum_{\mathbf{a}, \mathbf{a}'} \mathbf{B}_{j, \mathbf{a}; j', \mathbf{a}'; j'', \mathbf{a}''} e^{i(\mathbf{f} \cdot \mathbf{a}_{\mathbf{a}} + \mathbf{f}' \cdot \mathbf{a}_{\mathbf{a}'} + \mathbf{f}'' \cdot \mathbf{a}_{\mathbf{a}''})} \mathbf{v}_j(\mathbf{f}, s) \mathbf{v}_{j'}(\mathbf{f}', s') \mathbf{v}_{j''}(\mathbf{f}'', s''). \quad (2.40)$$

From the translational symmetry follows at once an important property of the b coefficients. We know that the equations remain unchanged if we displace the crystal by a lattice vector, which means adding a lattice vector \mathbf{a} to all the $\mathbf{a}_{\mathbf{a}}$ in (2.40). This multiplies the expression by

$$e^{i\mathbf{a}(\mathbf{f} + \mathbf{f}' + \mathbf{f}'')}. \quad (2.41)$$

Since the expression must remain unchanged, it follows that b must vanish, unless the exponential (2.41) is unity, which by (1.28) means that

$$b(\mathbf{f}, s; \mathbf{f}', s'; \mathbf{f}'', s'') = 0, \quad (2.42)$$

unless $\mathbf{f} + \mathbf{f}' + \mathbf{f}'' = \mathbf{K}$ is a vector of the reciprocal lattice. This means that, if two of the vectors, say \mathbf{f}, \mathbf{f}' , are given, all values of \mathbf{f}'' for which the coefficient is non-zero are equivalent, and only one of them lies in the basic cell of the reciprocal lattice, which by definition contains all our wave vectors \mathbf{f} . If \mathbf{f} and \mathbf{f}' are small, so that their sum lies itself in the basic cell, we must take $\mathbf{K} = 0$ in (2.42), otherwise it must be chosen so as to bring \mathbf{f}'' back into the basic cell.

We now write for the Boltzmann factor†

$$e^{-\beta E} = e^{-\beta E_{\text{kin}} - \beta U_h (1 - \beta U_c + \frac{1}{2} \beta^2 U_c^2 - \beta U_q)} \quad (2.43)$$

as in (2.35), where U_h , U_c , U_q stand for the harmonic, cubic, and quartic parts of the potential energy respectively. To obtain the partition function Z we have to integrate (2.43) over phase space, which amounts to taking the average values of U_c , U_c^2 , and U_q over the thermal distribution appropriate to harmonic motion. Now U_h is even in all the normal coordinates; hence the probability is not altered by reversing the value of all the q , and therefore the average of U_c , which is an odd function of the q , vanishes.

For the discussion of the term in U_c^2 we note that the normal coordinates are statistically independent and that the average potential energy for each of them must be $\frac{1}{2}kT = 1/2\beta$. Hence by (1.47)

$$\overline{q_{t,s}^2} = \{M^{(N)}\beta\omega^2(f, s)\}^{-1}, \quad (2.44)$$

where the bar over the symbol means the average value for harmonic motion.

Now the square of (2.39) contains products of the type (we form the product $U_c^* U_c$, which is the same since U_c is real)

$$q_{t,s}^* q_{t',s'}^* q_{t'',s''}^* q_{t,s} q_{t',s'} q_{t'',s''}. \quad (2.45)$$

Because of the statistical independence of the q , the average of this product vanishes, unless the six normal modes concerned are equal in pairs. The symmetry of the coefficients in (2.39) means that we can permute the first three between themselves and the last three between themselves without changing the expression. Hence there are only two types of term to be considered:

$$\left. \begin{aligned} (a) \quad & f = -f', f_1 = -f_2, f'' = f_3; s = s', s_1 = s_2, s'' = s_3 \\ (b) \quad & f = f_1, f' = f_2, f'' = f_3; s = s_1, s' = s_2, s'' = s_3 \end{aligned} \right\}. \quad (2.46)$$

At this point the further discussion is greatly simplified if we are dealing with a lattice for which the unit cell contains only one atom ($r = 1$), and I shall restrict myself to this case.‡ Now, in the case (a), (2.42) requires that $f'' = f_3 = 0$. If this is inserted in (2.40) for $r = 1$,

† The expansion of the exponential which has been used in deriving (2.43) looks doubtful, since for the whole crystal neither U_c nor U_q would be expected to be small compared with kT . However, a more rigorous justification of (2.43) can be given, based on the fact that in any configuration which occurs with reasonable probability that part of U_c or U_q which depends on any given normal coordinate is small, so that, in averaging over each coordinate, the expansion may be used.

‡ In a general lattice terms of the type (a) can be shown to be connected with the variation of the cell structure with temperature. In particular, they still vanish if the positions d_j of the atoms in a cell are determined by the crystal symmetry.

when the suffix j can be omitted, we see that the appropriate coefficient vanishes by (2.23). It represents the change in the harmonic terms caused by a uniform displacement of the lattice.

We are therefore left with case (b) and the equivalent ones obtained by permuting the first three normal modes. Hence

$$\frac{1}{2}\beta^2 U_c^2 = \frac{1}{12} \frac{1}{M^{(N)3}\beta} \sum_{\mathbf{f}, \mathbf{f}', \mathbf{f}''} \sum_{s, s', s''} \frac{|b(\mathbf{f}, s; \mathbf{f}', s'; \mathbf{f}'', s'')|^2}{\omega^2(\mathbf{f}, s)\omega^2(\mathbf{f}', s')\omega^2(\mathbf{f}'', s'')}. \quad (2.47)$$

Strictly speaking, this expression should be corrected for the case when two of the three normal modes in the sum coincide, since we are then concerned with the average of the fourth power of one of the normal coordinates, which is not the same as the square of the mean square. However, the contribution of such terms is of relative magnitude $1/N$, and hence negligible. The contribution to the energy can again be obtained from (2.37) and, neglecting higher-order corrections, yields

$$E_c = \frac{(kT)^2}{12M^{(N)3}} \sum_{\mathbf{f}, \mathbf{f}', \mathbf{f}''} \sum_{s, s', s''} \frac{|b(\mathbf{f}, s; \mathbf{f}', s'; \mathbf{f}'', s'')|^2}{\omega^2(\mathbf{f}, s)\omega^2(\mathbf{f}', s')\omega^2(\mathbf{f}'', s'')}. \quad (2.48)$$

Because of the restriction (2.42), there are 3^3N^2 terms in this sum. When the sum in (2.40) does not vanish, it is proportional to N . Hence, allowing for the mass denominator, (2.48) is proportional to N , as it should be. It is proportional to T^2 , as the simple model led us to expect. One might suspect that the frequency denominators would lead to trouble, since the lowest frequencies are practically zero. However, they belong to the acoustical limit when \mathbf{f} is very small, and in that case the numerator is also small, since we had already seen that then $b(\mathbf{f}, s; \mathbf{f}', s'; \mathbf{f}'', s'')$ vanishes if $\mathbf{f} = 0$; it will also be small if \mathbf{f} is small. The same applies for small \mathbf{f}' and \mathbf{f}'' .

For a better interpretation of the sum (2.48) it is therefore convenient to define a new coefficient \mathbf{b} by

$$\begin{aligned} b(\mathbf{f}, s; \mathbf{f}', s'; \mathbf{f}'', s'') \\ = \omega(\mathbf{f}, s)\omega(\mathbf{f}', s')\omega(\mathbf{f}'', s'')M^{(N)}\Delta(\mathbf{f}+\mathbf{f}'+\mathbf{f}'')\mathbf{b}(\mathbf{f}, s; \mathbf{f}', s'; s''). \end{aligned} \quad (2.49)$$

Here $\Delta(\mathbf{f})$ is a generalized Kronecker symbol for which

$$\Delta(\mathbf{f}) = \begin{cases} 1, & \text{if } \mathbf{f} \text{ is a vector in the reciprocal lattice,} \\ 0, & \text{otherwise.} \end{cases} \quad (2.50)$$

The factor $M^{(N)}$ is inserted to make \mathbf{b} independent of the size of the crystal. \mathbf{b} then approaches a finite limit when any of the frequencies vanishes, and may be supposed to have constant order of magnitude for all arguments.

Then the cubic contribution to the thermal energy becomes finally

$$E_c = \frac{(kT)^2}{12M^{(N)}} \sum_{\mathbf{f}, \mathbf{f}'} \sum_{s, s'} |b(\mathbf{f}, s; \mathbf{f}', s'; s'')|^2. \quad (2.51)$$

For the contribution of the quartic terms, we put these in a form analogous to (2.49)

$$U_q = \frac{1}{24} \sum c(\mathbf{f}, s; \mathbf{f}', s'; \mathbf{f}'', s''; \mathbf{f}''', s''') q_{\mathbf{f}, s} q_{\mathbf{f}', s'} q_{\mathbf{f}'', s''} q_{\mathbf{f}''', s'''} \quad (2.52)$$

Again only those terms contribute to the average for which the normal modes are equal in pairs. They can be grouped in pairs in three ways and we therefore have

$$\beta \bar{U}_q = \frac{1}{8} \sum_{\mathbf{f}, \mathbf{f}'} \sum_{s, s'} \frac{c(\mathbf{f}, s; \mathbf{f}, s; \mathbf{f}', s'; \mathbf{f}', s')}{\{M^{(N)}\}^2 \beta \omega^2(\mathbf{f}, s) \omega^2(\mathbf{f}', s')}. \quad (2.53)$$

We conclude, as before, that $c(\mathbf{f}, s; \dots)$ must vanish if any of its wave vectors tends to zero. Also, its non-vanishing elements will again contain a factor proportional to the size of the crystal. Hence, if we define

$$\begin{aligned} c(\mathbf{f}, s; \mathbf{f}', s'; \mathbf{f}'', s''; \mathbf{f}''', s''') \\ = M^{(N)} \omega(\mathbf{f}, s) \omega(\mathbf{f}', s') \omega(\mathbf{f}'', s'') \omega(\mathbf{f}''', s''') \times \\ \times \Delta(\mathbf{f} + \mathbf{f}' + \mathbf{f}'' + \mathbf{f}''') c(\mathbf{f}, s; \mathbf{f}', s'; \mathbf{f}'', s''; \mathbf{f}''', s'''), \end{aligned} \quad (2.54)$$

the coefficient c will be independent of the crystal size, and roughly constant in order of magnitude.

The contribution of the quartic terms to the thermal energy is now

$$E_q = - \frac{(kT)^2}{8M^{(N)}} \sum_{\mathbf{f}, \mathbf{f}'} \sum_{s, s'} c(\mathbf{f}, s; -\mathbf{f}, s; -\mathbf{f}', s'; \mathbf{f}', s'), \quad (2.55)$$

which again has the same temperature dependence as (2.51). One can also show that the two contributions are of the same order of magnitude.

These expressions could easily be generalized to their quantum-mechanical form, but this is not worth while since they are of no interest at low temperatures.

The results (2.51) and (2.55) represent the correction to the Dulong-Petit value of the specific heat if the volume of the crystal is kept constant at the equilibrium value. In actual fact, the crystal will expand as the temperature increases. This will result in a further correction term, which can be calculated from the thermal expansion coefficient and the elastic constants by using purely thermodynamic arguments. I shall not give this calculation here.

2.4. Thermal conductivity

We have seen that the thermal energy of the crystal consists of waves which travel with velocities of the order of sound velocity. They are therefore also capable of transporting energy. Using the familiar argument of the kinetic theory of gases, we may write the dimensional formula

$$\kappa = \gamma C c \lambda, \quad (2.56)$$

where κ is the heat conductivity, C the specific heat per unit volume, c the velocity of sound, λ a mean free path, and γ a numerical factor.

In the harmonic approximation the waves travel freely without attenuation, and therefore have an unlimited free path. In reality their free path is limited by (a) the anharmonic terms, (b) impurities and imperfections in the crystal, and (c) the finite dimensions of the crystal. We shall for the present consider only the first effect, which is dominant in good and pure crystals of not too small size at not too low temperatures.

For this problem we shall use quantum mechanics at once, since the case of low temperatures is of interest. The classical result will, of course, also come out as a limit. We must now regard the cubic part of the energy as a perturbation, and we may take it in the form (2.39). Since we found the most convenient variables for the quantum treatment to be the Q introduced by (1.32), we write

$$U_c = \frac{1}{6} \sum_{i, f, f''} \sum_{\sigma, \sigma', \sigma''} b(f, \sigma; f', \sigma'; f'', \sigma'') Q(f, \sigma) Q(f', \sigma') Q(f'', \sigma''), \quad (2.57)$$

where the sums over σ now cover positive and negative values.

Now we consider (2.57) as a small perturbation which causes transitions between the states of the unperturbed system. The general relation giving the transition probability per unit time from some initial state i to a final state f is†

$$\frac{dP_{if}}{dt} = \frac{2\pi}{\hbar} |(i|U_c|f)|^2 \delta(E_f - E_i). \quad (2.58)$$

Here δ is the Dirac delta-function, E_i , E_f are the energy values of initial and final state respectively, and $(i|U_c|f)$ is the matrix element of (2.57) between the two states. Now we have seen in (1.63) that, for positive σ , Q has matrix elements only corresponding to an increase of the corresponding quantum number by 1, for negative σ to a decrease. Each term in (2.57) therefore describes a process in which three quantum numbers each change by one unit. The corresponding change of energy is

$$\hbar\{\omega(f, \sigma) + \omega(f', \sigma') + \omega(f'', \sigma'')\}, \quad (2.59)$$

† See, for example, Schiff (1949), section 29.

and for the process to be possible according to (2.58) this must vanish. Since the sign of $\omega(\mathbf{f}, \sigma)$ is the sign of σ , it is clear that $\sigma, \sigma', \sigma''$ cannot be all positive or all negative. The actual process therefore involves either two positive and one negative, or vice versa, which means either the destruction of two phonons and the creation of a new one, or vice versa. Hence the process in which two phonons \mathbf{f}, \mathbf{s} and \mathbf{f}', \mathbf{s}' are combined into a single $\mathbf{f}'', \mathbf{s}''$ has the probability (allowing for permutations in (2.57))

$$|b(\mathbf{f}, \mathbf{s}; \mathbf{f}', \mathbf{s}'; -\mathbf{f}'', \mathbf{s}'')|^2 \frac{2\pi\hbar N(\mathbf{f}, \mathbf{s})N(\mathbf{f}', \mathbf{s}')\{N(\mathbf{f}'', \mathbf{s}'') + 1\}}{8\{M^{(N)}\}^3 \omega(\mathbf{f}, \mathbf{s})\omega(\mathbf{f}', \mathbf{s}')\omega(\mathbf{f}'', \mathbf{s}'')} \times \\ \times \delta\{\omega(\mathbf{f}, \mathbf{s}) + \omega(\mathbf{f}', \mathbf{s}') - \omega(\mathbf{f}'', \mathbf{s}'')\}. \quad (2.60)$$

The δ -function vanishes unless

$$\omega(\mathbf{f}, \mathbf{s}) + \omega(\mathbf{f}', \mathbf{s}') - \omega(\mathbf{f}'', \mathbf{s}'') = 0, \quad (2.61)$$

and by (2.42) the first factor vanishes unless also

$$\mathbf{f} + \mathbf{f}' - \mathbf{f}'' = \mathbf{K}, \quad (2.62)$$

where \mathbf{K} again stands for a lattice vector of the reciprocal lattice.

The first of these conditions expresses the conservation of energy in the collision between phonons. The second is similar to conservation of momentum. Indeed, if we were dealing with a continuous medium instead of a crystal, the only possible value of \mathbf{K} on the right-hand side of (2.62) would be zero, and in a continuous medium the momentum of a phonon of wave vector \mathbf{f} is $\hbar\mathbf{f}$. However, this analogy must not be taken too seriously, since for the normal vibrations which we have derived the total momentum certainly vanishes (except for the rather degenerate case $\mathbf{f} \simeq 0$).

With our convention, which restricts the \mathbf{f} values to the basic cell of the reciprocal lattice, there exists for given \mathbf{f} and \mathbf{f}' always just one value of \mathbf{f}'' which satisfies (2.62); whether the \mathbf{K} on the right is a finite reciprocal lattice vector or zero will depend on the choice of \mathbf{f} and \mathbf{f}' .

Processes for which $\mathbf{K} \neq 0$ in (2.62) are called 'Umklappprozesse' in the German literature. A typical example is the case when \mathbf{f} is a wave travelling in the $+x$ direction, almost at the edge of the basic cell, i.e. with a wavelength such that adjacent atoms move with almost the same phase in opposite directions. The wave \mathbf{f}' which interacts with it has a very small wave vector, also in the $+x$ -direction, but enough to bring the sum beyond the edge of the basic cell, so that it is equivalent to a vector near the left-hand face of the cell, \mathbf{K} being in that case the smallest non-zero reciprocal lattice vector in the x -direction.

It will be clear from this example that physically there is no important difference between processes in which the sum $\mathbf{f} + \mathbf{f}'$ just remains within the basic cell, and those in which it falls just outside and has to be brought back by adding a suitable \mathbf{K} , and indeed the distinction between the two depends on our convention in choosing the basic cell. What matters, however, is whether or not we can find a convention with which (2.62) would always hold with $\mathbf{K} = 0$.

Indeed, let us assume for the moment that the 'Umklapp' processes could be excluded and that we were allowed to put $\mathbf{K} = 0$ in (2.62). Then it is obvious that the sum of the wave vectors would not change in the process we have specified, and that therefore the quantity

$$\mathbf{J} = \sum_{\mathbf{f}} \sum_s \mathbf{f} N(\mathbf{f}, s) \quad (2.63)$$

would be conserved in these collisions. Hence the collisions would be incapable of establishing complete statistical equilibrium if once $\mathbf{J} \neq 0$. Rather they will make the system approach the most probable state which is compatible with a given \mathbf{J} . (The statistical problem is similar to that of collisions between the molecules of a gas in an infinitely long straight frictionless tube if the average velocity is non-zero.) Now a resultant \mathbf{J} in the positive x -direction means that the phonons in the positive x -direction will be more numerous than those travelling in the opposite direction, and this asymmetry will lead to a non-vanishing energy transport. In other words, in this hypothetical case a finite energy transport can persist without a temperature gradient to maintain it, and this implies an infinite thermal conductivity.

It follows, therefore, that the solutions of (2.61), (2.62) with $\mathbf{K} \neq 0$ are of vital importance for the thermal resistance.

The consequences of this conclusion are particularly obvious at very low temperatures ($T \ll \Theta$). In that case most of the phonons which make up the thermal motion of the crystal are long-wave ones, and for the interaction of long-wave phonons \mathbf{K} will vanish in (2.62). If the smallest non-zero value of \mathbf{K} is of magnitude K_0 , then $\mathbf{f} + \mathbf{f}'$ must in magnitude exceed $\frac{1}{2}K_0$, if the addition of a lattice vector is to lead to a reduction. Hence either \mathbf{f} or \mathbf{f}' must exceed $\frac{1}{4}K_0$ in magnitude. We can thus give a lower limit to the frequency of the phonons that must be present to make an Umklapp process possible. At low temperatures the number $N(\mathbf{f}, s)$ of such phonons is small, and hence the magnitude of the expression (2.60) is governed by the factors $N(\mathbf{f}, s)$, $N(\mathbf{f}', s')$ which will diminish exponentially with temperature if one of the frequencies is kept above a fixed limit. We see therefore that the rate at which

Umklapp processes take place diminishes with temperature as

$$e^{-\gamma\theta/T}, \quad (2.64)$$

where γ is some numerical factor less than 1. Since in the absence of such processes there is no thermal resistance, the thermal resistance itself must be proportional to (2.64). This conclusion is confirmed by experiments at Oxford.†

It is evident that this result is not altered if we consider also the reverse process, in which one phonon splits in two, since this will produce a non-vanishing K in (2.62) only if the frequency of the initial phonon, in this case $\omega(\mathbf{f}'', \mathbf{s}'')$, is high enough.

It is equally clear that the situation is not substantially changed if we include the quartic terms in the potential. These will give rise to four-phonon processes. Either two phonons collide and change into two new ones, or three merge into one, or lastly one splits into three. In each case we find conservation laws as above, and we find that the total wave vector (2.63) is conserved except for processes which require the initial presence of at least one high-energy phonon. However, if one were to attempt a closer estimate of the factor in (2.64), one would have to decide whether for this purpose the cubic or the quartic terms are dominant.

For a further understanding of the interactions between phonons it is obviously important to consider the conservation laws (2.61) and (2.62) to see the nature of the solutions which they admit. We shall carry out this discussion for a lattice with one atom per unit cell, for which there are then just three frequencies for any given \mathbf{f} . Consider, for further simplification, the case in which $\mathbf{f}, \mathbf{f}', \mathbf{f}''$ are all parallel to a main axis of the crystal. Then two of the normal modes will in each case be transverse and belong to the same frequency, the third will be longitudinal and have a higher frequency. The frequencies will be represented by curves of the shape of the full lines in Fig. 1. Then we may imagine the solutions of (2.61) and (2.62) constructed graphically as follows: Mark on the full line the point \mathbf{f} , belonging to one of the initial phonons, and then draw the frequency curves again, with that point as origin (broken lines), continuing them periodically as necessary; then their intersections with the original full lines give the required solution. The abscissa and ordinate of the intersection give \mathbf{f}'' and ω'' , whereas the horizontal and vertical distances of the intersection from the origin of the broken curves give \mathbf{f}' and ω' . If by this construction \mathbf{f}' falls outside the basic cell, it has to be reduced in the usual way, and we are then dealing with an Umklapp process. These quantities have been labelled in Fig. 1

† Cf. Berman (1951), (1953).

for one particular intersection, in which two transverse phonons combine to make up a longitudinal one. The figure also shows inter-

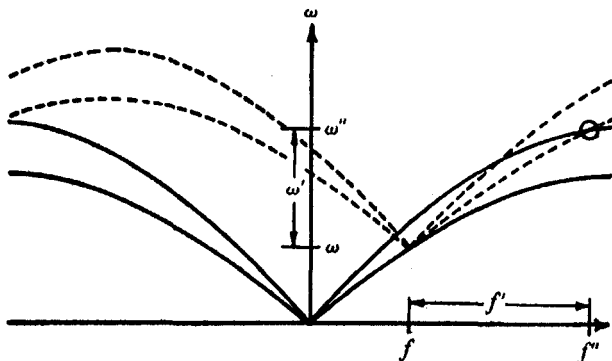


FIG. 1.

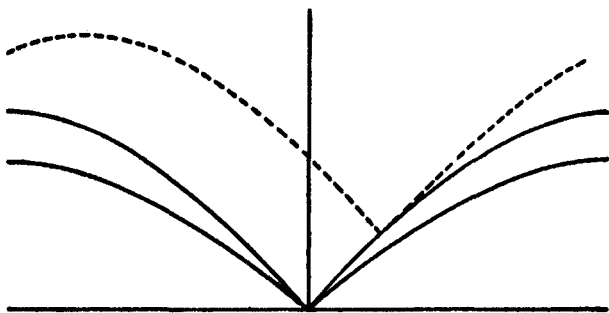


FIG. 2.

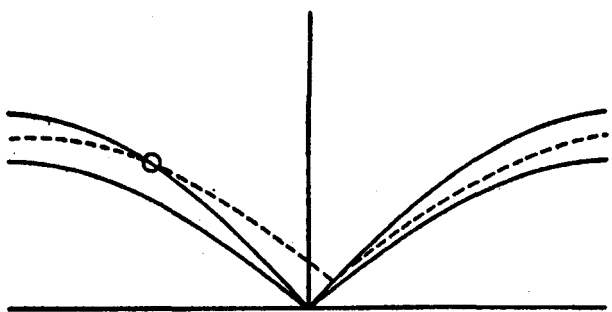


FIG. 3.

sections corresponding to one transverse and one longitudinal phonon combining into a longitudinal one. The same construction for two initial longitudinal quanta is shown in Fig. 2, and no solutions are obtained in this case. Fig. 3 shows that, if f is in particular very small (long waves)

and s longitudinal, then the only possible process is a collision with a transverse phonon of comparable wavelength.

All these arguments hold only for the very special direction of the three wave vectors. By imagining the figures extended first into two and then into three dimensions, it is, however, easy to see that, if we denote by $s = 1, 2, 3$ frequencies for given f in increasing order of magnitude, the following statements are still correct: no solution exists for which all phonons belong to the same s , or for the case

$$(3) + (3) \rightarrow \begin{cases} (1); \\ (2) \end{cases}$$

possible processes are

$$\begin{array}{lll} (1) + (1) \rightarrow (2), & (1) + (1) \rightarrow (3), & (1) + (2) \rightarrow (2), \\ (1) + (2) \rightarrow (3), & (1) + (3) \rightarrow (3), & (2) + (3) \rightarrow (3). \end{array}$$

In each of these cases we may give one of the initial phonons arbitrarily, and then find a surface on which the second wave vector must end. It is again true that, if in the last two cases we make the wavelength for $s = 3$ very long, the colliding phonon must have a wavelength of the same order.

2.5. Boltzmann equation

We shall now derive the integral equation whose solution would give a quantitative expression for the thermal conductivity, even though we shall not succeed in solving it. This seems worth while because it is possible to draw some qualitative conclusions, and also because it is of some interest to see the nature of the difficulties which stand in the way of a complete solution.

In order to describe heat conduction we must be able to describe a state of affairs in which the temperature is different at different points in space. For this purpose we should not use exact normal coordinates as we have done so far, but rather combinations of them in the form of wave packets, such that each belongs to a small spread δf of the wave vector, and is localized in space in a region of size δx . We have from the uncertainty principle

$$\delta f_x \delta x \sim 1, \quad (2.65)$$

and similarly for the other components. This means, of course, that we are considering vibrations which are not strictly normal modes, or quantum states which are not strictly stationary. The first effect of this is that each of these wave packets is going to travel with the appropriate group velocity, and this we shall, of course, take into account. Furthermore,

the energy of such a wave is not sharply defined, so that we must admit a slight spread in equation (2.61) if the frequencies in that equation are taken to be the mean values for each wave packet. However, this will make no difference in the results if all other energy-dependent factors in the equations are practically constant over the region of this uncertainty. Now in thermal equilibrium, or in the slight deviations from equilibrium that correspond to a reasonable heat flow, the excitation numbers of various phonon states change appreciably only over energy changes of the order of kT . Hence the use of wave packets causes no complication provided

$$kT > \delta E = \hbar \frac{\partial \omega}{\partial f} \delta f = \hbar v \delta f,$$

where v is the group velocity. Inserting for δf from (2.65), the condition becomes

$$\delta l > \frac{\hbar v}{kT} \sim \frac{\Theta}{T} a, \quad (2.66)$$

where in the last estimate we have replaced the group velocity by the sound velocity, and identified the length $1/f_0$ which enters in the definition of the Debye temperature with the lattice constant a . It is therefore sufficient to assume that the temperature should not vary appreciably over distances of the order (2.66), which is evidently a very mild restriction on the temperature gradient. In any case the coefficient of thermal conductivity refers by definition to an infinitesimal gradient; but (2.66) shows that there is no reason to expect in practice any dependence on the magnitude of the gradient from this cause.

We then regard the number of phonons as a function of their wave vector and polarization as well as of the space coordinates, and we formulate the condition for this distribution function to remain stationary. It is subject to change for two reasons: one is the motion of the phonons, carrying energy from the high-temperature to the low-temperature regions, the other is the effect of the collisions between phonons which we have just discussed. The probability of such collisions is given by (2.60), and to work out the average effect of this we should really require to know the average value of products of three occupation numbers, which may be replaced by the product of the averages only in the absence of correlations. In fact, if we assume that the numbers of phonons in different states are initially uncorrelated and then consider their rate of change by (2.60), we find that at a later instant there will be correlations between the numbers for those states between which collisions may have occurred. This is analogous to the situation in the kinetic

theory of gases where one can show that after a collision the distribution in phase space of the molecules which have just collided will show correlations. This point is then dealt with by remarking that it is most unlikely that the same pair of molecules will collide again before each of them has made many collisions with others, and that it is therefore reasonable to suppose the properties of any two molecules which do collide to be uncorrelated.

The same argument can be taken over in our case, provided conditions are such that we are dealing with large numbers of phonons, so that the chance of the same individual phonons colliding several times in succession is negligible.

There is one further condition to be satisfied before we can write an equation for the mean occupation numbers. This is that the occupation numbers should contain all the information that is obtainable about the system, and that there should be no phase relations between states with different phonon numbers. In terms of the concept of a statistical density matrix this means that the density matrix should be diagonal in the phonon numbers. I shall not here give a formal argument that this is a consistent assumption, i.e. that, inserting a diagonal density matrix for the initial state, we shall find it diagonal at later times, using only the assumption that we are dealing with large numbers of phonons, which we have used already. I want to point out, however, that this statement can be true only if we have chosen variables which are appropriate to the problem. For example, we might have chosen standing waves (sine and cosine waves) instead of the progressive waves which occurred in our definition of the normal modes. In that case a state in which there is an energy transport can be specified only by phase relations between the sine and cosine waves. If we simply omitted all phase relations, and hence all non-diagonal elements in all equations, we should come to the conclusion that a temperature gradient has no tendency to produce an energy flow, which would be patently incorrect. At the same time we should also be unable to recognize the importance of the total wave vector (2.63) whose average value for standing waves is, of course, zero, so that it would again depend on phase relations between different standing waves.

After these remarks we consider the number $N(\mathbf{f}, s, \mathbf{r})$ of phonons in the wave packet of wave vector \mathbf{f} , polarization s , and located at \mathbf{r} . Then its rate of change due to the motion of the phonons is

$$-\frac{\partial N}{\partial x} v_x$$

if the gradient is in the x -direction. Here v_x is the x -component of the group velocity, which equals $\partial\omega(\mathbf{f}, s)/\partial f_x$.

In computing the change due to collisions, we note that (2.60) is independent of the size of the crystal, so that we may retain its exact form even though we are now thinking of localized wave packets, which is equivalent to considering a smaller crystal. Indeed, the rate of change of $N(\mathbf{f}, s)$ by the process specified in (2.60) may be written, using (2.49),

$$-\frac{\pi\hbar}{4M^{(N)}} \sum_{\mathbf{f}'} \sum_{s', s''} |\mathbf{b}(\mathbf{f}, s; \mathbf{f}', s'; s'')|^2 \omega \omega' \omega'' \delta(\omega + \omega' - \omega'') N N' (N'' + 1). \quad (2.67)$$

Here we have written for brevity $\omega, \omega', \omega''$ in place of $\omega(\mathbf{f}, s), \omega(\mathbf{f}', s'), \omega(\mathbf{f}'', s'')$ respectively, and N, N', N'' for $N(\mathbf{f}, s), N(\mathbf{f}', s'), N(\mathbf{f}'', s'')$. We have also assumed that \mathbf{f}'' is the solution of (2.62) for given \mathbf{f} and \mathbf{f}' . The summation over \mathbf{f}' may now be replaced by an integration. We have seen earlier (§ 1.6) that there are $V/(2\pi)^3$ permissible values of \mathbf{f} per unit volume in f space, if V is the volume of the crystal. Since this is related to the total mass by $M^{(N)} = \rho V$, where ρ is the density, we have finally for (2.67)

$$-\frac{\hbar}{32\pi^2\rho} \sum_{s', s''} \int d^3\mathbf{f}' |\mathbf{b}(\mathbf{f}, s; \mathbf{f}', s'; s'')|^2 \omega \omega' \omega'' \delta(\omega + \omega' - \omega'') N N' (N'' + 1), \quad (2.68)$$

which is now indeed independent of the size. In addition to this process we have to take into account the inverse (a phonon with wave vector \mathbf{f}'' splits into those with \mathbf{f} and \mathbf{f}'), and also the process in which the phonon under consideration, \mathbf{f} , splits into two others or vice versa. Combining these four processes and the phonon motion, we have finally for the total rate of change of $N(\mathbf{f}, s)$

$$\begin{aligned} & -\frac{\partial N}{\partial x} \frac{\partial \omega}{\partial f_x} + \frac{\hbar}{32\pi^2\rho} \int d^3\mathbf{f}' \left[\sum_{s', s''} |\mathbf{b}(\mathbf{f}, s; \mathbf{f}', s'; s'')|^2 \times \right. \\ & \quad \times \omega \omega' \omega'' \delta(\omega + \omega' - \omega'') \{ (N+1)(N'+1)N'' - N N' (N''+1) \} + \\ & \quad + \sum_{s', s''} \frac{1}{2} |\mathbf{b}(\mathbf{f}, s; \mathbf{f}', s'; s'')|^2 \omega \omega' \omega'' \delta(\omega - \omega' - \omega'') \times \\ & \quad \times \{ (N+1)N'N'' - N(N'+1)(N''+1) \} \left. \right]. \quad (2.69) \end{aligned}$$

Here it is again understood that \mathbf{f}'' stands for the solution of (2.62) and correspondingly \mathbf{f}''' is the solution of

$$\mathbf{f} - \mathbf{f}' - \mathbf{f}''' = \mathbf{K}. \quad (2.70)$$

We now assume, to define the heat conduction problem, that

$$N(\mathbf{f}, s, x) = N^0(\mathbf{f}, s, T) + N^1(\mathbf{f}, s), \quad (2.71)$$

where N^0 is the mean phonon number for thermal equilibrium (eq. 2.4), i.e.

$$N^0 = \frac{1}{e^{\beta\hbar\omega} - 1}. \quad (2.72)$$

One easily verifies that

$$\frac{\partial N^0}{\partial T} = N^0(N^0 + 1) \frac{\hbar\omega}{kT^2}. \quad (2.73)$$

When inserting (2.71) in (2.69), we can neglect N^1 in the transport term, since this would otherwise give terms of second order in the temperature gradient. In the collision terms one verifies immediately that N^0 by itself gives no contribution (thus confirming that in the absence of a temperature gradient N^0 represents a stationary distribution) and we expect therefore in the collision terms contributions of at least the first order in N^1 . Hence N^1 will be proportional to the temperature gradient, and we shall neglect its square. Lastly it is convenient to take out of N^1 a factor similar to that occurring in (2.73),

$$N^1(\mathbf{f}, s) = N^0(\mathbf{f}, s) \{N^0(\mathbf{f}, s) + 1\} g(\mathbf{f}, s). \quad (2.74)$$

Then, using the identity

$$N^0(\mathbf{f}, s) N^0(\mathbf{f}', s') \{N^0(\mathbf{f}'', s'') + 1\} = \{N^0(\mathbf{f}, s) + 1\} \{N^0(\mathbf{f}', s') + 1\} N^0(\mathbf{f}'', s'') \quad (2.75)$$

if

$$\omega(\mathbf{f}, s) + \omega(\mathbf{f}', s') = \omega(\mathbf{f}'', s''),$$

and omitting the superscript 0 since now all phonon numbers refer to equilibrium, we have finally the 'Boltzmann equation'

$$\begin{aligned} N(N+1) \frac{\hbar\omega}{kT^2} \frac{\partial \omega}{\partial f_x} \frac{\partial T}{\partial x} &= \frac{\hbar}{32\pi^2\rho} \int d^3\mathbf{f}' \left\{ \sum_{s', s''} |\mathbf{b}(\mathbf{f}, s; \mathbf{f}', s'; s'')|^2 \times \right. \\ &\quad \times \omega\omega'\omega'' \delta(\omega + \omega' - \omega'') (N+1)(N'+1)N''(g'' - g - g') + \\ &\quad + \sum_{s', s''} \frac{1}{2} |\mathbf{b}(\mathbf{f}, s; \mathbf{f}', s'; s''')|^2 \omega\omega'\omega''' \delta(\omega - \omega' - \omega''') \times \\ &\quad \left. \times (N+1)N'N'''(g' + g''' - g) \right\} \quad (2.76) \end{aligned}$$

as the condition that the phonon distribution be stationary.

In this form it is obvious that, in the absence of a temperature gradient, the equation admits the solution

$$g(\mathbf{f}, s) = \text{constant} \times \omega(\mathbf{f}, s), \quad (2.77)$$

since with this value of g the brackets in (2.76) vanish by virtue of the properties of the δ -functions. This has a very simple physical meaning, since it is easy to see that inserting from (2.77) in (2.74) this yields an

expression proportional to (2.73) and thus represents simply an infinitesimal change of temperature. Evidently (2.72) must lead to a stationary distribution whatever the temperature. Now in general an inhomogeneous equation of the type (2.76) will be soluble only if the inhomogeneous part is orthogonal to all solutions of the corresponding homogeneous equation. This is all right for the solution (2.77) since this is even in its directional dependence, i.e. it does not change if we replace f_x by $-f_x$, whereas the left-hand side of (2.76) is odd. In other words, the temperature gradient has no tendency either to increase or to decrease the temperature at any given point.

If we were to omit the Umklapp processes, then the homogeneous equation would admit the further solution

$$g(\mathbf{f}, s) = \text{constant} \times f_x, \quad (2.78)$$

and this would not be orthogonal to the left-hand side.

This fact could be made the basis of a method of solving the equation for low temperatures, if the dispersion law was known with sufficient accuracy to determine the solutions of (2.61) and (2.62) in practice. We could then note that at low temperatures Umklapp collisions are rare, most collisions being of the kind which preserves the distribution (2.78). It is therefore reasonable to suppose that the actual distribution is given by (2.78) with a small correction, smaller in the ratio of Umklapp to ordinary processes. Then we can find the factor in (2.78) by multiplying (2.76) by f_x and summing over all \mathbf{f} and s . In other words, we compute the rate of change of J_x . On the right-hand side, then, only the Umklapp processes matter, and we may then neglect the deviation of the distribution from (2.78) as small of higher order. Then the right-hand side is known except for the constant, and the equation thus determines the constant in (2.78) and through it the energy transport. However, by writing all this down we should only confirm the result (2.64) which we have already derived by intuitive arguments; we should not be able to make it more quantitative without a much more extensive study of the dispersion law.

2.6. High temperatures

If we are in the region where classical mechanics is valid, $T > \Theta$, then all the phonon numbers occurring in (2.76) will be large, so that $N+1$ may be replaced by N , and they are all proportional to the temperature. Collecting the temperature factors in the equation, it is then easy to see that, for a given temperature gradient, g must be proportional to T^{-3} . Going back to (2.74) this makes the change in the

mean phonon number N^1 proportional to $1/T$, and therefore we expect an energy transport, and thermal conductivity, proportional to $1/T$. This law is usually stated to be in agreement with the behaviour of most crystals at high temperatures.

Its theoretical validity has been called in question by Pomeranchuk (1942). His reasoning starts from the fact, which we have already noted, that long-wave longitudinal phonons (or more precisely phonons with $s = 3$) occur only in collisions in which the other phonons have comparable wavelength. Now consider the Boltzmann equation (2.76) for the particular case $s = 3$, and very small f . Then the left-hand side is proportional to f^{-1} . Since f' is also of order f , the integration over f' covers a volume of order f^3 . However, the δ -function allows only a surface within this volume, which has an area proportional to f^2 . The phonon numbers are inversely proportional to the frequencies and therefore cancel the frequency factors. The coefficient b had been found constant for small frequencies. Hence the right-hand side is proportional to f^2 times some average value of g , averaged over arguments of the order f . The equation therefore requires that g be of the order of f^{-3} for small f . This makes N^1 in (2.74) proportional to f^{-5} , and hence the energy transport

$$\frac{V}{(2\pi)^3} \sum_s N^1 \hbar \omega \frac{d\omega}{df} f^2 df d\Omega$$

diverges for small f as $\int f^{-2} df$. Hence an exact solution of (2.76) would lead to an infinite thermal conductivity. Pomeranchuk also points out that the long waves will be much more strongly damped by the effect of the quartic terms, which involve four-phonon processes. In that case the collision of a long-wave with a short-wave phonon of any kind of polarization is always possible, and therefore the difficulty does not arise. However, the terms due to four-phonon processes contain an extra power of T , and if they alone were present the thermal conductivity would be proportional to T^{-2} . In actual fact we must assume that the cubic terms in (2.76) are the dominant ones, and that the quartic ones will come in only for the purpose of limiting the movement of the long-wave phonons. The temperature law should therefore be some compromise between $1/T$ and $1/T^2$. Pomeranchuk gives an argument which leads to a T^{-1} law, but, since this is based on the concept of mean free path, which is not really applicable in these circumstances, one cannot regard this conclusion as established. The only prediction that would seem to follow with certainty is that the law must be intermediate between T^{-1} and T^{-2} .

This seems a poor return for a long discussion, but progress beyond this stage is difficult, unless we could construct a dispersion law which was simple enough to allow us to list the solutions for the possible phonon collisions explicitly, and yet realistic enough to give the right kind of collisions including those of the Umklapp type.

2.7. Impurities and size effect

So far our discussion has been concerned with ideal crystals. If the lattice is disturbed by impurities or by imperfections in the growth of the crystal, these will also scatter phonons. Since in this case the scattering centres are present no matter what the temperature, the scattering probability of phonons of a given wave vector and polarization is independent of the temperature. At high temperatures, when the spectral distribution of phonons is fixed, and when the specific heat is constant, such imperfections therefore contribute an additional resistance which is independent of the temperature. The situation is more complicated at low temperatures when we are dealing with phonons of longer and longer wavelength. In that case the temperature variation depends on the variation of the scattering cross-section with wavelength. If the imperfections are small, perhaps single misplaced atoms, they will scatter long waves very inefficiently. They may, in fact, not be sufficient by themselves to give a finite resistance because, as in the case discussed in the preceding section, the long-wave phonons retain too great a mobility. Nevertheless, they may have a large effect on the resistance at low temperatures, if they can cause a sufficiently rapid change in the total wave vector \mathbf{J} , so as to make the Umklapp processes unnecessary. In such cases the thermal resistance is again the combined result of several different types of collisions, and any discussion of experimental results becomes accordingly very complex (cf., for example, the paper by Klemens (1951), whose use of the concept of relaxation time is not, however, very convincing).

A further point of interest can be seen by comparing the crude formula (2.56) with a result like (2.64). At low temperatures the conductivity increases rapidly, in spite of the decrease in the specific heat. It follows that the mean free path of the phonons must become very large.

For example, the thermal conductivity of pure KCl at 4° K. is of the order of 1 cal./sec. deg. cm. Since the specific heat at that temperature is about 10^4 cal./deg. cm.³ and the sound velocity about $6 \cdot 10^5$ cm./sec., the effective mean free path must be of the order of 10^{-1} cm. It is evident, therefore, that the size of the crystal actually used and the

condition of its surface are of great importance in the interpretation of the experiments. Experiments by de Haas and Biermasz (1935) and their analysis by Casimir (1938) have indeed verified this dependence on the size of the specimen.

Here again the problem is complicated by the fact that, even when the specimen is much smaller than the mean free path estimated from the crude relation (2.56), this does not mean that the collisions between phonons are completely negligible. The reason is that we have found the thermal resistance to be dependent on the rare Umklapp processes. In the circumstances specified we can therefore merely be sure that a phonon has a small probability of undergoing an Umklapp process on crossing the specimen once, but it may make many collisions in which the wave vector is conserved; these by themselves would not be sufficient to produce a finite resistance, but they may affect the phonon distribution. Hence it is in general necessary to discuss the effect of boundary scattering jointly with that of collisions between phonons. An attempt to do this has been made in the paper by Klemens to which I have already referred, but much remains to be done.

Lastly, it should be mentioned that the collisions between phonons which we have discussed in the last few sections are also responsible for the damping of sound waves in perfect crystals. This has been discussed by Slonimsky (1937). It would take us too far, however, to enter into details of this problem. As far as I am aware, there exist no experiments with which to compare this theory.

Note added in proof

The expansion of the potential energy in powers of the displacements might appear questionable in the case of displacements like (2.20), in which atoms far from the origin are necessarily displaced by an amount much larger than the lattice spacing. However, the potential energy is really a function of the distances between the atoms (hence the identities (1.22) and (2.23)), and the expansion is therefore valid provided the distance between any two atoms changes only by a small fraction. This is compatible with (2.20) provided ϵ is a small number.

Note added January 1956

C. Herring (*Phys. Rev.* **95**, 954, 1954) has shown that the frequency curves in a general direction in the lattice are sufficiently different from those shown in Figs. 1–3 to allow in most cases collisions of a long wave longitudinal phonon with other short wave phonons, and hence the arguments of section 2.6 do in fact give a $1/T$ law for most crystals.