Normal Vibrations of a Crystal Lattice

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SINCE the work of Debye[1] in 1912, the theory of the specific heat of solids has often been regarded as at least qualitatively satisfactory. This was in spite of the obviously crude approximations to the more exact treatment indicated by Born and von Karman.[2] Since, however, the available measurements did not, in most cases, extend to extremely low temperatures, and since the elastic constants were not too precisely known, the approximations of Debye were regarded as adequate. Within the last 15 years, however, more exact measurements of specific heats at very low temperatures have called attention to the fact that the Debye approximation is really very rough, and that it should be possible to make a more precise calculation in terms of the known elastic constants. Furthermore, the desire to understand the behavior of electrons in metals, and, in particular, their behavior at the superconducting transition point, had led to a revival of interest in this problem, and to the attempt to distinguish the specific heat associated with the lattice from the specific heat that must be due to the electrons.[3]

In 1935 Blackman[4] began a series of papers analyzing the vibrations of real and idealized lattices of various kinds. He pointed out that the Debye approximation can be valid at most in only a relatively small region. He further showed that there probably exist frequencies at which normal vibrations accumulate to such an extent as to suggest that the original hypothesis of Einstein,[5] as extended by Nernst and Lindemann,[6] might be almost as good an approximation as that of Debye. Since the general analysis seemed to be difficult and not too certain, detailed treatments of special cases appeared to offer a means of further progress, and in 1939 Fine[7] published calculations of the vibration frequencies of a body-centered cubic lattice, using simplified assumptions as to the force constants. By a laborious numerical procedure, he was able to calculate the frequency distribution and the specific heat, and to show moderate agreement with the experimental values for tungsten. More recently Leighton[8] has made a similar calculation, using a mechanical method of interpolation, and has determined the frequency spectrum and specific heat for a face-centered cubic lattice with suitable elastic constants. These results reproduce some of the major features of the specific heat curve for silver.

In 1941, Montroll[9] described a very elegant method of expanding the frequency distribution in terms of Legendre polynomials. This method would, in principle, give the exact frequency distribution if carried far enough. It appears, however, that its convergence is not very good without an almost impossible amount of labor, so that the attainable results are probably less accurate than those obtained by the numerical methods of Fine and Leighton. Since it appears that progress in this field will be aided by some detailed knowledge of actual or idealized frequency distributions, it is the purpose of this paper to describe a numerical procedure which appears to give valuable results with a reasonable amount of effort. Furthermore, it can be carried to any desired degree of precision.

The secular equation for the vibration frequencies of a crystal lattice can always be reduced to an equation of the $3N$th order in the square of the frequencies. Here N is the number

[1] P. Debye, Ann. d. Physik **39**, 789 (1912).
[2] M. Born and Th. von Karman, Physik. Zeits. **13**, 297 (1912); **14**, 15 (1913).
[3] A good outline of the historical development is given by M. Blackman, "Reports on Progress in Physics," Physical Society (London) **8**, 11 (1941).
[4] M. Blackman, Proc. Roy. Soc. **A148**, 365 (1935); **A148**, 384 (1935); **A149**, 117 (1935); **A149**, 126 (1935); **A159**, 416 (1937).
[5] A. Einstein, Ann. d. Physik **22**, 180 (1906); **34**, 170 (1911).
[6] W. Nernst and F. Lindemann, Zeits. f. Elektrochemie **17**, 817 (1911).
[7] P. C. Fine, Phys. Rev. **56**, 355 (1939).
[8] R. C. Leighton, Thesis, California Institute of Technology, June 1947.
[9] E. W. Montroll *et al.*, J. Chem. Phys. **10**, 218 (1942); **11**, 481 (1943).

of different atoms in a lattice cell. For a monatomic lattice this is a cubic equation, giving the frequencies of vibration in terms of the propagation vectors of the standing waves in question. The different propagation vectors fill uniformly the space in a Brillouin zone of the reciprocal lattice. Hence, the problem is to solve this cubic equation to find the frequency as a function of the coordinates inside this zone. The equation can always be solved, at least numerically, for a specified point. Solving the equation for enough points to give a frequency distribution is what requires so much labor.

Along any one radius vector from the center in the reciprocal lattice the frequency is a function of the distance only. If the cubic equation is solved along this particular line, the solution can be inverted to give the distance from the origin to the point at which the frequency has any assigned value. The quantity $r^2(dr/d\nu)d\nu$ will then give the number of points, per unit solid angle in the propagation vector space, whose vibration frequencies lie between ν and $\nu+d\nu$, and which are close to the line along which the equation has been solved. One can imagine a narrow cone along this line, and a function $F(\nu)$, which gives the distribution of frequencies in this particular direction. If the secular equation can be solved along a large number of such lines, the sum of the resulting distributions will be the desired frequency distribution. The closer together the lines are taken, the more accurate will be the result.

In order to approximate the desired result without an indefinite amount of labor, use may be made of the symmetry of the problem. The frequency as a function of the distance from the center, as well as the function $F(\nu)$, will be invariant to those rotations under which the crystal lattice itself is invariant. Hence, it is necessary to study the distribution in only a small portion of the whole solid angle, and in the case of the cubic lattice only 1/48 of the solid angle need be covered.

The function $F(\nu)$ along a line defined by the angles ϑ and φ may be expressed as a series of functions, each multiplied by a spherical harmonic.

$$F(\nu, \vartheta, \varphi)=\sum_i f_i(\nu)\, Y_i(\vartheta, \varphi). \tag{1}$$

The only harmonics Y_i that need be used are those with the symmetry of the lattice, that is, those which are invariant under the group of transformations to which the crystal lattice is invariant. The series in Eq. (1) can be carried as far as is desired, but it would appear that by a proper selection of the lines used to determine the functions $f_i(\nu)$, a small number, such as three or six, will already give a good approximation.

If the different directions along which the secular equation is solved are designated by the subscripts s, and if s has R different values, the R linear equations

$$F_s(\nu, \vartheta_s, \varphi_s)=\sum_{i=0}^{R-1} f_i(\nu)\, Y_i(\vartheta_s, \varphi_s) \tag{2}$$

can be solved for the R functions $f_i(\nu)$. The larger the value of R, the closer will the expansion (1) represent the actual distribution.

The total distribution function is then

$$N(\nu)=\int\int F(\nu, \vartheta, \varphi)\, \sin\vartheta d\vartheta d\varphi = 4\pi Y_0 f_0(\nu), \tag{3}$$

where $f_0(\nu)$ is the coefficient of the constant, Y_0.

As an illustration of the application of this method it is instructive to consider the ideal case of a simple cubic and monatomic lattice. This case has been considered by Blackman,[10] and so it is possible to compare the results obtained from the first three terms of Eq. (2) with those obtained by his more laborious method.

The secular equation for this case reduces to

$$\begin{vmatrix} 2\alpha(1-\cos x)+4\gamma(2-\cos x\cos y-\cos x\cos z)-m\omega^2 & 4\gamma\sin x\sin y & 4\gamma\sin x\sin z \\ 4\gamma\sin y\sin x & 2\alpha(1-\cos y)+4\gamma(2-\cos y\cos z-\cos y\cos x)-m\omega^2 & 4\gamma\sin y\sin z \\ 4\gamma\sin z\sin x & 4\gamma\sin z\sin y & 2\alpha(1-\cos z)+4\gamma(2-\cos z\cos x-\cos z\cos y)-m\omega^2 \end{vmatrix} = 0. \tag{4}$$

[10] M. Blackman, Proc. Camb. Phil. Soc. **33**, 94 (1937).

x, y, and z are the components of the propagation vectors of the normal vibrations. In this case the allowed values of x, y, and z fill a cube of edge 2π. α is the restoring force constant acting between adjacent atoms when the motion is in the line connecting them. γ is the restoring force constant between adjacent atoms when the motion is perpendicular to the line connecting them. For comparison with Blackman's results γ/α is taken to be 0.05.

Figure 1 shows the cones along whose axes the secular equation is solved. For $x=y=0$, the distance r from the origin is just z. Hence the three solutions, in terms of r, are

$$m\omega_1^2=(2\alpha+8\gamma)(1-\cos z)=(12/5)\alpha(1-\cos r), \quad (5)$$

$$m\omega_{2,3}^2=4\gamma(1-\cos z)=\tfrac{1}{5}\alpha(1-\cos r).$$

From these it follows that

$$r^2\frac{dr}{dq_1}=\frac{8\{\sin^{-1}(5/24)^{\frac{1}{2}}q_1\}^2}{(24/5-q_1^2)^{\frac{1}{2}}}, \quad (6a)$$

and

$$r^2\frac{dr}{dq_{2,3}}=\frac{8\{\sin^{-1}(5/2)^{\frac{1}{2}}q_{2,3}\}^2}{(2/5-q_{2,3}^2)^{\frac{1}{2}}}, \quad (6b)$$

where $q_i=(m/\alpha)^{\frac{1}{2}}\omega_i$.

The sum of these expressions gives the distribution of vibrations within the cone around the z axis. If it is denoted by F_1,

$$F_1=\frac{8\{\sin^{-1}(5/24)^{\frac{1}{2}}q\}^2}{(24/5-q^2)^{\frac{1}{2}}}+\frac{16\{\sin^{-1}(5/2)^{\frac{1}{2}}q\}^2}{(2/5-q^2)^{\frac{1}{2}}}. \quad (7)$$

Figure 2 shows F_1 as a function of q.

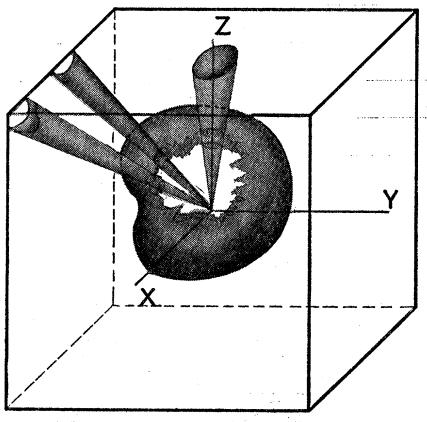

FIG. 1. First Brillouin zone of a simple cubic lattice showing elementary cones in three typical directions.

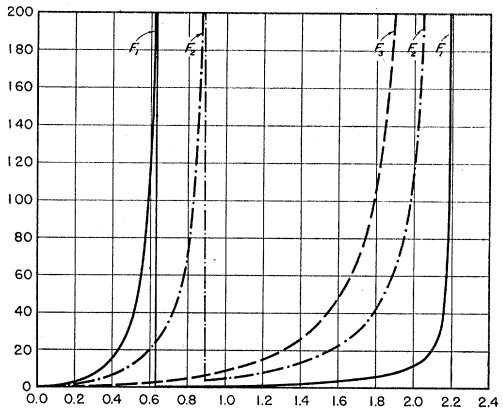

FIG. 2. Distribution of frequencies within the three cones shown in Fig. 1. F_i is shown as a function of q.

In a similar fashion let F_2 be the distribution in the cone about the line $x=0$, $y=z$. In this case $r=\sqrt{2}z$, and

$$F_2=\frac{16\sqrt{2}\{\sin^{-1}(5/4)^{\frac{1}{2}}q\}^2}{(22/5-q^2)^{\frac{1}{2}}}+\frac{16\sqrt{2}\{\sin^{-1}(5/22)^{\frac{1}{2}}q\}^2}{(4/5-q^2)^{\frac{1}{2}}}+\frac{64\sqrt{2}q\{\sin^{-1}[15/8-(15/8)Q]^{\frac{1}{2}}\}^2}{45(Q-7/15)^{\frac{1}{2}}(1-Q)^{\frac{1}{2}}Q}, \quad (8)$$

where $Q=[1-(8/45)q^2]^{\frac{1}{2}}$.

The distribution along the line $x=y=z$ is

$$F_3=\frac{80q\{\sin^{-1}(9/8)^{\frac{1}{2}}(1-R)^{\frac{1}{2}}\}^2}{3\sqrt{3}(9R-1)^{\frac{1}{2}}(1-R)^{\frac{1}{2}}R}+\frac{10q\{\sin^{-1}\sqrt{3}(1-S)^{\frac{1}{2}}\}^2}{3(S-\frac{2}{3})^{\frac{1}{2}}(1-S)^{\frac{1}{2}}S}, \quad (9)$$

where

$$R=[1-(20/81)q^2]^{\frac{1}{2}} \quad \text{and} \quad S=[1-(5/36)q^2]^{\frac{1}{2}}.$$

These functions also are shown in Fig. 2. The cones in Fig. 1 are in directions along which the functions F_1, F_2, and F_3 are also valid because of symmetry.

To express the distribution in other directions, the appropriate interpolation between these three functions must be made. Since the crystal has cubic symmetry, the three Kubic Harmonics[11]

[11] F. C. Von der Lage and H. A. Bethe, Phys. Rev. 71, 612 (1947).

of lowest order are needed. These may be taken to be

$$K_0=\frac{1}{(4\pi)^{\frac{1}{2}}}P_0(\cos\vartheta),$$

$$K_1=\frac{3}{(4\pi)^{\frac{1}{2}}}P_4(\cos\vartheta)+\frac{1}{56(4\pi)^{\frac{1}{2}}}P_4^4(\cos\vartheta)\cos4\varphi, \quad (10)$$

$$K_2=\frac{(13)^{\frac{1}{2}}}{(4\pi)^{\frac{1}{2}}}P_6(\cos\vartheta)-\frac{(13)^{\frac{1}{2}}}{720(4\pi)^{\frac{1}{2}}}P_6^4(\cos\vartheta)\cos4\varphi,$$

where the $P_n^m(\cos\theta)$ are the associated Legendre polynomials.

Substituting the values of the angles ϑ and φ corresponding to the three directions of Eqs. (7), (8), and (9) leads to the three equations

$$F_1(q,0,0)=\frac{1}{(4\pi)^{\frac{1}{2}}}f_0(q)+\frac{3}{(4\pi)^{\frac{1}{2}}}f_1(q)+\frac{(13)^{\frac{1}{2}}}{(4\pi)^{\frac{1}{2}}}f_2(q),$$

$$F_2\left(q,\frac{\pi}{4},0\right)=\frac{1}{(4\pi)^{\frac{1}{2}}}f_0(q)-\frac{3}{4(4\pi)^{\frac{1}{2}}}f_1(q)-\frac{(13)^{\frac{1}{2}}}{(4\pi)^{\frac{1}{2}}}\frac{13}{8}f_2(q),$$

$$F_3\left(q,\cos^{-1}\frac{1}{\sqrt{3}},\frac{\pi}{4}\right)=\frac{1}{(4\pi)^{\frac{1}{2}}}f_0(q)-\frac{10}{3(4\pi)^{\frac{1}{2}}}f_1(q)+\frac{(13)^{\frac{1}{2}}}{(4\pi)^{\frac{1}{2}}}\frac{16}{9}f_2(q).$$

From these it follows that

$$N(\nu)=(4\pi)^{\frac{1}{2}}f_0(\nu)=\frac{4\pi}{469}\left\{162F_1(q,0,0)+208F_2\left(q,\frac{\pi}{4},0\right)+99F_3\left(q,\cos^{-1}\frac{1}{\sqrt{3}},\frac{\pi}{4}\right)\right\}. \quad (11)$$

This is plotted as a function of q in Fig. 3. In the same figure is plotted the distribution obtained by Blackman and taken from his published curve.

The striking feature of the curves obtained by this method is the presence of very sharp peaks at several frequencies. The ordinates at these points actually approach infinity, although the area under the curve is finite. The method certainly exaggerates the importance of these peaks, and taking additional terms in the expansion would increase their number but decrease their individual importance. Nevertheless, the peaks do have some significance. The peaks in the function F_1 are probably correct because the line along which this distribution is taken intersects the bounding plane normally. Group theory considerations applied to the vibration near this line indicate one longitudinal vibration and two transverse vibrations. The two transverse vibrations will have the same frequency, and the longitudinal vibration will have a higher frequency for the ratio of force constants adopted in this illustration.

The longitudinal vibrations represent the motion of whole planes of atoms in phase with each other, and with a frequency determined by the constant α. For propagation vectors only slightly off the line $x=y=0$ the atoms of the plane will not be exactly in phase, but the wavelengths in the planes will be long and will have a negligible effect on the frequency. It then seems quite reasonable that the peaks in the distribution, which Eq. (7) shows to exist along the line $x=y=0$, should also exist along neighboring

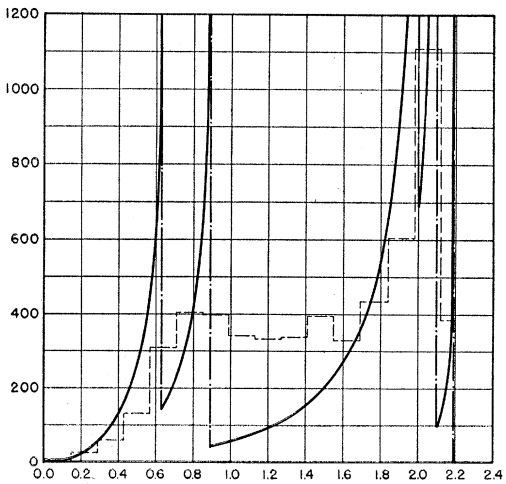

FIG. 3. Total distribution function compared with the step function obtained numerically by Blackman. $n(\nu)$ is plotted as a function of q. The broken curve shows the values obtained by Blackman.

lines. The method of approximation which takes this distribution F_1 as typical of much of the distribution is not far in error.

The peaks in the other functions are less satisfactory. Function F_2 is along a line ending at an edge. For other lines ending at the same edge the same peaks are to be expected, but for lines ending away from the edge the peaks will be displaced. In the case of function F_3 the peaks are probably not justified at all, since the line $x=y=z$ ends at a corner, and the decrease in solid angle around the line will more than compensate the infinity in the function F_3.

Most methods of approximation previously used have tended to obscure and smooth out the actually existing peaks. This method overemphasizes them and adds some extra ones, without, however, diminishing the accuracy of representation of the low frequencies. It must be further emphasized that the use of additional terms in the expansion will reduce the overemphasis and the spurious peaks, and will tend to approach the correct distribution.

The simple cubic lattice is particularly ill-adapted to this method because of the shape of the Brillouin zone. For a body-centered or a face-centered lattice the zones will have less acute angles and corners, and the method will be correspondingly more rapidly convergent.

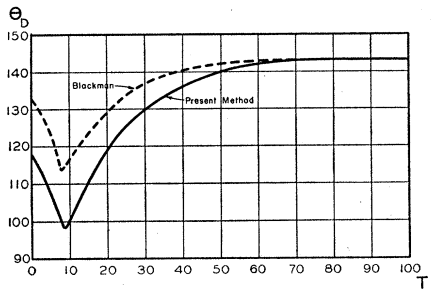

FIG. 4. The equivalent Debye characteristic temperature as a function of temperature for the distributions obtained by the present method and that of Blackman.

Figure 4 indicates the Debye characteristic temperature, as a function of temperature, derived from the frequency distribution of Fig. 3. The force constants are adjusted to make θ approach 142° at high temperature. The corresponding values obtained by Blackman are also shown in this curve, and the effect of the sharper peaks in making a deeper dip is evident.

It is proposed to apply this method to the model of Fine for a body-centered lattice and of Leighton for a face-centered lattice, as well as to investigate the effect of solving the secular equation along several other directions.

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The Vibrational Spectrum and Specific Heat of a Face-Centered Cubic Crystal

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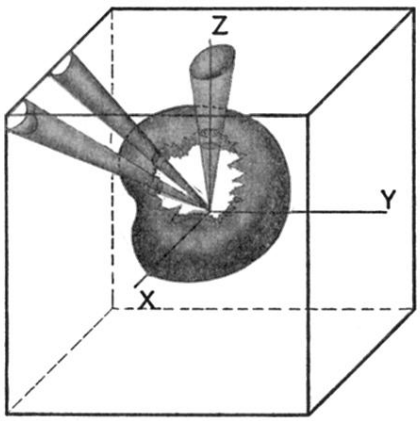
The frequency spectrum of a face-centered cubic crystal lattice is found by actually modeling the constant-frequency surfaces of the secular determinant in plaster of Paris and measuring the volume enclosed between successive surfaces. The frequency spectrum so obtained is used in the evaluation of the specific heat of a general crystal of the type treated, and numerical values are presented for the element silver. The present theory (that of Born and v. Karman) is in much better agreement with experimental values for temperatures below 100°K than is the Debye theory. Certain anomalies in the specific heat curves of silver and potassium chloride at temperatures below 10°K are not explicable in terms of the atomic model that is used.

MANY of the thermal properties of solids can be explained semiquantitatively by interpretation in terms of thermal vibrations of the atoms about their mean rest positions. Some of these properties can be treated satisfactorily by using only the qualitative features of the atomic



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