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Theory of Anharmonic Crystals*

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The anharmonic contributions to the energy, specific heat, frequency–wave-vector dispersion relations and damping of phonons in a crystal have been studied using the recent technique of thermodynamic Green's functions based on field-theoretic methods. General expressions for these quantities have been deduced. It has been shown that at absolute zero the number of density is finite for the anharmonic solid and it is of the same order as the square of the fractional change in the normal-mode frequencies. The cases of a linear chain and a simple model of a crystal have been studied in detail. The normal modes of a linear chain exhibit some unusual but interesting features for different amounts of anharmonicity. The half-width of the phonons of the anharmonic chain has been evaluated for all temperatures for both normal and umklapp processes. For a solid, the complicated integrals that occur because of anharmonicity are simplified by an approximation scheme suggested by us. Within the scope of this approximation it is found that the frequency–wave-vector dispersion curves for a solid show a dip at the maximum wave number, quite similar to that observed for solids like lead and copper. The width of phonons is proportional to the square of the wave number, and the thermal conductivity is seen to be finite at low temperatures and to vary inversely with temperature at high temperatures.

I. INTRODUCTION

THE potential energy of a crystal is usually expanded in a power series of nuclear displacements from their equilibrium positions. In the harmonic approximation one retains only the quadratic terms and then the problem is solved exactly in terms of the normal modes of vibration of the crystal. The system can be quantized and each quantum of normal mode is known as a "phonon." The thermodynamic properties are easily worked out by treating the crystal as an assembly of these phonons.

However, there are many features of a real solid which can not be explained by the harmonic approximation alone, for example, the thermal expansion, specific heat at high temperatures, thermal conductivity, and frequency–wave-vector dispersion relations, etc. Many of these features of a solid can be explained by going beyond the harmonic approximation. The next terms in the power series expansion of the potential energy are the cubic and quartic terms. The role of these anharmonic forces in determining the actual response of the crystal is by no means negligible, because these anharmonic terms contain phonon-phonon interactions which can explain some of the more interesting properties of the crystals.

Recently, the anharmonic free energy and specific heat of solids have been calculated by Maradudin and co-workers.[1–3] They have used the Bloch expansion formula which for a system described by the Hamiltonian $H=H_0+H_1$ is

$$e^{-\beta H}=e^{-\beta H_0}\left[1-\int_0^\beta d\beta' e^{\beta' H_0}H_1e^{-\beta' H_0}+\int_0^\beta d\beta' e^{\beta' H_0}H_1e^{-\beta' H_0}\int_0^{\beta'} d\beta'' e^{\beta'' H_0}H_1e^{-\beta'' H_0}-\cdots\right],$$

where $\beta=(k_BT)^{-1}$ and H_1 is a small anharmonic perturbation to the Hamiltonian H_0 of the harmonic approximation.

So far we have not come across any published work where the anharmonic contribution to the energy of the system has been evaluated quantum mechanically, either at low or at high temperatures, although the recent formulation of thermodynamic Green's functions leads naturally to the evaluation of the energy of the system through the correlation functions. In Sec. II we shall deduce an exact expression for the energy in the presence of cubic anharmonicity alone in terms of the one-particle correlation function. We shall treat the quartic anharmonicity in an approximate way.

Our Green's function will be similar to that of Thompson,[4] which gives directly the displacement and momentum correlation function. The approximation of limiting the chain of Green's function equations will be used to write the two-particle Green's function as a sum of products of one-particle Green's function and equal-time correlation functions. These approximations are not the usual perturbation approximation; indeed they are better than Hartree-Fock approximations as pointed out by Thompson.[4]

Once the decoupling scheme has been decided upon, it is easy to obtain a simple expression for the Green's function. Examining the Green's function in the complex energy plane, it is found that there are poles that lie above and below the real axis. The real part of the

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[1] A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. (N.Y.) **15**, 337 (1961).

[2] A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. (N.Y.) **15**, 360 (1961).

[3] P. A. Flinn and A. A. Maradudin, Ann. Phys. (N.Y.) **22**, 223 (1963).

[4] B. V. Thompson, Phys. Rev. **131**, 1420 (1963).

pole in the positive half-plane is identified as the perturbed mode, and the imaginary part as the half-width of the mode. When the poles lie close to the real axis one can meaningfully discuss a phonon number density and it turns out that at absolute zero of temperature this number density does not vanish as it does for a perfect crystal.

In Sec. III, the general formulas deduced in Sec. II have been used to calculate the properties of a linear chain. Detailed discussion of the dynamic properties of the anharmonic chain is given. The width of the phonons is obtained for all temperatures and is found to be proportional to the absolute temperature. In Sec. IV, we have performed similar calculations for a solid based on a very simplified approximation, which we have called the soft phonon approximation. The frequency–wave-vector dispersion curve is found to drop near the maximum wave number.

II. GENERAL FORMULATIONS

We consider a Bravais crystal of N atoms, each of mass M. Our Hamiltonian for the system is

$$H=\tfrac{1}{2}M\sum_i \dot{U}_i^2+\tfrac{1}{2}\sum_{i,j}\varphi_{ij}\mathbf{U}_i\mathbf{U}_j+\tfrac{1}{6}\sum_{i,j,k}\varphi_{ijk}\mathbf{U}_i\mathbf{U}_j\mathbf{U}_k+(1/24)\sum_{i,j,k,l}\varphi_{ijkl}\mathbf{U}_i\mathbf{U}_j\mathbf{U}_k\mathbf{U}_l\,,\quad(1)$$

where $\mathbf{U}_i$ is the displacement of the ith atom from the equilibrium position. The φ coefficients are general force constants of the lattice. We confine ourselves to quadratic, cubic, and quartic terms in the potential energy. In terms of phonon annihilation and creation operators, the atomic displacement can be expressed as

$$\mathbf{U}_i=\frac{1}{(2MN)^{1/2}}\sum_{\mathbf{k},j}\frac{\mathbf{e}(\mathbf{k},j)}{[\omega_{\mathbf{k}j}]^{1/2}}(a_{\mathbf{k}j}+a_{-\mathbf{k}j}{}^{\dagger})e^{2\pi i\mathbf{k}\cdot\mathbf{R}i}\quad(\hbar=1)\,.\quad(2)$$

In this expression $\omega_{\mathbf{k}j}$ is the frequency of the normal mode described by the wave vector $\mathbf{k}$ and polarization index j, and $\mathbf{e}(\mathbf{k}j)$ is the polarization vector for the mode $(\mathbf{k},j)$.

For convenience we define the operators

$$A_{\mathbf{k}j}=a_{\mathbf{k}j}+a_{-\mathbf{k}j}{}^{\dagger};\quad B_{\mathbf{k}j}=a_{\mathbf{k}j}-a_{-\mathbf{k}j}{}^{\dagger}\,.$$

$A_{\mathbf{k}j}$ and $B_{\mathbf{k}j}$ are directly related to the Fourier transforms of the displacement and momentum operators. Substitution of (2) in (1) gives the Hamiltonian in second quantized form as

$$H=\sum_{\mathbf{k}j}\omega_{\mathbf{k}j}(a_{\mathbf{k}j}{}^{\dagger}a_{\mathbf{k}j}+\tfrac{1}{2})+\sum_{\substack{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3\\ j_1,j_2,j_3}}V^{(3)}(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\mathbf{k}_3j_3)A_{\mathbf{k}_1j_1}A_{\mathbf{k}_2j_2}A_{\mathbf{k}_3j_3}+\sum_{\substack{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4\\ j_1,j_2,j_3,j_4}}V^{(4)}(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\mathbf{k}_3j_3,\mathbf{k}_4j_4)A_{\mathbf{k}_1j_1}A_{\mathbf{k}_2j_2}A_{\mathbf{k}_3j_3}A_{\mathbf{k}_4j_4}\,.\quad(3)$$

The coefficients $V^{(3)}$ and $V^{(4)}$ which appear in the anharmonic Hamiltonian are the Fourier transforms of the third- and fourth-order atomic force constants. They are completely symmetric in the indices $(\mathbf{k}_ij_i)$ and are given by[5]

$$\begin{aligned}V^{(3)}(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\mathbf{k}_3j_3)&=\frac{1}{(2)^{3/2}6N^{1/2}}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\frac{\varphi(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\mathbf{k}_3j_3)}{[\omega_{\mathbf{k}_1j_1}\omega_{\mathbf{k}_2j_2}\omega_{\mathbf{k}_3j_3}]^{1/2}}\,,\\ V^{(4)}(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\mathbf{k}_3j_3,\mathbf{k}_4j_4)&=\frac{1}{(2)^{2}24N}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\frac{\varphi(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\mathbf{k}_3j_3,\mathbf{k}_4j_4)}{[\omega_{\mathbf{k}_1j_1}\omega_{\mathbf{k}_2j_2}\omega_{\mathbf{k}_3j_3}\omega_{\mathbf{k}_4j_4}]^{1/2}}\,,\end{aligned}\quad(4)$$

where

$$\varphi(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\mathbf{k}_3j_3)=\sum_{i,j,k}(\varphi_{ijk}/M^{3/2})\mathbf{e}(\mathbf{k}_1j_1)\mathbf{e}(\mathbf{k}_2j_2)\mathbf{e}(\mathbf{k}_3j_3)e^{2\pi i(\mathbf{k}_1\cdot\mathbf{R}_i+\mathbf{k}_2\cdot\mathbf{R}_j+\mathbf{k}_3\cdot\mathbf{R}_k)}\,,$$

$$\varphi(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\mathbf{k}_3j_3,\mathbf{k}_4j_4)=\sum_{i,j,k,l}(\varphi_{ijkl}/M^{2})\mathbf{e}(\mathbf{k}_1j_1)\mathbf{e}(\mathbf{k}_2j_2)\mathbf{e}(\mathbf{k}_3j_3)\mathbf{e}(\mathbf{k}_4j_4)e^{2\pi i(\mathbf{k}_1\cdot\mathbf{R}_i+\cdots)}\,,$$

and

$$\begin{aligned}\Delta(\mathbf{k})&=1\quad\text{if}\quad k=0,\quad\text{or reciprocal lattice vector},\\ &=0\quad\text{otherwise}.\end{aligned}\quad(5)$$

Equations of motion for A_k and B_k are

$$\begin{aligned}i(\partial A_k/\partial t)&=[A_k,H]=\omega_kB_k\,,\\ i(\partial B_k/\partial t)&=[B_k,H]=\omega_kA_k\\ &\quad+6\sum_{k_1,k_2}V^{(3)}(k_1,k_2,-k)A_{k_1}A_{k_2}\\ &\quad+8\sum_{k_1,k_2,k_3}V^{(4)}(k_1,k_2,k_3,-k)A_{k_1}A_{k_2}A_{k_3}\,.\end{aligned}\quad(6)$$

Here and in what follows we use only one index k to denote $(\mathbf{k}j)$.

We define the one-phonon retarded Green's function as[6]

$$G_{kq}(t,t')=\langle\langle A_k(t),A_q{}^{\dagger}(t')\rangle\rangle=-i\theta(t-t')\langle[A_k(t),A_q{}^{\dagger}(t')]\rangle\,,$$

where

$$\langle 0\rangle=\mathrm{Tr}e^{-\beta H}0/\mathrm{Tr}e^{-\beta H}\,,$$
$$[A,B]=AB-BA\,,$$

and

$$\begin{aligned}\theta(x)&=1\quad\text{for}\quad x>0\\ &=0\quad\text{for}\quad x<0.\end{aligned}$$

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[5] A. A. Maradudin and A. E. Fein, Phys. Rev. **128**, 2589 (1962).

[6] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Physics—Uspekhi **3**, 320 (1960)].

We also define the one-particle correlation function as

$$F_{qk}(t,t')=\langle A_q^\dagger(t')A_k(t)\rangle.$$

The Fourier transforms $G_k(\omega)$ and $J_k(\omega)$ of the one-particle Green's function and the correlation function are defined as

$$G_k(t-t')=\int_{-\infty}^{+\infty} G_k(\omega)e^{-i\omega(t-t')}d\omega$$

and

$$F_k(t-t')=\int_{-\infty}^{+\infty} J_k(\omega)e^{-i\omega(t-t')}d\omega. \qquad (7)$$

Here we will just indicate the relation between the correlation function and the thermodynamic Green's function. Details of the formalism can be seen in Ref. 6. The spectral-density function $J_k(\omega)$ is related to the one-particle Green's function by the relation

$$G_k(\omega+i\epsilon)-G_k(\omega-i\epsilon)=-i(e^{\beta\omega}-1)J_k(\omega)$$

or

$$J_k(\omega)=-(2/(e^{\beta\omega}-1))\,\mathrm{Im}G_k(\omega+i\epsilon) \qquad (8)$$

where $\epsilon\to 0$ is implied.

(i) The Number Density

The spectral-density function $J_k(\omega)$ is directly related to the number density of the system. In terms of the operators A_k and B_k, the number density is

$$n_k=\langle a_k^\dagger a_k\rangle=\tfrac{1}{4}[\langle A_k^\dagger A_k\rangle+\langle A_k^\dagger B_k\rangle+\langle B_k^\dagger A_k\rangle+\langle B_k^\dagger B_k\rangle].$$

We now use the relations

$$\omega_k\langle B_k^\dagger(t')A_k(t)\rangle=-i\frac{\partial}{\partial t'}\langle A_k^\dagger(t')A_k(t)\rangle =\int_{-\infty}^{+\infty}\omega J_k(\omega)e^{-i\omega(t-t')}d\omega,$$

$$\omega_k\langle B_k^\dagger(t')B_k(t)\rangle=i\frac{\partial}{\partial t}\langle B_k^\dagger(t')A_k(t)\rangle =\int_{-\infty}^{+\infty}\omega^2 J_k(\omega)e^{-i\omega(t-t')}d\omega,$$

and

$$\omega_k\langle A_k^\dagger(t')B_k(t)\rangle=i\frac{\partial}{\partial t}\langle A_k^\dagger(t')A_k(t)\rangle =\int_{-\infty}^{+\infty}\omega J_k(\omega)e^{-i\omega(t-t')}d\omega, \qquad (9)$$

and take the limit $t=t'$; the number density comes out to be

$$n_k=\frac{1}{4}\int_{-\infty}^{+\infty}\left(1+\frac{\omega}{\omega_k}\right)^2 J_k(\omega)d\omega. \qquad (10)$$

(ii) The Energy of the System

The energy of the system is equal to the thermal average of the Hamiltonian which is

$$E=\langle H\rangle.$$

Therefore

$$E=E_0+\sum_k\omega_k\langle a_k^\dagger a_k\rangle+\sum_{k_1,k_2,k_3}V^{(3)}(k_1,k_2,k_3)\langle A_{k_1}A_{k_2}A_{k_3}\rangle +\sum_{k_1,k_2,k_3,k_4}V^{(4)}(k_1,k_2,k_3,k_4)\langle A_{k_1}A_{k_2}A_{k_3}A_{k_4}\rangle$$
$$=E_0+\sum_k\omega_k n_k+\langle V_3\rangle+\langle V_4\rangle, \qquad (11)$$

where E_0 is the usual zero point energy of the harmonic crystal. Now we differentiate the correlation function $\langle B_k^\dagger(t')A_k(t)\rangle$ with respect to t' and, after summing over all k, we get

$$-i(\partial/\partial t')\sum_k\langle B_k^\dagger(t')A_k(t)\rangle$$
$$=\sum_k\omega_k\langle A_k^\dagger(t')A_k(t)\rangle+6\sum_{k,k_1,k_2,k_3}V^{(3)}(k,k_1,k_2)\langle A_{k_1}A_{k_2}A_k\rangle +8\sum_{k,k_1,k_2,k_3}V^{(4)}(k,k_1,k_2,k_3)\langle A_{k_1}A_{k_2}A_{k_3}A_k\rangle. \qquad (12)$$

To evaluate the right-hand side of Eq. (12) we differentiate the first relation of Eq. (9) with respect to t' and then take the limit $t=t'$. We get a very useful relation:

$$\langle V_3\rangle=\tfrac{1}{6}\sum_k\frac{1}{\omega_k}\int_{-\infty}^{\infty}d\omega J_k(\omega)(\omega^2-\omega_k^2)-\tfrac{4}{3}\langle V_4\rangle. \qquad (13)$$

The usefulness of the above relation lies in the fact that $\langle V_3\rangle$ is now expressible in terms of the one-particle correlation function. Using the relations (10) and (13) we get an expression for the energy of the system from Eq. (11) as

$$E=E_0-\tfrac{1}{3}\langle V_4\rangle +\tfrac{1}{6}\sum_k\frac{1}{\omega_k}\int_{-\infty}^{+\infty}d\omega(5\omega^2+\omega_k^2+6\omega\omega_k)J_k(\omega). \qquad (14)$$

So far we have not made any approximation in obtaining (14), and it is clear from the expression for E that, if the quartic anharmonic term is absent, then E is exactly known in terms of $J_k(\omega)$. It is possible to write formally exact expressions for the thermodynamic functions when the anharmonic terms of all orders are present (e.g. free energy as an integral over coupling parameter). However, it is not possible to express the energy of the system in terms of the one-particle correlation function. For instance, to evaluate the cubic and quartic contributions we can express the energy in terms of one-particle and two-particle correlation functions. The complex problem of anharmonicity is considerably simplified if the two-particle correlation function is decoupled according to the scheme

$$\langle abcd\rangle=\langle ab\rangle\langle cd\rangle+\langle ac\rangle\langle bd\rangle+\langle ad\rangle\langle bc\rangle, \qquad (15)$$

where a, b, c, d are the operators A_k or B_k. Therefore, the approximate form of $\langle V_4\rangle$ is

$$\langle V_4\rangle=3\sum_{k_1,k_2}V^{(4)}(k_1,-k_1,k_2,-k_2) \times\langle A_{k_1}^\dagger A_{k_1}\rangle\langle A_{k_2}^\dagger A_{k_2}\rangle. \qquad (16)$$

(iii) The Green's Functions

The equation of motion for the Green's function G_{kq} is

$$-(d^2/dt^2+\omega_k^2)G_{kq}=2\omega_k\delta_{kq}\delta(t-t')+6\omega_k\sum_{k_1,k_2}V^{(3)}(k_1,k_2,-k)\langle\langle A_{k_1}A_{k_2},A_q^\dagger(t')\rangle\rangle$$
$$+8\omega_k\sum_{k_1,k_2,k_3}V^{(4)}(k_1,k_2,k_3,-k)\langle\langle A_{k_1}A_{k_2}A_{k_3},A_q^\dagger(t')\rangle\rangle. \quad (17)$$

The Green's function of the last term is now decoupled according to relation (15). To evaluate the Green's function $\Gamma_{k_1k_2q}^{(1)}=\langle\langle A_{k_1}A_{k_2},A_q^\dagger(t')\rangle\rangle$ contained in the second term, we need the Green's functions $\Gamma_{k_1k_2q}^{(2)}=\langle\langle B_{k_1}A_{k_2},A_q^\dagger(t')\rangle\rangle$, $\Gamma_{k_1k_2q}^{(3)}=\langle\langle A_{k_1}B_{k_2},A_q^\dagger(t')\rangle\rangle$ and $\Gamma_{k_1k_2q}^{(4)}=\langle\langle B_{k_1}B_{k_2},A_q^\dagger(t')\rangle\rangle$ as can be seen from the equations of motion given below.

$$i(d\Gamma^{(1)}/dt)=\omega_1\Gamma^{(2)}+\omega_2\Gamma^{(3)},$$
$$i(d\Gamma^{(2)}/dt)=\omega_2\Gamma^{(4)}+\omega_1\Gamma^{(1)}+6\sum_{q_1,q_2}V^{(3)}(q_1,q_2,-k)\langle\langle A_{q_1}A_{q_2}A_{k_2},A_q^\dagger(t')\rangle\rangle$$
$$+8\sum_{q_1,q_2,q_3}V^{(4)}(q_1,q_2,q_3,-k_1)\langle\langle A_{q_1}A_{q_2}A_{q_3}A_{k_2},A_q^\dagger(t')\rangle\rangle,$$
$$i(d\Gamma^{(3)}/dt)=\omega_2\Gamma^{(1)}+\omega_1\Gamma^{(4)}+6\sum_{q_1,q_2}V^{(3)}(q_1,q_2,-k_2)\langle\langle A_{q_1}A_{q_2}A_{k_1},A_q^\dagger(t')\rangle\rangle$$
$$+8\sum_{q_1,q_2,q_3}V^{(4)}(q_1,q_2,q_3,-k_2)\langle\langle A_{q_1}A_{q_2}A_{q_3}A_{k_1},A_q^\dagger(t')\rangle\rangle, \quad (18)$$
$$i(d\Gamma^{(4)}/dt)=\omega_2\Gamma^{(2)}+\omega_1\Gamma^{(3)}+6\sum_{q_1,q_2}V^{(3)}(q_1,q_2,-k)\langle\langle B_{k_1}A_{q_1}A_{q_2},A_q^\dagger(t')\rangle\rangle$$
$$+8\sum_{q_1,q_2,q_3}V^{(4)}(q_1,q_2,q_3,-k_2)\langle\langle B_{k_1}A_{q_1}A_{q_2}A_{q_3},A_q^\dagger(t')\rangle\rangle+6\sum_{q_1,q_2}V^{(3)}(q_1,q_2,-k_1)\langle\langle A_{q_1}A_{q_2}B_{k_2},A_q^\dagger(t')\rangle\rangle$$
$$+8\sum_{q_1,q_2,q_3}V^{(4)}(q_1,q_2,q_3,-k_1)\langle\langle A_{q_1}A_{q_2}A_{q_3}B_{k_2},A_q^\dagger(t')\rangle\rangle.$$

Thompson[4] has tried to shorten the procedure by writing the equations for $\Gamma^{(1)}$ and $\Gamma^{(4)}$ only, and his second-order differential equations for $\Gamma^{(1)}$ and $\Gamma^{(4)}$ are approximately true. The five-operator Green's functions can be decoupled as sums of products of the three-operator correlation functions (and Green's functions) and two-operator Green's functions (and correlation functions). After these decouplings are done, one can proceed to solve for G_{kq}. It is easily noticed that the contribution from the terms obtained from decoupling the five-operator Green's functions are small, being of the order of the product of cubic and quartic coupling parameters. We neglect them because such terms are comparable to the contributions that can arise from the higher order expansion of the potential energy of the crystal beyond the quartic anharmonic term. However, in an analysis of the type attempted by Thompson[4] (where he takes into account higher order effects in the neutron-scattering problem) these contributions have to be considered. So we obtain the following two equations for the Fourier transforms of the Green's functions.

$$(\omega^2-\omega_k^2)G_{kq}=\frac{\omega_k}{\pi}\delta_{kq}+6\omega_k\sum_{k_1,k_2}V^{(3)}(k_1,{}^{k}{}_{2},-k)\Gamma_{k_1k_2q}^{(1)}$$
$$+24\omega_k\sum_{k_1,k_2}V^{(4)}(k_1,k_2,-k_2,-k)G_{k_1q}N_{k_1}$$

and

$$\Gamma_{k_1k_2q}^{(1)}=F(k_1,k_2,\omega)\sum_{q_1}V^{(3)}(-k_1,-k_2,q_1)G_{q_1q}, \quad (19)$$

where[7]

$$F(k_1,k_2,\omega)=6(N_1+N_2)\frac{\omega_1+\omega_2}{\omega^2-(\omega_1+\omega_2)^2}$$
$$+6(N_2-N_1)\frac{\omega_1-\omega_2}{\omega^2-(\omega_1-\omega_2)^2}$$
$$+6(N_1'+N_2')\left[\frac{\omega}{\omega^2-(\omega_1+\omega_2)^2}-\frac{\omega}{\omega^2-(\omega_1-\omega_2)^2}\right]$$

and

$$N_k=\langle A_k^\dagger A_k\rangle,\ N_1'=\langle B_{k_1}A_{k_1}^\dagger\rangle \text{ and } N_2'=\langle A_{k_2}^\dagger B_{k_2}\rangle. \quad (20)$$

Finally we get from Eqs. (19)

$$G_k(\omega)=(\omega_k/\pi)(\omega^2-\omega_k^2-2\omega_kM_k(\omega))^{-1}, \quad (21)$$

where

$$M_k(\omega)=3\sum_{k_1,k_2}|V^{(3)}(-k,k_1,k_2)|^2F(k_1,k_2,\omega)$$
$$+12\sum_{k_1}V^{(4)}(k_1,-k_1,k,-k)N_{k_1}.$$

Let us define

$$M_k(\omega+i\epsilon)=\Delta_k(\omega)-i\Gamma_k(\omega),$$

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[7] The last term in first equation of (20) is missing from Ref. 4. It is, however, seen by evaluating $(N_1'+N_2')$ from (9) that $(N_1'+N_2')$ can be omitted in the desired degree of accuracy.

where

$$\Delta_k(\omega)=18\mathcal{P}\sum_{k_1,k_2}|V^{(3)}(-k,k_1,k_2)|^2$$
$$\times\left[(N_1+N_2)\frac{\omega_1+\omega_2}{\omega^2-(\omega_1+\omega_2)^2}+(N_2-N_1)\frac{\omega_1-\omega_2}{\omega^2-(\omega_1-\omega_2)^2}\right]$$
$$+12\sum_{k_1}V^{(4)}(-k,k,-k_1,k_1)N_{k_1}, \quad (22)$$

and

$$(\Gamma_k\omega)=18\pi\epsilon(\omega)\sum_{k_1,k_2}|V^{(3)}(-k,k_1,k_2)|^2$$
$$\times[(N_1+N_2)(\omega_1+\omega_2)\delta(\omega^2-(\omega_1+\omega_2)^2)$$
$$+(N_2-N_1)(\omega_1-\omega_2)\delta(\omega^2-(\omega_1-\omega_2)^2)], \quad (23)$$

where

$$\begin{aligned}\epsilon(\omega)&=1 \quad \text{for} \quad \omega>0\\ &=-1 \quad \text{for} \quad \omega<0.\end{aligned}$$

It is obvious also that $\Delta_k(\omega)$ and $\Gamma_k(\omega)$ are the Hilbert transforms of each other and $\Delta_k(\omega)$ is an even function of ω and $\Gamma_k(\omega)$ an odd function. The above results agree with previous calculations[4,5] if N_k is preassigned the value $N_k=2n_k+1$.

(iv) Physical Properties of the Anharmonic Solid

The poles of the Green's function will be given by the zeros of the denominator of Eq. (21). The real part of the pole gives the dispersion formula and the imaginary part gives the half-width of the phonons.[6] In our case the perturbed normal mode is given by the equation

$$\epsilon_k^2=\omega_k^2+2\omega_k\Delta_k(\epsilon_k). \quad (24)$$

The correlation function N_k which is obtained directly from the spectral density function is

$$N_k=-\frac{2\omega_k}{\pi}\,\mathrm{Im}\int_{-\infty}^{+\infty}\frac{d\omega}{(e^{\beta\omega}-1)}\,\frac{1}{(\omega^2-\omega_k^2-2\omega_k\Delta_k(\omega)+2i\omega_k\Gamma_k(\omega)\epsilon(\omega))}$$
$$=\frac{4\omega_k^2}{\pi}\int_0^{\infty}d\omega\frac{\coth\frac{1}{2}\beta\omega\;\Gamma_k(\omega)}{(\omega^2-\omega_k^2-2\omega_k\Delta_k)^2+4\omega_k^2\Gamma_k^2}. \quad (25)$$

The physical quantity n_k is given by Eq. (10) and after appropriate substitutions becomes

$$n_k=-\frac{1}{2\pi\omega_k}\,\mathrm{Im}\int_{-\infty}^{+\infty}d\omega\frac{\omega^2+\omega_k^2+2\omega\omega_k}{(e^{\beta\omega}-1)(\omega^2-\omega_k^2-2\omega_k\Delta_k(\omega)+2i\omega_k\Gamma_k(\omega)\epsilon(\omega))}$$
$$=\frac{1}{\pi}\int_0^{\infty}d\omega\frac{[(\omega^2+\omega_k^2)\coth\frac{1}{2}\beta\omega-2\omega\omega_k]\Gamma_k(\omega)}{(\omega^2-\omega_k^2-2\omega_k\Delta_k)^2+4\omega_k^2\Gamma_k^2}. \quad (26)$$

There is no direct relationship between N_k and n_k.

The idea of a number density is physically meaningful only when the damping is considered to be small. In this limit we see that the spectral density function $J_k(\omega)$ has a steep maximum at the value $\omega=\epsilon_k$. If we replace the Breit-Wigner form of the spectral density function by a Dirac δ function, then the integrals are easily done and we get the following fairly accurate expressions for the number density and the N_k:

$$n_k=(1/4\omega_k\epsilon_k)[(\omega_k-\epsilon_k)^2+(\omega_k^2+\epsilon_k^2)(\coth\tfrac{1}{2}\beta\epsilon_k-1)], \quad (27)$$

$$N_k=(\omega_k/\epsilon_k)\coth\tfrac{1}{2}\beta\epsilon_k. \quad (28)$$

When ω_k is close to ϵ_k one can replace N_k by $2n_k+1$. The expression for the number density n_k has been written in a form such that in the limit $\beta\to\infty$ the second term vanishes. At absolute zero the particles (phonons) are distributed over various normal modes and it follows from Eq. (27) that

$$n_k(T\to 0)=[(1/2\omega_k)\Delta_k(T\to 0)]^2. \quad (29)$$

In the harmonic approximation this number vanishes whereas it is proportional to the square of the fractional change in the normal mode frequencies. This may prove useful for qualitative discussion of the effect of anharmonicity on the thermodynamic properties of solids.

The contribution of quartic anharmonicity to the energy of the system, according to our approximation, is given in terms of N_ks as

$$\langle V_4\rangle=3\sum_{k_1,k_2}V^{(4)}(-k_1,k_1,k_2,-k_2)N_{k_1}N_{k_2}. \quad (30)$$

The total energy is

$$E=E_0-\tfrac{1}{3}\langle V_4\rangle-\frac{1}{6\pi}\,\mathrm{Im}\sum_k\int_{-\infty}^{+\infty}\frac{d\omega}{(e^{\beta\omega}-1)}\,\frac{5\omega^2+\omega_k^2+6\omega\omega_k}{(\omega^2-\omega_k^2-2\omega_k\Delta_k+2i\omega_k\Gamma_k\epsilon(\omega))}$$
$$=E_0-\tfrac{1}{3}\langle V_4\rangle+\frac{1}{3\pi}\sum_k\omega_k\int_0^{\infty}d\omega\frac{(5\omega^2+\omega_k^2)\coth\frac{1}{2}\beta\omega\;\Gamma_k(\omega)}{(\omega^2-\omega_k^2-2\omega_k\Delta_k)^2+4\omega_k^2\Gamma_k^2}-\frac{2}{\pi}\sum_k\omega_k^2\int_0^{\infty}\frac{d\omega\omega\Gamma_k(\omega)}{(\omega^2-\omega_k^2-2\omega_k\Delta_k)^2+4\omega_k^2\Gamma_k^2}. \quad (31)$$

This is our final expression for the energy of the system. The specific heat can be obtained by using the relation

$$C_v = -k_B\beta^2(\partial E/\partial\beta). \tag{32}$$

Very accurate results will be obtained if expression (31) can be evaluated for any specific model of a crystal. It seems to us that it is impossible to evaluate this expression in closed form in all generality without the aid of computers. Finally we obtain the energy in our approximation as

$$\begin{aligned} E = E_0 - \sum_{k_1,k_2} & V^{(4)}(-k_1, k_1, k_2, -k_2) \\ & \times((\omega_{k_1}/\epsilon_{k_1}) \coth\tfrac{1}{2}\beta\epsilon_{k_1})((\omega_{k_2}/\epsilon_{k_2}) \coth\tfrac{1}{2}\beta\epsilon_{k_2}) \\ & + \tfrac{1}{12}\sum_k((\omega_k^2+5\epsilon_k^2)/\epsilon_k) \coth\tfrac{1}{2}\beta\epsilon_k. \end{aligned} \tag{33}$$

The expression for the energy given by Eq. (33) is a useful nonperturbative result. The cubic anharmonicity does not enter explicitly. It alters the normal mode frequency in a significant way and hence the energy.

III. APPLICATION TO A MONATOMIC LINEAR CHAIN

In this section we shall work out various anharmonic properties of a monatomic linear chain. It is quite obvious that the model of a linear chain is nonphysical as well as unrealistic; however in the absence of accurate calculations of anharmonic properties of solids beyond perturbation theory, we feel that it is worthwhile to study the anharmonic properties of a linear chain. Apart from this, the one-dimensional model will serve as a guide for calculations in three-dimensional models. Similar calculations for the free energy of a linear chain have been made by Maradudin and co-workers.[1] They have shown there that for a monatomic linear chain

$$|V^{(3)}(-k, k_1, k_2)|^2 = (\delta^2/288\gamma^3 N)\Delta(-k+k_1+k_2)\omega_k\omega_{k_1}\omega_{k_2}$$

and

$$V^{(4)}(-k_1, k_1, k_2, -k_2) = (\epsilon/96\gamma^2 N)\omega_{k_1}\omega_{k_2}, \tag{34}$$

where γ, δ, and ϵ are harmonic, cubic, and quartic force constants (nearest neighbor) for the linear chain. The unperturbed normal mode frequencies are given by

$$\omega_k^2 = \omega_L^2 \sin^2\tfrac{1}{2}k, \quad \omega_L = (4\gamma/M)^{1/2}$$

$$k = 2\pi l/N \text{ where } l \text{ lies between } -\tfrac{1}{2}N \text{ and } +\tfrac{1}{2}N. \tag{35}$$

(i) Lifetime of Phonons

The cubic anharmonicity gives a finite width to the normal modes and is responsible for dissipation of energy, so that the transport properties (e.g. thermal conductivity) turn out to be finite. In fact at high temperatures the thermal conductivity is essentially governed by the cubic anharmonicity. We have already deduced in Eq. (23) an expression for the width at all temperatures and we shall see that it turns out to be finite. Furthermore the contribution from normal and umklapp processes can be discussed clearly and easily in the case of a linear chain. Maradudin[8] has also obtained a finite width at high temperatures.

For the linear chain we omit the polarization index, and we obtain the width from Eq. (23) after substitution for $V^{(3)}$. By rearranging the terms we write it as

$$\begin{aligned} \Gamma_k(\omega) = (\pi\omega_k\delta^2/16\gamma^3 N)\epsilon(\omega) & \sum_{k_1,k_2} \Delta(-k+k_1+k_2)\omega_1\omega_2 \\ & \times[(N_1\omega_2+N_2\omega_1)\{\delta(\omega^2-(\omega_1+\omega_2)^2) \\ & +\delta(\omega^2-(\omega_1-\omega_2)^2)\}+(N_1\omega_1+N_2\omega_2) \\ & \times\{\delta(\omega^2-(\omega_1+\omega_2)^2)-\delta(\omega^2-(\omega_1-\omega_2)^2)\}]. \end{aligned}$$

Strictly speaking, the observed width is of the perturbed normal mode. However we assume this to be equal to the width at the unperturbed frequency which can be written as

$$\begin{aligned} \Gamma_k(\omega_k) = (\pi\omega_k\delta^2/4\gamma^3 N) & \sum_{k_1,k_2} \Delta(-k+k_1+k_2)\omega_1^2\omega_2^2 \\ & \times\delta(\omega_k^4-2\omega_k^2(\omega_1^2+\omega_2^2)+(\omega_1^2-\omega_2^2)^2) \\ & \times[(N_1\omega_2+N_2\omega_1)+(N_1\omega_1+N_2\omega_2) \\ & \times\epsilon(\omega_k^2-\omega_1^2-\omega_2^2)], \end{aligned} \tag{36}$$

where we have used the formulas

$$\epsilon(x)\delta(x^2-a^2) = (|2a|)^{-1}[\delta(x-a)-\delta(x+a)]$$

and

$$\delta[(x-a)(x-b)] = (|a-b|)^{-1}[\delta(x-a)+\delta(x-b)].$$

The advantage of writing in this fashion is that the argument of the Dirac δ function now contains the square of the normal-mode frequencies and the troublesome modulus-of-the-sine functions do not arise. Furthermore, the roots of the argument of the Dirac delta function turn out to be very simple. The important point is to sum over k_2 (or k_1) keeping the properties of $\Delta(-k+k_1+k_2)$ in mind. We use the indices $l = Nk_1/2\pi$, $m = Nk_2/2\pi$, and $n = Nk/2\pi$ and write Eq. (36) as

$$\begin{aligned} \Gamma_n = (\pi\omega_n\delta^2/4\gamma^3 N)\sum_l & \sum_{m=-N/2}^{N/2} \Delta(-l+m+n)\omega_l^2\omega_m^2 \\ & \times\delta(\omega_n^4-2\omega_n^2(\omega_l^2+\omega_m^2)+(\omega_l^2-\omega_m^2)^2) \\ & \times[(N_l\omega_m+N_m\omega_l)+\epsilon(\omega_n^2-\omega_l^2-\omega_m^2) \\ & \times(N_l\omega_l+N_m\omega_m]. \end{aligned}$$

The Δ function implies that $m = n-l\pm M$, where $M = 0$, $\pm N$, $\pm 2N$, $\cdots$. Since the ranges of summation of l and m are only from $-N/2$ to $+N/2$, the value of M can only be 0 or $\pm N$. When $M = 0$ the process is called a normal process and when $M = \pm N$ the process is called

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[8] A. A. Maradudin, Phys. Letters 2, 298 (1962).

an umklapp process. However, for any value of M $(0, \pm N, \pm 2N, \cdots)$ $\omega_{n+M}=\omega_n$ so that the summand in Γ_n is independent of M. Therefore we can write

$$\Gamma_n=(\pi\omega_n\delta^2/4\gamma^3N)\sum_l\Big[\sum_{m=-N/2}^{+N/2}\Delta(-n+l+m)\Big]\omega_l^2\omega_{n-l}^2 \times\delta(f(\omega_n,\omega_l,\omega_{n-l}))g(N_l,N_{n-l},\omega_l,\omega_{n-l}). \quad (37)$$

The quantity in the square bracket can only be 1; i.e., there exists only one value of m such that $m=n-l$ or $n-l\pm N$. However, if $n>0$, it is easily seen that, for normal processes (i.e., $n-l=m$) to occur, we should have the range of l restricted by $n-\frac{1}{2}N<l<\frac{1}{2}N$ and for umklapp process (i.e., $n-l=m-N$) by $-\frac{1}{2}N<l<n-\frac{1}{2}N$. Thus the normal and umklapp contributions (for $k>0$) are

$$\Gamma_k^{\text{normal}}=\frac{\omega_k\delta^2}{8\gamma^3}\int_{k-\pi}^{\pi}dq\,\omega_q^2\omega_{k-q}^2 \times\delta(f(\omega_k,\omega_q,\omega_{k-q}))g(N_q,N_{k-q},\omega_q,\omega_{k-q})$$

and

$$\Gamma_k^{\text{umklapp}}=\frac{\omega_k\delta^2}{8\gamma^3}\int_{-\pi}^{k-\pi}dq\,\omega_q^2\omega_{k-q}^2 \times\delta(f(\omega_k,\omega_q,\omega_{k-q}))g(N_q,N_{k-q},\omega_q,\omega_{k-q}). \quad (38)$$

The argument of the Dirac δ function is

$$\begin{aligned} f(\omega_k,\omega_q,\omega_{k-q}) &=\omega_L^4[\sin^4\tfrac{1}{2}k-2\sin^2\tfrac{1}{2}k(\sin^2\tfrac{1}{2}q+\sin^2\tfrac{1}{2}(k-q)) \\ &\qquad+(\sin^2\tfrac{1}{2}q-\sin^2\tfrac{1}{2}(k-q))^2] \\ &=-4\omega_L^2\omega_k^2\sin^2\tfrac{1}{2}q\sin^2\tfrac{1}{2}(k-q) \end{aligned}$$

so that the poles are at $q=0$ and $q=k$. If we take $N_k=\coth\frac{1}{2}\beta\omega_k$ and use the property of the Dirac δ function

$$\delta(f(x))=\sum_i\delta(x-x_i)/|f'(x_i)|\,,$$

where x_i are the roots of $f(x)=0$, we obtain an expression for the half-width for all temperatures

$$\begin{aligned}\Gamma_k^{\text{normal}}=\frac{\delta^2}{32\gamma^3\omega_L^2}\sum_{\substack{q=0\\q=k}}\theta(\pi-q)\theta(q-k+\pi)\omega_q^2\omega_{k-q}^2 &\times[(N_q\omega_{k-q}+N_{k-q}\omega_q)+\epsilon(\sin\tfrac{1}{2}q\sin\tfrac{1}{2}(q-k)) \\ &\times(N_q\omega_q+N_{k-q}\omega_{k-q})][|\sin\tfrac{1}{2}q\sin^2\tfrac{1}{2}(k-q)\cos\tfrac{1}{2}q \\ &+\sin^2\tfrac{1}{2}q\sin\tfrac{1}{2}(k-q)\cos\tfrac{1}{2}(k-q)|]^{-1}.\end{aligned}$$

To evaluate the above expression we use the fact that $\lim_{q\to0}\omega_qN_q=2/\beta$ and we get

$$\Gamma_k^{\text{normal}}=(\delta^2/8\gamma^3)(\omega_L/\beta)\theta(\pi-k).$$

Similarly,

$$\Gamma_k^{\text{umklapp}}=(\delta^2/16\gamma^3)(\omega_L/\beta)\theta(k-\pi).$$

Finally we get the total contribution to the half-width as

$$\Gamma_k=(\delta^2/16\gamma^3)(\omega_L/\beta)[1+\theta(\pi-k)] \quad \text{for} \quad k>0. \quad (39)$$

In general the half-width is

$$\Gamma_k=(\delta^2/16\gamma^3)(\omega_L/\beta)[1+\theta(\pi-k)\theta(\pi+k)], \quad (40)$$

which can also be obtained directly from Eq. (37). If we take the implications of the Heaviside θ function seriously (i.e. $\theta(0)=\frac{1}{2}$), we see that when k falls on the zone boundary the width is reduced from $(4\delta^2/32\gamma^3)(\omega_L/\beta)$ to $\frac{3}{32}(\delta^2/\gamma^3)(\omega_L/\beta)$. (The experiments of Ref. 13 show such a drop in width.)

(ii) Frequency–Wave-Vector Relations and Energy Shifts

It is not possible to evaluate $\Delta_k(\omega)$ in closed form at all temperatures. Therefore one has to be satisfied with evaluating it at high and low temperatures only.

At high temperatures we have $N_1\sim2/\beta\omega_1$ so that we obtain for the energy shift, after substituting (34) in (22) and simplifying, the result

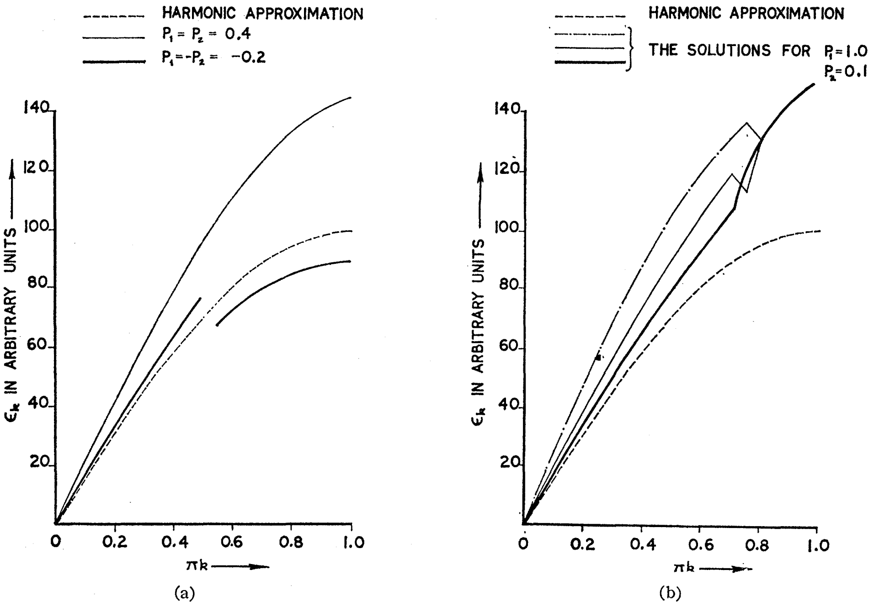
$$\Delta_k(\omega)=\frac{\omega_k}{4\beta}\left(\frac{\epsilon}{\gamma^2}-\frac{\delta^2}{\gamma^3}\right)+\frac{\delta^2\omega_k\omega^2}{8\pi\gamma^3\beta}\mathcal{P}\int_{-\pi}^{+\pi}dq\left[\omega^2-\omega_L^2+\omega_L^2\cos\frac{k}{2}\cos\left(q-\frac{k}{2}\right)\right] \times[\omega^4-2\omega^2\omega_L^2+2\omega^2\omega_L^2\cos\tfrac{1}{2}k\cos(q-\tfrac{1}{2}k)+\omega_L^4\sin^2\tfrac{1}{2}k\sin^2(q-\tfrac{1}{2}k)]^{-1}.$$

This integral is evaluated with due care to the principal value problem and the result for the shift is

$$\Delta_k(\omega)=\frac{\omega_k}{4\beta}\left(\frac{\epsilon}{\gamma^2}-\frac{\delta^2}{\gamma^3}\right)+\frac{\delta^2\omega_k\omega}{8\gamma^3\beta}[\theta(\omega^2-4\omega_L^2\sin^2\tfrac{1}{4}k)/(\omega^2-4\omega_L^2\sin^2\tfrac{1}{4}k)^{1/2}-\theta(\omega^2-4\omega_L^2\cos^2\tfrac{1}{4}k)/(\omega^2-4\omega_L^2\cos^2\tfrac{1}{4}k)^{1/2}]. \quad (41)$$

The modified normal mode frequency ϵ_k is determined by the equation

$$\epsilon_k^2=\omega_k^2+\frac{\omega_k^2}{2\beta}\left(\frac{\epsilon}{\gamma^2}-\frac{\delta^2}{\gamma^3}\right)+\frac{\delta^2\omega_k^2\epsilon_k}{4\gamma^3\beta} \times[\theta(\omega^2-4\omega_L^2\sin^2\tfrac{1}{4}k)/(\omega^2-4\omega_L^2\sin^2\tfrac{1}{4}k)^{1/2}-\theta(\omega^2-4\omega_L^2\cos^2\tfrac{1}{4}k)/(\omega^2-4\omega_L^2\cos^2\tfrac{1}{4}k)^{1/2}]. \quad (42)$$



(a) (b)

FIG. 1. (a) Dispersion curves for the linear chain. (b) Three solutions for the frequency of a linear chain.

This we rewrite as

$$\epsilon_k^2=\omega_k^2+P_1\omega_k^2+P_2\omega_k^2\epsilon_k\big[\theta(\epsilon_k^2-4\omega_L^2\sin^2\tfrac{1}{4}k)/(\epsilon_k^2-4\omega_L^2\sin^2\tfrac{1}{4}k)^{1/2}-\theta(\epsilon_k^2-4\omega_L^2\cos^2\tfrac{1}{4}k)/(\epsilon_k^2-4\omega_L^2\cos^2\tfrac{1}{4}k)^{1/2}\big],\quad(43)$$

where P_1 and P_2 are to be read from Eq. (42).

We notice that $\epsilon_k^2>4\omega_L^2\cos^2\frac{1}{4}k$ is not satisfied for any k. For values of k such that $\epsilon_k^2>4\omega_L^2\sin^2\frac{1}{4}k$, (43) becomes a cubic equation in ϵ_k. This cubic equation has been solved for various parameters which characterize anharmonicity, and temperatures and graphs for ϵ_k versus k have been plotted in Figs. 1(a) and 1(b) for $P_1=P_2=0.4$, $P_1=-P_2=-0.2$, and $P_1=1.0$, $P_2=0.1$. It appears to us that the existence of three acceptable roots is an interesting feature of the solution, although we can not comment on their significance. The drop at a particular value of k in Fig. 1(a) strongly resembles the Kohn type of effect in three-dimensional solids.

At low temperatures $N_1\simeq 1+2\sum_{n=1}^{\infty}e^{-\eta\beta\omega_1}$, and we get, after substituting (34) in (22),

$$\Delta_k(\omega)=\frac{\delta^2\omega_k\omega_L}{16\pi\gamma^3}\int_{-\pi}^{+\pi}dq\sin\left|\frac{q}{2}\right|\sin\left|\frac{k-q}{2}\right|\left(\sin\left|\frac{q}{2}\right|+\sin\left|\frac{k-q}{2}\right|\right)\left[\sin^2\frac{k}{2}-\left(\sin\left|\frac{q}{2}\right|+\sin\left|\frac{k-q}{2}\right|\right)^2\right]^{-1}+\frac{\epsilon\omega_k\omega_L}{4\pi\gamma^2}$$
$$+\frac{\delta^2\omega_k}{4\pi\gamma^3}\sum_{n=1}^{\infty}\int_{-\pi}^{+\pi}dq\omega_q\omega_{k-q}{}^2e^{-\eta\beta\omega_q}(\omega_k{}^2+\omega_q{}^2-\omega_{k-q}{}^2)\left[\omega_k{}^4-2\omega_k{}^2(\omega_q{}^2+\omega_{k-q}{}^2)+(\omega_q{}^2-\omega_{k-q}{}^2)^2\right]^{-1}$$
$$+\frac{\epsilon\omega_k\omega_L}{4\pi\gamma^2}\sum_{n=1}^{\infty}\int_0^{\pi}dq\sin\frac{q}{2}e^{-\eta\beta\omega_L\sin q/2}.\quad(44)$$

The first integral in (44) is evaluated by breaking it up into three integrals between the limits $-\pi$ to 0, 0 to k, and k to π, so that moduli are correctly accounted for and we obtain

$$\Delta_k=\frac{\omega_k}{4}\left(\frac{\epsilon}{\gamma^2}-\frac{\delta^2}{\gamma^3}\right)\frac{\omega_L}{\pi}+\frac{1}{12}\left(\frac{\epsilon}{\gamma^2}-\frac{\delta^2}{\gamma^3}\right)\frac{\pi\omega_k}{\beta^2\omega_L}.\quad(45)$$

The dispersion relation is

$$\epsilon_k^2=\omega_k^2\left[1+\frac{\omega_L}{2\pi}\left(\frac{\epsilon}{\gamma^2}-\frac{\delta^2}{\gamma^3}\right)+\frac{\pi}{\omega_L\beta^2}\left(\frac{\epsilon}{\gamma^2}-\frac{\delta^2}{\gamma^3}\right)\right].\quad(46)$$

This can be written as

$$\epsilon_k^2=\epsilon_L^2\omega_k^2.\quad(47)$$

In Eq. (47) ϵ_L is the new maximum frequency. Dispersion relation at low temperatures remains a sine curve except that the maximum frequency is changed.

(iii) Number Density

We have already shown that for a solid, the number density at absolute zero is nonvanishing. For a linear chain,

$$\Delta_k(T\to 0)=(\hbar\omega_L/4\pi)(\epsilon/\gamma^2-\delta^2/\gamma^3).$$

The number density at absolute zero is

$$n_k=\tfrac{1}{4}(\Delta_k/\omega_k)^2.$$

Maradudin and Fein[5] have given plausible values for ϵ, δ, γ, and ω_L for a model of lead which are

$$\epsilon=4.016\times10^{21}\ \text{erg/cm}^4,\quad \delta=-9.693\times10^{12}\ \text{erg/cm}^3$$
$$\gamma=1.819\times10^4\ \text{erg/cm}^2,\quad\text{and}\quad \omega_L=2.057\times10^{13}\ \text{sec}^{-1}.$$

Putting in these values we get the number of phonons to be $8.5\times10^{-4}\%$. This corresponds to about 10^{18} vibrations per mole.[9]

(iv) Energy and Specific Heat

For E_h, the energy at high temperatures, we obtain from Eqs. (33) and (43)

$$E_h=\frac{N}{6\beta}\left(5+\frac{\beta}{\beta+P}\right)-\frac{\epsilon N}{24\gamma^2\beta}\frac{1}{\beta+P},$$

where

$$P=\beta P_1.$$

The specific heat C_v is given by

$$\frac{C_v}{Nk_B}=\frac{1}{6}\left(5+\frac{\beta^2}{(\beta+P)^2}\right)-\frac{\epsilon}{24\gamma^2}\frac{2\beta+P}{(\beta+P)^2},\tag{48}$$

which of course agrees with the result of Maradudin and co-workers[1] if we make a perturbation expansion of (48) in powers of the parameter P_1.

At low temperatures, we obtain for the energy

$$E_l=\frac{N}{6\pi}\frac{\omega_L^2+5\epsilon_L^2}{\epsilon_L}+\frac{N\pi}{18\beta^2}\frac{(5\epsilon_L^2+\omega_L^2)}{\epsilon_L^3}-\frac{\epsilon N}{24\gamma^2}\left(\frac{\omega_L^2}{\pi\epsilon_L}+\frac{\pi^2\omega_L^2}{\beta^2\epsilon_L^3}\right)^2$$

from which the specific heat can be easily evaluated. The zero point energy is

$$E^{(0)}=\frac{N}{6\pi}\frac{\omega_L^2+5\epsilon_L^{0\,2}}{\epsilon_L^0}-\frac{\epsilon N\omega_L^4}{24\pi^2\gamma^2\epsilon_L^{0\,2}}\tag{49}$$

where ϵ_L^0 is the maximum frequency at absolute zero. In a perturbative sense our result (49) for the zero point energy does not agree with the result of Ref. 1.

However, if we make a series expansion of our Breit-Wigner function

$$\frac{2\omega_k\Gamma_k(\omega)}{(\omega^2-\epsilon_k^2)^2+4\omega_k^2\Gamma_k^2}\sim\pi\delta(\omega^2-\epsilon_k^2)+\frac{2\omega_k\Gamma_k(\omega)}{(\omega^2-\omega_k^2)^2}+\cdots\tag{50}$$

and integrate over ω, and then further expand the result for small Δ_k, we get the perturbation-theoretic results. If one adds the second term as above, one cannot be sure whether one can still talk of phonons in a meaningful way.[6] Using Eqs. (31) and (50), one can write the energy as the sum of three terms

$$E=E_1+E_2+E_3,\tag{51}$$

where

$$E_1=-\tfrac{1}{3}\langle V_4\rangle+\tfrac{1}{12}\sum_k((\omega_k^2+5\epsilon_k^2)/\epsilon_k)\coth\tfrac{1}{2}\beta\epsilon_k,$$

$$E_2=6\sum_{k,k_1,k_2}|V^{(3)}(-k,k_1,k_2)|^2\omega_k\left[\frac{(N_1+N_2)\coth\frac{1}{2}\beta(\omega_1+\omega_2)}{(\omega_1+\omega_2)^2-\omega_k^2}-\frac{(N_2-N_1)\coth\frac{1}{2}\beta(\omega_1-\omega_2)}{(\omega_1-\omega_2)^2-\omega_k^2}\right],$$

$$\begin{aligned}E_3=9\sum_{k,k_1,k_2}|V^{(3)}(-k,k_1,k_2)|^2\omega_k\Bigg\{&\frac{N_1+N_2}{((\omega_1-\omega_2)^2-\omega_k^2)^2}[((\omega_1+\omega_2)^2+\omega_k^2)\coth\tfrac{1}{2}\beta(\omega_1+\omega_2)-2\omega_k(\omega_1+\omega_2)]\\&+\frac{N_2-N_1}{((\omega_1-\omega_2)^2-\omega_k^2)^2}[((\omega_1-\omega_2)^2+\omega_k^2)\coth\tfrac{1}{2}\beta(\omega_1-\omega_2)-2\omega_k(\omega_1-\omega_2)]\Bigg\}.\end{aligned}\tag{52}$$

From Eqs. (52) we get for the zero-point energy

$$\begin{aligned}E_1^{(0)}&=\tfrac{1}{2}\sum_k\omega_k-\frac{\epsilon}{96\gamma^2N}\Big(\sum_k\omega_k\Big)^2+\frac{\epsilon\omega_L}{12\pi\gamma^2}\sum_k\omega_k+12\sum_{k,k_1,k_2}|\mathrm{V}^{(3)}(-k,k_1,k_2)|^2\frac{\omega_1+\omega_2}{\omega_k^2-(\omega_1+\omega_2)^2},\\E_2^{(0)}&=12\sum_{k,k_1,k_2}|V^{(3)}(-k,k_1,k_2)|^2\frac{\omega_k}{(\omega_1+\omega_2)^2-\omega_k^2},\\E_3^{(0)}&=18\sum_{k,k_1,k_2}|V^{(3)}(-k,k_1,k_2)|^2\frac{\omega_k}{(\omega_1+\omega_2+\omega_k)^2}.\end{aligned}\tag{53}$$

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[9] The author is thankful to Dr. A. A. Maradudin for bringing to his notice the importance of the number density.

Therefore from Eqs. (51) and (53) the zero-point energy is

$$E^{(0)}=\frac{N\omega_L}{\pi}+\frac{N\epsilon\omega_L{}^2}{8\pi^2\gamma^2}-\frac{\delta^2}{48\gamma^3N}\sum_{k,q}\frac{\omega_k\omega_q\omega_{k-q}}{\omega_k+\omega_q+\omega_{k-q}},\quad \frac{E^{(0)}}{N}=\frac{\omega_L}{\pi}+\frac{\epsilon\omega_L{}^2}{8\pi^2\gamma^2}-\frac{\omega_L{}^2\delta^2}{6\pi^3\gamma^3}\left[\frac{\pi}{16}(12-\pi^2)\right], \tag{54}$$

which is essentially the perturbation result of Ref. 1. Continuing as above, it can be shown that the specific heat at low temperature also agrees with the previously obtained result.

(v) Thermal Conductivity

Having calculated Γ_k one can use the expression[10] for lattice thermal conductivity

$$K=k_B\beta^2\sum_{\mathbf{q}j}\tau_{\mathbf{q}j}\omega_{\mathbf{q}j}{}^2C_{\mathbf{q}j}{}^2(e^{\beta\omega_{\mathbf{q}j}}/[e^{\beta\omega_{\mathbf{q}j}}-1]^2), \tag{55}$$

where $2\Gamma_k=(\tau_k)^{-1}$ and $C_{\mathbf{q}j}$ is the velocity of $(\mathbf{q}j)$ phonon, to calculate the thermal conductivity of a linear chain. It is

$$K=\frac{4k_B\beta^3\gamma^3}{\delta^2\omega_L}\sum_q\omega_q{}^2C_q{}^2\frac{e^{\beta\omega_q}}{[e^{\beta\omega_q}-1]^2}.$$

This reduces at high temperatures to

$$K_h/N=(k_B\beta\gamma^3\omega_La_0{}^2)/2\delta^2,$$

where a_0 is the separation between two atoms. At low temperatures

$$K_l/N=k_B\gamma^3a_0{}^2/\delta^2.$$

Thus the thermal conductivity at absolute zero is finite and at high temperature it decreases as $1/T$.

IV. APPLICATION TO SOLIDS

For a solid it is difficult to obtain any result without reference to a model. For the sake of simplicity we shall take the form of anharmonic coefficients $V^{(3)}$ and $V^{(4)}$ as taken by Klemens[11] in preference to the more realistic calculations of Maradudin, Fien and Vineyard[6,12]

$$V^{(3)}(-\mathbf{k}_1j_1,\,\mathbf{k}_2j_2,\,\mathbf{k}_3j_3)=(\lambda_j/288\omega_{Lj}N)\omega_1\omega_2\omega_3\Delta(-\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)$$

and

$$V^{(4)}(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\mathbf{k}_3j_3,\mathbf{k}_4j_4)=(\eta_j/96\omega_{Lj}N)(\omega_1\omega_2\omega_3\omega_4)^{1/2}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4), \tag{56}$$

where λ_j and η_j are dimensionless parameters. Further we assume that the summations over j_1 and j_2 implied in Eqs. (22) and (23) are such that the maximum contributions come when $j_1=j_2=j$. We can now write $\Delta_{\mathbf{k}j}$ and $\Gamma_{\mathbf{k}j}$ as

$$\begin{aligned}\Delta_{\mathbf{k}j}(\omega)&=\frac{\lambda_j\omega_{\mathbf{k}j}}{16\omega_{Lj}N}\sum_{\mathbf{k}_1,\mathbf{k}_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\omega_1\omega_2\left[(N_1+N_2)\frac{\omega_1+\omega_2}{\omega^2-(\omega_1+\omega_2)^2}+(N_1-N_2)\frac{(\omega_1-\omega_2)}{\omega^2-(\omega_1-\omega_2)^2}\right]\\&\qquad+\frac{\omega_{\mathbf{k}j}\eta_j}{8\omega_{Lj}N}\sum_{\mathbf{q}}\frac{\omega_{\mathbf{q}j}{}^2}{\epsilon_{\mathbf{q}j}}\coth\frac{\beta\epsilon_{\mathbf{q}j}}{2},\\ \Gamma_{\mathbf{k}j}(\omega)&=\frac{\pi\lambda_j\omega_{\mathbf{k}j}\epsilon(\omega)}{4\omega_{Lj}N}\sum_{\mathbf{k}_1,\mathbf{k}_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\omega_1{}^2\omega_2{}^2\\&\qquad\times[N_1\omega_2+N_2\omega_1+(N_1\omega_1+N_2\omega_2)\epsilon(\omega^2-\omega_1{}^2-\omega_2{}^2)]\delta(\omega^4-2\omega^2(\omega_1{}^2+\omega_2{}^2)+(\omega_1{}^2-\omega_2{}^2)^2).\end{aligned} \tag{57}$$

To proceed further, we have to (i) assume a particular form of harmonic dispersion relation which we have taken as

$$\omega_{kj}{}^2=\omega_{Lj}{}^2\sin^2\tfrac{1}{2}\pi ka_0,$$

where a_0 is the lattice constant, (ii) indicate the method of evaluating the summation $\mathbf{k}_1$, $\mathbf{k}_2$. We replace $\sum_{\mathbf{k}_1}\rightarrow(N/\Omega)\int k_1{}^2dk_1\sin\theta d\theta d\varphi$, where Ω is the volume of the first Brillouin zone.

A simple Debye model calculation of $\Delta_{\mathbf{k}j}$ has a logarithmic singularity due to poles at forward and backward angles. This means that the self-energy term is divergent for the anharmonic phonon whose frequency is proportional to wave number. It appears to us that this is sufficient reason not to use the Debye approximation for calculating anharmonic contributions because there is no way of getting rid of this infinity. A phonon with Debye dispersion relation (or a photon) can disintegrate into two phonons (or two photons) only in the forward direction, according to momentum and energy conservation considerations. Thus, the probability for disintegration into a pair and subsequent recombination to form a phonon is maximum at forward and backward

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[10] P. Carruthers, Rev. Mod. Phys. **33**, 72 (1961).

[11] P. G. Klemens, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 1.

[12] A. A. Maradudin, A. E. Fien, and G. H. Vineyard, Phys. Status Solidi **2**, 1479 (1962).

angles. It is not unreasonable to assume that the kernel of Eqs. (57) [call it $K\,(k_1, \cos\theta)$] possesses maxima for $\cos\theta = \pm 1$. We approximate the kernel by

$$K(k_1, \cos\theta) = \tfrac{1}{2}[K(k_1, +1) + K(k_1, -1)],$$

which implies that the kernel goes linearly from its maximum to zero at 90° and then rises linearly to a maximum at 180°. To us this appears to be a very reasonable approximation and may be termed a soft phonon approximation. With this approximation the integrals involved in calculating physical quantities are very similar to those encountered in the linear chain. Proceeding exactly as in Sec. II, the following results are obtained:

(i) Width

It is difficult to separate the normal and umklapp processes. In view of the approximation for ω_{kj}, the summand is no longer invariant under translation by a reciprocal lattice vector. Ignoring the distinction between these processes, we obtain for the width

$$\begin{aligned}\Gamma_{\mathbf{k}j} = \frac{\pi\lambda_j\omega_{\mathbf{k}j}}{4\omega_{Lj}}\left(\frac{N\pi}{\Omega}\right)\int_0^{k_m} dq\; q^2\omega_{\mathbf{q}}{}^2\omega_{\mathbf{k}-\mathbf{q}}{}^2 \\ \times[N_{\mathbf{q}}\omega_{\mathbf{k}-\mathbf{q}} + N_{\mathbf{k}-\mathbf{q}}\omega_{\mathbf{q}} + (N_{\mathbf{q}}\omega_{\mathbf{q}} + N_{\mathbf{k}-\mathbf{q}}\omega_{\mathbf{k}-\mathbf{q}}) \\ \times\epsilon(\sin\tfrac{1}{2}\pi q a_0 \sin\tfrac{1}{2}\pi(q-k)a_0)] \\ \times\delta(-4\omega_{Lj}{}^2\omega_{\mathbf{k}j}{}^2 \sin^2\tfrac{1}{2}\pi q a_0 \sin^2\tfrac{1}{2}\pi(k-q)a_0).\end{aligned} \tag{58}$$

The integral in (58) is evaluated in the same way as the integral of Eq. (37) and we get

$$\Gamma_{kj} = (3\lambda_j/32\beta)(ka_0)^2\theta(k_m - k). \tag{59}$$

This final result is not invariant under reciprocal lattice vector translation even though the original expression for Γ_k, [Eq. (23)] is invariant. A possible translationally invariant quantity could be

$$\Gamma_{kj} = (3\lambda_j/8\pi^2\beta\omega_{Lj})\omega_{kj}{}^2\theta(\omega_{Lj} - \omega_{kj}). \tag{60}$$

In our opinion this is a very good estimate of the phonon width.

The results of Brockhouse and co-workers[13] for lead indicate a $\sin^2\frac{1}{2}\pi k a_0$ variation for the width. There are, however, large experimental uncertainties for higher k values. We have evaluated Γ_{kj} for $\omega = \omega_{kj}$. In view of this (and our previous) approximations, the k^2 variation as obtained here is not inconsistent with experiment. An approximate comparison with the results of Ref. 13 shows that for the width to be of the order of 2 to 4 MeV at $ka_0 = 1$, we need $P_1 = (\lambda_j/4\beta\omega_{Lj})$ to be of the order of unity. It will be seen below that for this value of P_1, the dispersion relation shows a dip for ka_0 close to unity.

(ii) Thermal Conductivity

Since the width is proportional to temperature, the anharmonic contribution to the lattice thermal conductivity is inversely proportional to temperature at high temperatures. At low temperatures however, it is constant because the width varies as $(ka_0)^2$. Thus the variation of the thermal conductivity with temperature is similar to that of a linear chain.

(iii) Frequency–Wave-Vector Relations

We now proceed to calculate the energy shift and subsequently the dispersion relations for solids. We will consider both the high temperature and low temperature limits, and make use of our "soft-phonon" approximation.

At low temperatures, as before, we have

$$\Delta_{\mathbf{k}j} = \frac{\lambda_j\omega_{\mathbf{k}j}}{8\omega_{Lj}N}\sum_{\mathbf{q}}\omega_{\mathbf{q}}\omega_{\mathbf{k}-\mathbf{q}}\frac{\omega_{\mathbf{q}} + \omega_{\mathbf{k}-\mathbf{q}}}{\omega_{\mathbf{k}}{}^2 - (\omega_{\mathbf{q}} + \omega_{\mathbf{k}-\mathbf{q}})^2} + \frac{\omega_{\mathbf{k}j}\eta_j}{8\omega_{Lj}N}\sum_{\mathbf{q}}\omega_{\mathbf{q}}. \tag{61}$$

In the soft-phonon approximation the first term of (61) gives two integrals which have been evaluated by breaking the interval into 0 to k and k to k_m so that moduli are correctly accounted for and we obtain

$$\begin{aligned}\Delta_{kj} = (-3\lambda_j\omega_{kj}/4\pi^3)[\pi - 4 + \pi k a_0 \cot\tfrac{1}{2}\pi k a_0 \\ + (\tfrac{1}{2}\pi k a_0)^2] + 3\omega_{kj}\eta_j(\pi - 2)/\pi^3.\end{aligned} \tag{62}$$

Temperature-dependent terms have been omitted from (61). Finally we obtain the dispersion relation

$$\begin{aligned}\epsilon_{kj}{}^2 = \omega_{kj}{}^2[1 - (3\lambda_j/2\pi^3)(\pi - 4 + \pi k a_0 \cot\tfrac{1}{2}\pi k a_0 \\ + (\tfrac{1}{2}\pi k a_0)^2) + 6\eta_j(\pi - 2)/\pi^3].\end{aligned} \tag{63}$$

At high temperatures as usual, we have

$$\begin{aligned}\Delta_{\mathbf{k}j} = \frac{-\lambda_j\omega_{\mathbf{k}j}}{4\beta\omega_{Lj}} + \frac{\omega_{\mathbf{k}j}{}^3\lambda_j}{4\beta\omega_{Lj}N}\mathcal{P}\sum_{\mathbf{q}}[\omega_{\mathbf{k}j}{}^2 - \omega_{\mathbf{q}j}{}^2 - \omega_{\mathbf{k}-\mathbf{q},j}{}^2] \\ \times[\omega_{\mathbf{k}j}{}^4 - 2\omega_{\mathbf{k}j}{}^2(\omega_{\mathbf{q}j}{}^2 + \omega_{\mathbf{k}-\mathbf{q},j}{}^2) \\ + (\omega_{\mathbf{q}j}{}^2 - \omega_{\mathbf{k}-\mathbf{q},j}{}^2)^2]^{-1} + \frac{\omega_{\mathbf{k}j}\eta_j}{4\beta\omega_{Lj}}.\end{aligned} \tag{64}$$

Here again the soft-phonon approximation leads to two integrals. They combine together into one integral and we obtain

$$\Delta_{kj} = -\frac{\lambda_j\omega_{kj}}{4\beta\omega_{Lj}} + \frac{\lambda_j\omega_{kj}}{8\beta\omega_{Lj}}\cos^2(\tfrac{1}{2}\pi k a_0)I(ka_0) + \frac{\omega_{kj}\eta_j}{4\beta\omega_{Lj}}, \tag{65}$$

where

$$I(ka_0) = \frac{3}{\pi^3}\mathcal{P}\int_0^{\pi} dq\frac{q^2}{\cos q - \cos\pi k a_0}. \tag{66}$$

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[13] B. N. Brockhouse, T. Arase, G. Caglioti, M. Sakamoto, R. N. Sinclair, and A. D. B. Woods, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 531.

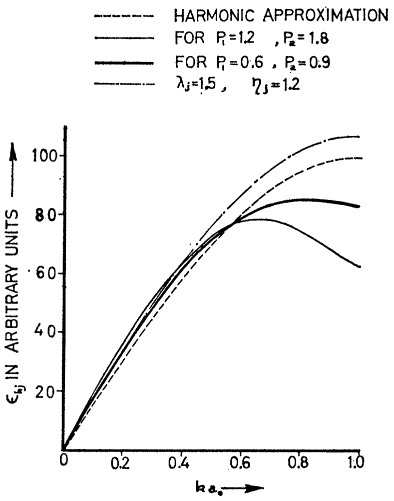

FIG. 2. Dispersion curves for solids.

The dispersion relation is

$$\epsilon_{kj}{}^2=\omega_{kj}{}^2\left[1-\frac{\lambda_j}{4\beta\omega_{Lj}}(2+\cos^2(\tfrac{1}{2}\pi ka_0)I(ka_0))+\frac{\eta_j}{2\beta\omega_{Lj}}\right]$$

$$=\omega_{kj}{}^2[1-P_1(2+\cos^2\tfrac{1}{2}(\pi ka_0)I(ka_0))+P_2]. \tag{67}$$

Integral (66), as it stands, has poles at $q=\pm\pi ka_0$. We subtract an integral which is zero to remove these poles, and evaluate the following integral numerically:

$$I(ka_0)=\frac{3}{\pi^3}\int_0^\pi dq\frac{q^2-\pi^2k^2a_0{}^2}{\cos q-\cos\pi ka_0}. \tag{68}$$

Curves depicting the $\epsilon_k(k)$ relation from Eqs. (63) and (67) are presented in Fig. 2. It is easily seen that the shape of the curve for $P_1=1.2$, $P_2=1.8$ is very similar to the experimentally observed dispersion curves for lead.[13,14] The dip however depends on the relative values of λ_j and η_j.

We repeat that the calculations on solids have been done using our soft phonon approximation which has made most calculations possible. A comparison with the more exact computer calculation of Maradudin and Fein[5] for lead will now be made to examine the extent to which our approximation can be trusted. For transverse modes they obtain (and also the experiments[13] agree) that $2\Gamma_k=0.25\times10^{-3}$ eV for $ka_0=0.2$ at 425°K. Using these values we get from our Eq. (59) for the transverse mode $\lambda_T\sim0.03$. From Eq. (65) we now calculate

$$\text{for } ka_0=0.25,\quad \frac{\Delta_k}{\omega_L}=-0.0035\times T/\theta_\infty,$$

$$\text{for } ka_0=0.50,\quad \frac{\omega_k}{\omega_L}=-0.0061\times T/\theta_\infty;$$

whereas, Maradudin and Fein[5] obtain $-0.00306\times T/\theta_\infty$ and $-0.0033\times T/\theta_\infty$, respectively, where $\theta_\infty=143.4$°K. In view of this agreement as to order of magnitude with an entirely different model, the approximation scheme suggested here seems to be reliable for obtaining estimates of anharmonic contributions to properties of a solid.

ACKNOWLEDGMENT

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[14] B. N. Brockhouse, T. Arase, G. Caglioti, K. R. Rao, and A. D. B. Woods, Phys. Rev. **128**, 1099 (1962).