

Anharmonic Contributions to Specific Heat*

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At temperatures appreciably above the Debye temperature, anharmonic parts of the lattice potential of a crystal make a contribution to the specific heat at constant volume that is nearly linear with the temperature, but of uncertain sign. Calculations on bcc and fcc crystals with a single atom per unit cell, based on central Lennard-Jones forces, show that the net effect is one of specific heat decreasing as temperature increases. The complicated sums involved can be simplified by use of a matrix inverse to the harmonic dynamical matrix, or by neglecting the dependence of phonon frequency on polarization. The latter method is used here. Forces between nearest and next-nearest neighbors are considered, and phonon dispersion is included approximately.

INTRODUCTION

THE harmonic approximation to lattice potential energy gives rise to a specific heat c_v of a solid that is independent of temperature, once the Debye temperature has been appreciably exceeded. Including terms in the potential energy cubic and quartic in lattice displacements provides a contribution to the specific heat that is nearly proportional to temperature, in this same temperature range. Many solid materials have a specific heat that appears to increase more or less linearly with temperature well above the Debye temperature (although an accurate $c_p - c_v$ correction is difficult to make). This rise is often attributed to the anharmonic forces and partly, in the case of metals, to specific heat of conduction electrons. (Throughout this paper, specific heat is to be understood as at constant volume except where the contrary is explicitly stated.)

The cubic and quartic parts of the lattice energy probably contribute with opposite signs to the specific heat, and it is not at all clear from the general theory¹ that the over-all effect is positive, i.e., specific heat increasing with increasing temperature. Since the cubic terms contribute to energies only in even orders of perturbation, the sign of this term is unique and positive. The sign of the contribution to specific heat due to the quartic part of the potential depends on the sign of this part of the potential itself. The effect can easily be understood for a collection of noninteracting oscillators. If the quartic term is such as to steepen the oscillator potential, this term increases the spacing between oscillator energy levels, reduces the number of levels effectively available at a given temperature, and so reduces the specific heat. The effect of quartic terms in the potential is indeed expected to be in this direction, since quartic terms arise principally from the strong interatomic repulsions at small distances. Our calculations on crystals confirm this conclusion, even though

in a solid the principal effect of anharmonic forces is to couple the different normal modes to one another.

The sign of the anharmonic contribution to specific heat is the principal concern of the present paper.

Concerning previous related theoretical studies, we do not believe that any work based on independent oscillators is adequate for our purpose. The studies of MacDonald and his colleagues² on a linear chain with nearest-neighbor interactions, and using a wide variety of interatomic potentials, showed conclusively that for this one-dimensional model, the anharmonic specific heat is negative. Henkel³ has obtained a similar result for a three-dimensional crystal, and the success that has been achieved in interpreting properties of solidified inert gases on the basis of Henkel's work implies that the specific heat in these materials does decrease with increasing temperature above the Debye temperature. Henkel's calculations, however, are based on an "Einstein model" in which each atom is considered as moving independently in a static potential. And, as Leech⁴ has pointed out for the case of a linear chain, an Einstein model automatically discards the effects of odd powers of displacements in the potential if the atom equilibrium positions are centers of inversion symmetry. Stern⁵ has made an ingenious calculation for c_p of a bcc crystal, based on a partition function for constant pressure p . Stern's calculation, however, rests on the assertion that a partition function for a small positive (constant) pressure and an effective Hamiltonian $H_0 + pV$ is identical with the partition function for zero pressure and effective Hamiltonian H_0 , an assertion with which we disagree.

Ludwig⁶ has obtained expressions for c_v , and an explicit formula for an fcc crystal with nearest-neighbor central forces, by replacing all frequencies by their root-mean-square values. Rather than use these expressions, we have attempted to include in at least an approximate way the variation of frequency with

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¹ R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955).

² J. S. Dugdale and D. K. C. MacDonald, *Phys. Rev.* **96**, 57 (1954); D. K. C. MacDonald and S. K. Roy, *Phys. Rev.* **97**, 673 (1955).

³ J. H. Henkel, *J. Chem. Phys.* **23**, 681 (1955).

⁴ J. W. Leech, *Can. J. Phys.* **37**, 1067 (1959).

⁵ E. A. Stern, *Phys. Rev.* **111**, 786 (1958).

⁶ W. Ludwig, *J. Phys. Chem. Solids* **4**, 283 (1958).

wavelength. A calculation by Coldwell-Horsfall *et al.*,⁷ reported when the present work was nearly completed, neglects certain force terms, but treats the frequencies exactly. Both this last work and that of Ludwig agree with ours in predicting that anharmonic forces decrease the specific heat.

GENERAL FORMULATION

We shall concern ourselves only with moderate temperatures, that is, with temperatures large enough so that we may neglect quantum (zero-point) effects and small enough so that (a) we may neglect anharmonic potential terms higher than quartic in the displacements, and (b) the anharmonic energy per atom (roughly proportional to T^2) is small compared to KT . (K is the Boltzmann factor, T the absolute temperature.)

Let us write the Hamiltonian for the system

$$H = H_0 + H_2 + H_3 + H_4, \quad (2.1)$$

where the successive terms represent the kinetic energy and the parts of the potential energy, respectively, quadratic, cubic, and quartic in the displacements of the atoms from equilibrium positions at the appropriate volume. Then we may make the usual expansion for the partition function Z and the Helmholtz function F in powers of the anharmonic energy divided by KT , keeping only the lowest contributing terms.

$$\begin{aligned} Z &= \sum \exp[-\beta(H_0 + H_2 + H_3 + H_4)] \\ &\approx \sum \exp[-\beta(H_0 + H_2)](1 - \beta H_4 + \frac{1}{2}\beta^2 H_3^2). \\ F &\approx F_0 + F_3 + F_4, \end{aligned} \quad (2.2)$$

where $\beta = (KT)^{-1}$, and F_0 is the harmonic approximation to F ,

$$\begin{aligned} F_3 &= -\frac{1}{2}\beta \langle H_3^2 \rangle \\ F_4 &= \langle H_4 \rangle. \end{aligned} \quad (2.3)$$

and $\langle \rangle$ indicates values averaged over the distribution unperturbed by the anharmonic terms. Since F_3 and F_4 turn out to be each proportional to T^2 , the anharmonic contribution to specific heat at constant volume is given by

$$\begin{aligned} c_v &\approx -T(\partial^2(F_3 + F_4)/\partial T^2)_v \\ &= -(2/T)(F_3 + F_4). \end{aligned} \quad (2.4)$$

Let us indicate by \mathbf{u} the displacement of an atom from its equilibrium position \mathbf{R} . Where a detailed indexing is necessary we shall refer to a particular Cartesian coordinate by i , a particular atom in a unit cell by j (in this section only), and a particular unit cell by n . A single symbol ρ , standing for both Cartesian coordinate i and atom j , will often be convenient. In this language, the potential-energy terms may be

written as

$$\begin{aligned} H_2 &= (1/2!) \sum \mathbf{A}(n\rho, n'\rho') \mathbf{u}\mathbf{u}', \\ H_3 &= (1/3!) \sum \mathbf{B}(n\rho, n'\rho', n''\rho'') \mathbf{u}\mathbf{u}'\mathbf{u}'', \\ H_4 &= (1/4!) \sum \mathbf{C}(n\rho, n'\rho', n''\rho'', n'''\rho''') \mathbf{u}\mathbf{u}'\mathbf{u}''\mathbf{u}'''. \end{aligned} \quad (2.5)$$

The sums are to be taken over all coordinates of all atoms of all cells, and \mathbf{u}' has been written for $\mathbf{u}(n'\rho')$, etc. The tensors \mathbf{A} , \mathbf{B} , \mathbf{C} are symmetric in the sense that

$$\mathbf{B}(n\rho, n'\rho', n''\rho'') = \mathbf{B}(n'\rho', n\rho, n''\rho''),$$

etc., and the invariance of the potential energy to uniform displacement of the entire crystal gives rise to a number of convenient identities⁸:

$$\begin{aligned} \sum_{nj} \mathbf{A}(n\rho, n'\rho') &= \sum_{n'j'} \mathbf{A}(n\rho, n'\rho') = 0, \\ \sum_{nj} \mathbf{B}(n\rho, n'\rho', n''\rho'') &= \sum_{n'j'} \mathbf{B}(n\rho, n'\rho', n''\rho'') \\ &= \sum_{n''j''} \mathbf{B}(n\rho, n'\rho', n''\rho'') = 0, \\ \sum_{nj} \mathbf{C}(n\rho, n'\rho', n''\rho'', n'''\rho''') &= \sum_{n'j'} \mathbf{C}(n\rho, n'\rho', n''\rho'', n'''\rho''') \\ &= \sum_{n''j''} \mathbf{C}(n\rho, n'\rho', n''\rho'', n'''\rho''') \\ &= \sum_{n'''j'''} \mathbf{C}(n\rho, n'\rho', n''\rho'', n'''\rho''') = 0. \end{aligned} \quad (2.6)$$

In order to work in wave-vector space, it is convenient to introduce Fourier transforms of the potential energy tensors

$$\begin{aligned} \mathbf{a}(\mathbf{k}, \mathbf{k}'\rho') &= \sum_n \mathbf{A}(n\rho, n'\rho') \exp[i(\mathbf{k} \cdot \mathbf{R} + \mathbf{k}' \cdot \mathbf{R}')] \delta(\mathbf{k} + \mathbf{k}'), \\ \mathbf{b}(\mathbf{k}, \mathbf{k}'\rho', \mathbf{k}''\rho'') &= \sum_{n'n''} \mathbf{B}(n\rho, n'\rho', n''\rho'') \\ &\quad \times \exp[i(\mathbf{k} \cdot \mathbf{R} + \mathbf{k}' \cdot \mathbf{R}' + \mathbf{k}'' \cdot \mathbf{R}'')] \delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}''), \\ \mathbf{c}(\mathbf{k}, \mathbf{k}'\rho', \mathbf{k}''\rho'', \mathbf{k}'''\rho''') &= \sum_{n'n''n'''} \mathbf{C}(n\rho, n'\rho', n''\rho'', n'''\rho''') \\ &\quad \times \exp[i(\mathbf{k} \cdot \mathbf{R} + \mathbf{k}' \cdot \mathbf{R}' + \mathbf{k}'' \cdot \mathbf{R}'' + \mathbf{k}''' \cdot \mathbf{R}''')] \delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}'' + \mathbf{k}'''). \end{aligned} \quad (2.7)$$

The function $\delta(\mathbf{k})$ has value unity if its argument is zero or 2π times a reciprocal vector, and is zero otherwise. It is introduced into the above expressions because the sums in Eq. (2.5) over all unit cells eliminate all Fourier transforms for which the corresponding δ 's vanish. The harmonic approximation is handled in the customary way by the introduction of normal-mode vectors $\mathbf{v}_\rho(\mathbf{k}\lambda)$. Components of each normal-mode vector are characterized by ρ , i.e., by a particular atom of the unit cell as well as by a particular Cartesian coordinate. Different normal-mode vectors (enumerated by the "polarization" index λ) belonging to a particular wave vector \mathbf{k} are orthogonal since they are eigenvectors of the \mathbf{a} matrices:

$$\sum_{\rho'} \mathbf{a}(-\mathbf{k}, \mathbf{k}\rho') \mathbf{v}_{\rho'}(\mathbf{k}\lambda) = m_j \omega^2(\mathbf{k}\lambda) \mathbf{v}_\rho(\mathbf{k}\lambda). \quad (2.8)$$

Here m_j is the mass of the j th atom of the unit cell, and

⁸ See reference 1, pp. 15, 33.

⁷ R. A. Coldwell-Horsfall, P. A. Flinn, and A. A. Maradudin, Bull. Am. Phys. Soc. **6**, 119 (1961); A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. (New York) **15**, 360 (1961).

ω is the circular frequency of the normal mode. The \mathbf{v} 's are normalized so that

$$\sum_{\rho} m_j \mathbf{v}_{\rho}(-\mathbf{k}\lambda) \mathbf{v}_{\rho}(\mathbf{k}\lambda') = M_c \delta_{\lambda\lambda'}, \quad (2.9)$$

where M_c is the mass of a unit cell. There is also a completeness relation between the \mathbf{v} 's for each wave vector, namely

$$m_j \sum_{\lambda} \mathbf{v}_{\rho}(\mathbf{k}\lambda) \mathbf{v}_{\rho'}(-\mathbf{k}\lambda) = M_c \delta_{\rho\rho'}. \quad (2.10)$$

It is often convenient to use a single symbol σ to stand for $(\mathbf{k}\lambda)$, and to use $-\sigma$ for $(-\mathbf{k}\lambda)$.

For a crystal containing N unit cells, the displacement for any atom can be written in terms of the normal-mode vectors and their associated amplitudes or normal coordinates $q(\sigma)$ as

$$\mathbf{u}(n\rho) = N^{-1/2} \sum_{\sigma} q(\sigma) \mathbf{v}_{\rho}(\sigma) \exp(i\mathbf{k} \cdot \mathbf{R}). \quad (2.11)$$

$$F_3 = -\frac{1}{72NKT} \left(\frac{KT}{M_c} \right)^3 \sum \frac{\mathbf{v}_{\rho}(\sigma) \mathbf{v}_{\rho'''}(-\sigma) \mathbf{v}_{\rho'}(\sigma') \mathbf{v}_{\rho''}(-\sigma') \mathbf{v}_{\rho'''}(\sigma'') \mathbf{v}_{\rho''}(-\sigma'')}{\omega^2(\sigma) \omega^2(\sigma') \omega^2(\sigma'')} \\ \times [6\mathbf{b}(\mathbf{k}\rho, \mathbf{k}'\rho', \mathbf{k}''\rho'') \mathbf{b}(-\mathbf{k}\rho''', -\mathbf{k}'\rho^{iv}, -\mathbf{k}''\rho^v) + 9\mathbf{b}(\mathbf{k}\rho, -\mathbf{k}\rho''', 0\rho'') \mathbf{b}(\mathbf{k}'\rho', -\mathbf{k}'\rho^{iv}, 0\rho^v) \delta(\mathbf{k}'')], \quad (2.14)$$

$$F_4 = \frac{1}{8N} \left(\frac{KT}{M_c} \right)^2 \sum \frac{\mathbf{v}_{\rho}(\sigma) \mathbf{v}_{\rho'}(-\sigma) \mathbf{v}_{\rho''}(\sigma'') \mathbf{v}_{\rho'''}(-\sigma'')}{\omega^2(\sigma) \omega^2(\sigma'')} \mathbf{c}(\mathbf{k}\rho, -\mathbf{k}\rho', \mathbf{k}''\rho'', -\mathbf{k}'''\rho''').$$

Equations (2.14) constitute the usual formulation for F_3 and F_4 in the classical limit. It is possible to make a formal simplification by observing that if we consider $\mathbf{a}(-\mathbf{k}\rho, \mathbf{k}\rho')$ as the $\rho\rho'$ element of a matrix $\mathbf{a}(\mathbf{k})$, then

$$F_3 = -(1/72NKT)(KT)^3 \sum [(\mathbf{a}(\mathbf{k}))^{-1}]_{\rho\rho'''} [(\mathbf{a}(\mathbf{k}'))^{-1}]_{\rho'\rho^{iv}} \\ \times \left\{ 6[(\mathbf{a}(\mathbf{k}''))^{-1}]_{\rho''\rho^v} \mathbf{b}(\mathbf{k}\rho, \mathbf{k}'\rho', \mathbf{k}''\rho'') \mathbf{b}(-\mathbf{k}\rho''', -\mathbf{k}'\rho^{iv}, -\mathbf{k}''\rho^v) \right. \\ \left. + 9\delta(\mathbf{k}'') \sum_{\lambda''} \frac{\mathbf{v}_{\rho''}(\lambda'') \mathbf{v}_{\rho'''}(\lambda'')}{M_c \omega^2(\lambda'')} \mathbf{b}(\mathbf{k}\rho, -\mathbf{k}\rho''', 0\rho'') \mathbf{b}(\mathbf{k}'\rho', -\mathbf{k}'\rho^{iv}, 0\rho^v) \right\}, \quad (2.16)$$

$$F_4 = (1/8N)(KT)^2 \sum \mathbf{c}(\mathbf{k}\rho, -\mathbf{k}\rho', \mathbf{k}''\rho'', -\mathbf{k}'''\rho''') [(\mathbf{a}(\mathbf{k}))^{-1}]_{\rho\rho'} [(\mathbf{a}(\mathbf{k}''))^{-1}]_{\rho''\rho'''}.$$

Except for $\mathbf{k}=0$ [for which $\mathbf{a}(\mathbf{k})$ is an improper matrix], the normal mode vectors and the polarizations have been eliminated in expressions (2.16). These equations are probably a useful starting point for an exact calculation.

The second term in brackets in the expressions for F_3 in both Eqs. (2.14) and (2.16) arises only if there is more than one atom per cell, as it involves optic modes for $\mathbf{k}=0$.¹⁰

ONE ATOM PER UNIT CELL

To this point, no approximations have been made beyond the application of lowest order perturbation

⁹ The fact that terms of 4th and 6th degree in the q 's are averaged correctly by this method is (the classical counterpart of) a consequence of the extension of Wick's theorem by C. Bloch and C. de Domenicis, Nuclear Phys. 7, 459 (1958).

¹⁰ See reference 1, pp. 37 and 38.

Then the various terms in the energy become

$$H_0 + H_2 = \frac{1}{2} M_c \sum_{\sigma} [\dot{q}(\sigma) \dot{q}(-\sigma) + \omega^2(\sigma) q(\sigma) q(-\sigma)], \\ H_3 = (1/3!) N^{-1/2} \sum \mathbf{b}(\mathbf{k}\rho, \mathbf{k}'\rho', \mathbf{k}''\rho'') q q' q'' \mathbf{v} \mathbf{v}' \mathbf{v}'', \\ H_4 = (1/4!) N^{-1} \sum \mathbf{c}(\mathbf{k}\rho, \mathbf{k}'\rho', \mathbf{k}''\rho'', \mathbf{k}'''\rho''') \\ \times q q' q'' q''' \mathbf{v} \mathbf{v}' \mathbf{v}'' \mathbf{v}'''. \quad (2.12)$$

The sums in these last two expressions are over all Cartesian components, all atoms in the unit cell, all wave numbers and all polarizations. Now to obtain the averages required for expressing the free energy [Eqs. (2.3)] it is only necessary to observe that

$$M_c \omega^2(\sigma) \langle q(\sigma) q(-\sigma) \rangle = KT, \quad (2.13)$$

and that all quantities of odd degree in the q 's, as well as all other quadratic functions of the q 's, average to zero.⁹ The results are

$$\sum_{\lambda} \mathbf{v}_{\rho}(\mathbf{k}\lambda) \mathbf{v}_{\rho'}(-\mathbf{k}\lambda) \omega^{-2}(\mathbf{k}\lambda) = M_c [(\mathbf{a}(\mathbf{k}))^{-1}]_{\rho\rho'}. \quad (2.15)$$

Equation (2.15) is precisely the eigenvector expansion for the inverse matrix $[\mathbf{a}(\mathbf{k})]^{-1}$. This relation enables the expressions for free energy to be rewritten as

theory. But for crystals with only a single atom per unit cell, all normal modes are acoustic. From now on we limit our discussion to this class, and for these substances it is a reasonable approximation to neglect the dependence of frequency on polarization, and treat all modes for a given wave vector as having the same frequency. In this approximation, the sums over polarization in Eqs. (2.14) are accomplished by Eq. (2.10), and one finds for F_3 and F_4

$$F_3 = -\frac{(KT)^2}{12N\bar{m}^3} \sum_{kk'k''} \frac{|\mathbf{b}(\mathbf{k}, \mathbf{k}', \mathbf{k}'')_{ijl}|^2}{\omega^2(\mathbf{k}) \omega^2(\mathbf{k}') \omega^2(\mathbf{k}''')}, \quad (3.1)$$

$$F_4 = \frac{(KT)^2}{8N\bar{m}^2} \sum_{kk'k''} \frac{\mathbf{c}(\mathbf{k}, -\mathbf{k}, \mathbf{k}', -\mathbf{k}')_{iiij}}{\omega^2(\mathbf{k}) \omega^2(\mathbf{k}')}. \quad (3.2)$$

(A slight change has been made in the form for writing

the potential tensors; also all Latin subscripts now indicate Cartesian components.)

In order to do the sums over k space, it is necessary to restore the explicit k dependence of the coefficients \mathbf{b} and \mathbf{c} , Eq. (2.7). It is convenient now to limit the discussion to anharmonic forces describable by two-particle potentials, that is, to central forces. This limitation is not essential and is made primarily to restrict the number of parameters entering the calculation; but it does introduce some convenient simplifications. The potential tensors \mathbf{B} and \mathbf{C} can involve at most two different atoms (n and n'). And translational invariance [Eqs. (2.6)] requires that

$$\begin{aligned} \mathbf{B}(n, n, n)_{ijl} + \sum_{n' \neq n} \mathbf{B}(n, n', n')_{ijl} &= 0, \\ \mathbf{B}(n, n', n)_{ijl} + \mathbf{B}(n, n', n')_{ijl} &= 0, \quad (n' \neq n) \\ \mathbf{C}(n, n, n, n)_{ijlm} + \sum_{n' \neq n} \mathbf{C}(n, n, n, n')_{ijlm} &= 0, \\ \mathbf{C}(n, n, n', n)_{ijlm} + \mathbf{C}(n, n, n', n')_{ijlm} &= 0 \quad (n' \neq n). \end{aligned} \quad (3.3)$$

The first of these relations is obtained by applying Eq. (2.6) to \mathbf{B} 's having the first two atoms both equal to n , summing over the third atom; the second relation arises from \mathbf{B} 's with the first two atoms different. The relations between the \mathbf{C} 's are obtained similarly. The sums of Eq. (2.6) can also be carried out on atoms other than the last. If the results are compared with those already written in Eqs. (3.3), one observes that for $n' \neq n$

$$\begin{aligned} \mathbf{B}(n, n', n)_{ijl} &= \mathbf{B}(n, n, n')_{ijl} = -\mathbf{B}(n, n', n')_{ijl} = -\mathbf{B}(n', n', n)_{ijl}, \\ \mathbf{C}(n, n', n, n)_{ijlm} &= \mathbf{C}(n, n, n', n')_{ijlm} \\ &= -\mathbf{C}(n, n, n', n')_{ijlm} = -\mathbf{C}(n, n', n', n)_{ijlm} \\ &= -\mathbf{C}(n, n', n', n)_{ijlm} = \mathbf{C}(n, n', n', n')_{ijlm}. \end{aligned} \quad (3.4)$$

Explicit forms for the Fourier transformed tensors \mathbf{b} and \mathbf{c} , for the cases of interest, are now

$$\begin{aligned} \mathbf{b}(\mathbf{k}, \mathbf{k}', \mathbf{k}'')_{ijl} &= - \sum_{n' \neq n} \mathbf{B}(n, n, n')_{ijl} [1 - \exp(i\mathbf{k}' \cdot (\mathbf{R}' - \mathbf{R}))] \\ &\quad \times [1 - \exp(i\mathbf{k}'' \cdot (\mathbf{R}' - \mathbf{R}))] \delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}''). \quad (3.5) \\ \mathbf{c}(\mathbf{k}, -\mathbf{k}, \mathbf{k}', -\mathbf{k}')_{iijj} &= 2 \sum_{n' \neq n} \mathbf{C}(n, n, n', n')_{iijj} [1 - \cos(\mathbf{k}' \cdot (\mathbf{R}' - \mathbf{R}))] \\ &\quad \times [1 - \exp(-i\mathbf{k} \cdot (\mathbf{R}' - \mathbf{R}))]. \end{aligned}$$

The sum over \mathbf{k} and \mathbf{k}' in expression (3.2) for F_4 is seen to factor into two independent sums. The sum in expression (3.1) for F_3 is more formidable. It appears as a sum over \mathbf{k} and \mathbf{k}' , each wave-vector summation extended over the Brillouin zone. But the sums are

not independent, being coupled by $\omega^{-2}(\mathbf{k}'')\delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}'')$. We can, however, remove $\delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}'')$ by the identity

$$N^{-1} \sum_n \exp(i\mathbf{k} \cdot \mathbf{R}_n) = \delta(\mathbf{k}). \quad (3.6)$$

(In fact, the δ arose in the first place from just such a sum.) We also replace sums over k space by integrals. Thus, for a crystal of volume V ,

$$\begin{aligned} F_3 &= - \frac{(KT)^2}{12N^2m^3} \left(\frac{V}{8\pi^3} \right)^3 \sum_{i,j,l,n',n''} \mathbf{B}(n, n, n')_{ijl} \mathbf{B}(n, n, n'')_{ijl} \\ &\quad \times \sum_n \int d^3k \exp(i\mathbf{k} \cdot \mathbf{R}) \omega^{-2}(\mathbf{k}) \int d^3k' \exp(i\mathbf{k}' \cdot \mathbf{R}) \\ &\quad \times [1 - \exp(i\mathbf{k}' \cdot (\mathbf{R}' - \mathbf{R}))] \\ &\quad \times [1 - \exp(-i\mathbf{k}'' \cdot (\mathbf{R}'' - \mathbf{R}))] \omega^{-2}(\mathbf{k}'') \\ &\quad \times \int d^3k'' \exp(i\mathbf{k}'' \cdot \mathbf{R}) [1 - \exp(i\mathbf{k}'' \cdot (\mathbf{R} - \mathbf{R}))] \\ &\quad \times [1 - \exp(-i\mathbf{k}'' \cdot (\mathbf{R}'' - \mathbf{R}))] \omega^{-2}(\mathbf{k}''). \end{aligned} \quad (3.7)$$

The integrals over wave-vector space are now all independent and all of the same type. We approximate to them by (a) replacing the actual Brillouin zone by a sphere of radius $k_0 = (6\pi^2 N/V)^{1/3}$, (b) ignoring the dependence of $\omega(\mathbf{k})$ on direction, and (c) assuming a standard form for the dependence of $\omega(k)$ on the magnitude of k . As to the latter, ω^2 should be proportional to k^2 for small k . The periodicity of ω^2 in k space is simulated by requiring $\omega^2(k)$ to have a vanishing slope at $k = k_0$. A simple function with these properties, nearly equal to $\sin^2(\pi k/2k_0)$ but more convenient for the radial integrals in Eq. (3.7), is

$$\omega^2(k) = \pi^2 x^2 [4 + (\pi^2 - 8)x^2 + 4x^4]^{-1} \omega_0^2, \quad (3.8)$$

where

$$x = k/k_0.$$

With these various approximations, all the integrals over k space reduce to the single integral

$$J(R) = \pi^{-2} \int_0^1 [4 + (\pi^2 - 8)x^2 + 4x^4]^{-1} \times [\sin(k_0 R x)/k_0 R x] dx, \quad (3.9)$$

which depends only on the magnitude $k_0 R$ and can be expressed in terms of the sine integral and elementary functions.

$$J(0) = 32/15\pi^2 + \frac{1}{3}. \quad (3.9a)$$

The free energies now take the forms

$$F_3 = -(9/4) [N(KT)^2/m^3 \omega_0^6] \sum_{i,j,l,n',n''} D(n', n'') \times \mathbf{B}(n, n, n')_{ijl} \mathbf{B}(n, n, n'')_{ijl}, \quad (3.10)$$

$$F_4 = (9/4) [N(KT)^2/m^2 \omega_0^4] \sum_{i,j,n'} [J(0) - J(R')]^2 \times \mathbf{C}(n, n, n', n')_{ii jj}, \quad (3.11)$$

where $\mathbf{r}' = \mathbf{R}' - \mathbf{R}$, etc., and

$$D(n', n'') \equiv \sum_n J(R_n) [J(R_n) - J(|\mathbf{R}_n + \mathbf{r}'|) - J(|\mathbf{R}_n - \mathbf{r}''|) + J(|\mathbf{R}_n + \mathbf{r}' - \mathbf{r}''|)]^2. \quad (3.12)$$

BODY- AND FACE-CENTERED CUBIC CRYSTALS

Equations (3.10) and (3.11) have been evaluated numerically in four cases. In each case, a Lennard-Jones 6-12 potential of the form

$$\phi = V_0 [(s/r)^{12} - 2(s/r)^6] \quad (4.1)$$

was assumed to represent the interaction between atoms, where V_0 and s are constants. Calculations were made for a bcc lattice and for an fcc lattice assuming nearest-neighbor interactions only. For each lattice, the calculations were repeated including second-neighbor interactions as well; for these cases, both interactions were described by the same potential (4.1).

The constant s in the potential was chosen in each case to make the potential energy a minimum at the equilibrium arrangement. In so doing, zero-point energy was neglected. For nearest-neighbor-only interactions, s was thus equated to the nearest-neighbor distance ($\sqrt{3}a/2$ for bcc, $\sqrt{2}a/2$ for fcc, where a is the cubic lattice spacing). Inclusion of second-neighbor interactions increases s slightly.

To evaluate the interaction tensors **A**, **B**, and **C** it is convenient to consider ϕ as a function of r^2 , the squared distance between the two atoms. Then ϕ can be expanded about \bar{r}^2 , the squared equilibrium distance. If the equilibrium position of one atom is considered at the origin, and indicated by a subscript 0,

$$\begin{aligned} \phi(r^2) = & \phi(\bar{r}^2) + 2[\bar{\mathbf{r}} \cdot (\mathbf{u} - \mathbf{u}_0)]\phi' \\ & + \{(\mathbf{u} - \mathbf{u}_0)^2\phi' + 2[\bar{\mathbf{r}} \cdot (\mathbf{u} - \mathbf{u}_0)]^2\phi''\} \\ & + \{2[\bar{\mathbf{r}} \cdot (\mathbf{u} - \mathbf{u}_0)](\mathbf{u} - \mathbf{u}_0)^2\phi'' + \frac{4}{3}[\bar{\mathbf{r}} \cdot (\mathbf{u} - \mathbf{u}_0)]^3\phi'''\} \\ & + \{\frac{1}{2}(\mathbf{u} - \mathbf{u}_0)^4\phi'' + 2[\bar{\mathbf{r}} \cdot (\mathbf{u} - \mathbf{u}_0)]^2(\mathbf{u} - \mathbf{u}_0)^2\phi'' \\ & + \frac{2}{3}[\bar{\mathbf{r}} \cdot (\mathbf{u} - \mathbf{u}_0)]^4\phi'''\} + \dots \quad (4.2) \end{aligned}$$

A prime indicates differentiation with respect to r^2 evaluated at \bar{r}^2 .

The total potential energy of the crystal [Eqs. (2.5)] is made up of sums of interatomic potentials of the form of Eq. (4.2). It simplifies the comparison between these two expressions if the crystal energy is written in a form appropriate for two-body potentials. For example, Eqs. (3.3) and (3.4) allow the cubic part of the crystal potential to be written as

$$H_3 = -(1/3!) \sum'_{n, n', i, j, l} \mathbf{B}(n, n')_{ijl} \times u_i(u_j' - u_j)(u_l' - u_l). \quad (4.3)$$

The symbol \sum' indicates that the sum is restricted to different atoms n and n' . If the primed and unprimed atoms are interchanged in expression (4.3), and use is again made of Eq. (3.4), the resulting form may be

TABLE I. Cubic and quartic potential energy tensors.

n'	ijl	$\mathbf{B}(0, 0, n')_{ijl}$
$a/2, a/2, a/2$	111, 222, 333 112, 113, 223, etc. 123	$6a\phi'' + a^3\phi'''$ $2a\phi'' + a^3\phi'''$ $a^3\phi'''$
$0, a/2, a/2$	112, 113 222, 333 223, 233 odd number of Cartesian indices equal to 1	$2a\phi''$ $6a\phi'' + a^3\phi'''$ $2a\phi'' + a^3\phi'''$ 0
$a, 0, 0$	111 122, 133 123 even number of Cartesian indices equal to 1	$12a\phi'' + 8a^3\phi'''$ $4a\phi''$ 0 0
n'	$ijlm$	$\mathbf{C}(0, 0, n', n')_{ijlm}$
$a/2, a/2, a/2$	1111, 2222, 3333 1112, 1113, 2223, etc. 1122, 1133, 2233 1123, 1223, 1233	$12\phi'' + 12a^2\phi''' + a^4\phi''''$ $6a^2\phi''' + a^4\phi''''$ $4\phi'' + 4a^2\phi''' + a^4\phi''''$ $2a^2\phi''' + a^4\phi''''$
$0, a/2, a/2$	1111 2222, 3333 2223, 2333 1122, 1133 2233 1123 odd number of Cartesian indices equal to 1	$12\phi''$ $12\phi'' + 12a^2\phi''' + a^4\phi''''$ $6a^2\phi''' + a^4\phi''''$ $4\phi'' + 2a^2\phi'''$ $4\phi'' + 4a^2\phi''' + a^4\phi''''$ $2a^2\phi'''$ 0
$a, 0, 0$	1111 2222, 3333 1122, 1133 2233 odd number of Cartesian indices equal to 1, 2, or 3	$12\phi'' + 48a^2\phi''' + 16a^4\phi''''$ $12\phi''$ $4\phi'' + 8a^2\phi'''$ $4\phi''$ 0

averaged with expression (4.3) to give

$$H_3 = \frac{1}{12} \sum'_{n, n', i, j, l} \mathbf{B}(n, n')_{ijl} \times (u_i' - u_i)(u_j' - u_j)(u_l' - u_l). \quad (4.4)$$

An identical procedure applied to the quartic part of the potential energy yields the form

$$H_4 = \frac{1}{48} \sum'_{n, n', i, j, l, m} \mathbf{C}(n, n', n', n')_{ijlm} \times (u_i' - u_i)(u_j' - u_j)(u_l' - u_l)(u_m' - u_m). \quad (4.5)$$

Table I lists the **B** and **C** tensors for some pairs of atoms. In each case, the atom n is considered at the origin, and the other atom is a nearest or next-nearest neighbor. The tensors for other neighbors can be obtained from those listed by the following two rules found by studying Eq. (4.2):

(a). If the atom n is at the origin, and if n'' is obtained from n' by interchanging, for example, x and y Cartesian coordinates, an element of a tensor coupling n with n'' is equal to that element of the corresponding tensor coupling n and n' , in which every Cartesian index equal to x is replaced by y , and vice versa.

TABLE II. Values of $J(R)$ and $D(n, n')$.^a

bcc			fcc		
$J(0)$	0.54949		$J(0)$	0.54949	
$J(\sqrt{3}a/2)$	0.15917		$J(\sqrt{2}a/2)$	0.14942	
$J(a)$	0.11452		$J(a)$	0.07859	
n'	n''	$D(n', n'')$	n'	n''	$D(n', n'')$
$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	0.38831	$\frac{1}{2}, \frac{1}{2}, 0$	$\frac{1}{2}, \frac{1}{2}, 0$	0.40396
$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}$	0.12258	$\frac{1}{2}, \frac{1}{2}, 0$	$\frac{1}{2}, 0, \frac{1}{2}$	0.15493
$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}$	0.10965	$\frac{1}{2}, \frac{1}{2}, 0$	$-\frac{1}{2}, 0, \frac{1}{2}$	0.12700
$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}$	0.17665	$\frac{1}{2}, \frac{1}{2}, 0$	$-\frac{1}{2}, -\frac{1}{2}, 0$	0.18180
$1, 0, 0$	$1, 0, 0$	0.46726	$1, 0, 0$	$1, 0, 0$	0.54507
$1, 0, 0$	$-1, 0, 0$	0.19676	$1, 0, 0$	$-1, 0, 0$	0.20377
$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$1, 0, 0$	0.17747	$\frac{1}{2}, \frac{1}{2}, 0$	$1, 0, 0$	0.20221
$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$-1, 0, 0$	0.14144	$\frac{1}{2}, \frac{1}{2}, 0$	$-1, 0, 0$	0.15820

^a Cartesian components of n' and n'' are expressed in units of the cubic lattice parameter a .

(b). If the atom n'' is obtained from n' by reversing, for example, the x Cartesian coordinate, the **C** tensors are unaltered, and the **B** tensor elements are multiplied by -1 for each Cartesian index that equals x .

It has already been noted that the tensors **B** and **C** are completely symmetric.

Numerical values of the integrals $J(R)$ and of the sums $D(n', n'')$, defined by Eqs. (3.9) and (3.12), respectively, are listed in Table II. They were obtained

from high-speed computing machines. Because of the slow convergence of the sums, the machine results for the D 's were supplemented by estimates of remainders (about 0.2% of the totals) based on the asymptotic behavior of the J 's.

A comparison of the approximate expressions (3.10) and (3.11) for the cubic and quartic parts of the free energy shows a somewhat different dependence on the assumed maximum frequency ω_0 . Before numerical estimates for F_3 and F_4 can be compared, it is necessary to express ω_0 in terms of the strength V_0 of the interatomic potential. Equation (3.8) gives for the mean value of ω^{-2} averaged over the Brillouin zone

$$\langle \omega^{-2} \rangle = 3J(0)\omega_0^{-2}. \quad (4.6)$$

The somewhat involved procedure by which this same quantity was estimated from the harmonic forces, and the proportionality constants between ω_0^2 and V_0/ma^2 determined, is described in the appendix.

Some of the numerical details of the calculations are shown in Table III.

DISCUSSION

In each of the cases calculated, the contribution to the Helmholtz function of the anharmonic terms in the potential comes predominantly from the terms quartic

TABLE III. Numerical details of the calculations.

$(s/a)^2$	Body-centered cubic				Face-centered cubic	
	Nearest neighbors only	Nearest and next-nearest neighbors		Nearest neighbors only	Nearest and next-nearest neighbors	
	0.75	0.788		0.5	0.509	
	Nearest	Next		Nearest	Next	
$a^2\phi'/V_0$	0	-1.50	1.50	0	-0.69	0.69
$a^4\phi''/V_0$	32	51.2	-1.7	72	85.5	-2.43
$a^6\phi'''/V_0$	-512	-744	-21.9	-1728	-1976	9.98
$a^8\phi''''/V_0$	7282	10 248	373	36 864	41 362	-42.4
$a^6V_0^{-2} \sum_{ijl} \mathbf{B}(0,0,n')_{ijl} \mathbf{B}(0,0,n'')_{ijl}$						
	n'	n''		n'	n''	
5 493 000	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	11 302 000	18 538 000	$0, \frac{1}{2}, \frac{1}{2}$	23 989 000
-266 000	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	-660 000	311 000	$0, \frac{1}{2}, \frac{1}{2}$	287 000
	$1, 0, 0$	$1, 0, 0$	38 000		$1, 0, 0$	3 000
	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$1, 0, 0$	111 000		$0, \frac{1}{2}, \frac{1}{2}$	-26 000
$a^6V_0^{-2} \sum_{i,j,l,n',n''} D(n', n'') \mathbf{B}(0,0,n')_{ijl} \mathbf{B}(0,0,n'')_{ijl}$						
9 218 000			19 091 000	49 838 000		64 316 000
$a^4V_0^{-1} \sum_{ij} \mathbf{C}(0,0,n',n')_{ijij}$						
	n'			n'		
36 700	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$		50 700	82 700	$0, \frac{1}{2}, \frac{1}{2}$	91 600
	$1, 0, 0$		4 100		$1, 0, 0$	-26
$a^4V_0^{-1} \sum_{i,j,n'} [J(0) - J(r')]^2 \mathbf{C}(0,0,n',n')_{ijij}$						
$V_0/ma^2\omega_0^2$	0.00280		0.00184	0.00122		0.00107
$[ma^2\omega_0^2/N(KT)^2]F_3$	-163		-145	-167		-167
$[ma^2\omega_0^2/N(KT)^2]F_4$	282		274	436		425

in atomic displacements. The ratio of the magnitudes of F_4 to F_3 is about 1.7 and 2.5 for bcc and fcc crystals, respectively. It follows that the anharmonic forces decrease the specific heat at constant volume. The effect of including second-neighbor forces is very slight, which is not surprising in view of the short-range nature of the forces considered.

Including second-neighbor forces, we find for the anharmonic specific heat

$$c_v = -(KT/ma^2\omega_0^2) \times \begin{cases} 1025 \text{ cal/mole } ^\circ\text{K for fcc} \\ 515 \text{ cal/mole } ^\circ\text{K for bcc.} \end{cases} \quad (5.1)$$

The factor in parentheses is dimensionless. We can relate ω_0 to a Debye temperature Θ by matching acoustic velocity as obtained from Eq. (3.8) with that of a Debye model, with the result

$$\hbar\omega_0 = (2/\pi)K\Theta. \quad (5.2)$$

Table IV contains values for the temperature coefficient of specific heat obtained by using constants appropriate to the elements listed.

It is perhaps of interest to compare our results with those of Ludwig.⁶ The principal difference between the two calculations lies in the factors by which the different potential tensor elements are weighted in Eqs. (3.10) and (3.11). Ludwig's approximation weights all the tensors equally. Our expressions would essentially reduce to Ludwig's if we were to replace $D(n', n'')$ in Eq. (3.10) by $\delta_{n', n''} J^3(0)$, and all expressions $[J(0) - J(r')]^2$ in Eq. (3.11), including the term with $n' = n$, by $\frac{1}{2}J^2(0)$. Ludwig's results for F_3 and F_4 for an fcc crystal with nearest-neighbor forces only are

$$ma^2\langle\omega^2\rangle F_3/N(KT)^2 = -111.8,$$

$$ma^2\langle\omega^2\rangle F_4/N(KT)^2 = 430.5.$$

[We have dropped terms proportional to negative powers of T , and have based our comparison on Ludwig's Eqs. (4.3) and (4.5) because we have been unable to verify his Eq. (4.6)]

One recent confirmation of the sign of the anharmonic contribution to specific heat comes from Martin's¹¹ low-temperature measurements on Li. (While our calculations were carried out for temperatures above the Debye temperature, conclusions on sign should still be valid at lower temperatures.) Dugdale *et al.*¹² observe that on the basis of the harmonic approximation, the lattice specific heats c_v of Li⁶ and of natural Li should be the same functions of a reduced temperature. The theoretical value of 1.074 for the ratio of

TABLE IV. Typical calculated values for anharmonic specific heat.

Element	Structure	Atomic weight	$a(\text{\AA})$	$\Theta(^{\circ}\text{K})$	c_v/T (cal/mole $^{\circ}\text{K}^2$)
Li	bcc	6.94	3.50	380	-5.02×10^{-3}
Al	fcc	27.0	4.04	418	-1.60×10^{-3}
A	fcc	39.9	5.31	80	-1.70×10^{-2}
Ag	fcc	107.9	4.08	225	-1.35×10^{-3}
α -W	bcc	183.9	3.16	379	-2.34×10^{-4}
Pb	fcc	207.2	4.94	94.5	-2.72×10^{-3}

T_6/T_{nat} for equal specific heats is in good agreement with the experimental value extrapolated to 0°K . But at higher temperatures, as vibrational amplitudes increase and specific heats approach the classical value, the ratio T_6/T_{nat} increases to a value of 1.127 for $c_v = 5.3$ cal/mole deg. Such behavior could be due to anharmonic contributions. An increase in the ratio of temperatures would follow from a negative anharmonic specific heat. At a given temperature, anharmonic contributions would be roughly the same for different isotopes, since the mass enters in Eq. (5.1) only in the product $m\omega^2$. However, the comparison of Dugdale *et al.* is at different temperatures, and there will be a greater anharmonic contribution at the higher temperature (T_6). If the anharmonic specific heat may still be represented as $c_{\text{anh}} = -\gamma T$ over the small temperature range involved, we can determine the value of γ for $c_v = 5.3$ cal/mole deg from Martin's data (taking 0.0072 cal/mole deg² as the average of Martin's values for dc_v/dT for Li⁶ and Li⁷) to be

$$\gamma = (1.127 - 1.074)/(1.074 - 1) \times 0.0072 = 0.0046 \text{ cal/mole deg}^2,$$

in surprising agreement with the prediction of Eq. (5.1).

To what extent does our result of a negative sign for the anharmonic specific heat of solids depend on the limitations of our model? The essential limitations seem to be the following: (a) Use of a 6-12 potential. The calculated ratio of F_4/F_3 seems large enough to conclude that any reasonable short-range potential would give the same result for the sign. (b) Restriction to two-body potentials (central forces). Lacking information on the nature of the anharmonic aspects of other potentials and forces, we can only speculate that their effects would be similar to those of central forces and generally less important. (c) Exclusion of long-range (Coulomb) forces. Such forces have a much smaller ratio of quartic to cubic content than the short-range forces we have considered. Even in polar crystals, however, the predominant anharmonicities probably arise from short-range repulsions.

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¹¹ D. L. Martin, *Physica* **25**, 1193 (1959); *Proc. Roy. Soc. (London)* **A254**, 444 (1960).

¹² J. S. Dugdale, D. Guban and K. Okumura, *Proc. Roy. Soc. (London)* **A263**, 407 (1961). We are grateful to Dr. Dugdale for pointing out to us the significance of these results prior to publication.

APPENDIX

We wish to estimate $\langle \omega^{-2} \rangle$ in terms of the potential constants, in order to compare with Eq. (4.6) and thus obtain the relation between ω_0 and V_0 . For a particular wave number, the average of $\omega^2(\mathbf{k})$ is equal to one-third the sum over polarizations of ω^2 and is readily obtained from the trace of the matrix $\mathbf{a}(\mathbf{k})$ [see Eq. (2.8)]. Since we have consistently ignored the dependence of frequency on polarization, we now ignore the difference between $\langle \omega^{-2}(\mathbf{k}) \rangle$ and $\langle \omega^2(\mathbf{k}) \rangle^{-1}$ for each wave vector and proceed to average $\langle \omega^2(\mathbf{k}) \rangle^{-1}$ over all wave vectors.

Wave vectors may be expressed in terms of reciprocal lattice vectors \mathbf{b} as

$$\mathbf{k} = p_1 \mathbf{b}_1 + p_2 \mathbf{b}_2 + p_3 \mathbf{b}_3. \quad (\text{A1})$$

For an fcc structure, the \mathbf{b} 's have Cartesian components $(-1/a, 1/a, 1/a)$, $(1/a, -1/a, 1/a)$ and $(1/a, 1/a, -1/a)$, respectively. Then

$$m \langle \omega^2(\mathbf{k}) \rangle = g_1(1-f_1) + g_2(1-f_2), \quad (\text{A2})$$

where

$$\begin{aligned} f_1 &= \frac{1}{6} [\cos p_1 + \cos p_2 + \cos p_3 + \cos(p_2 - p_3) \\ &\quad + \cos(p_3 - p_1) \cos(p_1 - p_2)], \\ f_2 &= \frac{1}{3} [\cos(-p_1 + p_2 + p_3) + \cos(p_1 - p_2 + p_3) \\ &\quad + \cos(p_1 + p_2 - p_3)], \end{aligned} \quad (\text{A3})$$

$$g_1 = 8(3\phi_1' + a^2\phi_1''),$$

$$g_2 = 4(3\phi_2' + 2a^2\phi_2'').$$

(Subscripts 1 and 2 on ϕ' and ϕ'' refer, respectively, to nearest- and next-nearest-neighbor distances. When only nearest-neighbor forces are considered, g_2 must be set equal to zero.) If

$$\begin{aligned} h_1 &= g_1/(g_1 + g_2), \\ h_2 &= g_2/(g_1 + g_2), \\ y &= h_1 f_1 + h_2 f_2, \end{aligned} \quad (\text{A4})$$

we may write

$$[m \langle \omega^2(\mathbf{k}) \rangle]^{-1} = (g_1 + g_2)^{-1} (1 - y)^{-1},$$

and

$$\langle \omega^{-2} \rangle \approx m (g_1 + g_2)^{-1} (1 + (1 - y)^{-1} y). \quad (\text{A5})$$

Since f_1 and f_2 are periodic functions of the p 's with periods 2π , we can make a triple Fourier expansion of $y/(1-y)$:

$$y/(1-y) = \sum_{c_1, c_2, c_3} (c_1, c_2, c_3) \cos(c_1 p_1 + c_2 p_2 + c_3 p_3). \quad (\text{A6})$$

The mean value of this quantity is given by the particular Fourier coefficient (0,0,0). The Fourier coefficients in Eq. (A6) are invariant to permutation of the c 's and to simultaneous change in the sign of all three c 's. They are determined in principle by a sequence of algebraic equations obtained by multiplying both sides of Eq. (A6) by $1-y$ and then equating coefficients of the corresponding cosines in the two members of the

equation. The vanishing of the constant term requires that

$$0 = (0,0,0) - \frac{1}{2} h_1 [(1,0,0) + (1,0,\bar{1})] - h_2 (1,1,\bar{1}). \quad (\text{A7})$$

Similarly, the inhomogeneous equations are

$$\begin{aligned} \frac{1}{6} h_1 &= 2(1,0,0) - \frac{1}{6} h_1 [(0,0,0) + 2(1,0,0) + 2(1,0,\bar{1}) \\ &\quad + 2(1,1,\bar{1}) + \dots] - \frac{1}{3} h_2 [2(1,0,\bar{1}) + \dots], \\ \frac{1}{6} h_1 &= 2(1,0,\bar{1}) - \frac{1}{6} h_1 [(0,0,0) + 2(1,0,0) + 2(1,0,\bar{1}) \\ &\quad + 2(1,1,\bar{1}) + \dots] - \frac{1}{3} h_2 [2(1,0,0) + \dots], \\ \frac{1}{3} h_2 &= 2(1,1,\bar{1}) - \frac{1}{6} h_1 [2(1,0,0) + 2(1,0,\bar{1}) + \dots] \\ &\quad - \frac{1}{3} h_2 (0,0,0) \dots \end{aligned} \quad (\text{A8})$$

The dots in Eqs. (A8) refer to Fourier coefficients other than the four that appear in Eq. (A7). The approximation used to estimate (0,0,0) was to neglect these other coefficients, and then to solve Eqs. (A7) and (A8), with the result

$$(0,0,0) = \frac{3h_1^2 + 4h_2^2 + 2h_1^2 h_2}{24 - 5h_1^2 - 4h_2^2 - 2h_1^2 h_2}. \quad (\text{A9})$$

In obtaining this form, use was made of the fact that $h_1 + h_2 = 1$.

An exactly similar procedure may be used for the bcc structure. We again express wave vectors by Eq. (A1) in terms of reciprocal lattice vectors with Cartesian components $(0,1/a,1/a)$, $(1/a,0,1/a)$ and $(1/a,1/a,0)$. In this case

$$m \langle \omega^2(\mathbf{k}) \rangle = g_3(1-f_3) + g_4(1-f_4), \quad (\text{A10})$$

where

$$\begin{aligned} f_3 &= \frac{1}{4} [\cos p_1 + \cos p_2 + \cos p_3 + \cos(p_1 + p_2 + p_3)], \\ f_4 &= \frac{1}{3} [\cos(p_2 + p_3) + \cos(p_3 + p_1) + \cos(p_1 + p_2)], \\ g_3 &= 8(2\phi_1' + a^2\phi_1''), \\ g_4 &= 4(3\phi_2' + 2a^2\phi_2''). \end{aligned} \quad (\text{A11})$$

Equations (A4)–(A6) can now be applied directly to the bcc case by replacing subscripts 1 and 2 by 3 and 4. The equations determining the Fourier coefficients become

$$\begin{aligned} 0 &= (0,0,0) - \frac{1}{4} h_3 [3(1,0,0) + (1,1,1)] - h_4 (1,1,0), \\ \frac{1}{4} h_3 &= 2(1,0,0) - \frac{1}{4} h_3 [(0,0,0) + 3(1,1,0) + \dots] \\ &\quad - \frac{1}{3} h_4 [2(1,0,0) + (1,1,1) + \dots], \\ \frac{1}{4} h_3 &= 2(1,1,1) - \frac{1}{4} h_3 [(0,0,0) + 3(1,1,0) + \dots] \\ &\quad - \frac{1}{3} h_4 [3(1,0,0) + \dots], \\ \frac{1}{3} h_4 &= 2(1,1,0) - \frac{1}{4} h_3 [3(1,0,0) + (1,1,1) + \dots] \\ &\quad - \frac{1}{3} h_4 [(0,0,0) + \dots], \end{aligned} \quad (\text{A12})$$

and, with the same approximations as in the fcc case, we find that

$$(0,0,0) = \frac{6h_3^2(1+h_4) + 4h_4^2(2-h_4)}{4(6-h_4^2)(2-h_4) - 3h_3^2(5+2h_4)}. \quad (\text{A13})$$