

ANHARMONIC CONTRIBUTIONS TO THE VIBRATORY FREE ENERGY OF A LATTICE

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[Manuscript received December 23, 1963]

Summary

The anharmonic contribution to the free energy of a lattice is evaluated by means of a Bethe approximation. The approximation is accurate to within 3% for the model evaluated by Maradudin, Flinn, and Coldwell-Horsfall. The anharmonic contribution to the specific heat at constant volume of a model of sodium is evaluated. The specific heat is found to increase as the temperature rises but the rate of increase is lower than the observed value.

I. INTRODUCTION

The evaluation of the anharmonic contribution to the free energy of a lattice has proved to be extremely difficult. It has, however, been known since the work of Born and Brody (1921) and Schrodinger (1922) that at high temperatures the contribution to the free energy is quadratic in its dependence on temperature, or alternatively the contribution to the specific heat is linear in temperature. This anharmonic contribution, F_{AH} , is known to be the sum of two terms. The first of these, $F_{\text{AH}}^{(4)}$, is the contribution of fourth-order differentials of the interatomic potentials and is positive. The second of these, $F_{\text{AH}}^{(3,3)}$, is the contribution of the square of the third-order differentials of the interatomic potential and is negative. $F_{\text{AH}} = F_{\text{AH}}^{(4)} + F_{\text{AH}}^{(3,3)}$ may then be either positive or negative. However, several authors (using approximate methods of calculating the contribution) have found that for simple potentials, such as a Morse or Leonard-Jones potential, the contribution to the specific heat is negative (cf. Dugdale and MacDonald 1954; Keller and Wallace 1962).

Stern (1958) evaluated some of these complicated expressions exactly by analytical methods. However, this has been disputed by Maradudin, Flinn, and Coldwell-Horsfall (1961) and so the evaluation must be considered an approximation. Maradudin, Flinn, and Coldwell-Horsfall have evaluated the expressions for a simple model, using a computer to estimate the coefficients which appeared. This calculation can be used to check other analytic approximations by applying them to the same model. An important approximation of this type was introduced by Ludwig (1958) in a method of averaging over the mode function of the solid. In the model treated by Maradudin, Flinn, and Coldwell-Horsfall this approximation evaluates $F_{\text{AH}}^{(4)}$ exactly and underestimates $F_{\text{AH}}^{(3,3)}$ by 16%.

Most approximations for evaluating the anharmonic contribution to the specific heat are based on approximating the mode functions, even though the interest has been in high temperature contributions where classical statistics may be used. In the present paper an approximation based on the classical partition

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function is used. This is the analogue of the approximation introduced by Bethe (1935) in order to approximate the classical partition function of the Ising model of ferromagnetism. This approximation can be easily solved for the anharmonic contribution to the specific heat and when applied to the simple model studied by Maradudin, Flinn, and Coldwell-Horsfall it gives $F_{\text{AH}}^{(4)}$ exactly and $F_{\text{AH}}^{(3,3)}$ to within 3%. When this approximation is applied to a simple model of sodium, with a Morse interatomic potential, it leads to a positive increase in specific heat with temperature. This is in agreement with the observed behaviour of sodium, but the numerical value obtained is very low.

II. THE BETHE APPROXIMATION

The Bethe approximation as used in the study of the Ising model of ferromagnetism is used with nearest neighbour potentials only. The exact relation between expansions of the classical partition function and the Bethe approximation together with other treatments of the Ising model are given in a review article by Domb (1960). While the above treatment is written for the Ising model it is easy to transliterate these equations into the present case and so this will not be presented here. We shall, however, present the Bethe approximation in a heuristic physical way, suitable for the present application to the calculation of the free energy of a lattice.

Firstly, let us consider the case where only nearest neighbour potentials exist in the lattice and we can write the total potential in the form

$$U = \sum_{\alpha} U_{\alpha}(\mathbf{r}_1, \mathbf{r}_2), \quad (2.1)$$

where α is a subscript labelling the different nearest neighbour pairs of atoms. Then the idea of the Bethe approximation is that the behaviour of two nearest neighbour atoms is determined by the potential

$$\sum_i' \Psi_i(\mathbf{r}_1) + U_0(\mathbf{r}_1, \mathbf{r}_2) + \sum_j' \Psi_j(\mathbf{r}_2).$$

Here $U_0(\mathbf{r}_1, \mathbf{r}_2)$ is the interparticle potential ($\alpha = 0$) and $\Psi_i(\mathbf{r}_1)$ is the effective potential on atom 1 due to the nearest neighbour bond, i . The prime on the summation is to show that the bond represented by the potential term $U_0(\mathbf{r}_1, \mathbf{r}_2)$ is not to be counted.

This leads to a distribution function given by

$$e^{-2\beta F_c} \rho_2(\mathbf{r}_1, \mathbf{r}_2) = \exp\{-\beta[\sum_i' \Psi_i(\mathbf{r}_1) + U_0(\mathbf{r}_1, \mathbf{r}_2) + \sum_j' \Psi_j(\mathbf{r}_2)]\}, \quad (2.2)$$

where F_c is the configurational free energy per particle, $\beta = 1/kT$ is the inverse temperature, and $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ is the probability distribution function for finding the first atom at position \mathbf{r}_1 and the second atom at position \mathbf{r}_2 . The probability distribution function satisfies

$$\int \rho_2(\mathbf{r}_1, \mathbf{r}_2) d^3r_2 = \rho_1(\mathbf{r}_1), \quad (2.3)$$

where $\rho_1(\mathbf{r}_1)$ is the one-particle probability distribution function. This satisfies

$$\int \rho_1(\mathbf{r}_1) d^3r_1 = 1. \quad (2.4)$$

Now the one-particle distribution function can be found in a similar manner, since one particle will be in the potential $\sum_i \Psi_i(\mathbf{r}_1)$. This time there is no restriction on the summation over i . The one-particle distribution is then given by

$$e^{-\beta F_0 \rho_1(\mathbf{r}_1)} = \exp\{-\beta[\sum_i \Psi_i(\mathbf{r}_1)]\}. \quad (2.5)$$

When it is remembered that the potentials acting due to different bonds will be simply related by coordinate rotations, this equation may be combined with (2.2), (2.3), and (2.4) to give a consistency relation from which both the effective potentials due to the nearest neighbour bonds and the configurational free energy may be found.

When non-nearest neighbour potentials are present we shall represent these by a mean field or Einstein approximation as used by Henkel (1955). With these additional terms in both $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ and $\rho_1(\mathbf{r}_1)$, the equations will be used exactly as before.

We may expect the approximation to be most accurate when the effective potential due to any one bond is small compared to the total effective potential that one atom moves in. This will imply that the approximation is better the greater the number of nearest neighbours.

III. THE HARMONIC FREE ENERGY

The model which we are going to treat is one where the nearest neighbour potential can be written as

$$U_a = U_a^{(2)} + U_a^{(3)} + U_a^{(4)},$$

where $U_a^{(2)}$ is a quadratic contribution,

$U_a^{(3)}$ is a cubic contribution, and

$U_a^{(4)}$ is a quartic contribution.

We shall also limit the discussion to the case where the potential has cylindrical symmetry about the line joining the two nearest neighbour atoms. Then

$$\begin{aligned} U_a^{(2)} &= \frac{1}{2}a_1(\mathbf{p} \cdot \Delta\mathbf{r})^2 + \frac{1}{2}a_2[(\Delta\mathbf{r})^2 - (\mathbf{p} \cdot \Delta\mathbf{r})^2], \\ U_a^{(3)} &= \frac{1}{3!}\gamma_1(\mathbf{p} \cdot \Delta\mathbf{r})^3 + \frac{1}{3!}\gamma_2(\mathbf{p} \cdot \Delta\mathbf{r})[(\Delta\mathbf{r})^2 - (\mathbf{p} \cdot \Delta\mathbf{r})^2], \\ U_a^{(4)} &= \frac{1}{4!}\delta_1(\mathbf{p} \cdot \Delta\mathbf{r})^4 + \frac{1}{4!}\delta_2(\mathbf{p} \cdot \Delta\mathbf{r})^2[(\Delta\mathbf{r})^2 - (\mathbf{p} \cdot \Delta\mathbf{r})^2] + \frac{1}{4!}\delta_3[(\Delta\mathbf{r})^2 - (\mathbf{p} \cdot \Delta\mathbf{r})^2]^2, \end{aligned} \quad (3.1)$$

where

$$\Delta\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$$

and \mathbf{p} is a unit vector in the direction of atom 1 to atom 2.

In particular, if the interatomic potential is a central potential, then we have

$$a_1 = \Phi^{\text{II}}(a), \quad a_2 = \frac{1}{a}\Phi^{\text{I}}(a),$$

$$\begin{aligned}
\gamma_1 &= \Phi^{\text{iii}}(a), & \gamma_2 &= \frac{3}{a}\Phi^{\text{ii}}(a) - \frac{3}{a^2}\Phi^{\text{i}}(a), \\
\delta_1 &= \Phi^{\text{iv}}(a), & \delta_2 &= \frac{6}{a}\Phi^{\text{iii}}(a) - \frac{12}{a^2}\Phi^{\text{ii}}(a) + \frac{12}{a^3}\Phi^{\text{i}}(a), \\
\delta_3 &= \frac{3}{a^2}\Phi^{\text{ii}}(a) - \frac{3}{a^3}\Phi^{\text{i}}(a),
\end{aligned} \tag{3.2}$$

where a is the nearest neighbour distance between atoms.

Let us first solve the Bethe approximation equations ignoring $U_a^{(3)}$ and $U_a^{(4)}$. If now we use a coordinate system such that two atoms lie on the x -axis we have

$$U_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\alpha_1(x_2 - x_1)^2 + \frac{1}{2}\alpha_2[(y_2 - y_1)^2 + (z_2 - z_1)^2]. \tag{3.3}$$

Let the effective potential due to a bond in the direction of the unit vector \mathbf{p} be

$$\Psi(\mathbf{r}_1) = \frac{1}{2}\eta_1(\mathbf{p} \cdot \mathbf{r}_1)^2 + \frac{1}{2}\eta_2[(\mathbf{r}_1)^2 - (\mathbf{p} \cdot \mathbf{r}_1)^2] + \eta_0. \tag{3.4}$$

Then we have

$$\sum_p \Psi(\mathbf{r}_1) = \frac{1}{2}\chi(x_1^2 + y_1^2 + z_1^2) + q\eta_0, \tag{3.5}$$

where q is the number of nearest neighbours and

$$\chi = \frac{1}{3}q[\eta_1 + 2\eta_2].$$

If non-nearest neighbour potentials are present then this last equation will be replaced by

$$\chi = \frac{1}{3}q[\eta_1 + 2\eta_2] + K, \tag{3.6}$$

where K is the contribution of the non-nearest neighbour potentials treated in an Einstein approximation.

The other quantity we need is

$$\sum_p \Psi(\mathbf{r}_1) = \frac{1}{2}[\chi - \eta_1]x_1^2 + \frac{1}{2}[\chi - \eta_2](y_1^2 + z_1^2) + (q-1)\eta_0. \tag{3.7}$$

When equations (3.3), (3.5), (3.7) are substituted into the consistency conditions (2.2), (2.3), (2.4), and (2.5) we obtain

$$\begin{aligned}
\eta_1 &= \alpha_1 - \alpha_1^2/A_1, \\
\eta_2 &= \alpha_2 - \alpha_2^2/A_2, \\
\beta\eta_0 &= \frac{1}{4}\{\ln A_1/\chi + 2 \ln A_2/\chi\}, \\
\beta F_c &= \frac{3}{2} \ln\{\beta\chi/2\pi\} + q\beta\eta_0,
\end{aligned} \tag{3.8}$$

where

$$\begin{aligned}
A_1 &= \chi - \eta_1 + \alpha_1, \\
A_2 &= \chi - \eta_2 + \alpha_2.
\end{aligned} \tag{3.9}$$

The distribution functions are given by

$$\begin{aligned} \rho_2(\mathbf{r}_1, \mathbf{r}_2) &= (1/2\pi)(A_1^2 - a_1^2)^{\frac{1}{2}} \exp\{-\frac{1}{2}\beta[A_1x_1^2 - 2a_1x_1x_2 + A_1x_2^2]\} \\ &\quad \times (1/2\pi)(A_2^2 - a_2^2)^{\frac{1}{2}} \exp\{-\frac{1}{2}\beta[A_2y_1^2 - 2a_2y_1y_2 + A_2y_2^2]\} \\ &\quad \times (1/2\pi)(A_2^2 - a_2^2)^{\frac{1}{2}} \exp\{-\frac{1}{2}\beta[A_2z_1^2 - 2a_2z_1z_2 + A_2z_2^2]\}, \end{aligned} \quad (3.10)$$

$$\rho_1(\mathbf{r}_1) = (\chi/2\pi)^{3/2} \exp\{-\frac{1}{2}\beta\chi[x_1^2 + y_1^2 + z_1^2]\}. \quad (3.11)$$

In order to obtain the total free energy from the configurational free energy we must add the contribution from the kinetic energy of the atoms,

$$\frac{3}{2} \ln\{2\pi\hbar^2\beta/m\},$$

to give the harmonic free energy as

$$\beta F_{\text{H}} = \frac{3}{2} \ln \beta^2 \hbar^2 \chi / m + \frac{1}{4} q \{ \ln A_1 / \chi + 2 \ln A_2 / \chi \}. \quad (3.12)$$

From the harmonic free energy we may calculate the Gruneisen constant, γ .

$$\gamma = -\frac{\overline{\partial \ln \omega}}{\partial \ln v},$$

where ω are the mode frequencies of the lattice. Now the classical free energy is

$$\beta F_{\text{H}} = 3 \overline{\ln \beta \hbar \omega},$$

and so we have

$$\begin{aligned} \gamma &= -\frac{1}{3} v \frac{d}{dv} [\beta F_{\text{H}}] \\ &= -\frac{1}{3} a \frac{d}{da} [\beta F_{\text{H}}]. \end{aligned}$$

In terms of the Bethe approximation this may be evaluated if we write the relations for the effective potentials (3.8) in the equivalent form

$$\begin{aligned} 2/\chi &= 1/(\chi - \eta_1) + 1/(\chi - \eta_1 + 2a_1), \\ 2/\chi &= 1/(\chi - \eta_2) + 1/(\chi - \eta_2 + 2a_2), \\ \chi &= \frac{1}{3} q [\eta_1 + 2\eta_2] + K, \end{aligned} \quad (3.13)$$

and the harmonic contribution to the free energy as

$$\begin{aligned} \beta F_{\text{H}} &= \frac{3}{2} \ln \beta^2 \hbar^2 \chi / m + \frac{1}{4} q \{ \ln(\chi - \eta_1) + \ln(\chi - \eta_1 + 2a_1) + 2 \ln(\chi - \eta_2) \\ &\quad + 2 \ln(\chi - \eta_2 + 2a_2) - 6 \ln \chi \}. \end{aligned} \quad (3.14)$$

If now we substitute the expression for χ into this equation and consider it as an equation in η_1 and η_2 we find

$$\begin{aligned} \frac{\partial \beta F_{\text{H}}}{\partial \eta_1} &= 0, \\ \frac{\partial \beta F_{\text{H}}}{\partial \eta_2} &= 0, \end{aligned}$$

which allows us to obtain

$$\begin{aligned} \gamma &= -\frac{a}{9} \frac{d}{da} [\beta F_{\text{H}}] \\ &= \frac{q}{18} \left(\frac{-a da_1/da}{\chi - \eta_1 + 2\alpha_1} - 2 \frac{a da_2/da}{\chi - \eta_2 + 2\alpha_2} \right) - \frac{a}{6\chi} \frac{dK}{da}. \end{aligned} \quad (3.15)$$

IV. THE ANHARMONIC FREE ENERGY

The anharmonic contribution to the free energy can be found in the same manner. The Bethe approximation equations can be expanded in a perturbation series which gives the desired contribution to the free energy. However, an approach which gives an identical result and which is somewhat easier may be used. This approach uses the fact that the Bethe approximation gives an exact answer for a pseudo lattice which consists of non-intersecting chains of atoms (cf. Domb 1960). As this is so we can use the usual expansion for the anharmonic contribution to the free energy only applied to this pseudo lattice. This gives us at once

$$F_{\text{AH}}^{(4)} = \frac{1}{2} q \langle U_0^{(4)} \rangle_{\text{H}}, \quad (4.1)$$

$$F_{\text{AH}}^{(3,3)} = -\frac{1}{4} q \beta \sum_{\alpha} \langle U_0^{(3)} U_{\alpha}^{(3)} \rangle_{\text{H}}, \quad (4.2)$$

where the subscript 0 refers to a particular pair of atoms in the lattice and the subscript α is summed over all pairs of atoms in the lattice. The bracket $\langle \rangle_{\text{H}}$ means an expectation over the probability function for all atoms calculated as if they had only harmonic forces between them.

The expression for $F_{\text{AH}}^{(4)}$ can be evaluated immediately as the expectation reduces to an integral over the two-particle probability distribution function. Hence

$$\beta F_{\text{AH}}^{(4)} = \frac{1}{2} q \beta \iint U_0^{(4)}(\mathbf{r}_1, \mathbf{r}_2) \rho_2(\mathbf{r}_1, \mathbf{r}_2) d^3 r_1 d^3 r_2. \quad (4.3)$$

On substituting (3.1) for $U^{(4)}$ and (3.10) for ρ_2 we obtain

$$\beta F_{\text{AH}}^{(4)} = \frac{q}{\beta} \left\{ \frac{1}{4} \frac{\delta_1}{(A_1 + \alpha_1)^2} + \frac{1}{6} \frac{\delta_2}{(A_1 + \alpha_1)(A_2 + \alpha_2)} + \frac{2}{3} \frac{\delta_3}{(A_2 + \alpha_2)^2} \right\}. \quad (4.4)$$

The equation for $F_{\text{AH}}^{(3,3)}$ cannot be evaluated as straightforwardly as $F_{\text{AH}}^{(4)}$ for the expectation does not immediately reduce to an integral over the two-atom distribution function. We can, however, reduce the evaluation of $F_{\text{AH}}^{(3,3)}$ to that of a separate integral equation and then an expectation over the two-atom distribution function. Firstly, imagine that the integrals involved in the expectation have been taken over all atoms except the two atoms in the pair we have labelled $\alpha = 0$. Then, remembering that the Bethe approximation is equivalent to an exact evaluation over this lattice of non-intersecting chains, we may write

$$\begin{aligned} \beta F_{\text{AH}}^{(3,3)} &= -q/4\beta^2 \{ \langle U_0^{(3)}(\mathbf{r}_1, \mathbf{r}_2) U_0^{(3)}(\mathbf{r}_1, \mathbf{r}_2) \rangle_{\text{H}} \\ &\quad + \sum_i \langle \theta_i(\mathbf{r}_1) U_0^{(3)}(\mathbf{r}_1, \mathbf{r}_2) \rangle_{\text{H}} + \sum_j \langle U_0^{(3)}(\mathbf{r}_1, \mathbf{r}_2) \theta_j(\mathbf{r}_2) \rangle_{\text{H}} \}. \end{aligned} \quad (4.5)$$

Here $\theta_i(\mathbf{r}_1)$ is the effect of all the terms in $\sum_{\alpha} \langle U_0^{(3)} U_{\alpha}^{(3)} \rangle$ (equation (4.2)) where the

pairs of nearest neighbour atoms a lie in chains which join atom 1 through the nearest neighbour bond i .

If now we consider the process of taking the integrals and the summation involved, then we see that θ_i satisfies the integral equation

$$\int [\sum'_i \theta_i(\mathbf{r}_1) + U_0^{(3)}(\mathbf{r}_1, \mathbf{r}_2)] \rho_2(\mathbf{r}_1, \mathbf{r}_2) d^3 r_1 = \theta_0(\mathbf{r}_2) \rho_1(\mathbf{r}_2). \quad (4.6)$$

Substituting equation (3.1) for $U^{(3)}$ and equations (3.10) and (3.11) for ρ_2 and ρ_1 we may solve this integral equation to give

$$\begin{aligned} \theta_i(\mathbf{r}_1) = \gamma_1 & \left\{ \frac{(A_1 - a_1)^3}{A_1^3 - a_1^3} (\mathbf{p} \cdot \mathbf{r}_1)^3 + \frac{3[A_1 - a_1][A_1 + 2a_1]}{A_1^3 - a_1^3} (\mathbf{p} \cdot \mathbf{r}_1) \right\} \\ & + \gamma_2 \left\{ \frac{(A_1 - a_1)(A_2 - a_2)^2}{A_2^2 A_1 - a_2^2 a_1} (\mathbf{p} \cdot \mathbf{r}_1) [(\mathbf{r}_1)^2 - (\mathbf{p} \cdot \mathbf{r}_1)^2] + \frac{2[A_1 A_2 + a_1 A_2 - 2a_1 a_2]}{A_2^2 A_1 - a_2^2 a_1} (\mathbf{p} \cdot \mathbf{r}_1) \right\}. \end{aligned} \quad (4.7)$$

Here \mathbf{p} is a unit vector directed along the bond i towards atom 1.

When this is substituted into equation (4.2) we obtain, after some algebra,

$$\beta F_{\text{AH}}^{(3,3)} = -\frac{q}{\beta} \left\{ \frac{\gamma_1^2}{4} \frac{[A_1 - a_1]}{[A_1 + a_1][A_1^3 - a_1^3]} + \frac{\gamma_2^2}{18} \frac{[3A_1 A_2 - a_2 A_1 + a_1 A_2 - 3a_1 a_2]}{[A_1 + a_1][A_2 + a_2][A_2^2 A_1 - a_2^2 a_1]} \right\}. \quad (4.8)$$

Equation (3.12) for the harmonic free energy, together with equation (4.4) for the quartic contribution to the anharmonic free energy and equation (4.8) for the cubic squared contribution, gives the solution to the problem.

V. APPLICATION TO A FACE-CENTRED CUBIC CRYSTAL MODEL

Maradudin, Flinn, and Coldwell-Horsfall (1961) have treated exactly a simple nearest neighbour model with central forces. They have, however, ignored all terms of order $1/a$ (where a is the nearest neighbour distance) in the expansion of the potential given in equations (3.1) and (3.2). Hence in the model treated by these authors

$$\begin{aligned} a_2 &= K = 0, \\ a_1 &= \Phi^{\text{II}}, \end{aligned} \quad (5.1)$$

$$\begin{aligned} \gamma_2 &= \delta_2 = \delta_3 = 0, \\ \gamma_1 &= \Phi^{\text{III}}, \\ \delta_1 &= \Phi^{\text{IV}}. \end{aligned} \quad (5.2)$$

When the relation (5.1) is substituted into relations (3.6), (3.8), and (3.9), which relate the effective potentials to the harmonic constants of the interatomic potential, we have

$$\begin{aligned} \eta_1 &= a_1 - \frac{a_1^2}{\chi - \eta_1 + a_1}, \\ \chi &= 4a_1, \end{aligned}$$

as $q = 12$ in a face-centred cubic crystal. These may be easily solved to give

$$\eta_1 = \frac{2}{3}a_1, \quad (5.3)$$

and

$$\chi = \frac{8}{3}a_1, \quad (5.4)$$

$$A_1 = 3a_1. \quad (5.5)$$

Substituting these in the relation (3.12) for the harmonic contribution to the free energy we obtain

$$\beta F_{\text{H}} = \frac{3}{2} \ln \left\{ \beta^2 \frac{\hbar^2}{m} \times \frac{27}{8} \Phi_{\text{H}} \right\}. \quad (5.6)$$

Maradudin, Flinn, and Coldwell-Horsfall obtained for the harmonic contribution

$$\beta F_{\text{H}} = \frac{3}{2} \ln \left\{ \beta^2 \frac{\hbar^2}{m} \times 3 \cdot 385 \Phi_{\text{H}} \right\}. \quad (5.7)$$

As $\frac{27}{8} = 3 \cdot 375$, these two expressions agree to within 0.3%.

When the relations (5.2), (5.3), (5.4), and (5.5) are substituted into the relations (4.4) and (4.8) for the anharmonic contribution to the free energy we obtain

$$\beta F_{\text{AH}} = \frac{1}{\beta} \left\{ \frac{3}{16} \frac{\Phi^{\text{iv}}}{[\Phi_{\text{H}}]^2} - \frac{3}{52} \frac{[\Phi_{\text{H}}^{\text{iii}}]^2}{[\Phi_{\text{H}}]^3} \right\}. \quad (5.8)$$

This may be compared with the relation obtained by Maradudin, Flinn, and Coldwell-Horsfall

$$\beta F_{\text{AH}} = \frac{1}{\beta} \left\{ \frac{3}{16} \frac{\Phi^{\text{iv}}}{[\Phi_{\text{H}}]^2} - \frac{172 \cdot 3}{3072} \frac{[\Phi_{\text{H}}^{\text{iii}}]^2}{[\Phi_{\text{H}}]^3} \right\}. \quad (5.9)$$

The Bethe approximation then calculates the terms $\beta F_{\text{AH}}^{(4)}$ exactly for this model and, as $3/52 = 177 \cdot 2/3072$, it calculates $\beta F_{\text{AH}}^{(3,3)}$ to within 3%.

The approximation introduced by Ludwig (1958) has been compared with the above calculation by Maradudin, Flinn, and Coldwell-Horsfall and shown to calculate $\beta F_{\text{AH}}^{(4)}$ exactly for this model and to underestimate the coefficient in $\beta F_{\text{AH}}^{(3,3)}$ by 16%. On the other hand, the mean field or Einstein approximation used by Henkel (1955) in the study of solid argon gives, when applied to this model,

$$\begin{aligned} \beta F_{\text{AH}}^{(4)} &= \frac{1}{\beta} \frac{3}{32} \frac{\Phi^{\text{iv}}}{[\Phi_{\text{H}}]^2}, \\ \beta F_{\text{AH}}^{(3,3)} &= 0. \end{aligned} \quad (5.10)$$

It may be noted that these two errors tend to cancel.

It is interesting to see whether or not the terms in $1/a$ can be ignored in the expansion of the potential in equation (3.2). If all the terms for a central potential in this model are retained we obtain

$$\begin{aligned} \beta F_{\text{AH}}^{(4)} &= \frac{1}{\beta} \left\{ \frac{3}{16} \Phi^{\text{iv}} + \frac{9}{8} \frac{1}{a} \Phi_{\text{H}}^{\text{iii}} + \frac{9}{8} \frac{1}{a^2} \Phi_{\text{H}}^{\text{ii}} \right\} \frac{1}{[\Phi_{\text{H}}]^2}, \\ \beta F_{\text{AH}}^{(3,3)} &= -\frac{1}{\beta} \left\{ \frac{3}{52} [\Phi_{\text{H}}^{\text{iii}}]^2 + \frac{45}{64} \frac{1}{a^2} [\Phi_{\text{H}}^{\text{ii}}]^2 \right\} \frac{1}{[\Phi_{\text{H}}]^3}. \end{aligned} \quad (5.11)$$

Now, in order to estimate the importance of these terms, we shall substitute a Morse potential given by

$$\Phi(r) = \frac{1}{2} \frac{D}{A^2} \left[\exp \left\{ -2A \left(\frac{r-a}{a} \right) \right\} - 2 \exp \left\{ -A \left(\frac{r-a}{a} \right) \right\} \right]. \quad (5.12)$$

With this potential we have

$$\begin{aligned} \Phi^i(a) &= 0, \\ \Phi^{ii}(a) &= D/a^2, \\ \Phi^{iii}(a) &= -3AD/a^3, \\ \Phi^{iv}(a) &= 7A^2D/a^4. \end{aligned} \quad (5.13)$$

Substituting this into (5.11) gives

$$\begin{aligned} \beta F_{\text{AH}}^{(4)} &= \frac{1}{\beta D} \left(\frac{21}{16} A^2 - \frac{27}{8} A + \frac{9}{8} \right), \\ \beta F_{\text{AH}}^{(3,3)} &= -\frac{1}{\beta D} \left(\frac{27}{52} A^2 + \frac{45}{64} \right). \end{aligned} \quad (5.14)$$

Using a typical value of $A = 5$ we see that $\beta F_{\text{AH}}^{(4)}$ drops from $(1/\beta D)(525/16)$ if only the first term is retained to $(1/\beta D)(273/16)$ if all terms are retained. It would appear then that the term $(1/a)\Phi^{iii}$ cannot be ignored. The terms of order $1/a^2$, however, do not contribute strongly. It may be noted that, because of the term $(1/a)\Phi^{iii}$, the total anharmonic free energy will be negative for this model when $A < 4.12$.

VI. APPLICATION TO A BODY-CENTRED CUBIC CRYSTAL MODEL

The anharmonic contribution to the specific heat of sodium has been treated by both Stern (1958) and Leibfried and Ludwig (1961). Both these authors use models based on generalized coupling parameters. However, a simple model is suggested by the work of Fuchs (1935) in his calculation of the elastic constants. This work suggests that the forces between atoms in the alkali metals are central forces but that the contribution of the conduction electrons must be taken into account separately in calculating the elastic constants and the specific heat. This has been the basis of several calculations of the vibratory spectrum of these metals (cf. de Launay 1956). The elastic constants of the metal are then related to the elastic constants of the lattice by the Fuchs relations

$$\begin{aligned} c_{11} - c_{12} &= c'_{11} - c'_{12}, \\ c_{44} &= c'_{44}. \end{aligned} \quad (6.1)$$

The contribution of nearest neighbour forces is relatively more important for effects which depend on higher order terms in the interatomic potential. In the model studied here we shall assume that nearest and non-nearest harmonic forces are important, but that only the nearest neighbours need be considered in calculating the anharmonic contribution to the specific heat. The magnitude of the harmonic

potentials may then be estimated from the elastic constants. The assumption will then be made that the interatomic central potential is a Morse potential. This will allow us to calculate the anharmonic contribution to the specific heat after fitting the Morse potential to the observed Gruneisen constant.

The harmonic constants are then taken to be α_1 and α_3 , where the potential between non-nearest neighbours is taken as $\frac{1}{2}\alpha_3(\mathbf{p}\cdot\Delta\mathbf{r})^2$. \mathbf{p} is a unit vector to the non-nearest neighbour and α_1 is given in (3.1). It is assumed that $\alpha_2 = 0$. α_1 and α_3 are then related to the elastic constants (cf. de Launay 1956) by

$$\begin{aligned} 3^{\frac{1}{2}}\alpha_1/3a &= c_{44}, \\ 3^{\frac{1}{2}}\alpha_2/a &= c_{11}-c_{12}, \end{aligned} \quad (6.2)$$

where a is the nearest neighbour distance. Put

$$\begin{aligned} \alpha_3 &= ra_1, \\ r &= (c_{11}-c_{12})/3c_{44}. \end{aligned} \quad (6.3)$$

The effective potentials are then given by equations (3.6) and (3.8), which in the present case give

$$\begin{aligned} \eta_1 &= \alpha_1 - \alpha_1^2/(\chi - \eta_1 + \alpha_1), \\ \chi &= 8\eta_1/3 + 2\alpha_3, \end{aligned} \quad (6.4)$$

as there are eight nearest neighbours and six next-nearest neighbours in a body-centred cubic lattice. Solving these equations

$$\eta_1 = (3\alpha_1/5)[1 - r + \{(1-r)^2 + 10r/3\}^{\frac{1}{2}}]. \quad (6.5)$$

For the numerical data on the elastic constants of sodium we use the figures of Quimby and Siegel (1938) and of Siegel and Quimby (1938) linearly extrapolated to zero by Leibfried and Ludwig (1961) (for the justification of this procedure see Leibfried and Ludwig).

These figures are

$$\begin{aligned} c_{11} &= 0.65 \times 10^{11} \text{ erg cm}^{-3}, \\ c_{12} &= 0.49 \times 10^{11} \text{ erg cm}^{-3}, \\ c_{44} &= 0.665 \times 10^{11} \text{ erg cm}^{-3}, \end{aligned} \quad (6.6)$$

which give

$$r = 0.0804. \quad (6.7)$$

Substituting into equation (6.5) for the effective potential we obtain

$$\begin{aligned} \eta_1 &= 0.50\alpha_1, \\ \chi &= 1.33\alpha_1, \\ A_1 &= 1.83\alpha_1. \end{aligned} \quad (6.8)$$

When these are substituted into equation (3.12) for the harmonic free energy we obtain

$$\beta F_H = \frac{3}{2} \ln \left\{ \beta^2 \frac{\hbar^2}{m} 2 \cdot 46 \alpha_1 \right\}. \quad (6.9)$$

The anharmonic energy can now be calculated using the relation between the potentials for a Morse potential as given in equation (5.13) and the expressions for the anharmonic contributions to the free energy as given in equations (4.4) and (4.8). These give us

$$\beta F_{AH}^{(4)} = \frac{1}{\beta D} \left[1 \cdot 75 A^2 - 6 \cdot 40 A + 4 \cdot 29 \right],$$

$$\beta F_{AH}^{(3,3)} = -\frac{1}{\beta D} \left[1 \cdot 03 A^2 + 5 \cdot 21 \right],$$

which, when added together, give

$$\beta F_{AH} = \frac{1}{\beta D} \left[0 \cdot 72 A^2 - 6 \cdot 40 A - 0 \cdot 92 \right]. \quad (6.10)$$

Combining this equation with equation

$$C_v/k = -\beta^2 \frac{\partial^2}{\partial \beta^2} \left[\beta F \right], \quad (6.11)$$

we obtain the specific heat at constant volume per particle divided by Boltzmann's constant as

$$C_v/k = 3 + (1/\beta D) \{-1 \cdot 44 A^2 + 12 \cdot 8 A + 1 \cdot 84\}.$$

Differentiating, this expression leads to

$$\frac{d}{dT} \left(\frac{C_v}{k} \right) = \frac{k}{D} \{-1 \cdot 44 A^2 + 12 \cdot 8 A + 1 \cdot 84\}. \quad (6.12)$$

In order to complete the evaluation of this expression for sodium, we know that D is given by equations (5.13) as

$$D = a^2 \alpha_1.$$

When this is combined with the equations for the elastic constants (6.2) we have

$$D = 3^{\frac{1}{2}} a^3 c_{44}. \quad (6.13)$$

Using the value of the elastic constants, extrapolated linearly to zero temperature (6.6) and the nearest neighbour distance (Leibfried and Ludwig 1961)

$$a = \frac{1}{2} \times 3^{\frac{1}{2}} \times 4 \cdot 206 \times 10^{-8} \text{ cm}, \quad (6.14)$$

we obtain the value

$$D = 5 \cdot 57 \times 10^{-12} \text{ erg}. \quad (6.15)$$

In order to obtain Λ we shall relate it to Gruneisen's constant. Using equation (3.15), together with

$$-a \frac{d\alpha_1}{da} = 3\Lambda\alpha_1,$$

$$a \frac{d\alpha_2}{da} = \alpha_1,$$

$$\frac{dk}{da} = 0,$$

$$\alpha_2 = \eta_2 = 0,$$

gives

$$\gamma = \frac{4}{3} \frac{\Lambda\alpha_1}{\chi - \eta_1 + 2\alpha_1} - \frac{8}{9} \frac{\alpha_1}{\chi}. \quad (6.16)$$

Substituting the numerical values given in (6.8)

$$\gamma = 0.472\Lambda - 0.670. \quad (6.17)$$

Using the value $\gamma = 1.00$ given by Leibfried and Ludwig,

$$\Lambda = 3.54. \quad (6.18)$$

Substituting this value and the value of D given by (6.15) into (6.12) gives

$$\frac{d}{dT} \left(\frac{C_v}{k} \right) = +6.95 \times 10^{-4} \text{ deg}^{-1}. \quad (6.19)$$

This value is similar to the value

$$\frac{d}{dT} \left(\frac{C_v}{k} \right) = 6.43 \times 10^{-4} \text{ deg}^{-1}$$

obtained by Leibfried and Ludwig (1961), who used generalized coupling parameters instead of a simple model potential. Stern (1958) obtained

$$\frac{d}{dT} \left(\frac{C_v}{k} \right) = -1.80 \times 10^{-4} \text{ deg}^{-1}.$$

However, none of these values are extremely close to the measured value of

$$\frac{d}{dT} \left(\frac{C_v}{k} \right) = +20.9 \times 10^{-4} \text{ deg}^{-1}. \quad (6.20)$$

The experimental value (6.20) was obtained from Dauphinee, MacDonald, and Preston-Thomas (1954) who measured

$$\frac{d}{dT} \left(\frac{C_p}{k} \right) = 27.7 \times 10^{-4} \text{ deg}^{-1}.$$

As we have calculated the lattice contribution to the specific heat at constant volume we must subtract from this the thermal expansion contribution

$$9K\gamma^2k/V_2 = 6.2 \times 10^{-4} \text{ deg}^{-1}$$

and the electronic contribution

$$0.6 \times 10^{-4} \text{ deg}^{-1}.$$

These figures are also taken from Leibfried and Ludwig.

VII. CONCLUSION

The Bethe approximation can be used to evaluate the anharmonic contribution to the free energy of a lattice. When applied to the exactly evaluated face-centred cubic model of Maradudin, Flinn, and Coldwell-Horsfall the approximation produces an answer within 3% of the exact value. It is found that if the forces in the lattice are actually central forces then the anharmonic contribution to the free energy is quite different from that predicted by the model of Maradudin, Flinn, and Coldwell-Horsfall.

The approximation has been used to evaluate the anharmonic contribution to the specific heat of a simple model of sodium. Only fair agreement with experiment is obtained.

The approximation may be extended to other types of lattices if this is required.

VIII. ACKNOWLEDGMENT

The author sincerely wishes to thank Professor J. J. O'Dwyer for many helpful discussions on this problem.

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