

## Thermal and Elastic Properties of Crystals at Low Temperatures

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It is shown that to a first approximation (first-order perturbation theory in the quartic terms and second order in the cubic terms) the thermal free energy of an anharmonic crystal at low temperatures is given by an effective harmonic frequency distribution. The limiting form of this distribution at low frequencies can be calculated from the velocity of long elastic waves just as for a harmonic crystal, which implies that the Debye temperature  $\Theta_0^e$  calculated from the heat capacity at low temperatures is equal to  $\Theta_0^{e1}$  calculated from the elastic constants at low temperatures. Discrepancies between  $\Theta_0^e$  and  $\Theta_0^{e1}$  found in earlier theoretical work are discussed, and it is suggested that they are mainly due to a specific approximation employed in deriving  $\Theta_0^{e1}$ .

### INTRODUCTION

IT was suggested some time ago by Ludwig<sup>1</sup> that one consequence of anharmonicity in the theory of crystal vibrations is that the well-known relation between lattice-heat capacity and elastic constants at low temperatures breaks down. This relation can be concisely stated in the form

$$\Theta_0^e = \Theta_0^{e1}, \quad (1)$$

where  $\Theta_0^e$  is the Debye equivalent temperature derived from the heat capacity as  $T \rightarrow 0$  and  $\Theta_0^{e1}$  is the corresponding Debye temperature calculated from the velocity of elastic waves at  $T=0$ . In approximate calculations on particular models Leibfried and Ludwig<sup>2</sup> (L.L.) have estimated that  $\Theta_0^{e1} > \Theta_0^e$  by 1 or 2%. Since present experimental errors in both  $\Theta_0^e$  and  $\Theta_0^{e1}$  are of the order of 1%, such differences are relevant in the discussion of experimental data but cannot be conclusively confirmed or disproved thereby.<sup>2-7</sup>

The main purpose of this article is to point out that a rigorous theoretical analysis predicts no difference between  $\Theta_0^e$  and  $\Theta_0^{e1}$ , since the general expression for the thermal free energy  $F_T$  can be shown to correspond at low temperatures to a modified harmonic frequency distribution, which at low frequencies is identical to that derived from the velocity of elastic waves. First, however, we consider briefly the exact analytic solution for the linear chain,<sup>8</sup> since this has been cited incorrectly by L.L. as a model for which  $\Theta_0^e \neq \Theta_0^{e1}$ .

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<sup>2</sup> G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 275.

<sup>3</sup> G. A. Alers and J. R. Neighbours, *Revs. Modern Phys.* **31**, 675 (1959).

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<sup>5</sup> W. W. Scales, *Phys. Rev.* **112**, 49 (1958).

<sup>6</sup> T. H. K. Barron and J. A. Morrison, *Phys. Rev.* **115**, 1439 (1959).

<sup>7</sup> R. N. Claytor and B. J. Marshall, *Phys. Rev.* **120**, 332 (1960).

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### LINEAR CHAIN

L.L. take a linear chain of  $N$  atoms of mass  $M$ , with an interatomic potential between nearest neighbors which is expanded about the equilibrium distance  $\bar{l}$ :

$$\phi(\bar{l} + \delta l) = \phi(\bar{l}) + (1/2!) \tilde{f}(\delta l)^2 + (1/3!) \tilde{g}(\delta l)^3 + (1/4!) \tilde{h}(\delta l)^4 + \dots \quad (2)$$

This potential can also be expanded about an arbitrary distance  $l$ :

$$\phi(l + \delta l) = \phi(l) + e\delta l + (1/2!) f(\delta l)^2 + (1/3!) g(\delta l)^3 + (1/4!) h(\delta l)^4 + \dots \quad (3)$$

At  $T=0$ , the zero-point energy expands the lattice, and (3) is used. Here, (L.L., p. 347)

$$f = \tilde{f} - (\tilde{g}^2/2\tilde{f}^2)\bar{\epsilon}_z, \quad (4)$$

where  $\bar{\epsilon}_z$  is the mean zero-point energy per atom. Maradudin, Flinn, and Coldwell-Horsfall<sup>8</sup> [their equation (4.53)] give the heat capacity at low temperatures corresponding to a potential of the form (3), from which we find

$$k\Theta_0^e = \pi\hbar(f/M)^{1/2} [1 - \bar{\epsilon}_z \{ (g^2/8f^3) - (h/4f^2) \}]. \quad (5)$$

To this approximation we can neglect the difference between  $f$ ,  $g$ ,  $h$  and  $\tilde{f}$ ,  $\tilde{g}$ ,  $\tilde{h}$  except in the term  $(f/M)^{1/2}$ , so that from (4) and (5), we have

$$k\Theta_0^e = \pi\hbar(\tilde{f}/M)^{1/2} [1 - \bar{\epsilon}_z \{ (3\tilde{g}^2/8\tilde{f}^3) - (\tilde{h}/4\tilde{f}^2) \}]. \quad (6)$$

This is in perfect agreement with the expression for  $\Theta_0^{e1}$  [L.L., Eq. (9.16)].

We have confirmed this result by deriving  $\Theta_0^e$  independently from the general expressions [L.L., Eqs. (7.6a) and (7.10)] for the free energy of this model. The discrepancy between  $\Theta_0^e$  and  $\Theta_0^{e1}$  reported by L.L. is due partly to the use of the Debye approximation and partly to a trivial but unlucky error in deriving their Eq. (9.11) from (9.7).

## THREE-DIMENSIONAL CRYSTALS

The standard anharmonic theory of crystal vibrations<sup>2,8</sup> treats the cubic and quartic terms ( $\Phi_3$  and  $\Phi_4$ ) in the lattice-potential energy as perturbations added to the harmonic Hamiltonian; the first-order contribution of  $\Phi_3$  to the energy levels is zero, but its second-order contribution is of the same magnitude as the first-order contribution of  $\Phi_4$ . To this order of perturbation the expressions of L.L. for the contributions  $F_3$  and  $F_4$  to the Helmholtz free energy are rigorous [L.L., Eqs. (10.2) and (10.4b)]. We take these as our starting point, and use L.L.'s notation.

It is helpful first to consider the simple theoretical concept underlying the equality of  $\Theta_0^c$  and  $\Theta_0^{el}$ . This is that, regardless of detailed lattice structure, the lowest excited states are composed of quantised long elastic waves, so that as  $T \rightarrow 0$  the thermal free energy  $F_T$  depends upon the wave velocities precisely as in a harmonic crystal. If this is true, anharmonic effects can enter only through the effect of the zero-point energy  $E_z$  on the elastic constants and hence on the frequencies of long waves. The frequency dependence of the thermal free energy  $f_T$  of a harmonic oscillator is given by

$$(\partial/\partial\omega)f_T(\omega, T) = \epsilon_T(\omega, T)/\omega, \quad (7)$$

where  $\omega$  is the angular frequency and  $\epsilon_T(\omega, T)$  the internal energy; and so the anharmonic contribution to  $F_T$  as  $T \rightarrow 0$  must, to the first approximation, have the limiting form

$$F_T^{(anh)} = \sum_{\mathbf{k}, \lambda} \{ \epsilon_T(\omega, T)/\omega \} \delta\omega, \quad (8)$$

where  $\mathbf{k}$  is the wave vector of a normal mode,  $\lambda$  is its branch label, and  $\delta\omega$  is the change in its frequency due to  $E_z$ .

The general expression for  $F_4$  (L.L., p. 351) is

$$F_4 = \frac{1}{8Ns} \sum_{\mathbf{k}, \lambda} \sum_{\mathbf{k}', \lambda'} \Phi_{\lambda\lambda\lambda\lambda'}^{\mathbf{k}-\mathbf{k}'-\mathbf{k}'} \frac{\epsilon(\omega, T)\epsilon(\omega', T)}{\omega^2\omega'^2}, \quad (9)$$

where  $N$  is the number of primitive cells,  $s$  the number of atoms within a cell, and  $\Phi_{\lambda\lambda\lambda\lambda'}^{\mathbf{k}-\mathbf{k}'-\mathbf{k}'}$  is a coefficient occurring when  $\Phi_4$  is expressed in terms of the harmonic normal coordinates  $a_{\lambda}^{\mathbf{k}}$  (L.L., p. 306). To get  $F_{4,T}$  we separate  $\epsilon(\omega, T)$  into zero point and thermal components; with an obvious notation,

$$\epsilon\epsilon' = \epsilon_z\epsilon_z' + (\epsilon_T\epsilon_z' + \epsilon_z\epsilon_T') + \epsilon_T\epsilon_T'. \quad (10)$$

Here,  $\epsilon_z\epsilon_z'$  merely contributes to  $E_z$ , and it is the term  $\epsilon_T\epsilon_z' + \epsilon_z\epsilon_T'$  that is dominant in  $F_{4,T}$  at low temperatures.

Thus, at temperatures where the contribution  $\epsilon_T\epsilon_T'$  can be neglected,<sup>9</sup>  $F_{4,T}$  reduces to the form of Eq. (8) with

$$\delta\omega_4 = (\hbar/8Ns) \sum_{\mathbf{k}'\lambda'} \{ \Phi_{\lambda\lambda\lambda\lambda'}^{\mathbf{k}-\mathbf{k}'-\mathbf{k}'} / \omega\omega' \}. \quad (11)$$

By considering the change in the ground-state energy when a long-wave distortion  $a_{\lambda}^{\mathbf{k}}$  is applied to the crystal, it is easy to show<sup>10</sup> that this is indeed the change in frequency brought about by the effect of  $\Phi_4$  upon  $E_z$ .

A similar analysis can be carried out<sup>10</sup> for  $\Phi_3$ , where the change in effective frequency is

$$\delta\omega_3 = -(\hbar/8Ns) \sum_{\mathbf{k}', \lambda', \mathbf{k}'', \lambda''} \{ |\Phi_{\lambda\lambda'\lambda''}^{\mathbf{k}\mathbf{k}'\mathbf{k}''}|^2 / \omega\omega'\omega'' \} \times \frac{\omega' + \omega''}{(\omega' + \omega'')^2 - \omega^2}. \quad (12)$$

In the limit as  $\omega \rightarrow 0$  the last factor can be replaced by  $(\omega' + \omega'')^{-1}$ , when the expression becomes identical to that calculated from the distortion energy of a long elastic wave.

## FINAL REMARKS

Since the general theory implies that  $\Theta_0^c = \Theta_0^{el}$ , any differences found between them in theoretical calculations must be due to approximations in their explicit evaluation. We suggest that in L.L.'s calculations for cubic crystals the most serious approximation may be the replacement of  $\ln(\omega^2)$  by  $\ln(\omega^2)_{av}$  (L.L., p. 355), which will give elastic constants similar to those estimated by Salter.<sup>11</sup> Calculations on the fcc lattice with central forces<sup>12,13</sup> indicate that here Salter's approximation overestimates the contribution of  $E_z$  to the shear constants, corresponding to an error of about 3% in  $\Theta_0^{el}$  for argon. After correction for this error, the value of  $\Theta_0^{el}$  is in good agreement with the value of  $\Theta_0^c$  estimated by L.L. [their Eq. (12.14)].

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<sup>9</sup> Terms like this, involving the product of thermal energies, cannot be accounted for by an effective harmonic distribution. When they are appreciable, the properties of the crystal become explicitly anharmonic. *Note added in proof.* Dr. G. V. Chester (private communication) has pointed out that this explicit anharmonicity due to the term  $\epsilon_T\epsilon_T'$  can be described by a *temperature-dependent* harmonic distribution.

<sup>10</sup> T. H. K. Barron (to be published).

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<sup>12</sup> T. H. K. Barron, D. Phil. thesis, Oxford, 1955 (unpublished).

<sup>13</sup> T. H. K. Barron and M. L. Klein (to be published).