occurrence of ferromagnetism at low temperatures. Data obtained on the powder sample indicate an onset of magnetic ordering at 32°K. In this ordered state the magnetic moment per molecule is 0.10 μ_B. In the case of the solid rod, we have a sample which contains Ta as a chemical impurity and which has been severely cold worked. The main effect of all this is the lowering of the Curie point by only about 8°K. Thus we cannot agree with the idea that the ferromagnetism of ZrZn$_2$ can be easily destroyed by impurities and other lattice disturbances.[17] We also find no evidence for the existence of any magnetic ordering at temperatures between 32 and 120°K.

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[17] B. T. Matthias *et al.*, Phys. Rev. Letters **7**, 7 (1961).

Note added in proof: The behavior of the high-temperature susceptibility of ZrZn$_2$ has been the subject of a recent publication: E. P. Wohlfarth, Phys. Letters **20**, 253 (1966).

ACKNOWLEDGMENTS

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Lattice-Dynamical Calculation of the Surface Specific Heat of a Crystal at Low Temperatures

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A lattice-dynamical calculation of the surface contribution to the low-temperature specific heat of a crystal is presented. The free boundary surfaces of a crystal are treated as a perturbation of an unperturbed crystal in which the atomic displacements satisfy the cyclic boundary condition. The general theory developed in this paper is illustrated by applying it to a nearest- and next-nearest-neighbor central-force model of a simple cubic crystal, whose force constants are chosen in such a way that it is elastically isotropic in the long-wavelength limit. The result for the low-temperature surface specific heat obtained here agrees with the results of earlier calculations by Dupuis, Mazo, and Onsager, and by Stratton, which were based on elasticity theory.

1. INTRODUCTION

In this paper we present a lattice-dynamical calculation of the surface contribution to the specific heat of a crystal at low temperatures.

The majority of the previous calculations of the surface specific heat of a crystal were carried out for finite or semi-infinite isotropic elastic continua. The earliest such calculation seems to have been carried out by Breger and Zhukhovitskii[1–3] who determined the normal-mode frequencies of a semi-infinite incompressible isotropic continuum, from which the frequency spectrum and consequently the specific heat were computed. The assumption of incompressibility, while unphysical, is a mathematically convenient one because only transverse waves will propagate in such a medium. The result for the specific heat obtained in this way can be written in the low-temperature limit in the form

$$C_v(T)=AVT^3+BST^2+\cdots, \qquad (1.1)$$

where A and B are constants, V is the crystal volume, and S is its surface area. The first term is just the well-known "Debye-T^3" contribution to the low-temperature bulk specific heat, and the second term is the surface contribution.

Subsequently, Montroll[4] calculated the surface specific heat of an isotropic elastic rectangular parallelepiped whose faces are clamped. The normal-mode frequencies of such a solid can be written down explicitly, and the resulting specific heat has the form given by Eq. (1.1), although the coefficient B obtained by Montroll of course differed from that obtained by Breger and Zhukhovitskii.

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[1] A. Kh. Breger and A. A. Zhukhovitskii, J. Phys. Chem. U.S.S.R. **20**, 1459 (1946).

[2] A. Kh. Breger and A. A. Zhukhovitskii, Acta Physiochim. U.R.S.S. **21**, 1001 (1946).

[3] A. Kh. Breger and A. A. Zhukhovitskii, J. Chem. Phys. **14**, 569 (1946).

[4] E. W. Montroll, J. Chem. Phys. **18**, 183 (1950).

The first calculation of the surface specific heat for a physically realistic model of a solid was carried out by Stratton.[5] He considered a semi-infinite elastically isotropic plate, bounded by two planes perpendicular to the z axis and of infinite extent in the x and y directions. The displacement field satisfied the cyclic boundary conditions at boundaries of the solid normal to the x and y axes, and the condition that the solid be stress free on the two boundary surfaces normal to the z axis. Stratton determined the frequency–wave-vector relation for this solid, and from it the specific heat, which was found to have the form given by Eq. (1.1) at low temperatures.

The surface contribution to the low-temperature specific heat of the model studied by Stratton was recently calculated by Dupuis, Mazo, and Onsager.[6] In contrast with earlier calculations these authors bypassed the task of computing the frequency–wave-vector relationship explicitly by carrying out the sum over normal-mode frequencies in the expression for the specific heat by means of a contour integral. Their result for the surface specific heat has a remarkably simple analytic form:

$$C(T)_{\text{surface}}=3\pi\frac{k_B{}^2}{\hbar^2}\zeta(3)\frac{2C_t{}^4-3C_t{}^2C_l{}^2+3C_l{}^4}{C_t{}^2C_l{}^2(C_l{}^2-C_t{}^2)}ST^2. \quad (1.2)$$

Here C_l and C_t are the speeds of sound for longitudinal and transverse waves in the solid, and $\zeta(x)$ is the Riemann zeta function. The coefficient of ST^2 given by Eq. (1.2) differs from the original result of Stratton. However, in a recent note Stratton[7] has corrected two errors in his earlier calculation and has obtained agreement with the result given by Dupuis *et al.*

In this paper rather than assume a finite or semi-infinite crystal from the start in a calculation of the surface contribution to the low-temperature specific heat, we base our calculation on a perfect crystal in which the atomic displacements satisfy the cyclic boundary condition. We create a pair of adjacent free surfaces in the crystal by setting equal to zero all of the interactions between atoms on opposite sides of a hypothetical plane through the crystal, which plane contains no atoms itself. In other words, we cut the bonds joining the atoms on opposite sides of this hypothetical plane and in so doing create a semi-infinite plate bounded by the two free surfaces.

To set these interactions equal to zero we subtract their contribution from the potential energy of the perfect, cyclic crystal. The negatives of these interactions are treated as a perturbation on the potential energy of the perfect uncut crystal. The difference between the specific heat of the cut crystal and the specific heat of the unperturbed crystal caused by the perturbation is the surface contribution. This difference will be calculated by a Green's-function method.

The method underlying the present calculations will be developed quite generally in Secs. 2 and 3 of this paper. However, in order that the evaluation of the various integrals arising in this work can be carried out analytically rather than numerically we apply our methods in the succeeding sections of this paper to a nearest- and next-nearest-neighbor central-force model of a simple cubic crystal, whose force constants are chosen in such a way that the crystal is elastically isotropic in the long wavelength limit.

A preliminary account of this method was given in a short note by Maradudin and Ashkin.[8] Unfortunately, in that note an error in the evaluation of one matrix element led to a result for the surface specific heat which while of the same form as that obtained by Dupuis *et al.*[6] and by Stratton,[7] differed from it by a numerical factor. In this paper the error is corrected and the result of Dupuis *et al.* is obtained.

The only previous calculation of the surface contribution to the low temperature specific heat of a crystal which is lattice dynamical in character rather than proceeding directly from the assimilation of a crystal into an elastic continuum was carried out by Patterson.[9] The crystal model used in these calculations was a finite simple cubic crystal with nearest-neighbor central and noncentral force interactions between atoms. The eigenfrequencies of this crystal model can be obtained explicitly, so that the calculation of the specific heat can be carried out in a fairly straightforward fashion. Patterson found a surface contribution to the specific heat which at low temperatures has the form (constant)ST^2. However, Lengeler and Ludwig[10] have shown recently that for this crystal model it is not possible to satisfy simultaneously the conditions for elastic stability and the conditions on the atomic force constants which follow from the invariance of the crystal potential energy against infinitesimal rigid-body rotations of the crystal. Consequently the results obtained by Patterson have primarily a qualitative rather than a quantitative significance.

The method developed in this paper for the calculation of the surface contribution to the specific heat of a crystal may not be any simpler in its computational aspects than the earlier methods which were based on elasticity theory. However, inasmuch as it is essentially a perturbation calculation, although carried out exactly by Green's-function methods, we feel that it may be more easily understood than some of the previous calculations.

Finally we remark that we will not enter here into a

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[5] R. Stratton, Phil. Mag. 44, 519 (1953).

[6] M. Dupuis, R. Mazo, and L. Onsager, J. Chem. Phys. 33, 1452 (1960).

[7] R. Stratton, J. Chem. Phys. 37, 2972 (1962).

[8] A. A. Maradudin and M. Ashkin, *Proceedings of the IX International Conference on Low Temperature Physics, Columbus, Ohio, 1964* (Plenum Press, Inc., New York, to be published).

[9] D. Patterson, Can. J. Chem. 33, 1079 (1955).

[10] B. Lengeler and W. Ludwig, *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963* (Pergamon Press, Inc., New York, 1965), p. 439.

comparison of the predictions of theory and the results of experimental studies of the specific heats of assemblies of fine particles. Such comparisons have been given in the paper by Dupuis *et al.*,[6] and in a forthcoming review article by one of the present authors.[11]

2. THE SPECIFIC HEAT OF A PERTURBED CRYSTAL

In this section we obtain a formal expression for the change in the specific heat of a crystal brought about by the introduction of a perturbation into it. The expression is designed to be particularly useful for the calculation of this change at low temperatures. For much of the following discussion it is not necessary to specify the nature of the perturbation, so that several of the intermediate results we obtain are quite general. However, we will not lose sight of the fact that finally it is the surface contribution to the specific heat that we wish to calculate, and that the type of perturbation which we are required to consider for this purpose consists of changes in only the forces between the constituent atoms and not in the atomic masses. Our final expressions accordingly apply only for perturbations of this type.

The specific heat of an arbitrary crystal can be written in the harmonic approximation as

$$C_v(T)=k_B\sum_s\frac{(\frac{1}{2}\beta\hbar\omega_s)^2}{\sinh^2\frac{1}{2}\beta\hbar\omega_s}, \tag{2.1}$$

where T is the absolute temperature, k_B is Boltzmann's constant, $\beta=(k_BT)^{-1}$, and ω_s is the frequency of the sth normal mode of vibration. If we expand the hyperbolic sine in the denominator of the summand in Eq. (2.1) in powers of $\exp(-\beta\hbar\omega_s)$, we obtain an expression for the specific heat which, although valid at all finite temperatures, is particularly well suited for its calculation in the limit of low temperatures

$$C_v(T)=k_B\sum_{n=1}^{\infty}n\sum_s(\beta\hbar\omega_s)^2e^{-n\beta\hbar\omega_s}. \tag{2.2}$$

We begin the evaluation of $C_v(T)$ by introducing the function $F(z^2)$ of the complex variable z,

$$F(z^2)=\sum_s(1/(z^2-\omega_s^2)). \tag{2.3}$$

This function has simple poles at $z=\pm\omega_s$ with residues of $\pm\frac{1}{2}\omega_s$, respectively. Because only positive values of the frequencies $\{\omega_s\}$ appear in the expressions for the specific heat given by Eqs. (2.1) and (2.2), we can rewrite Eq. (2.2) as a contour integral involving the function $F(z^2)$,

$$C_v(T)=\frac{k_B(\beta\hbar)^2}{\pi i}\sum_{n=1}^{\infty}n\int_{C_1}z^3e^{-n\beta\hbar z}F(z^2)dz, \tag{2.4}$$

provided that we take for C_1 the contour shown in Fig. 1.

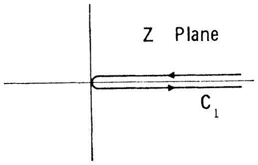

FIG. 1. The integration contour C_1.

The result expressed by Eqs. (2.3) and (2.4) is based only on the harmonic approximation. It therefore applies equally well to perturbed crystals and to perfect crystals.

If we denote functions associated with a perfect crystal by a superscript zero, then the specific heat for such a crystal can be written

$$C_v^{(0)}(T)=\frac{k_B(\beta\hbar)^2}{\pi i}\sum_{n=1}^{\infty}n\int_{C_1}z^3e^{-n\beta\hbar z}F^{(0)}(z^2)dz, \tag{2.5}$$

where

$$F^{(0)}(z^2)=\sum_s(1/(z^2-\omega_{0s}^2)). \tag{2.6}$$

In writing Eq. (2.6) we have denoted the normal mode frequencies of a perfect crystal by $\{\omega_{0s}\}$.

Combining Eqs. (2.4) and (2.5) we see that the change in the specific heat of a crystal caused by the introduction of impurities or imperfections into it is given by

$$\Delta C_v(T)=\frac{k_B(\beta\hbar)^2}{\pi i}\sum_{n=1}^{\infty}n\int_{C_1}z^3e^{-n\beta\hbar z}[F(z^2)-F^{(0)}(z^2)]dz. \tag{2.7}$$

From Eqs. (2.3) and (2.6) we find that in the limit as $|z|\to\infty$

$$\begin{aligned}F(z^2)-F^{(0)}(z^2)&=\sum_s\left\{\left[\frac{1}{z^2}+\frac{\omega_s^2}{z^4}+\frac{\omega_s^4}{z^6}+\cdots\right]\right.\\&\qquad\left.-\left[\frac{1}{z^2}+\frac{\omega_{0s}^2}{z^4}+\frac{\omega_{0s}^4}{z^6}+\cdots\right]\right\}\\&=\frac{1}{z^4}\sum_s[\omega_s^2-\omega_{0s}^2]+O(z^{-6}).\end{aligned} \tag{2.8}$$

The fact that the difference $F(z^2)-F^{(0)}(z^2)$ is of $O(z^{-4})$ in the limit as $|z|\to\infty$, together with the presence of the descending exponential in the integrand of Eq. (2.7) means that we may deform the integration contour C_1 in Eq. (2.7) into the contour C_2 (shown in Fig. 2), which consists of an infinite semicircle in the right half-plane together with the imaginary axis, and know that the contribution from the semicircle vanishes.

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[11] A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, to be published), Vol. 19.

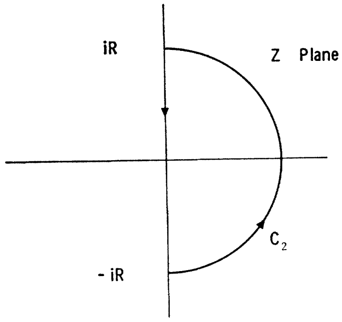

FIG. 2. The integration contour C_2.

With the change of variable $z=iy$, we obtain therefore that

$$\Delta C_v(T) = -\frac{2k_B(\beta\hbar)^2}{\pi}\sum_{n=1}^{\infty} n\int_0^\infty y^3 \sin n\beta\hbar y\,\Omega(y^2)dy, \quad (2.9)$$

where we have put

$$\Omega(y^2) = -F(-y^2)+F^{(0)}(-y^2). \quad (2.10)$$

Inasmuch as we are primarily interested in the specific heat in the limit of low temperatures, we may use a result from the theory of the asymptotic behavior of Fourier integrals[12] to simplify our subsequent analysis. In the limit of low temperatures β is large. The summation index n is always greater than or equal to unity. We therefore require the asymptotic behavior of the integral

$$J=\int_0^\infty y^3 \sin n\beta\hbar y\,\Omega(y^2)dy \quad (2.11)$$

in the limit as $n\beta\hbar$ becomes infinite. From the results of Lighthill's[12] analysis we can state that if the function $\Omega(y^2)$ has as its only singularity a logarithmic dependence on $|y|$ in the limit as $|y|\rightarrow 0$, i.e., if

$$\Omega(y^2) \sim -A\ln|y|+o(\ln|y|) \quad (2.12)$$

as $|y|\rightarrow 0$, then the dominant term in the asymptotic behavior of the integral J in the limit as $n\beta\hbar\rightarrow\infty$ is given by

$$J\sim -3\pi A/(n\beta\hbar)^4+o(n^{-4}), \quad (n\beta\hbar)\rightarrow\infty. \quad (2.13)$$

That the function $F_0(-y)^2$ can have its only singular (i.e., nonanalytic) behavior in the limit as $|y|\rightarrow 0$ was proved in the Appendix of Ref. 13. A proof of the same result for the function $F(-y^2)$ runs along the very same lines. It was also shown in Ref. 13 that a logarithmic dependence of $F_0(-y^2)$ on $|y|$ of the type given by the right-hand side of Eq. (2.12) is characteristic of two-dimensional crystals. It was this last result which in fact provided the heuristic motivation for the development of the method used in this paper for the calculation of the surface contribution to the specific heat of a crystal.

When the result given by Eq. (2.13) is substituted into Eq. (2.9), we obtain for the change in the specific heat

$$\Delta C_v(T) = 6A\zeta(3)k_B(k_BT/\hbar)^2+o(T^2) \quad (2.14)$$

in the limit as $T\rightarrow 0$, where $\zeta(x)$ is the Riemann zeta function.

It is shown in the Appendix that the specific heat of the unperturbed or perfect crystal contains no contribution proportional to its surface area, if the atomic displacements satisfy the cyclic boundary condition. It follows, therefore, that the entire surface contribution to the specific heat is given by the change $\Delta C_v(T)$, when the perturbation of the crystal is the introduction of a pair of free surfaces into it in the manner described in the Introduction.

The problem of calculating the surface contribution to the low-temperature specific heat of a crystal is thus seen to reduce to the problem of showing that the function $\Omega(y^2)$ associated with the introduction of free surfaces into a crystal has the asymptotic behavior given by Eq. (2.12) in the limit as $|y|\rightarrow 0$, and of determining the coefficient A.

3. THE FUNCTION $\Omega(y^2)$

We now must ask, what is a convenient way of calculating $F(z^2)$, $F^{(0)}(z^2)$, and consequently $\Omega(y^2)$? In the present paper we have adopted the following course.

The (time-independent) equations of motion for an arbitrary perfect crystal can be written as[14]

$$\sum_{l'\kappa'\beta}\{M_\kappa\omega^2\delta_{ll'}\delta_{\kappa\kappa'}\delta_{\alpha\beta}-\Phi_{\alpha\beta}^{(0)}(l\kappa;l'\kappa')\}u_\beta(l'\kappa')=0. \quad (3.1)$$

In this equation M_κ is the mass of the κth atom in the lth unit cell of the crystal, $u_\alpha(l\kappa)$ is the α-Cartesian component of the (time-independent) displacement of the atom $(l\kappa)$ from its equilibrium position, and the $\{\Phi_{\alpha\beta}^{(0)}(l\kappa;l'\kappa')\}$ are the atomic force constants. Equation (3.1) can be rewritten compactly in matrix form as

$$\mathbf{L}\mathbf{u}=0. \quad (3.2)$$

The time-independent equations of motion for an arbitrary imperfect crystal can be written in a similar fashion:

$$\sum_{l'\kappa'\beta}\{M_{l\kappa}\omega^2\delta_{ll'}\delta_{\kappa\kappa'}\delta_{\alpha\beta}-\Phi_{\alpha\beta}(l\kappa;l'\kappa')\}u_\beta(l'\kappa')=0, \quad (3.3)$$

or compactly as

$$(\mathbf{L}-\delta\mathbf{L})\mathbf{u}=0. \quad (3.4)$$

The elements of the matrix $\delta\mathbf{L}$, which expresses the effects of the perturbation on the equations of motion,

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[12] M. J. Lighthill, *Fourier Analysis and Generalized Functions* (Cambridge University Press, Cambridge, 1958), Chap. IV.

[13] J. Mahanty, A. A. Maradudin, and G. H. Weiss, Progr. Theoret. Phys. (Kyoto) 24, 648 (1960).

[14] A. A. Maradudin, in *Astrophysics and the Many Body Problem* (W. A. Benjamin, Inc., New York, 1963), p. 109.

are given explicitly by

$$\delta L_{\alpha\beta}(l\kappa;l'\kappa')=(M_\kappa-M_{l\kappa})\delta_{ll'}\delta_{\kappa\kappa'}\delta_{\alpha\beta}-(\Phi_{\alpha\beta}^{(0)}(l\kappa;l'\kappa')-\Phi_{\alpha\beta}(l\kappa;l'\kappa')). \quad (3.5)$$

We now define the Green's-function matrix for the perfect crystal, **G**, and for the perturbed crystal, **U**, by

$$\mathbf{G}=\mathbf{L}^{-1}, \quad (3.6a)$$

$$\mathbf{U}=(\mathbf{L}-\delta\mathbf{L})^{-1}. \quad (3.6b)$$

Combining Eqs. (3.6a) and (3.6b) we see that the matrix **U** is the solution of the equation

$$\mathbf{U}=\mathbf{G}+\mathbf{G}\delta\mathbf{L}\mathbf{U} \quad (3.7a)$$

$$=\mathbf{G}+\mathbf{GTG}, \quad (3.7b)$$

where the matrix **T** is defined by

$$\mathbf{T}=\delta\mathbf{L}+\delta\mathbf{LGT} \quad (3.8a)$$

$$=(\mathbf{I}-\delta\mathbf{LG})^{-1}\delta\mathbf{L}. \quad (3.8b)$$

The interest in these matrices lies in the fact that the elements of U can be written in the form

$$U_{\alpha\beta}(l\kappa;l'\kappa';\omega^2)=\frac{1}{(M_{l\kappa}M_{l'\kappa'})^{1/2}}\sum_s\frac{B_\alpha^{(s)}(l\kappa)B_\beta^{(s)}(l'\kappa')}{\omega^2-\omega_s^2}, \quad (3.9)$$

where ω_s is the frequency of the sth normal mode of the crystal, and $B_\alpha^{(s)}(l\kappa)$ is the $(l\kappa\alpha)$ component of the associated unit polarization vector. These two sets of quantities are defined through the eigenvalue equation

$$\sum_{l'\kappa'\beta}\frac{\Phi_{\alpha\beta}(l\kappa;l'\kappa')}{(M_{l\kappa}M_{l'\kappa'})^{1/2}}B_\beta^{(s)}(l'\kappa')=\omega_s^2B_\alpha^{(s)}(l\kappa), \quad (3.10)$$

together with the normalization and closure conditions

$$\sum_{l\kappa\alpha}B_\alpha^{(s)}(l\kappa)B_\alpha^{(s')}(l\kappa)=\delta_{ss'} \quad (3.11a)$$

$$\sum_s B_\alpha^{(s)}(l\kappa)B_\beta^{(s)}(l'\kappa')=\delta_{ll'}\delta_{\kappa\kappa'}\delta_{\alpha\beta}. \quad (3.11b)$$

Combining Eqs. (3.9) and (3.11a) we see that the function $F(\omega^2)$ is given by

$$F(\omega^2)=\sum_{l\kappa\alpha}M_{l\kappa}U_{\alpha\alpha}(l\kappa;l\kappa;\omega^2). \quad (3.12)$$

In a completely analogous fashion we can write the elements of the matrix **G** in the form

$$G_{\alpha\beta}(l\kappa;l'\kappa';\omega^2)=\frac{1}{(M_\kappa M_{\kappa'})^{1/2}}\sum_s\frac{B_\alpha^{(0s)}(l\kappa)B_\beta^{(0s)}(l'\kappa')}{\omega^2-\omega_{0s}^2}, \quad (3.13)$$

from which it follows that

$$F_0(\omega^2)=\sum_{l\kappa\alpha}M_\kappa G_{\alpha\alpha}(l\kappa;l\kappa;\omega^2). \quad (3.14)$$

In the special case, and the only one we consider from now on, that the perturbation of the crystal consists only of force constant changes with no mass changes, $M_{l\kappa}=M_\kappa$, and we have the result that

$$\Omega(y^2)=-\sum_{l\kappa\alpha}M_\kappa[U_{\alpha\alpha}(l\kappa;l\kappa;-y^2)-G_{\alpha\alpha}(l\kappa;l\kappa;-y^2)] \quad (3.15a)$$

$$=-\sum_{l\kappa\alpha}M_\kappa\sum_{l'l''}\sum_{\kappa'\kappa''}\sum_{\beta\gamma}G_{\alpha\beta}(l\kappa;l'\kappa';-y^2)\times T_{\beta\gamma}(l'\kappa';l''\kappa'';-y^2)G_{\gamma\alpha}(l''\kappa'';l\kappa;-y^2). \quad (3.15b)$$

The elements of the Green's-function matrix for the perfect crystal can be written equivalently as[14]

$$G_{\alpha\beta}(l\kappa;l'\kappa';\omega^2)=\frac{1}{N(M_\kappa M_{\kappa'})^{1/2}}\sum_{\mathbf{k}j}\frac{e_\alpha(\kappa|\mathbf{k}j)e_\beta^*(\kappa'|\mathbf{k}j)}{\omega^2-\omega_j^2(\mathbf{k})}\times e^{i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}. \quad (3.16)$$

In this expression N is the number of unit cells in the crystal, $\omega_j(\mathbf{k})$ is the frequency of the normal mode described by the wave vector $\mathbf{k}$ and the phonon branch index j, while $\mathbf{e}(\kappa|\mathbf{k}j)$ is the associated unit eigenvector. $\mathbf{x}(l)$ is the position vector to the lth unit cell. The fact that $G_{\alpha\beta}(l\kappa;l'\kappa';\omega^2)$ depends on l and l' only through their difference is a consequence of the invariance of the perfect crystal against a displacement through any of its translation vectors.

The eigenvectors $\{\mathbf{e}(\kappa|\mathbf{k}j)\}$ satisfy the orthogonality and closure conditions

$$\sum_{\kappa\alpha}e_\alpha^*(\kappa|\mathbf{k}j)e_\alpha(\kappa|\mathbf{k}j')=\delta_{jj'} \quad (3.17a)$$

$$\sum_j e_\alpha^*(\kappa|kj)e_\beta(\kappa'|kj)=\delta_{\kappa\kappa'}\delta_{\alpha\beta}. \quad (3.17b)$$

Let us expand $T_{\alpha\beta}(l\kappa;l'\kappa';\omega^2)$ formally in a double Fourier series according to

$$T_{\alpha\beta}(l\kappa;l'\kappa';\omega^2)=\frac{1}{N}(M_\kappa M_{\kappa'})^{1/2}\sum_{\mathbf{k}_1j_1}\sum_{\mathbf{k}_2j_2}e_\alpha(\kappa|\mathbf{k}_1j_1)t(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\omega^2)\times e_\beta(\kappa'|\mathbf{k}_2j_2)e^{i\mathbf{k}_1\cdot\mathbf{x}(l)+i\mathbf{k}_2\cdot\mathbf{x}(l')}. \quad (3.18)$$

That a double Fourier series is necessary is a consequence of the loss of translational symmetry by the crystal in the presence of the perturbation.

If we substitute Eqs. (3.16) and (3.18) into Eq. (3.15b) we find the following simple result for $\Omega(y^2)$

$$\Omega(y^2)=-\sum_{\mathbf{k}j}\frac{t(\mathbf{k}j;-\mathbf{k}j;-y^2)}{[y^2+\omega_j^2(\mathbf{k})]^2}. \quad (3.19)$$

The equation satisfied by the Fourier coefficient $t(kj;k'j';\omega^2)$ is obtained by substituting Eqs. (3.16) and (3.18) into Eq. (3.8a). When we do so we find that

$$t(\mathbf{k}j;\mathbf{k}'j';\omega^2)=V(\mathbf{k}j;k'j';\omega^2)+\sum_{\mathbf{k}_1 j_1}\frac{V(\mathbf{k}j;-\mathbf{k}_1 j_1;\omega^2)}{\omega^2-\omega_{j_1}{}^2(\mathbf{k}_1)}\times t(\mathbf{k}_1 j_1;\mathbf{k}'j';\omega^2)\,, \quad (3.20)$$

where

$$V(\mathbf{k}j;\mathbf{k}'j';\omega^2)=\frac{1}{N}\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta}e_\alpha{}^*(\kappa|\mathbf{k}j)\frac{\delta L_{\alpha\beta}(l\kappa;l'\kappa')}{(M_\kappa M_{\kappa'})^{1/2}}\times e_\beta{}^*(\kappa'|\mathbf{k}'j')e^{-i\mathbf{k}\cdot\mathbf{x}(l)-i\mathbf{k}'\cdot\mathbf{x}(l')}\,. \quad (3.21)$$

In the remainder of this paper we apply the results of this and the preceding section to the calculation of the surface contribution to the low-temperature specific heat for a particular crystal model.

4. THE CRYSTAL MODEL USED IN THIS PAPER

The crystal model for which we evaluate the function $\Omega(y^2)$ in this paper is a simple cubic crystal with nearest- and next-nearest-neighbor central-force interactions between atoms. This model was chosen for study because it is the simplest nontrivial model of a cubic crystal on which the condition of elastic isotropy can be imposed, and the imposition of this condition ultimately enables us to calculate the surface contribution to the specific heat of this crystal analytically, rather than numerically.

The translation vectors of this crystal are given by

$$\mathbf{x}(l)=l_x\mathbf{a}_1+l_y\mathbf{a}_2+l_z\mathbf{a}_3,\quad -\tfrac{1}{2}L<l_x,\,l_y,\,l_z\leq\tfrac{1}{2}L \quad (4.1\text{a})$$

$$\mathbf{a}_1=(a_0,0,0),\quad \mathbf{a}_2=(0,a_0,0),\quad \mathbf{a}_3=(0,0,a_0)\,, \quad (4.1\text{b})$$

where l_x, l_y, l_z are three integers, which can be positive, negative or zero, and where a_0 is the lattice parameter. The total number of atoms in the crystal is $N=L^3$.

The primitive translation vectors $\{\mathbf{b}_i\}$ of the reciprocal lattice for our crystal model, defined by

$$\mathbf{a}_i\cdot\mathbf{b}_j=2\pi\delta_{ij}\,, \quad (4.2)$$

are found to be

$$\mathbf{b}_1=\frac{2\pi}{a_0}(1,0,0),\quad \mathbf{b}_2=\frac{2\pi}{a_0}(0,1,0),\quad \mathbf{b}_3=\frac{2\pi}{a_0}(0,0,1)\,. \quad (4.3)$$

The potential energy of the crystal in the harmonic approximation can be written as

$$\Phi=\tfrac{1}{4}\sum_{ll'}{}'\sum_{\alpha\beta}\varphi_{\alpha\beta}(r^{ll'})(u_\alpha(l)-u_\alpha(l'))\times(u_\beta(l)-u_\beta(l'))\,. \quad (4.4)$$

The prime on the sum in this expression means that the terms with $l=l'$ are to be excluded from it. $r^{ll'}$ is the magnitude of the distance between the equilibrium positions of the atoms l and l', $r^{ll'}=|\mathbf{x}(l)-\mathbf{x}(l')|$. The coefficient $\varphi_{\alpha\beta}(r^{ll'})$ is given by

$$\varphi_{\alpha\beta}(r^{ll'})=\left.\frac{\partial^2\varphi(r)}{\partial x_\alpha\partial x_\beta}\right|_{r=r^{ll'}}=\left\{\frac{x_\alpha x_\beta}{r^2}\left[\varphi''(r)-\frac{1}{r}\varphi'(r)\right]+\delta_{\alpha\beta}\frac{1}{r}\varphi'(r)\right\}_{r=r^{ll'}} \quad (4.5)$$

where $\varphi(r)$ is the potential energy of interaction between two atoms separated by a distance r, and primes denote differentiation with respect to argument. In what follows, for a reason which will be clear below, we approximate Eq. (4.5) by

$$\varphi_{\alpha\beta}(r^{ll'})=\frac{x_\alpha(ll')x_\beta(ll')}{(r^{ll'})^2}\varphi''(r^{ll'})\,. \quad (4.6)$$

Thus we work with what is in fact de Launay's two-force-constant model[15] for a simple cubic crystal.

It should be pointed out here that our use of either of the expressions (4.5) or (4.6) for $\varphi_{\alpha\beta}(r^{ll'})$ ensures that the conditions imposed on the atomic force constants by the invariance of the crystal potential energy against rigid-body rotations of the crystal, viz.,[16]

$$\sum_{l'}\varphi_{\alpha\beta}(r^{ll'})x_\gamma(l')=\sum_{l'}\varphi_{\alpha\gamma}(r^{ll'})x_\beta(l')\,, \quad (4.7)$$

are automatically satisfied for every atom l in the crystal, regardless of whether it is in a surface layer or in the interior.

We will impose the cyclic boundary condition on the atomic displacements in this crystal model,

$$u_\alpha(l_x+L,l_y,l_z)=u_\alpha(l_x,l_y+L,l_z)=u_\alpha(l_x,l_y,l_z+L)=u_\alpha(l_x,l_y,l_z)\,. \quad (4.8)$$

The elements of the crystal dynamical matrix which follows from this assumption, are given by

$$D_{\alpha\beta}(\mathbf{k})=\frac{1}{M}\sum_{l'}{}'\varphi_{\alpha\beta}(r^{ll'})(1-e^{-i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]})\,. \quad (4.9)$$

The allowed values of the wave vector $\mathbf{k}$ appearing in this expression are given by

$$\mathbf{k}=\frac{1}{L}(h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3)=\frac{2\pi}{La_0}(h_1,h_2,h_3),\quad -\frac{L}{2}+1\leq h_1,\,h_2,\,h_3\leq\frac{L}{2}, \quad (4.10)$$

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[15] J. de Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 219.

[16] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963), p. 13.

where h_1, h_2, h_3, are three integers, which can be positive, negative, or zero. They are, therefore, uniformly distributed throughout the cube $(\pm\pi/a_0, \pm\pi/a_0, \pm\pi/a_0)^3$, with a density $V/(2\pi)^3$, where $V=(La_0)^3$ is the volume of the crystal.

Substituting Eq. (4.6) into Eq. (4.9), we find that

$$D_{xx}(\mathbf{k})=(2/M)\{\varphi''(a_0)(1-\cos k_xa_0)+\varphi''(2^{1/2}a_0) \times[2-\cos k_xa_0(\cos k_ya_0+\cos k_za_0)]\} \quad (4.11\text{a})$$

$$D_{xy}(\mathbf{k})=(2/M)\varphi''(2^{1/2}a_0)\sin k_xa_0 \sin k_ya_0. \quad (4.11\text{b})$$

Comparing the long-wavelength forms of these expressions with the analogous elements of the Green-Christoffel tensor of elasticity theory,

$$D_{xx}(\mathbf{k})=\frac{1}{\rho}\left\{\left[\frac{\varphi''(a_0)}{a_0}+\frac{2\varphi''(2^{1/2}a_0)}{a_0}\right]k_x^2 +\frac{\varphi''(2^{1/2}a_0)}{a_0}(k_y^2+k_z^2)\right\}, \quad (4.12\text{a})$$

$$D_{xy}(\mathbf{k})=\frac{1}{\rho}\frac{2\varphi''(2^{1/2}a_0)}{a_0}k_xk_y, \quad (4.12\text{b})$$

$$D_{xx}(\mathbf{k})_{\text{elastic}}=(1/\rho)\{c_{11}k_x^2+c_{44}(k_y^2+k_z^2)\}, \quad (4.13\text{a})$$

$$D_{xy}(\mathbf{k})_{\text{elastic}}=(1/\rho)(c_{12}+c_{44})k_xk_y, \quad (4.13\text{b})$$

we obtain the following relations between the elastic constants and atomic force constants for our crystal model:

$$\begin{aligned} c_{11}&=\frac{\varphi''(a_0)}{a_0}+\frac{2\varphi''(2^{1/2}a_0)}{a_0} \\ c_{12}=c_{44}&=\frac{\varphi''(2^{1/2}a_0)}{a_0}. \end{aligned} \quad (4.14)$$

In the equations $\rho=M/a_0^3$ is the mass density. The fact that the Cauchy relation $c_{12}=c_{44}$ is satisfied is of course a consequence of our assumption of central-force interactions between atoms.

The isotropy condition for cubic crystals is[17]

$$c_{11}-c_{12}=2c_{44}. \quad (4.15)$$

From Eqs. (4.14) we see that the satisfaction of this condition requires that

$$\varphi''(a_0)=\varphi''(2^{1/2}a_0). \quad (4.16)$$

In all that follows we adopt the condition (4.16).

In the long-wavelength limit the normal-mode frequencies, which are the eigenvalues of the matrix $D(\mathbf{k})$ whose elements are given by Eq. (4.13), are found to be

$$\omega_1^2(\mathbf{k})=(3c_{44}/\rho)k^2 \quad (4.17\text{a})$$

$$\omega_{2,3}^2(\mathbf{k})=(c_{44}/\rho)k^2, \quad (4.17\text{b})$$

when Eqs. (4.14) and (4.16) have been used. The eigenvector $\mathbf{e}(\mathbf{k}1)$ is found to have the simple form

$$\mathbf{e}(\mathbf{k}1)=\left(\frac{k_x}{k},\frac{k_y}{k},\frac{k_z}{k}\right). \quad (4.18)$$

The modes labeled by $j=1$ therefore are pure longitudinal modes. Since the modes labeled by $j=2$ and $j=3$ must be perpendicular to the mode $j=1$, and to each other, according to Eq. (3.17a), they must be pure transverse modes. Explicit expressions for the eigenvectors $\mathbf{e}(\mathbf{k}2)$ and $\mathbf{e}(\mathbf{k}3)$ will not be required in what follows, because they can always be eliminated in favor of $\mathbf{e}(\mathbf{k}1)$ through the use of Eq. (3.17b) and the degeneracy of the modes $j=2$ and $j=3$.

In what follows we will find it convenient to introduce the notation

$$c_t^2=c_{44}/\rho \quad (4.19\text{a})$$

$$c_l^2=3c_{44}/\rho=3c_t^2, \quad (4.19\text{b})$$

where c_l and c_t are, respectively, the speeds of propagation of longitudinal and transverse sound waves in our model of a crystal.

5. THE FUNCTION $\Omega(y^2)$ FOR THE ASSUMED CRYSTAL MODEL

We now introduce a pair of adjacent (100) free surfaces into the crystal by setting equal to zero all atomic interactions between atoms on opposite sides of the plane $z=\frac{1}{2}a_0$. For the present model this means setting to zero all interactions between an atom in the plane $l_z=0$ with its nearest- and next-nearest-neighbors in the plane $l_z=1$. We do this by subtracting from the potential energy of the crystal, as given by Eq. (4.4), the contribution from all interactions of this type. In this way we obtain the result that

$$\begin{aligned}\Phi_{\text{cut crystal}} &=\tfrac{1}{4}\sum_{ll'}{}'\sum_{\alpha\beta}\varphi_{\alpha\beta}(r^{ll'})(u_\alpha(l)-u_\alpha(l'))(u_\beta(l)-u_\beta(l')) \\ &-\tfrac{1}{4}\sum_{ll'}{}'\sum_{\alpha\beta}\varphi_{\alpha\beta}(r^{ll'})[\delta_{l_z0}\delta_{l_z'1}+\delta_{l_z'0}\delta_{l_z1}] \\ &\times(u_\alpha(l)-u_\alpha(l'))(u_\beta(l)-u_\beta(l')). \end{aligned} \quad (5.1)$$

From the relations

$$\begin{aligned}\Phi_{\alpha\beta}^{(0)}(ll')&=-\varphi_{\alpha\beta}(r^{ll'}) \qquad (l\neq l') \\ \Phi_{\alpha\beta}^{(0)}(ll)&=\sum_{l'}{}'\varphi_{\alpha\beta}(r^{ll'}), \end{aligned} \quad (5.2)$$

together with Eqs. (3.5), (5.1), and (5.2) we find that

$$\delta L_{\alpha\beta}(ll')=\varphi_{\alpha\beta}(r^{ll'})[\delta_{l_z0}\delta_{l_z'1}+\delta_{l_z'0}\delta_{l_z1}], \qquad l\neq l \quad (5.3\text{a})$$

$$\delta L_{\alpha\beta}(ll)=-\sum_{l'}{}'\varphi_{\alpha\beta}(r^{ll'})[\delta_{l_z0}\delta_{l_z'1}+\delta_{l_z'0}\delta_{l_z1}]. \quad (5.3\text{b})$$

The Fourier coefficient $V(\mathbf{k}j;\mathbf{k}'j';\omega^2)$, defined by

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[17] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1953), 1st ed., p. 52.

Eq. (3.21), for the present crystal model becomes

$$V(\mathbf{k}j;\mathbf{k}'j';\omega^2)$$

$$=\frac{1}{NM}\sum_{ll'}{}'\sum_{\alpha\beta}e_\alpha(\mathbf{k}j)e_\beta(\mathbf{k}'j')\varphi_{\alpha\beta}(r^{ll'})$$

$$\times[\delta_{l_z0}\delta_{l_z'1}+\delta_{l_z'0}\delta_{l_z1}][e^{-i\mathbf{k}\cdot\mathbf{x}(l)-i\mathbf{k}'\cdot\mathbf{x}(l')}$$

$$-e^{-i\mathbf{k}\cdot\mathbf{x}(l)-i\mathbf{k}'\cdot\mathbf{x}(l)}],\quad(5.4)$$

where we have used the fact that the eigenvectors $\{\mathbf{e}(\mathbf{k}j)\}$ for Bravais crystals can be chosen to be real, and to satisfy the condition[18]

$$\mathbf{e}(-\mathbf{k}j)=\mathbf{e}(\mathbf{k}j).\quad(5.5)$$

Replacing l' as a summation variable by a new independent variable $\bar{l}$ through the relation

$$\mathbf{x}(\bar{l})=\mathbf{x}(l)-\mathbf{x}(l'),\quad(5.6)$$

we can rewrite Eq. (5.4) as

$$V(kj;k'j';\omega^2)$$

$$=\frac{-1}{NM}\sum_{l}{}'\delta_{l_z0}e^{-i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{x}(l)}\sum_{\bar{l}\alpha\beta}\delta_{\bar{l}_z,-1}$$

$$\times e_\alpha(\mathbf{k}j)e_\beta(\mathbf{k}'j')\varphi_{\alpha\beta}(r^{\bar{l}})(e^{i\mathbf{k}\cdot\mathbf{x}(\bar{l})}-1)(e^{i\mathbf{k}'\cdot\mathbf{x}(\bar{l})}-1)$$

$$=\delta(k_x+k_x')\delta(k_y+k_y')\sum_{\bar{l}}v_{\bar{l}}(\mathbf{k}j)v_{\bar{l}}(\mathbf{k}j'),\quad(5.7)$$

with

$$v_{\bar{l}}(\mathbf{k}j)=\delta_{\bar{l}_z,-1}\frac{2}{(LM)^{1/2}}\frac{(\varphi''^{(r^{\bar{l}})})^{1/2}}{r^{\bar{l}}}(\mathbf{x}(\bar{l})\cdot\mathbf{e}(\mathbf{k}j))$$

$$\times e^{(i/2)\mathbf{k}\cdot\mathbf{x}(\bar{l})}\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l}).\quad(5.8)$$

It is the separable form (5.7) for the coefficient $V(\mathbf{k}j;\mathbf{k}'j';\omega^2)$ to which it gives rise that prompted our adoption of the approximation (4.6) in this work.

Because of the restrictions that $\bar{l}_z$ must equal -1 and that $\varphi''(r^{\bar{l}})$ is nonzero only if the vector $\mathbf{x}(\bar{l})$ $[r^{\bar{l}}=|\mathbf{x}(\bar{l})|]$ connects a given atom with its nearest- and next-nearest-neighbors, the vector $\mathbf{x}(\bar{l})$ can assume only the following five values:

$$\begin{array}{ll}(1) & \mathbf{x}(\bar{l})=a_0(0,0,-1)\\ (2) & \qquad =a_0(-1,0,-1)\\ (3) & \qquad =a_0(0,-1,-1)\\ (4) & \qquad =a_0(1,0,-1)\\ (5) & \qquad =a_0(0,1,-1)\,.\end{array}\quad(5.9)$$

The numbers (1)–(5) are merely a conventional labeling of these five vectors which will be useful below for labeling matrix elements.

The equation (3.20) for the Fourier coefficient $t(\mathbf{k}j;\mathbf{k}'j';\omega^2)$ takes the following simple form when the result given by Eq. (5.7) is substituted into it:

$$t(\mathbf{k}j;\mathbf{k}'j';\omega^2)$$

$$=\delta(k_x+k_x')\delta(k_y+k_y')\sum_{\bar{l}}v_{\bar{l}}(\mathbf{k}j)v_{\bar{l}}(\mathbf{k}'j')$$

$$+\sum_{\bar{l}}\sum_{\mathbf{k}_1j_1}\delta(k_x-k_{1x})\delta(k_y-k_{1y})v_{\bar{l}}(\mathbf{k}j)v_{\bar{l}}(-\mathbf{k}_1j_1)$$

$$(\omega^2-\omega_{j_1}{}^2(\mathbf{k}_1))^{-1}t(\mathbf{k}_1j_1;\mathbf{k}'j';\omega^2).\quad(5.10)$$

This equation is an integral equation with a degenerate kernel. To solve it we define the function $g_{\bar{l}}(k_xk_y;k'j';\omega^2)$ by

$$g_{\bar{l}}(k_xk_y;\mathbf{k}'j';\omega^2)$$

$$=\sum_{\mathbf{k}_1j_1}\delta(k_x-k_{1x})\delta(k_y-k_{1y})\frac{v_{\bar{l}}(-\mathbf{k}_1j_1)}{\omega^2-\omega_{j_1}{}^2(\mathbf{k}_1)}$$

$$\times t(\mathbf{k}_1j_1;\mathbf{k}'j';\omega^2).\quad(5.11)$$

In terms of this function the Fourier coefficient $t(\mathbf{k}j;\mathbf{k}'j';\omega^2)$ is given by

$$t(\mathbf{k}j;\mathbf{k}'j';\omega^2)$$

$$=\sum_{\bar{l}}\delta(k_x+k_x')\delta(k_y+k_y')v_{\bar{l}}(\mathbf{k}j)v_{\bar{l}}(k'j')$$

$$+\sum_{\bar{l}}v_{\bar{l}}(\mathbf{k}j)g_{\bar{l}}(k_xk_y;\mathbf{k}'j';\omega^2).\quad(5.12)$$

Combining Eqs. (5.11) and (5.12) we find that $g_{\bar{l}}(k_xk_y;\mathbf{k}'j';\omega^2)$ is the solution of the equation

$$g_{\bar{l}}(k_xk_y;\mathbf{k}'j';\omega^2)$$

$$=\delta(k_x+k_x')\delta(k_y+k_y')\sum_{\bar{l}}M_{\bar{l}\bar{l}'}(k_xk_y;\omega^2)v_{\bar{l}'}(k'j')$$

$$+\sum_{\bar{l}}M_{\bar{l}\bar{l}'}(k_xk_y;\omega^2)g_{\bar{l}'}(k_xk_y;\mathbf{k}'j';\omega^2),\quad(5.13\text{a})$$

where we have introduced a 5×5 matrix $\mathbf{M}(k_xk_y;\omega^2)$, whose elements are given by

$$M_{\bar{l}\bar{l}'}(k_xk_y;\omega^2)=\sum_{k_zj}\frac{v_{\bar{l}}(-\mathbf{k}j)v_{\bar{l}'}(\mathbf{k}j)}{\omega^2-\omega_j{}^2(\mathbf{k})}.\quad(5.13\text{b})$$

The solution of Eq. (5.13a) is readily found to be

$$g_{\bar{l}}(k_xk_y;\mathbf{k}'j';\omega^2)$$

$$=\delta(k_x+k_x')\delta(k_y+k_y')\sum_{\bar{l}'}\{[\mathbf{I}-\mathbf{M}(k_xk_y;\omega^2)]^{-1}$$

$$\times\mathbf{M}(k_xk_y;\omega^2)\}_{\bar{l}\bar{l}'}v_{\bar{l}'}(\mathbf{k}'j'),\quad(5.14)$$

from which it follows directly that

$$t(\mathbf{k}j;\mathbf{k}'j';\omega^2)$$

$$=\delta(k_x+k_x')\delta(k_x+k_y')\sum_{\bar{l}\bar{l}'}v_{\bar{l}}(\mathbf{k}j)$$

$$\times[\mathbf{I}-\mathbf{M}(k_xk_y;\omega^2)]^{-}{}_{\bar{l}\bar{l}'}v_{\bar{l}'}(\mathbf{k}'j').\quad(5.15)$$

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[18] See, for example, A. Walfisz, *Gitterpunkte in Mehrdimensionalen Kugeln* (Pandstwowe Wydawnictwo Naukowe, Warsaw, 1957), Monografie Matematyczne No. 33.

When we substitute Eq. (5.8) into Eq. (5.13b) we obtain the following expression for the matrix element $M_{\bar{l}\bar{l}'}(k_xk_y;\omega^2)$

$$M_{\bar{l}\bar{l}'}(k_xk_y;\omega^2)$$
$$=-\frac{4}{LM}\frac{(\varphi''(r^{l})\varphi''(r^{\bar{l}'}))^{1/2}}{r^{\bar{l}}r^{\bar{l}'}}\sum_{k_zj}(\mathbf{x}(\bar{l})\cdot\mathbf{e}(\mathbf{k}j))e^{-(i/2)\mathbf{k}\cdot\mathbf{x}(\bar{l})}$$
$$\times\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l})(\omega^2-\omega_j^2(\mathbf{k}))^{-1}(\mathbf{x}(\bar{l}')\cdot\mathbf{e}(\mathbf{k}j))e^{(i/2)\mathbf{k}\cdot\mathbf{x}(\bar{l}')}$$
$$\times\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l}'). \quad (5.16)$$

As it stands, this element is complex in general. For computational purposes, however, it is more convenient to work with a real matrix. If we recall that $\bar{l}_z=\bar{l}_z'=-1$, we see that we can rewrite Eq. (5.16) as

$$M_{\bar{l}\bar{l}'}(k_xk_y;\omega^2)=e^{-(i/2)a_0(k_x\bar{l}_x+k_y\bar{l}_y)}m_{\bar{l}\bar{l}'}(k_xk_y;\omega^2)$$
$$\times e^{(i/2)a_0(k_x\bar{l}_x'+k_y\bar{l}_y')}, \quad (5.17)$$

where

$$m_{\bar{l}\bar{l}'}(k_xk_y;\omega^2)$$
$$=-\frac{4}{LM}\frac{(\varphi''(r^{\bar{l}})\varphi''(r^{\bar{l}'}))^{1/2}}{r^{\bar{l}}r^{\bar{l}'}}$$
$$\times\sum_{k_zj}(\mathbf{x}(\bar{l})\cdot\mathbf{e}(\mathbf{k}j))\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l})(\omega^2-\omega_j^2(\mathbf{k}))^{-1}$$
$$\times(\mathbf{x}(\bar{l}')\cdot\mathbf{e}(\mathbf{k}j))\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l}'). \quad (5.18)$$

If we introduce a diagonal 5×5 matrix $\mathbf{E}(k_xk_y)$ whose elements are given by

$$E_{\bar{l}\bar{l}'}(k_xk_y)=\delta_{\bar{l}\bar{l}'}e^{(i/2)a_0(k_x\bar{l}_x+k_y\bar{l}_y)}, \quad (5.19)$$

the relation (5.17) between the matrices $\mathbf{M}(k_xk_y;\omega^2)$ and $\mathbf{m}(k_xk_y;\omega^2)$ can be written

$$\mathbf{M}(k_xk_y;\omega^2)=\mathbf{E}^{-1}(k_xk_y)\mathbf{m}(k_xk_y;\omega^2)\mathbf{E}(k_xk_y). \quad (5.20)$$

It follows, therefore, that

$$(\mathbf{I}-\mathbf{M}(k_xk_y;\omega^2))^{-1}$$
$$=\mathbf{E}^{-1}(k_xk_y)(\mathbf{I}-\mathbf{m}(k_xk_y;\omega^2))^{-1}\mathbf{E}(k_xk_y). \quad (5.21)$$

The Fourier coefficient $t(\mathbf{k}j;\mathbf{k}'j';\omega^2)$ accordingly can be written as

$$t(\mathbf{k}j;\mathbf{k}'j';\omega^2)=\delta(k_x+k_x')\delta(k_y+k_y')\sum_{\bar{l}\bar{l}'}v_{\bar{l}}(\mathbf{k}j)$$
$$\times e^{-/i(a_02)(k_x\bar{l}_x+k_y\bar{l}_y)}[\mathbf{I}-\mathbf{m}(k_xk_y;\omega^2)]^{-1}{}_{\bar{l}\bar{l}'}$$
$$\times e^{i(a_0/2)(k_x\bar{l}_x'+k_yl_y')}v_{\bar{l}'}(\mathbf{k}'j'). \quad (5.22)$$

Substituting into Eq. (5.22) the explicit expression for $v_{\bar{l}}(\mathbf{k}j)$ given by Eq. (5.8), we obtain

$$t(\mathbf{k}j,\mathbf{k}'j';\omega^2)$$
$$=\delta(k_x+k_x')\delta(k_y+k_y')\frac{4}{LM}\sum_{\bar{l}\bar{l}'}\frac{(\varphi''(r^{\bar{l}})\varphi''(r^{\bar{l}'}))^{1/2}}{r^{\bar{l}}r^{\bar{l}'}}$$
$$\times(\mathbf{x}(\bar{l})\cdot\mathbf{e}(\mathbf{k}j))(\mathbf{x}(\bar{l}')\cdot\mathbf{e}(\mathbf{k}'j'))\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l})\sin\tfrac{1}{2}\mathbf{k}'\cdot\mathbf{x}(\bar{l}')$$
$$\times e^{-i(a_0/2)(k_z+k_z')}[\mathbf{I}-\mathbf{m}(k_xk_y;\omega^2)]^{-1}{}_{\bar{l}\bar{l}'}. \quad (5.23)$$

For the calculation of the function $\Omega(y^2)$ according to Eq. (3.19) it is the coefficient $t(\mathbf{k}j;-\mathbf{k}j;-y^2)$ that is required. From Eq. (5.23) we see that this function has the comparatively simple form

$$t(kj;-kj;-y^2)$$
$$=-\frac{4}{LM}\sum_{\bar{l}\bar{l}'}\frac{(\varphi''(r^{\bar{l}})\varphi''(r^{\bar{l}'}))^{1/2}}{r^{\bar{l}}r^{\bar{l}'}}(\mathbf{x}(\bar{l})\cdot\mathbf{e}(\mathbf{k}j))$$
$$\times(\mathbf{x}(\bar{l}')\cdot\mathbf{e}(\mathbf{k}j))\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l})\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l}')$$
$$\times[\mathbf{I}-\mathbf{m}(k_xk_y;-y^2)]^{-1}{}_{\bar{l}\bar{l}'}. \quad (5.24)$$

Finally, combining Eqs. (3.19) and (5.24) we obtain for the function $\Omega(y^2)$ the result

$$\Omega(y^2)=\frac{4}{LM}\sum_{\bar{l}\bar{l}'}\frac{(\varphi''(r^{\bar{l}})\varphi''(r^{\bar{l}'}))^{1/2}}{r^{\bar{l}}r^{\bar{l}'}}$$
$$\times\sum_{\mathbf{k}j}\frac{(\mathbf{x}(\bar{l})\cdot\mathbf{e}(\mathbf{k}j))(\mathbf{x}(\bar{l}')\cdot\mathbf{e}(\mathbf{k}j))}{[y^2+\omega_j^2(\mathbf{k})]^2}\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l})$$
$$\times\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l}')[\mathbf{I}-\mathbf{m}(\mathbf{k}_x\mathbf{k}_y;-y^2)]^{-1}{}_{\bar{l}\bar{l}'}. \quad (5.25)$$

6. THE EVALUATION OF $\Omega(y^2)$

If $\Omega(y^2)$ is to have a singular dependence on $|y|$ in the limit as $|y|\rightarrow 0$, e.g., of the type of $\ln|y|$, the sum on $\mathbf{k}$ on the right-hand side of Eq. (5.25) must diverge at the point $y=0$. Since the sum on $\mathbf{k}$ is a finite sum (because it extends over the N allowed values of $\mathbf{k}$ in the first Brillouin zone of the crystal), this divergence cannot come from large values of $\mathbf{k}$. On the other hand, the form of the summand in Eq. (5.25) strongly suggests that it is the region of small $\mathbf{k}$ values which leads to a divergence of $\Omega(y^2)$ at $y=0$, i.e., that part of $\mathbf{k}$ space for which the summand is largest as $|y|\rightarrow 0$.

We see from the expression given by Eq. (5.25) that in the limit as $|y|\rightarrow 0$, considered as a function of the wave vector $\mathbf{k}$ the summand is given by

$$(\mathbf{x}(\bar{l})\cdot\mathbf{e}(\mathbf{k}j))(\mathbf{x}(\bar{l}')\cdot\mathbf{e}(\mathbf{k}j))$$
$$\times\frac{\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l})\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l}')}{\omega_j^4(\mathbf{k})}[\mathbf{I}-\mathbf{m}(k_xk_y;0)]^{-1}{}_{\bar{l}\bar{l}'}.$$

It is not difficult to see from Eq. (5.18) that $m_{\bar{l}\bar{l}}(k_xk_y;0)$ is finite. Inasmuch as $\omega_j(\mathbf{k})\sim|\mathbf{k}|$ for $|\mathbf{k}|$ tending to zero, while $e_\alpha(\mathbf{k}j)$ becomes a function of $(\mathbf{k}/|\mathbf{k}|)$ in this limit, it follows that on converting the sum over $\mathbf{k}$ to an integral, the integrand is a function of the magnitude of $\mathbf{k}$ of the form

$$\frac{(\mathbf{k}\cdot\mathbf{x}(\bar{l}))(\mathbf{k}\cdot\mathbf{x}(\bar{l}))}{k^4}[\mathbf{I}-\mathbf{m}(k_xk_y;0)]^{-1}{}_{\bar{l}\bar{l}}k^2dk$$
$$\sim[\mathbf{I}-\mathbf{m}(k_xk_y;0)]^{-1}{}_{\bar{l}\bar{l}'}dk,$$

as $|\mathbf{k}|\rightarrow 0$. If the sum on $\mathbf{k}$ is to diverge in the neighborhood of $\mathbf{k}=0$ it can only do so if the matrix elements $[\mathbf{I}-\mathbf{m}(k_xk_y;0)]^{-1}$ are at least as singular as $|\mathbf{k}|^{-1}$ in the limit as $\mathbf{k}\rightarrow 0$. An explicit calculation of $[\mathbf{I}-\mathbf{m}(k_xk_y;-y^2)]^{-1}{}_{\bar{l}\bar{l}'}$ in the limit of small k_x and k_y in part B of this section shows that this matrix element in fact is proportional to $(k_x^2+k_y^2)^{-1/2}$ in this limit. Therefore, all calculations in this section are carried out in the long wavelength, i.e., small $\mathbf{k}$ limit. Intuitively this is what we would expect to do because it is only the small $\mathbf{k}$ modes which survive the approximation of a crystal by an elastic continuum, and which contribute to the low temperature specific heat.

From the expression for $\Omega(y^2)$ given by Eq. (5.25) we see that in the sum over $\mathbf{k}$ one factor, $[\mathbf{I}-\mathbf{m}(k_xk_y;-y^2)]^{-1}{}_{\bar{l}\bar{l}'}$, is independent of the variable k_z, while the remaining factors are functions of k_z. Converting a sum over k_x to an integral with the aid of the equivalence

$$\sum_{k_x}\rightarrow\frac{La_0}{2\pi}\int_{-\pi/a_0}^{\pi/a_0}dk_x, \tag{6.1}$$

we can express $\Omega(y^2)$ conveniently as

$$\Omega(y^2)=a_0\frac{Sc_t^2}{16\pi^3}\sum_{\bar{l}\bar{l}'}\frac{1}{\bar{l}\bar{l}'}\int_{-\pi/a_0}^{\pi/a_0}dk_x\int_{-\pi/a_0}^{\pi/a_0}dk_yJ_{\bar{l}\bar{l}'}(k_xk_y;y^2)\times[\mathbf{I}-\mathbf{m}(k_xk_y;-y^2)]^{-1}{}_{\bar{l}\bar{l}'}, \tag{6.2}$$

where

$$J_{\bar{l}\bar{l}'}(k_xk_y;y^2)=\frac{4}{a_0^4}\sum_j\int_{-\pi/a_0}^{\pi/a_0}dk_z\frac{(\mathbf{x}(\bar{l})\cdot\mathbf{e}(\mathbf{k}j))(\mathbf{x}(\bar{l}')\cdot\mathbf{e}(\mathbf{k}j))}{[y^2+\omega_j^2(\mathbf{k})]^2}\times\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l})\,\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{x}(\bar{l}'). \tag{6.3}$$

In writing Eq. (6.2) we have made use of the fact that because $\varphi''(a_0)=\varphi''(2^{1/2}a_0)$, the factor $[\varphi''(r^{\bar{l}})\varphi''(r^{\bar{l}'})]^{1/2}$ has the same value, viz., $\varphi''(a_0)=a_0c_{44}$, for each allowed value of $\bar{l}$ and $\bar{l}'$, and can therefore be removed outside the sums on $\bar{l}$ and $\bar{l}'$. We have also introduced into Eq. (6.2) the area S of the two adjacent free surfaces introduced into the cyclic crystal by our cutting of all atomic bonds crossing the plane $z=\frac{1}{2}a_0$. This surface area is clearly given by

$$S=2L^2a_0^2. \tag{6.4}$$

Finally, we introduce the dimensionless vector $\mathbf{l}$ with integer components through the relation

$$\mathbf{x}(\bar{l})=a_0\mathbf{l}. \tag{6.5}$$

(The bar is omitted from $\mathbf{l}$ for simplicity in typesetting.)

In this section we evaluate the elements of the matrices $\mathbf{J}(k_xk_y;y^2)$ and $[\mathbf{I}-\mathbf{m}(k_xk_y;-y^2)]^{-1}$ in turn. Because we need to know only the small $|y|$ limiting behavior of $\Omega(y^2)$, we can evaluate them in the long-wavelength limit, and this makes our task much simpler than it would be otherwise.

A. The Evaluation of $J_{\bar{l}\bar{l}'}(k_xk_y;y^2)$

We obtain the long-wavelength limit for $J_{\bar{l}\bar{l}'}(k_xk_y;y^2)$ by retaining only the terms of lowest order in the lattice parameter a_0 in the expression (6.3). This procedure yields the result that in the long-wavelength limit

$$J_{\bar{l}\bar{l}'}(k_xk_y;y^2)=\sum_j\int_{-\pi/a_0}^{\pi/a_0}dk_z\frac{(\mathbf{l}\cdot\mathbf{e}(\mathbf{k}j))(\mathbf{l}'\cdot\mathbf{e}(\mathbf{k}j))}{[y^2+c_j^2k^2]^2}\times(\mathbf{k}\cdot\mathbf{l})(\mathbf{k}\cdot\mathbf{l}'). \tag{6.6}$$

We now carry out the sum over j using the degeneracy of the modes labeled by $j=2, 3$ and the closure property of the eigenvectors. With the aid of Eq. (4.18) we find that

$$\sum_j\frac{(\mathbf{l}\cdot\mathbf{e}(\mathbf{k}j))(\mathbf{l}'\cdot\mathbf{e}(\mathbf{k}j))}{[y^2+c_j^2k^2]^2}=\frac{(\mathbf{k}\cdot\mathbf{l})(\mathbf{k}\cdot\mathbf{l}')}{k^2}\left[\frac{1}{[y^2+c_l^2k^2]^2}-\frac{1}{[y^2+c_t^2k^2]^2}\right]+\frac{(\mathbf{l}\cdot\mathbf{l}')}{[y^2+c_t^2k^2]^2}. \tag{6.7}$$

When this result is substituted into Eq. (6.6), and we note that only the terms in the integrand which are even in k_z give a nonvanishing contribution to the integral, we find that $J_{\bar{l}\bar{l}'}(k_xk_y;y^2)$ is given by

$$\begin{aligned}J_{\bar{l}\bar{l}'}(k_xk_y;y^2)=&(\mathbf{r}\cdot\mathbf{l})^2(\mathbf{r}\cdot\mathbf{l}')^2[T_l-T_t]\\&+[(\mathbf{r}\cdot\mathbf{l})^2+4(\mathbf{r}\cdot\mathbf{l})(\mathbf{r}\cdot\mathbf{l}')+(\mathbf{r}\cdot\mathbf{l}')^2]\\&\times[U_l-U_t]+[V_l-V_t]\\&+(\mathbf{l}\cdot\mathbf{l}')(\mathbf{r}\cdot\mathbf{l})(\mathbf{r}\cdot\mathbf{l}')R_t+(\mathbf{l}\cdot\mathbf{l}')S_t.\end{aligned} \tag{6.8}$$

To write this expression in a compact form and at the same time to make its dependence on $\mathbf{l}$ and $\mathbf{l}'$ explicit, we have introduced the following notation:

$$\mathbf{r}=(k_x,k_y,0),\quad d^2=y^2+c^2r^2, \tag{6.9}$$

$$R=\int_{-\infty}^{\infty}dk_z\frac{1}{[d^2+c^2k_z^2]^2}=\frac{\pi}{2}\frac{1}{d^3c}, \tag{6.10a}$$

$$S=\int_{-\infty}^{\infty}dk_z\frac{k_z^2}{[d^2+c^2k_z^2]^2}=\frac{\pi}{2}\frac{1}{dc^3}, \tag{6.10b}$$

$$T=\int_{-\infty}^{\infty}dk_z\frac{1}{r^2+k_z^2}\frac{1}{[d^2+c^2k_z^2]^2}=\frac{\pi}{2}\frac{1}{d^3r}\frac{2d+cr}{(d+cr)^2}, \tag{6.10c}$$

$$U=\int_{-\infty}^{\infty}dk_z\frac{k_z^2}{r^2+k_z^2}\frac{1}{[d^2+c^2k_z^2]^2}=\frac{\pi}{2}\frac{1}{dc}\frac{1}{(d+cr)^2}, \tag{6.10d}$$

$$V=\int_{-\infty}^{\infty}dk_z\frac{k_z^4}{r^2+k_z^2}\frac{1}{[d^2+c^2k_z^2]^2}=\frac{\pi}{2}\frac{1}{c^3}\frac{d+2cr}{(d+cr)^2}. \tag{6.10e}$$

The subscripts l or t on the integrals appearing on the right-hand side of Eq. (6.8) indicate that it is c_l or c_t, respectively, that appears as c in the defining equations, Eqs. (6.9) and (6.10). Because the integrals R, S, T, U, V, all converge when evaluated between infinite limits, we have passed to the limit $a_0 \to 0$ in obtaining the results expressed by Eqs. (6.10).

From the expression given by Eq. (6.8) it is found that there are several relations among the elements of the matrix $\mathbf{J}(k_xk_y;y^2)$. If the labeling of the rows and columns of this matrix is carried out according to the scheme given by Eq. (5.9), it is found to have the form

$$\mathbf{J}(k_xk_y;y^2)=\begin{bmatrix} \alpha & \delta & \epsilon & \delta & \epsilon \\ \delta & \beta & \zeta & \eta & \theta \\ \epsilon & \zeta & \gamma & \theta & \kappa \\ \delta & \eta & \theta & \beta & \zeta \\ \epsilon & \theta & \kappa & \zeta & \gamma \end{bmatrix}. \tag{6.11}$$

B. The Evaluation of $[I-m(k_xk_y;\,-y^2)]^{-1}{}_{\bar{l}\bar{l}'}$

In the long-wavelength limit the matrix element $m_{\bar{l}\bar{l}'}(k_xk_y;\,-y^2)$ is found from Eq. (5.18) to be given by

$$m_{\bar{l}\bar{l}'}(k_xk_y;\,-y^2) =\frac{a_0}{2\pi}\frac{c_t^2}{\bar{l}\bar{l}'}\sum_j\int_{-\pi/a_0}^{\pi/a_0}dk_z\frac{(\mathbf{l}\cdot\mathbf{e}(\mathbf{k}j))(\mathbf{l}'\cdot\mathbf{e}(\mathbf{k}j))}{y^2+c_j^2k^2} \times(\mathbf{k}\cdot\mathbf{l})(\mathbf{k}\cdot\mathbf{l}'). \tag{6.12}$$

The evaluation of the sum over j is carried out in exactly the same way as the sum in Eq. (6.7) was carried out. The result in the present context differs from that given by Eq. (6.7) only in that the first power of $[y^2+c_{l,t}{}^2k^2]$ now appears in the several denominators. We therefore find that

$$m_{\bar{l}\bar{l}'}(k_xk_y;\,-y^2) =\frac{a_0}{2\pi}\frac{c_t^2}{\bar{l}\bar{l}'}\int_{-\pi/a_0}^{\pi/a_0}dk_z\left\{\frac{(\mathbf{k}\cdot\mathbf{l})^2(\mathbf{k}\cdot\mathbf{l}')^2}{k^2}\left[\frac{1}{y^2+c_l^2k^2}-\frac{1}{y^2+c_t^2k^2}\right] +\frac{(\mathbf{l}\cdot\mathbf{l}')(\mathbf{k}\cdot\mathbf{l})(\mathbf{k}\cdot\mathbf{l}')}{y^2+c_t^2k^2}\right\}. \tag{6.13}$$

However, unlike the situation which obtains in the evaluation of the integral $J_{\bar{l}\bar{l}'}(k_xk_y;y^2)$, the integrals appearing in Eq. (6.13) do not all converge when the limits of integration are extended to $\pm\infty$. We must, therefore, keep a_0 finite in those integrals which diverge when the limits are extended to infinity; in the remaining integrals we pass to the limit $a_0\to 0$. In this way we obtain the result that

$$\begin{aligned} m_{\bar{l}\bar{l}'}(k_xk_y;\,-y^2) &=\frac{c_t^2}{\bar{l}\bar{l}'}\left[\frac{1}{c_l^2}+\frac{(\mathbf{l}\cdot\mathbf{l}')-1}{c_t^2}\right]+\frac{a_0}{2\pi}\frac{c_t^2}{\bar{l}\bar{l}'}\{(\mathbf{r}\cdot\mathbf{l})^2(\mathbf{r}\cdot\mathbf{l}')^2(T_l'-T_t') \\ &+[(\mathbf{r}\cdot\mathbf{l})^2+4(\mathbf{r}\cdot\mathbf{l})(\mathbf{r}\cdot\mathbf{l}')+(\mathbf{r}\cdot\mathbf{l}')^2](U_l'-U_t') \\ &-(V_l'-V_t')+(\mathbf{l}\cdot\mathbf{l}')(\mathbf{r}\cdot\mathbf{l})(\mathbf{r}\cdot\mathbf{l}')R_t' \\ &-(\mathbf{l}\cdot\mathbf{l}')S_t'\}, \end{aligned} \tag{6.14}$$

where

$$R'=\int_{-\infty}^{\infty}dk_z\frac{1}{d^2+c^2k_z^2}=\frac{\pi}{dc}, \tag{6.15a}$$

$$S'=(d^2/c^2)R'=\pi d/c^3, \tag{6.15b}$$

$$T'=\int_{-\infty}^{\infty}dk_z\frac{1}{r^2+k_z^2}\frac{1}{d^2+c^2k_z^2}=\frac{\pi}{rd}\frac{1}{d+cr}, \tag{6.15c}$$

$$U'=\int_{-\infty}^{\infty}dk_z\frac{k_z^2}{r^2+k_z^2}\frac{1}{d^2+c^2k_z^2}=\frac{\pi}{c}\frac{1}{d+cr}, \tag{6.15d}$$

$$V'=\int_{-\infty}^{\infty}dk_z\frac{r^2d^2+k_z^2(d^2+c^2r^2)}{c^2(r^2+k_z^2)(d^2+c^2k_z^2)}=\frac{\pi}{c^3}\frac{d^2+c^2r^2+crd}{d+cr}. \tag{6.15e}$$

The notation not identified in these expressions is that given in Eq. (6.9).

It may be thought that because we are interested in retaining only terms of lowest order in a_0 in the long-wavelength limit, we should neglect the contribution to $m_{\bar{l}\bar{l}'}(k_xk_y;\,-y^2)$ from the terms in curly brackets in Eq. (6.14). However, we will see below that this is not permissible.

From Eq. (6.14) we find that the elements of the matrix $\mathbf{m}(k_xk_y;\,-y^2)$ are related among themselves in such a way that the matrix $\mathbf{I}-\mathbf{m}(k_xk_y;\,-y^2)$ has the form

$$\mathbf{I}-\mathbf{m}(k_xk_y;\,-y^2) =\begin{bmatrix} 1-A & -D & -E & -D & -E \\ -D & 1-B & -F & -G & -H \\ -E & -F & 1-C & -H & -J \\ -D & -G & -H & 1-B & -F \\ -E & -H & -J & -F & 1-C \end{bmatrix}. \tag{6.16}$$

We exploit the structure of this matrix to invert it in the following way. The matrix $\mathbf{I}-\mathbf{m}$ is block diagonalized into a 3×3 and a 2×2 matrix by a similarity transformation with the matrix $\mathbf{S}$, which is given explicitly by

$$\mathbf{S}=\begin{bmatrix} (1/\sqrt{2}) & 0 & 0 & 0 & 0 \\ 0 & \tfrac{1}{2} & 0 & -1 & 0 \\ 0 & 0 & \tfrac{1}{2} & 0 & -1 \\ 0 & \tfrac{1}{2} & 0 & 1 & 0 \\ 0 & 0 & \tfrac{1}{2} & 0 & 1 \end{bmatrix} \quad \mathbf{S}^{-1}=\begin{bmatrix} \sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ 0 & -\tfrac{1}{2} & 0 & \tfrac{1}{2} & 0 \\ 0 & 0 & -\tfrac{1}{2} & 0 & \tfrac{1}{2} \end{bmatrix}. \tag{6.17}$$

Thus we find that

$$\mathbf{S}^{-1}(\mathbf{I}-\mathbf{m})\mathbf{S}=\left[\begin{array}{c|c} \mathbf{a} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{b} \end{array}\right], \tag{6.18}$$

where

$$\mathbf{a}=\begin{bmatrix} 1-A & -2^{1/2}D & -2^{1/2}E \\ -2^{1/2}D & 1-B-G & -(F+H) \\ -2^{1/2}E & -(F+H) & 1-C-J \end{bmatrix}, \tag{6.19}$$

$$\mathbf{b}=\begin{bmatrix} 1-B+G & -(F-H) \\ -(F-H) & 1-C+J \end{bmatrix}. \tag{6.20}$$

It follows, therefore, that

$$(\mathbf{I}-\mathbf{m})^{-1}=\mathbf{S}\left[\begin{array}{c|c}\mathbf{a}^{-1} & 0\\ \hline 0 & \mathbf{b}^{-1}\end{array}\right]\mathbf{S}^{-1}. \tag{6.21}$$

At this point it is worth while to write out explicitly the expressions for the elements of the matrices **a** and **b**:

$$a_{11}=\tfrac{2}{3}+(a_0c_t^2/2\pi)[(V_l'-V_t')+S_t'], \tag{6.22a}$$

$$a_{12}=-\tfrac{1}{3}-(a_0c_t^2/2\pi)[k_x^2(U_l'-U_t') -(V_l'-V_t')-S_t'], \tag{6.22b}$$

$$a_{13}=-\tfrac{1}{3}-(a_0c_t^2/2\pi)[k_y^2(U_l'-U_t') -(V_l'-V_t')-S_t'], \tag{6.22c}$$

$$a_{22}=\tfrac{2}{3}-(a_0c_t^2/2\pi)[k_x^4(T_l'-T_t')+2k_x^2(U_l'-U_t') -(V_l'-V_t')+k_x^2R_t'-S_t'], \tag{6.22d}$$

$$a_{23}=-\tfrac{1}{3}-(a_0c_t^2/2\pi)[k_x^2k_y^2(T_l'-T_t')+r^2(U_l'-U_t') -(V_l'-V_t')-S_t'], \tag{6.22e}$$

$$a_{33}=\tfrac{2}{3}-(a_0c_t^2/2\pi)[k_y^4(T_l'-T_t')+2k_y^2(U_l'-U_t') -(V_l'-V_t')+k_y^2R_t'-S_t']; \tag{6.22f}$$

$$b_{11}=-(a_0c_t^2/2\pi)\{k_x^2[4(U_l'-U_t')+R_t']-S_t'\} =-(a_0c_t^2/2\pi)(\alpha k_x^2-\beta), \tag{6.23a}$$

$$b_{12}=-(a_0c_t^2/2\pi)k_xk_y[4(U_l'-U_t')+R_t'] =-(a_0c_t^2/2\pi)\alpha k_xk_y, \tag{6.23b}$$

$$b_{22}=-(a_0c_t^2/2\pi)\{k_y^2[4(U_l'-U_t')+R_t']-S_t'\} =-(a_0c_t^2/2\pi)(\alpha k_y^2-\beta). \tag{6.23c}$$

In writing these results we have used the relation $c_l^2=3c_t^2$ which is a consequence of our assumption of elastic isotropy.

We note first of all that the elements of the matrix **b** are all of $O(a_0)$. This means that the elements of the inverse matrix $\mathbf{b}^{-1}$ are of $O(a_0^{-1})$ in the limit as $a_0\to 0$ In fact, the inverse matrix $\mathbf{b}^{-1}$ is readily found to be

$$\mathbf{b}^{-1}=\frac{2\pi}{a_0c_t^2}\frac{1}{\beta(\beta-\alpha r^2)}\begin{bmatrix}-(\alpha k_y^2-\beta) & \alpha k_xk_y\\ \alpha k_xk_y & -(\alpha k_x^2-\beta)\end{bmatrix} \equiv\begin{bmatrix}b_{11}^{-1} & b_{12}^{-1}\\ b_{21}^{-1} & b_{22}^{-1}\end{bmatrix}. \tag{6.24}$$

Although the elements of the matrix **a** are of $O(1)$ in the limit as $a_0\to 0$, this does not imply that the elements of the inverse matrix $\mathbf{a}^{-1}$ are also of $O(1)$ in this limit. For if we set $a_0=0$ in Eq. (6.22), we see that the matrix **a** takes the form

$$\lim_{a_0\to 0}\mathbf{a}=\begin{pmatrix}\tfrac{2}{3} & -\tfrac{1}{3} & -\tfrac{1}{3}\\ -\tfrac{1}{3} & \tfrac{2}{3} & -\tfrac{1}{3}\\ -\tfrac{1}{3} & -\tfrac{1}{3} & \tfrac{2}{3}\end{pmatrix}. \tag{6.25}$$

But this matrix is singular.[19] This means that the determinant of **a** must be at least of $O(a_0)$, so that the elements of $\mathbf{a}^{-1}$ are at least of $O(a_0^{-1})$ in the limit as $a_0\to 0$. If we write the elements of the matrix **a** in the form

$$a_{ij}=a_{ij}^{(0)}+a_{ij}^{(1)}, \tag{6.26}$$

where the superscript denotes the power of a_0 to which the coefficient is proportional, the inverse matrix $\mathbf{a}^{-1}$ is readily found to have the very simple form

$$\mathbf{a}^{-1}=\{\sum_{ij}a_{ij}^{(1)}\}^{-1}\begin{pmatrix}1 & 1 & 1\\ 1 & 1 & 1\\ 1 & 1 & 1\end{pmatrix} \tag{6.27}$$

to lowest order in a_0. More explicitly, we have that

$$\mathbf{a}^{-1}=(2\pi/a_0c_t^2)\{-r^4(T_l'-T_t')-r^2[6(U_l'-U_t')+R_t']+9[(V_l'-V_t')+S_t']\}^{-1}\begin{pmatrix}1 & 1 & 1\\ 1 & 1 & 1\\ 1 & 1 & 1\end{pmatrix}\equiv\begin{pmatrix}a^{-1} & a^{-1} & a^{-1}\\ a^{-1} & a^{-1} & a^{-1}\\ a^{-1} & a^{-1} & a^{-1}\end{pmatrix}. \tag{6.28}$$

We see that each element of $\mathbf{a}^{-1}$ is of $O(a_0^{-1})$ in the limit as $a_0\to 0$.

Combining Eqs. (6.21), (6.24), and (6.28) we obtain finally the result that the matrix $(\mathbf{I}-\mathbf{m})^{-1}$ is given by

$$(\mathbf{I}-\mathbf{m})^{-1}=\begin{pmatrix}a^{-1} & \frac{1}{\sqrt{2}}a^{-1} & \frac{1}{\sqrt{2}}a^{-1} & \frac{1}{\sqrt{2}}a^{-1} & \frac{1}{\sqrt{2}}a^{-1}\\ \frac{1}{\sqrt{2}}a^{-1} & \tfrac{1}{2}(a^{-1}+b_{11}^{-1}) & \tfrac{1}{2}(a^{-1}+b_{12}^{-1}) & \tfrac{1}{2}(a^{-1}-b_{11}^{-1}) & \tfrac{1}{2}(a^{-1}-b_{12}^{-1})\\ \frac{1}{\sqrt{2}}a^{-1} & \tfrac{1}{2}(a^{-1}+b_{21}^{-1}) & \tfrac{1}{2}(a^{-1}+b_{22}^{-1}) & \tfrac{1}{2}(a^{-1}-b_{21}^{-1}) & \tfrac{1}{2}(a^{-1}-b_{22}^{-1})\\ \frac{1}{\sqrt{2}}a^{-1} & \tfrac{1}{2}(a^{-1}-b_{11}^{-1}) & \tfrac{1}{2}(a^{-1}-b_{12}^{-1}) & \tfrac{1}{2}(a^{-1}+b_{11}^{-1}) & \tfrac{1}{2}(a^{-1}+b_{12}^{-1})\\ \frac{1}{\sqrt{2}}a^{-1} & \tfrac{1}{2}(a^{-1}-b_{21}^{-1}) & \tfrac{1}{2}(a^{-1}-b_{22}^{-1}) & \tfrac{1}{2}(a^{-1}+b_{21}^{-1}) & \tfrac{1}{2}(a^{-1}+b_{22}^{-1})\end{pmatrix}. \tag{6.29}$$

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[19] It was in the calculation of the matrix element a_{11} that the error in the paper of Maradudin and Ashkin (Ref. 8) occurred. Through a transcription error the $a_0=0$ limit of a_{11} was found to be 5/3, which in turn implied that the inverse $\mathbf{a}^{-1}$ existed and was of O(1) in the limit as $a_0\to 0$. Consequently, the contribution to $\mathbf{a}^{-1}$ to $\Omega(y^2)$ was erroneously omitted as being of higher order in a_0 than the contribution from $\mathbf{b}^{-1}$.

C. The Asymptotic Behavior of $\Omega(y^2)$

When the result given by Eq. (6.29) is substituted into Eq. (6.2) for $\Omega(y^2)$, and the sums over $\bar{l}$ and $\bar{l}'$ are carried out, the result can be expressed in the form

$$\Omega(y^2)=\Omega_1(y^2)+\Omega_2(y^2), \tag{6.30}$$

where

$$\Omega_1(y^2)=a_0\frac{Sc_t^2}{16\pi^3}\int_{-\pi/a_0}^{\pi/a_0}dk_x\int_{-\pi/a_0}^{\pi/a_0}dk_y a^{-1}[J_{11}+2J_{13}+2J_{14}+\tfrac{1}{2}J_{22}+J_{23}+\tfrac{1}{2}J_{24}+J_{25}+\tfrac{1}{2}J_{33}+\tfrac{1}{2}J_{35}] \tag{6.31a}$$

$$\Omega_2(y^2)=a_0\frac{Sc_t^2}{32\pi^3}\int_{-\pi/a_0}^{\pi/a_0}dk_x\int_{-\pi/a_0}^{\pi/a_0}dk_y[b_{11}^{-1}(J_{22}-J_{24})+2b_{12}^{-1}(J_{23}-J_{25})+b_{22}^{-1}(J_{33}-J_{35})]. \tag{6.31b}$$

We have used the relations among the matrix elements $J_{\bar{l}\bar{l}'}(k_xk_y;y^2)$ expressed by Eq. (6.11) in writing these expressions.

We have separated $\Omega(y^2)$ into the two parts given by $\Omega_1(y^2)$ and $\Omega_2(y^2)$ because the former contains the factor a^{-1} in the integrand which was incorrectly taken to be identically zero in the work of Maradudin and Ashkin,[8] who computed only the contribution from $\Omega_2(y^2)$. The contribution to the specific heat from $\Omega_1(y^2)$ may therefore be regarded as providing a correction to the result of Maradudin and Ashkin, which, as we will see shortly, brings it into agreement with that of Dupuis *et al.*[6] and of Stratton.[7]

Let us evaluate the small $|y|$ limiting form of $\Omega_2(y^2)$ first. From Eq. (6.8) we find that

$$J_{22}-J_{24}=2k_x^2[4(U_l-U_t)+R_t]+2S_t, \tag{6.32a}$$

$$J_{23}-J_{25}=2k_xk_y[4(U_l-U_t)+R_t], \tag{6.32b}$$

$$J_{33}-J_{35}=2k_y^2[4(U_l-U_t)+R_t]+2S_t. \tag{6.32c}$$

Combining these expressions with the expressions for the elements of b^{-1} given by Eq. (6.24), it is found to be convenient to write $\Omega_2(y^2)$ itself as the sum of two contributions,

$$\Omega_2(y^2)=\Omega_{21}(y^2)+\Omega_{22}(y^2), \tag{6.33a}$$

where

$$\Omega_{21}(y^2)=\frac{S}{8\pi^2}\int_{-\pi/a_0}^{\pi/a_0}dk_x\int_{-\pi/a_0}^{\pi/a_0}dk_y\frac{r^2}{\beta-\alpha r^2}[4(U_l-U_t)+R_t] \tag{6.33b}$$

$$\Omega_{22}(y^2)=\frac{S}{8\pi^2}\int_{-\pi/a_0}^{\pi/a_0}dk_x\int_{-\pi/a_0}^{\pi/a_0}dk_yS_t\left[\frac{1}{\beta}+\frac{1}{\beta-\alpha r^2}\right]. \tag{6.33c}$$

Because the integrands of these expressions depend on k_x and k_y only in the combination $r=(k_x^2+k_y^2)^{1/2}$, it is convenient to transform to polar coordinates for the evaluation of these integrals. This transformation is made according to

$$\int_{-\pi/a_0}^{\pi/a_0}dk_x\int_{-\pi/a_0}^{\pi/a_0}dk_y\approx\int_0^{\pi/a_0}rdr\int_0^{2\pi}d\theta=2\pi\int_0^{\pi/a_0}rdr. \tag{6.34}$$

The replacement of the square bounded by the points $(\pm\pi/a_0, \pm\pi/a_0)$ by a circle of radius π/a_0 in the k_xk_y plane introduces a negligible error into our final results. The second equality in Eq. (6.34) follows from the independence of the integrands in Eq. (6.33) on the variable θ.

If we now substitute into Eqs. (6.33) the explicit expressions for the integrals U_l, U_t, R_t, S_t, α, and β from Eqs. (6.10) and (6.23), make the change of variable $r=(|y|/c_t)u$, and recall that $c_l^2=3c_t^2$ for our crystal model, we obtain the following expressions for $\Omega_{21}(y^2)$ and $\Omega_{22}(y^2)$:

$$\Omega_{21}(y^2)=\frac{S}{8\pi c_t^2}\int_0^{(\pi c_t/a_0|y|)} du\,u^3\left\{4\left[\frac{1}{3^{1/2}(1+3u^2)^{1/2}}\frac{1}{((1+3u^2)^{1/2}+3^{1/2}u)^2}-\frac{1}{(1+u^2)^{1/2}}\frac{1}{((1+u^2)^{1/2}+u)^2}\right]+\frac{1}{(1+u^2)^{3/2}}\right\}$$
$$\times\left\{(1+u^2)^{1/2}-4u^2\left[\frac{1}{3^{1/2}}\frac{1}{(1+3u^2)^{1/2}+3^{1/2}u}-\frac{1}{(1+u^2)^{1/2}+u}\right]-\frac{u^2}{(1+u^2)^{1/2}}\right\}^{-1} \tag{6.35a}$$

$$\Omega_{22}(y^2)=\frac{S}{8\pi c_t^2}\int_0^{(\pi c_t/a_0|y|)} du\frac{u}{(1+u^2)^{1/2}}\left\{\frac{1}{(1+u^2)^{1/2}}\right.$$
$$\left.+\left[(1+u^2)^{1/2}-4u^2\left(\frac{1}{3^{1/2}}\frac{1}{(1+3u^2)^{1/2}+3^{1/2}u}-\frac{1}{(1+u^2)^{1/2}+u}\right)-\frac{u^2}{(1+u^2)^{1/2}}\right]^{-1}\right\}. \tag{6.35b}$$

Fortunately, the completion of our calculation does not depend on our being able to evaluate these integrals exactly.

The parameter y appears only in the upper limit of each integral, not in the integrand itself. It is clear that the forms that $\Omega_{21}(y^2)$ and $\Omega_{22}(y^2)$ take in the limit as $|y|\to 0$ are determined only by the large u behaviors of the corresponding integrands. [This is easily demonstrated by splitting the range of integration $(0,\pi c_t/a_0|y|)$ into two parts $(0,T)$ and $(T,\pi c_t/a_0|y|)$, and expanding the integrands in powers of u and of u^{-1} in the two intervals, respectively. The cutoff T is arbitrary, but as a practical matter would be chosen in such a way that the series in T^{-1} which come from the upper limit of the interval $(0,T)$ and from the lower limit of the interval $(T,\pi c_t/a_0|y|)$ converge, or are at least asymptotic series.] Expanding the integrand of $\Omega_{21}(y^2)$ in powers of u^{-1} and retaining only the leading term, we find that in the limit as $|y|\to 0$

$$\Omega_{21}(y^2)\sim\frac{S}{8\pi c_t^2}\int^{(\pi c_t/a_0|y|)}\frac{du}{12u}=\frac{S}{8\pi c_t^2}\frac{1}{12}\ln\left(\frac{\pi c_t}{a_0|y|}\right)+\text{constant}=-\frac{S}{8\pi c_t^2}\frac{1}{12}\ln|y|+\text{constant}'. \tag{6.36a}$$

Similarly, we find that as $|y|\to 0$

$$\Omega_{22}(y^2)\sim\frac{S}{8\pi c_t^2}\int^{(\pi c_t/a_0|y|)}\frac{7du}{4u}=\frac{S}{8\pi c_t^2}\frac{7}{4}\ln\left(\frac{\pi c_t}{a_0|y|}\right)+\text{constant}=-\frac{S}{8\pi c_t^2}\frac{7}{4}\ln|y|+\text{constant}'. \tag{6.36b}$$

Combining the results given by Eqs. (6.36a) and (6.36b), we find that

$$\Omega_2(y^2)=-\frac{S}{8\pi c_t^2}\frac{11}{6}\ln|y|+o(\ln|y|), \tag{6.37}$$

as $|y|\to 0$. This is the result obtained by Maradudin and Ashkin.[8]

Turning now to the contribution to $\Omega(y^2)$ arising from $\Omega_1(y^2)$, when the explicit expressions for the elements $J_{ll'}(k_xk\mathrm{r};y^2)$ and a^{-1} are substituted into it we find that it is given by

$$\Omega_1(y^2)=\frac{S}{8\pi^2}\int_{-\pi/a_0}^{\pi/a_0}dk_x\int_{-\pi/a_0}^{\pi/a_0}dk_y\frac{r^4(T_l-T_t)+r^2[6(U_l-U_t)+R_t]+9(V_l-V_t+S_t)}{-r^4(T_l'-T_t')-r^2[6(U_l'-U_t')+R_t']+9(V'_l-V'_t+S'_t)}. \tag{6.38}$$

When we transform to polar coordinates, substitute into this integral the explicit expressions for the integrals T_l, T_t, $\cdots$, and make the change of variable $r=(|y|/c_t)u$, we obtain

$$\Omega_1(y^2)=\frac{S}{4\pi}\frac{y^2}{c_t^2}\int_0^{(\pi c_t/a_0|y|)}du\,u\frac{N(u)}{D(u)}, \tag{6.39a}$$

where

$$N(u)=\frac{\pi}{2c_t^3y}\left\{u^3\left[\frac{1}{(1+3u^2)^{3/2}}\frac{2(1+3u^2)^{1/2}+3^{1/2}u}{((1+3u^2)^{1/2}+3^{1/2}u)^2}-\frac{1}{(1+u^2)^{3/2}}\frac{2(1+u^2)^{1/2}+u}{((1+u^2)^{1/2}+u)^2}\right]\right.$$
$$+u^2\left[\frac{1}{(1+u^2)^{3/2}}+6\left[\frac{1}{3^{1/2}(1+3u^2)^{1/2}}\frac{1}{((1+3u^2)^{1/2}+3^{1/2}u)^2}-\frac{1}{(1+u^2)^{1/2}}\frac{1}{((1+u^2)^{1/2}+u)^2}\right]\right]$$
$$\left.+9\left[\frac{1}{3^{3/2}}\frac{(1+3u^2)^{1/2}+2(3^{1/2})u}{((1+3u^2)^{1/2}+3^{1/2}u)^2}-\frac{(1+u^2)^{1/2}+2u}{((1+u^2)^{1/2}+u)^2}+\frac{1}{(1+u^2)^{1/2}}\right]\right\}, \tag{6.39b}$$

$$D(u)=\frac{\pi y}{c_t^3}\left\{-u^3\left[\frac{1}{(1+3u^2)^{1/2}}\frac{1}{(1+3u^2)^{1/2}+3^{1/2}u}-\frac{1}{(1+u^2)^{1/2}}\frac{1}{(1+u^2)^{1/2}+u}\right]\right.$$

$$-u^2\left[\frac{1}{(1+u^2)^{1/2}}+6\left(\frac{1}{3^{1/2}}\frac{1}{(1+3u^2)^{1/2}+3^{1/2}u}-\frac{1}{(1+u^2)^{1/2}+u}\right)\right]$$

$$\left.+9\left[(1+u^2)^{1/2}+\frac{1}{3^{3/2}}\frac{1+6u^2+3^{1/2}u(1+3u^2)^{1/2}}{(1+3u^2)^{1/2}+3^{1/2}u}-\frac{1+2u^2+u(1+u^2)^{1/2}}{(1+u^2)^{1/2}+u}\right]\right\}. \qquad (6.39c)$$

By the same kind of reasoning as before, it follows that the small $|y|$ behavior of $\Omega_1(y^2)$ is determined by the large u behavior of the quotient $N(u)/D(u)$. Expanding this quotient in powers of u^{-1} we find that in the limit as $|y|\rightarrow 0$

$$\Omega_1(y^2)\sim\frac{S}{8\pi c_t^2}\int^{(\pi c_t/a_0|y|)}\frac{3du}{2u}=\frac{S}{8\pi c_t^2}\tfrac{3}{2}\ln\left(\frac{\pi c_t}{a_0|y|}\right)+\text{constant}=-\frac{S}{8\pi c_t^2}\tfrac{3}{2}\ln|y|+\text{constant}'. \qquad (6.40)$$

When we add together the results given by Eqs. (6.37) and (6.40), we finally obtain the result that in the limit as $|y|\rightarrow 0$

$$\Omega(y^2)=-\frac{S}{8\pi c_t^2}\frac{10}{3}\ln|y|+o(\ln|y|). \qquad (6.41)$$

7. THE SURFACE CONTRIBUTION TO THE SPECIFIC HEAT

Comparing the result given by Eq. (6.41) with Eq. (2.12), we find that the coefficient A appearing in the latter equation is

$$A=(S/8\pi c_t^2)(10/3). \qquad (7.1)$$

It only remains to substitute this value for A into Eq. (2.14) to obtain the result that the surface contribution to the specific heat of our crystal model is given in the limit of low temperatures by

$$\Delta C_v(T)=\frac{5}{2\pi}\frac{k_B^3}{\hbar^2}\zeta(3)\frac{1}{c_t^2}ST^2+o(T^2)$$

$$=3\pi\frac{k_B^3}{h^2}\zeta(3)\frac{10}{3c_t^2}ST^2+o(T^2).$$

The latter expression is just that obtained by Dupuis *et al.*[6] and by Stratton,[7] [see Eq. (1.2)] in the special case that $c_l^2=3c_t^2$.

We have therefore succeeded in showing that the method suggested by Maradudin and Ashkin[8] for evaluating the surface contribution to the specific heat of a crystal is a practical method. It is of course clear that the numerical computations which will accompany the application of this method to anisotropic crystals will have to be carried out on a high-speed computer. This, however, will also be the case for any other method of computing the surface contribution to the low-temperature specific heat of such crystals.

Finally, we remark that the present method may find its greatest utility when it is applied to an anisotropic crystal which from the start has been assimilated into an elastic continuum. In this case, the difference equations of motion, Eq. (3.3), and the matrix equation for the matrix $\mathbf{T}(\omega^2)$, Eq. (3.8a), become differential and integral equations, respectively. All of the parameters, such as the atomic masses, the range of interatomic forces, atomic force constants, and lattice parameters, which characterize the crystal on a microscopic level, are now absorbed into the parameters, such as mass density and elastic constants, which characterize the crystal on a macroscopic level. The equations with which one has to work are considerably simplified as a result. This approach to the calculation of surface specific heats is now being pursued.

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APPENDIX

By counting the number of normal modes in a given frequency interval more carefully than the calculation is ordinarily done we prove in this Appendix that the low-temperature specific heat of a crystal for which the atomic displacements satisfy the cyclic boundary condition contains no contribution which is proportional to the surface area of the crystal. This negative result establishes that the change in the specific heat of such a crystal brought about by the introduction of a pair of free surfaces in the manner described in the text in fact represents the entire surface contribution to the specific heat. The proof will be carried out for the crystal model employed in the text, but it is felt that the result is more general than the model. A proof of this conjecture on the basis of arguments of the kind employed here, however, would be difficult.

Our demonstration is greatly simplified if we use the result, which can be obtained by integrating Eq. (2.2) by parts, that the low-temperature specific heat of a crystal is given by

$$C_v = k_B\beta\hbar \sum_{n=1}^{\infty} \int_0^{\infty} N(\omega) e^{-n\beta\hbar\omega} [(n\beta\hbar\omega)^2 - 2(n\beta\hbar\omega)] d\omega . \tag{A.1}$$

In this expression $N(\omega)$ is the integrated frequency spectrum of the crystal, and is defined so that $N(\omega)$ is the number of normal modes with frequencies less than or equal to ω. Our extending the upper limit of integration to infinity is prompted by the fact that in the limit as $\beta \to \infty$, only the low-frequency part of the factor $N(\omega)[(n\beta\hbar\omega)^2 - 2(n\beta\hbar\omega)]$ contributes significantly to the integral.

We will establish that the low-frequency limit of the integrated spectrum of a crystal for which the atomic displacements satisfy the cyclic boundary condition has no part which is proportional to the surface area of the crystal. For this purpose we will use a result from the theory of numbers.

The temperature dependence of the specific heat of a crystal at low temperatures is determined by the low-frequency end of $N(\omega)$, which in turn is determined by the limiting forms the normal mode frequencies take as functions of $\mathbf{k}$ in the long-wavelength limit. If we recall the expressions for the frequencies of the normal modes of the unperturbed, cyclic, crystal in the long wavelength limit given by Eqs. (4.17) and (4.19), we can write the low-frequency limit of $N(\omega)$ in the form

$$N(\omega) = N_l(\omega) + 2N_t(\omega) , \tag{A.2a}$$

where

$$N_l(\omega) = \sum_{\substack{h_1h_2h_3 = -\infty \\ 0 \le (4\pi^2 c_l^2 / L^2 a_0^2)(h_1^2 + h_2^2 + h_3^2) \le \omega^2}}^{\infty} 1 \tag{A.2b}$$

$$N_t(\omega) = \sum_{\substack{h_1h_2h_3 = -\infty \\ 0 \le (4\pi^2 c_t^2 / L^2 a_0^2)(h_1^2 + h_2^2 + h_3^2) \le \omega^2}}^{\infty} 1 . \tag{A.2c}$$

The functions $N_l(\omega)$ and $N_t(\omega)$ can be given a simple geometrical interpretation. $N_{l,t}(\omega)$ is the number of points on a simple cubic lattice of lattice constant unity contained in or on a sphere of radius $(\omega L a_0 / 2\pi c_{l,t})$.

As a first approximation, the function $N_{l,t}(\omega)$ is given by the volume of the sphere,

$$N_{l,t}(\omega) = \tfrac{4}{3}\pi(\omega L a_0 / 2\pi c_{l,t}) . \tag{A.3}$$

The result given by Eq. (A.3) is proportional to the crystal volume, $V = (La_0)^3$, and yields the well known Debye T^3 law for the bulk contribution to the low-temperature specific heat of an isotropic solid. Our concern is with the leading correction to the expression given by Eq. (A.3), which is of lower order in L than $O(L^3)$.

The problem of determining the number of lattice points of an n-dimensional simple cubic lattice contained inside or on an n-dimensional sphere of radius r centered on one of the lattice points has been well studied in the context of the theory of numbers.[18] However, we were not able to find estimates of this function for three-dimensional spheres which are sufficiently precise for our purposes. Such an estimate can be made in the following manner.

Let us denote by $A_p(r^2)$ the number of lattice points of a p-dimensional simple cubic lattice which lie inside or on a p-dimensional sphere of radius r which is centered on one of the lattice points. Thus we have that

$$A_p(r^2) = \sum_{\substack{n_1, n_2, \cdots, n_p \\ 0 \le n_1^2 + n_2^2 + \cdots + n_p^2 \le r^2}} 1 . \tag{A.4}$$

As a function of a continuous variable r, $A_p(r)$ is discontinuous. It increases by some integer each time r achieves the value of the radius of a shell of lattice sites. Because $n_1, n_2, \cdots, n_p$ are all integers, $n_1^2 + n_2^2 + \cdots + n_p^2$ must also be an integer. Consequently, we are led to the conclusion that

$$A_p(r^2) = A_p([r^2]) , \tag{A.5}$$

where $[x]$ is the greatest integer contained in x (including x itself, if x is an integer). In other words, the number of lattice points inside or on a sphere of radius r is equal to the number of lattice points inside or on a sphere of radius $[r^2]^{1/2}$. To emphasize that $[r^2]$ is a non-negative integer we will set $[r^2] = n$, where n is now a non-negative integer.

The function $A_p(r^2)$ satisfies a useful recurrence relation

$$\begin{aligned} A_p(r^2) = A_p(n) &= \sum_{\substack{n_1, n_2, \cdots, n_p \\ 0 \le n_1^2 + n_2^2 + \cdots + n_p^2 \le n}} 1 \\ &= \sum_{-n^{1/2} \le m \le n^{1/2}} \; \sum_{0 \le n_1^2 + \cdots + n_{p-1}^2 \le n - m^2} 1 \\ &= \sum_{m=-[n^{1/2}]}^{[n^{1/2}]} A_{p-1}(n - m^2) \\ &= A_{p-1}(n) + 2 \sum_{m=1}^{[n^{1/2}]} A_{p-1}(n - m^2) . \end{aligned} \tag{A.6}$$

In particular, we have that

$$A_3(n) = A_2(n) + 2 \sum_{m=1}^{[n^{1/2}]} A_2(n - m^2) . \tag{A.7}$$

It was shown in 1906 by Sierpinski[20] that a constant B exists such that

$$-Bn^{1/3} < A_2(n) - \pi n < Bn^{1/3} \tag{A.8}$$

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[20] W. Sierpinski, Prace Mat.-Fiz. **17**, 77 (1906). This result is mentioned in the following, more accessible, reference: W. Sierpinski, *Elementary Theory of Numbers* (Pandstwowe Wydawnictwo Naukowe, Warsaw, 1964), Monografie Matematyczne No. 42, p. 346.

for any positive integer n. The exponent $\frac{1}{3}$ appearing in these inequalities is not the best known. It is known[21] to be greater than or equal to $\frac{1}{4}$, and less than or equal to $37/112<\frac{1}{3}$. However, the estimate given above is adequate for our purposes.

Combining Eqs. (A.7) and (A.8) we find that

$$\pi n-Bn^{1/3}+2\sum_{m=1}^{[n^{1/2}]}\{\pi(n-m^2)-B(n-m^2)^{1/3}\}<A_3(n)$$

$$<\pi n+Bn^{1/3}+2\sum_{m=1}^{[n^{1/2}]}\{\pi(n-m^2)+B(n-m^2)^{1/3}\}. \tag{A.9}$$

With the aid of the results

$$\pi n+2\pi\sum_{m=1}^{[n^{1/2}]}(n-m^2)=2\pi\{n[n^{1/2}]-\tfrac{1}{3}[n^{1/2}]^3\}+\pi\{n-[n^{1/2}]^2\}-\frac{\pi}{3}[n^{1/2}]$$

$$Bn^{1/3}+2B\sum_{m=1}^{[n^{1/2}]}(n-m^2)^{1/3}<2Bn^{1/3}[n^{1/2}],$$

we can write that

$$\left|A_3(n)-2\pi\{n[n^{1/2}]-\tfrac{1}{3}[n^{1/2}]^3\}-\pi\{n-[n^{1/2}]^2\}+\frac{\pi}{3}[n^{1/2}]\right|<2Bn^{1/3}[n^{1/2}]. \tag{A.10}$$

The function

$$\epsilon(n^{1/2})=n^{1/2}-[n^{1/2}] \tag{A.11}$$

satisfies the inequalities

$$0\leq\epsilon(n^{1/2})<1 \tag{A.12}$$

for all non-negative n. In terms of this function we can rewrite Eq. (A.10) as

$$|A_3(n)-\tfrac{4}{3}\pi n^{3/2}-(-\tfrac{1}{3}\pi+2\pi\epsilon-2\pi\epsilon^2)n^{1/2}-(\tfrac{1}{3}\pi\epsilon-\pi\epsilon^2+\tfrac{2}{3}\pi\epsilon^3)|<2B\{n^{5/6}-\epsilon n^{1/3}\} \tag{A.13}$$

or, less sharply as

$$|A_3(n)-\tfrac{4}{3}\pi n^{3/2}|<2B'n^{5/6}. \tag{A.14}$$

If we recall that $n=[r^2]$ and that $0\leq r^2-[r^2]<1$, for all positive r^2, it follows from Eq. (A.14) that

$$|A_3(r^2)-\tfrac{4}{3}\pi r^3|<2B''r^{5/3}. \tag{A.15}$$

Finally, the content of Eq. (A.15) in the context of the problem studied in this paper is that

$$\left|N_{l,t}(\omega)-\frac{4\pi}{3}V\left(\frac{\omega}{2\pi c_{l,t}}\right)^3\right|<2B''V^{5/9}\left(\frac{\omega}{2\pi c_{l,t}}\right)^{5/3}. \tag{A.16}$$

Inasmuch as the right side of this inequality is of lower order in V than $V^{2/3}\sim S$, we conclude that the low-temperature specific heat of our cyclic crystal has no contribution which is proportional to its surface area.

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[21] See, for example, E. Landau, *Elementary Number Theory* (Chelsea Publishing Company, New York, 1958), p. 5.