PHYSICAL REVIEW B VOLUME 14, NUMBER 6 15 SEPTEMBER 1976

Surface contribution to the low-temperature specific heat of a hexagonal crystal

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(Received 6 October 1975)

We derive for the first time an exact analytic result for the surface contribution to the low-temperature specific heat of an anisotropic medium. The system we consider is a semi-infinite hexagonal crystal with a stress-free planar surface parallel to the basal plane.

I. INTRODUCTION

The surface contribution to the specific heat of a finite crystal has been studied extensively, both theoretically and experimentally.

Some[1-5] of the previous calculations of the low-temperature surface specific heat of a crystal were carried out for finite or semi-infinite isotropic elastic continua, giving qualitative[1,2] and quantitative[3-5] results. Other calculations[6-12] of the surface specific heat of a crystal which are lattice dynamical in character have also been published. A few of them[6-9] are of a qualitative nature because they are based on a simple isotropic-crystal model for which 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. Maradudin and Wallis[10] derived for the first time from a lattice-dynamical model the surface specific heat of an isotropic crystal at low temperatures. Their analytic result is that obtained by Stratton,[3] Dupuis *et al.*,[4] and Burt[5] in the elastic approximation. Among the lattice-dynamical approaches to this problem a few[7,8,11,12] give the surface specific heat at all temperatures and show that this quantity has a maximum at a given temperature and then decreases to zero at higher temperatures. Allen and de Wette[11] give numerical results for the (100), (110), and (111) surfaces of the noble-gas solids neon, argon, krypton, and xenon. Chen, Alldredge, de Wette, and Allen[12] use the same numerical method for a (100) surface of NaCl. Their results are in rather good agreement with experimental results of Barkman, Anderson, and Brackett[13] for NaCl powder. Their method, however, is incapable of giving an analytic result at low temperatures, as the other lattice-dynamical calculations do.[7-10] Dobrzynski and Mills[8] and Allen, Alldredge, and de Wette[14] also studied the variation of the surface specific heat when a monolayer of isotopic impurities is present at the surface.

Among all the preceding analytic calculations of the surface specific heat only that of Cunningham[9] deals with an anisotropic surface, namely, the (110) surface of a simple-cubic crystal. But, as we have noted above, his result is qualitative only.

In the present paper we derive for the first time an exact analytic result for the surface contribution to the low-temperature specific heat of an anisotropic medium. The system we consider is a hexagonal crystal with a stress-free planar surface parallel to the basal plane. We obtain this result by using the Green's-function method introduced by Maradudin and Wallis[10] (Sec. II), but in the present work we calculate the necessary surface Green's function for a hexagonal crystal with a stress-free surface parallel to the basal plane in the elastic approximation rather than for a discrete crystal model (Sec. III). The knowledge of this surface Green's function enables us to obtain in analytic form the surface specific heat at low temperature and the speed c_R of Rayleigh waves (Sec. IV). The speed of Rayleigh waves in hexagonal crystals has been calculated numerically,[15] but to our knowledge the analytic result in Sec. IV is derived here for the first time.

II. GREEN'S-FUNCTION EXPRESSION FOR THE SURFACE SPECIFIC HEAT

We consider an elastic medium occupying the half space $x_3 \geq 0$, bounded by a stress-free surface at the plane $x_3 = 0$. The elastic moduli of such a system are position dependent and are given by

$$C_{\alpha\beta\mu\nu}(\vec{x}) = \Theta(x_3) C_{\alpha\beta\mu\nu}, \tag{2.1}$$

where the $\{C_{\alpha\beta\mu\nu}\}$ are the ordinary position-independent elastic moduli of the material out of which the semi-infinite medium is formed, and $\Theta(x_3)$ is the Heaviside unit step function:

$$\Theta(x_3) = \begin{cases} 1, & x_3 > 0 \\ 0, & x_3 < 0. \end{cases} \tag{2.2}$$

The equations of motion of the system are

$$\rho \ddot{u}_\alpha = \sum_\beta \frac{\partial T_{\alpha\beta}}{\partial x_\beta}, \tag{2.3}$$

where ρ is the mass density of the medium, $u_\alpha(\vec{x}, t)$ is the α Cartesian component of the displacement of the medium at the point $\vec{x}$ at time t, and $T_{\alpha\beta}$ is the stress tensor. The stress tensor is related to the displacement field by Hooke's law

$$T_{\alpha\beta}(\vec{x}) = \sum_{\mu\nu} C_{\alpha\beta\mu\nu}(\vec{x})\eta_{\mu\nu}(\vec{x}), \tag{2.4}$$

where the $\{\eta_{\mu\nu}(\vec{x})\}$ are the components of the strain tensor:

$$\eta_{\mu\nu}(\vec{x}) = \frac{1}{2}\left(\frac{\partial u_\mu(\vec{x})}{\partial x_\nu} + \frac{\partial u_\nu(\vec{x})}{\partial x_\mu}\right). \tag{2.5}$$

When we substitute Eqs. (2.1), (2.4), and (2.5) into Eq. (2.3) and use the symmetry of $C_{\alpha\beta\mu\nu}$ in μ and ν, we obtain for the equations of motion of the semi-infinite medium

$$\rho\ddot{u}_\alpha = \delta(x_3)\sum_{\mu\nu} C_{\alpha 3\mu\nu}\frac{\partial u_\mu}{\partial x_\nu} + \Theta(x_3)\sum_{\beta\mu\nu} C_{\alpha\beta\mu\nu}\frac{\partial^2 u_\mu}{\partial x_\beta \partial x_\nu}. \tag{2.6}$$

We assume a harmonic time dependence for the displacement field,

$$u_\alpha(\vec{x}, t) = u_\alpha(\vec{x})e^{-i\omega t}, \tag{2.7}$$

and obtain the time-independent equations of motion of the semi-infinite medium in the form:

$$\rho\omega^2 u_\alpha(\vec{x}) + \delta(x_3)\sum_{\mu\nu} C_{\alpha 3\mu\nu}\frac{\partial u_\mu(\vec{x})}{\partial x_\nu} + \sum_{\beta\mu\nu} C_{\alpha\beta\mu\nu}\frac{\partial^2 u_\mu(\vec{x})}{\partial x_\beta \partial x_\nu} = 0, \quad \alpha = 1, 2, 3, \quad x_3 \geq 0. \tag{2.8}$$

In writing Eq. (2.8) we have dropped the factor $\Theta(x_3)$ from the last term on the left-hand side, with the understanding there and in all that follows that $x_3 \geq 0$.

If we now make the substitution

$$u_\alpha(\vec{x}) = v_\alpha(\vec{x})/\sqrt{\rho}, \tag{2.9}$$

and require that $v_\alpha(\vec{x})$ be a solution of the set of equations

$$-\frac{1}{\rho}\sum_{\beta\mu\nu} C_{\alpha\beta\mu\nu}\frac{\partial^2 v_\mu^{(s)}(\vec{x})}{\partial x_\beta \partial x_\nu} = \omega_s^2 v_\alpha^{(s)}(\vec{x}), \quad \alpha = 1, 2, 3, \quad x_3 \geq 0 \tag{2.10a}$$

subject to the boundary conditions

$$\sum_{\mu\nu} C_{\alpha\beta\mu\nu}\left(\frac{\partial v_\mu^{(s)}(\vec{x})}{\partial x_\nu}\right)_{x_3=0} = 0, \quad \alpha = 1, 2, 3 \tag{2.10b}$$

at the plane $x_3 = 0$, and outgoing or exponentially decaying wave conditions at $x_3 = +\infty$, then the displacement field $u_\alpha(\vec{x})$ determined in this way clearly satisfies Eqs. (2.8). In general, there is an infinity of solutions of Eqs. (2.10), and we label these solutions by an index $s = 1, 2, 3, \ldots$.

The partial differential operator appearing on the left-hand side of Eq. (2.10a), supplemented by the boundary conditions (2.10b), is Hermitian. The eigenfunctions $\{v_\alpha^{(s)}(\vec{x})\}$ can therefore be shown to be orthonormal and complete:

$$\sum_\alpha \int d^2x_\parallel \int_0^\infty dx_3 v_\alpha^{(s)}(\vec{x})^* v_\alpha^{(s')}(\vec{x}) = \delta_{ss'}, \tag{2.11a}$$

$$\sum_s v_\alpha^{(s)}(\vec{x})^* v_\beta^{(s)}(\vec{x}') = \delta_{\alpha\beta}\delta(\vec{x} - \vec{x}'). \tag{2.11b}$$

The frequencies $\{\omega_s\}$ are clearly the normal-mode frequencies of the semi-infinite elastic medium bounded by a stress-free surface at the plane $x_3 = 0$.

We now introduce the Green's function $U_{\alpha\beta}(\vec{x}, \vec{x}'; \omega)$ as the solution of the equation:

$$\sum_\mu \left(\delta_{\alpha\mu}\omega^2 + \frac{1}{\rho}\delta(x_3)\sum_\nu C_{\alpha 3\mu\nu}\frac{\partial}{\partial x_\nu} + \frac{1}{\rho}\sum_{\beta\nu} C_{\alpha\beta\mu\nu}\frac{\partial^2}{\partial x_\beta \partial x_\nu}\right) U_{\mu\beta}(\vec{x}, \vec{x}'; \omega) = \delta_{\alpha\beta}\delta(\vec{x} - \vec{x}'), \tag{2.12}$$

subject to outgoing or exponentially decaying wave conditions at $x_3 = +\infty$. From the preceding results it follows that this function can be represented in the form:

$$U_{\alpha\beta}(\vec{x}, \vec{x}'; \omega) = \sum_s \frac{v_\alpha^{(s)}(\vec{x}) v_\beta^{(s)}(\vec{x}')^*}{\omega^2 - \omega_s^2}. \tag{2.13}$$

Our interest in the Green's function $U_{\alpha\beta}(\vec{x}, \vec{x}'; \omega)$ derives from the following considerations. If we denote by $U_{\alpha\beta}^{(0)}(\vec{x}, \vec{x}'; \omega)$ the corresponding Green's function for an infinitely extended medium, which is the solution of Eq. (2.12) with the term containing $\delta(x_3)$ omitted, and subject to outgoing or exponentially decaying wave conditions at $x_3 = +\infty$, we can construct a function $\Omega(y)$ according to

$$\Omega(y) = -\sum_\alpha \int d^2x_\parallel \int_0^\infty dx_3 \left[U_{\alpha\alpha}(\vec{x}, \vec{x}; iy) - U_{\alpha\alpha}^{(0)}(\vec{x}, \vec{x}; iy)\right]. \tag{2.14}$$

It has been shown by Maradudin and Wallis[10] that if the function $\Omega(y)$ has as its only singularity a logarithmic dependence on $|y|$ in the limit as $|y| \to 0$, i.e., if

$$\Omega(y) \sim -A \ln|y| + o(\ln|y|), \quad |y| \to 0, \tag{2.15}$$

the surface contribution to the specific heat of a crystal is given by

$$\Delta C_v(T) = 6A\zeta(3)k_B(k_B T/\hbar)^2 + o(T^2) \tag{2.16}$$

in the limit as the absolute temperature $T \to 0$, where $\zeta(x)$ is the Riemann ζ function and k_B is Boltzmann's constant.

The problem of calculating the surface contribution to the specific heat of a crystal is therefore reduced to showing that the function $\Omega(y)$ has the asymptotic form given by Eq. (2.15) in the limit as $|y| \to 0$, and of determining the coefficient A.

If it were necessary to solve Eqs. (2.10a)–(2.10b) for the eigenvectors $\{v_\alpha^{(s)}(\vec{x})\}$ and the corresponding eigenvalues $\{\omega_s^2\}$, and carry out the sum over s in Eq. (2.13) to obtain the Green's function $U_{\alpha\beta}(\vec{x}, \vec{x}'; \omega)$, the determination of the surface contribution to the low-temperature specific heat of a crystal by the methods of this paper would be virtually impossible. However, we will show in Sec. III that it is possible in fact to obtain $U_{\alpha\beta}(\vec{x}, \vec{x}'; \omega)$ [and $U_{\alpha\beta}^{(0)}(\vec{x}, \vec{x}'; \omega)$] in closed form for a medium of hexagonal symmetry by solving the partial differential equations (2.12) directly. With this result in hand, the determination of the surface contribution to the low-temperature specific heat of such a medium is straightforward and is carried out in Sec. IV.

III. DYNAMICAL GREEN'S FUNCTION FOR A HEXAGONAL ELASTIC HALF SPACE

The Green's function $U_{\alpha\beta}(\vec{x}, \vec{x}'; \omega)$ for an elastic medium of arbitrary symmetry occupying the half space $x_3 > 0$ can be Fourier analyzed in the following manner:

$$U_{\alpha\beta}(\vec{x}, \vec{x}'; \omega) = \int \frac{d^2k}{(2\pi)^2} e^{i\vec{k}\cdot(\vec{x}_\parallel - \vec{x}'_\parallel)} d_{\alpha\beta}(\vec{k}\omega|x_3 x_3'), \tag{3.1}$$

where $\vec{x}_\parallel$ and $\vec{k}$ are both two-dimensional vectors with components $(x_1, x_2, 0)$ and $(k_1, k_2, 0)$, respectively. The form of the expansion (3.1) is dictated by the fact that our elastic half space possesses infinitesimal translational invariance in directions parallel to its surface (the plane $x_3 = 0$), so that $U_{\alpha\beta}(\vec{x}, \vec{x}'; \omega)$ can depend on $\vec{x}_\parallel$ and $\vec{x}'_\parallel$ only through their difference. Because this system is no longer translationally invariant in the direction normal to the surface $x_3 = 0$, $U_{\alpha\beta}(\vec{x}, \vec{x}'; \omega)$ cannot depend on x_3 and x_3' only through their difference, but has a more complicated dependence on these variables whose form is one of the objects of this section.

When Eq. (3.1), together with the representation

$$\delta(\vec{x} - \vec{x}') = \delta(x_3 - x_3') \int \frac{d^2k}{(2\pi)^2} e^{i\vec{k}\cdot(\vec{x}_\parallel - \vec{x}'_\parallel)} \tag{3.2}$$

is substituted into Eq. (2.12), and the resulting equation is specialized to the case of an hexagonal medium with the six fold rotation axis in the x_3 direction, i.e., a medium belonging to one of the crystal classes $6, \bar{6}, 6/m, 6mm, \bar{6}m2, 62, 6/mm$, in the Hermann-Maugin notation, the equation satisfied by the Fourier coefficients $\{d_{\alpha\beta}(\vec{k}\omega|x_3 x_3')\}$ takes the form

$$\sum_\mu L_{\alpha\mu}(\vec{k}\omega|x_3) d_{\mu\beta}(\vec{k}\omega|x_3 x_3') = \delta_{\alpha\beta}\delta(x_3 - x_3'), \tag{3.3}$$

where the elements of the matrix differential operator $\vec{L}(\vec{k}\omega|x_3)$ are given explicitly by

$$L_{11}(\vec{k}\omega|x_3) = \omega^2 - \frac{c_{11}}{\rho}k_1^2 - \frac{1}{2\rho}(c_{11} - c_{12})k_2^2 + \frac{c_{44}}{\rho}\frac{d^2}{dx_3^2} + \delta(x_3)\frac{c_{44}}{\rho}\frac{d}{dx_3}, \tag{3.4a}$$

$$L_{12}(\vec{k}\omega|x_3) = -(1/2\rho)(c_{11} + c_{12})k_1 k_2, \tag{3.4b}$$

$$L_{13}(\vec{k}\omega|x_3) = \frac{i}{\rho}(c_{13} + c_{44})k_1\frac{d}{dx_3} + \delta(x_3)i\frac{c_{44}}{\rho}k_1, \tag{3.4c}$$

$$L_{21}(\vec{k}\omega|x_3) = -(1/2\rho)(c_{11} + c_{12})k_1 k_2, \tag{3.4d}$$

$$L_{22}(\vec{k}\omega|x_3) = \omega^2 - \frac{1}{2\rho}(c_{11} - c_{12})k_1^2 - \frac{c_{11}}{\rho}k_2^2 + \frac{c_{44}}{\rho}\frac{d^2}{dx_3^2} + \delta(x_3)\frac{c_{44}}{\rho}\frac{d}{dx_3}, \tag{3.4e}$$

$$L_{23}(\vec{k}\omega|x_3) = \frac{i}{\rho}(c_{13} + c_{44})k_2\frac{d}{dx_3} + \delta(x_3)i\frac{c_{44}}{\rho}k_2, \tag{3.4f}$$

$$L_{31}(\vec{k}\omega|x_3) = \frac{i}{\rho}(c_{13} + c_{44})k_1\frac{d}{dx_3} + \delta(x_3)i\frac{c_{13}}{\rho}k_1, \tag{3.4g}$$

$$L_{32}(\vec{k}\omega|x_3) = \frac{i}{\rho}(c_{13} + c_{44})k_2\frac{d}{dx_3} + \delta(x_3)i\frac{c_{13}}{\rho}k_2, \tag{3.4h}$$

$$L_{33}(\vec{k}\omega|x_3) = \omega^2 - \frac{c_{44}}{\rho}k^2 + \frac{c_{33}}{\rho}\frac{d^2}{dx_3^2} + \delta(x_3)\frac{c_{33}}{\rho}\frac{d}{dx_3}. \tag{3.4i}$$

In these expressions the $\{c_{ij}\}$ are the elastic moduli in the contracted Voigt notation, and $k = (k_1^2 + k_2^2)^{1/2}$.

We now exploit the isotropy of hexagonal media in the plane perpendicular to the sixfold rotation axis (the plane $x_3 = 0$ in the present case) to simplify the set of equations (3.3)–(3.4). We carry out a similarity transformation on the set of equations (3.3) with respect to the matrix $\vec{S}(\vec{k})$ given by

$$\tilde{S}(\vec{k}) = \begin{pmatrix} \hat{k}_1 & \hat{k}_2 & 0 \\ -\hat{k}_2 & \hat{k}_1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\tilde{S}^{-1}(\vec{k}) = \begin{pmatrix} \hat{k}_1 & -\hat{k}_2 & 0 \\ \hat{k}_2 & \hat{k}_1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \qquad (3.5)$$

where $\hat{k}_1 = k_1/k$ and $\hat{k}_2 = k_2/k$. The real orthogonal matrix $\tilde{S}(\vec{k})$ is the matrix which rotates the vector $\vec{k}$ into the vector $(k, 0, 0)$. As a result of this transformation Eq. (3.3) becomes

$$\sum_{\mu} \mathfrak{L}_{\alpha\mu}(k\omega|x_3) g_{\mu\beta}(k\omega|x_3x_3') = \delta_{\alpha\beta}\delta(x_3 - x_3'), \qquad (3.6)$$

where

$$\tilde{\mathfrak{L}}(k\omega|x_3) = \tilde{S}(\vec{k})\tilde{L}(\vec{k}\omega|x_3)\tilde{S}^{-1}(\vec{k}) \qquad (3.7)$$

and

$$d_{\alpha\beta}(\vec{k}\omega|x_3x_3') = \sum_{\mu\nu} S_{\mu\alpha}(\vec{k}) S_{\nu\beta}(\vec{k}) g_{\mu\nu}(k\omega|x_3x_3'). \qquad (3.8)$$

The elements of the matrix differential operator $\tilde{\mathfrak{L}}(k\omega|x_3)$ are given by

$$\mathfrak{L}_{11}(k\omega|x_3) = \omega^2 - \frac{c_{11}}{\rho}k^2 + \frac{c_{44}}{\rho}\frac{d^2}{dx_3^2} + \delta(x_3)\frac{c_{44}}{\rho}\frac{d}{dx_3}, \qquad (3.9a)$$

$$\mathfrak{L}_{12}(k\omega|x_3) = 0, \qquad (3.9b)$$

$$\mathfrak{L}_{13}(k\omega|x_3) = \frac{i}{\rho}(c_{13} + c_{44})k\frac{d}{dx_3} + \delta(x_3) i\frac{c_{44}}{\rho}k, \qquad (3.9c)$$

$$\mathfrak{L}_{21}(k\omega|x_3) = 0, \qquad (3.9d)$$

$$\mathfrak{L}_{22}(k\omega|x_3) = \omega^2 - \frac{c_{11} - c_{12}}{2\rho}k^2 + \frac{c_{44}}{\rho}\frac{d^2}{dx_3^2} + \delta(x_3)\frac{c_{44}}{\rho}\frac{d}{dx_3}, \qquad (3.9e)$$

$$\mathfrak{L}_{23}(k\omega|x_3) = 0, \qquad (3.9f)$$

$$\mathfrak{L}_{31}(k\omega|x_3) = \frac{i}{\rho}(c_{13} + c_{44})k\frac{d}{dx_3} + \delta(x_3) i\frac{c_{13}}{\rho}k, \qquad (3.9g)$$

$$\mathfrak{L}_{32}(k\omega|x_3) = 0, \qquad (3.9h)$$

$$\mathfrak{L}_{33}(k\omega|x_3) = \omega^2 - \frac{c_{44}}{\rho}k^2 + \frac{c_{33}}{\rho}\frac{d^2}{dx_3^2} + \delta(x_3)\frac{c_{33}}{\rho}\frac{d}{dx_3}. \qquad (3.9i)$$

The similarity transformation thus eliminates certain elements of the matrix differential operator and forces the remaining ones to depend on the vector $\vec{k}$ only through its magnitude.

To solve Eqs. (3.6) we proceed as follows: We first solve the form of Eqs. (3.6) which results when the terms proportional to $\delta(x_3)$ are omitted from the elements of the matrix operator $\tilde{\mathfrak{L}}(k\omega|x_3)$:

$$\begin{bmatrix} \omega^2 - \frac{c_{11}}{\rho}k^2 + \frac{c_{44}}{\rho}\frac{d^2}{dx_3^2} & 0 & \frac{i}{\rho}(c_{13}+c_{44})k\frac{d}{dx_3} \\ 0 & \omega^2 - \frac{c_{11}-c_{12}}{2\rho}k^2 + \frac{c_{44}}{\rho}\frac{d^2}{dx_3^2} & 0 \\ \frac{i}{\rho}(c_{13}+c_{44})k\frac{d}{dx_3} & 0 & \omega^2 - \frac{c_{44}}{\rho}k^2 + \frac{c_{33}}{\rho}\frac{d^2}{dx_3^2} \end{bmatrix} \begin{pmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{pmatrix} = \delta(x_3 - x_3') \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \qquad (3.10)$$

The solutions of Eq. (3.10) are then required to satisfy the following boundary conditions at the plane $x_3 = 0$, which are obtained by equating to zero the coefficients of $\delta(x_3)$ appearing on the left-hand sides of Eqs. (3.6):

$$\frac{c_{44}}{\rho}\frac{d}{dx_3}g_{x\alpha} + i\frac{c_{44}}{\rho}kg_{z\alpha} = 0,$$

$$\frac{c_{44}}{\rho}\frac{d}{dx_3}g_{y\alpha} = 0, \qquad (3.11)$$

$$i\frac{c_{13}}{\rho}kg_{x\alpha} + \frac{c_{33}}{\rho}\frac{d}{dx_3}g_{z\alpha} = 0,$$

where $\alpha = x, y, z$. The solutions of Eqs. (3.10) and (3.11) are clearly solutions of Eqs. (3.6).

When Eqs. (3.10) are written out explicitly, it is found that the Green's functions g_{yx} and g_{yz} satisfy homogeneous equations, while g_{xy} and g_{zy} satisfy a pair of coupled homogeneous equations. These Green's functions therefore vanish identically. The problem of obtaining the Green's function $U_{\alpha\beta}(\vec{x}, \vec{x}; \omega)$ is therefore reduced to that of obtaining the five functions g_{xx}, g_{zx}, g_{yy}, g_{xz}, and g_{zz} as the solutions of the following boundary-value problems for $x_3 \geq 0$:

$$\left(\omega^2 - \frac{c_{11}}{\rho}k^2 + \frac{c_{44}}{\rho}\frac{d^2}{dx_3^2}\right)g_{xx} + \frac{i}{\rho}(c_{13}+c_{44})k\frac{d}{dx_3}g_{zx} = \delta(x_3 - x_3'), \quad (3.12a)$$

$$\frac{i}{\rho}(c_{13}+c_{44})k\frac{d}{dx_3}g_{xx} + \left(\omega^2 - \frac{c_{44}}{\rho}k^2 + \frac{c_{33}}{\rho}\frac{d^2}{dx_3^2}\right)g_{zx} = 0, \quad (3.12b)$$

$$\left(\frac{d}{dx_3}g_{xx} + ikg_{zx}\right)_{x_3=0} = 0, \quad (3.12c)$$

$$\left(i\frac{c_{13}}{c_{33}}kg_{xx} + \frac{d}{dx_3}g_{zx}\right)_{x_3=0} = 0; \quad (3.12d)$$

$$\left(\omega^2 - \frac{c_{11}-c_{12}}{2\rho}k^2 + \frac{c_{44}}{\rho}\frac{d^2}{dx_3^2}\right)g_{yy} = \delta(x_3 - x_3'), \quad (3.13a)$$

$$\left(\frac{d}{dx_3}g_{yy}\right)_{x_3=0} = 0; \quad (3.13b)$$

$$\omega^2 - \frac{c_{11}}{\rho}k^2 + \frac{c_{44}}{\rho}\frac{d^2}{dx_3^2}\ g_{xz} + \frac{i}{\rho}(c_{13}+c_{44})k\frac{d}{dx_3}g_{zz} = 0, \quad (3.14a)$$

$$\frac{i}{\rho}(c_{13}+c_{44})k\frac{d}{dx_3}g_{xz} + \left(\omega^2 - \frac{c_{44}}{\rho}k^2 + \frac{c_{33}}{\rho}\frac{d^2}{dx_3^2}\right)g_{zz} = \delta(x_3 - x_3'), \quad (3.14b)$$

$$\left(\frac{d}{dx_3}g_{xz} + ikg_{zz}\right)_{x_3=0} = 0, \quad (3.14c)$$

$$\left(i\frac{c_{13}}{c_{33}}kg_{xz} + \frac{d}{dx_3}g_{zz}\right)_{x_3=0} = 0. \quad (3.14d)$$

In solving these equations the following results are useful:

$$\left(\frac{d^2}{dx_3^2} - \alpha^2\right)\frac{e^{-\alpha|x_3-x_3'|}}{-2\alpha} = \delta(x_3 - x_3'), \quad (3.15)$$

$$\left(\frac{d^2}{dx_3^2} - \alpha^2\right)\frac{1}{\alpha^2}\left[\Theta(x_3' - x_3) + \tfrac{1}{2}e^{-\alpha|x_3-x_3'|}\operatorname{sgn}(x_3 - x_3')\right] = -\theta(x_3' - x_3). \quad (3.16)$$

We will not present here the details of the determination of each of the five functions g_{xx}, g_{zx}, g_{yy}, g_{zx}, and g_{zz}. However, to illustrate the way in which this was done we outline the determination of g_{xx} and g_{zx}.

By eliminating g_{zx} between Eqs. (3.12a) and (3.12b) we find that g_{xx} satisfies the equation

$$\left(\frac{d^2}{dx_3^2} - \alpha_1^2\right)\left(\frac{d^2}{dx_3^2} - \alpha_2^2\right)g_{xx} = \frac{\rho}{c_{44}}\left[\frac{d^2}{dx_3^2} - \left(\frac{c_{44}}{c_{33}}k^2 - \frac{\rho\omega^2}{c_{33}}\right)\right]\delta(x_3 - x_3'), \quad (3.17)$$

where

$$\alpha_1^2 = \tfrac{1}{2}[x + (x^2 - 4y^2)^{1/2}], \quad (3.18a)$$

$$\alpha_2^2 = \tfrac{1}{2}[x - (x^2 - 4y^2)^{1/2}], \quad (3.18b)$$

with

$$x = (c_{33}c_{44})^{-1}[(c_{44}^2 + c_{11}c_{33})k^2 - (c_{13}+c_{44})^2k^2 - (c_{33}+c_{44})\rho\omega^2], \quad (3.19a)$$

$$y^2 = (c_{33}c_{44})^{-1}(c_{44}k^2 - \rho\omega^2)(c_{11}k^2 - \rho\omega^2). \quad (3.19b)$$

The functions α_1 and α_2 are obtained uniquely from Eqs. (3.18) with the aid of the following restrictions, which follow from the boundary conditions at $x_3 = +\infty$:

$$\operatorname{Re}\alpha_{1,2} > 0, \quad \operatorname{Im}\alpha_{1,2} < 0. \quad (3.20)$$

With the aid of Eq. (3.15) we find that the particular solution of Eq. (3.17) is given by

$$g_{xx}^p = -\frac{\rho}{2\alpha_1c_{44}}\frac{1}{\alpha_1^2 - \alpha_2^2}\left(\alpha_1^2 - \frac{c_{44}}{c_{33}}k^2 + \frac{\rho\omega^2}{c_{33}}\right)e^{-\alpha_1|x_3-x_3'|} + \frac{\rho}{2\alpha_2c_{44}}\frac{1}{\alpha_1^2 - \alpha_2^2}\left(\alpha_2^2 - \frac{c_{44}}{c_{33}}k^2 + \frac{\rho\omega^2}{c_{33}}\right)e^{-\alpha_2|x_3-x_3'|}. \quad (3.21)$$

The general solution of Eq. (3.17) is therefore

$$g_{xx} = g_{xx}^p + ae^{-\alpha_1x_3} + be^{-\alpha_2x_3}. \quad (3.22)$$

Turning now to g_{zx}, on eliminating g_{xx} between Eqs. (3.12a) and (3.12b), we find that it satisfies the equation

$$\left(\frac{d^2}{dx_3^2} - \alpha_1^2\right)\left(\frac{d^2}{dx_3^2} - \alpha_2^2\right)g_{zx} = -i\rho\frac{c_{13}+c_{44}}{c_{33}c_{44}}k\frac{d}{dx_3}\delta(x_3 - x_3'). \quad (3.23)$$

With the aid of Eq. (3.16) we obtain as the particular solution of this equation

$$g_{zx}^p = \frac{-i\rho(c_{13}+c_{44})k}{2c_{33}c_{44}(\alpha_1^2 - \alpha_2^2)}\left(e^{-\alpha_1|x_3-x_3'|} - e^{-\alpha_2|x_3-x_3'|}\right) \times \operatorname{sgn}(x_3 - x_3'). \quad (3.24)$$

The general solution of Eq. (3.23) is therefore

$$g_{zx} = g_{zx}^p + ce^{-\alpha_1x_3} + de^{-\alpha_2x_3}. \quad (3.25)$$

The four constants a, b, c, and d appearing in Eqs. (3.22) and (3.25) are not independent, however. When we substitute Eqs. (3.22) and (3.25) back into Eq. (3.12a) or (3.12b) we find that c and d can be expressed in terms of a and b according to

$$c = -i\frac{c_{44}}{\alpha_1(c_{13}+c_{44})k}\left(\alpha_1^2 - \frac{c_{11}}{c_{44}}k^2 + \frac{\rho\omega^2}{c_{44}}\right)a, \quad (3.26a)$$

$$d = -i\frac{c_{44}}{\alpha_2(c_{13}+c_{44})k}\left(\alpha_2^2 - \frac{c_{11}}{c_{44}}k^2 + \frac{\rho\omega^2}{c_{44}}\right)b. \quad (3.26b)$$

The constants which remain, a and b, are now determined by substituting Eqs. (3.21), (3.22), and (3.25), and (3.26) into the two boundary conditions, Eqs. (3.12c) and (3.12d). The results can be expressed in the following form:

$$g_{xx}(k\omega|x_3x_3')=[D(k\omega)]^{-1}[A_{11}(k\omega)e^{-\alpha_1(x_3+x_3')}+A_{12}(k\omega)e^{-\alpha_1x_3-\alpha_2x_3'}+A_{21}(k\omega)e^{-\alpha_2x_3-\alpha_1x_3'}+A_{22}(k\omega)e^{-\alpha_2(x_3+x_3')}]+g^{p}_{xx}(k\omega|x_3x_3'), \tag{3.27}$$

$$g_{zx}(k\omega|x_3x_3')=-i\frac{c_{44}}{(c_{13}+c_{44})\alpha_1k}\left(\alpha_1^2-\frac{c_{11}}{c_{44}}k^2+\frac{\rho\omega^2}{c_{44}}\right)\frac{1}{D(k\omega)}[A_{11}(k\omega)e^{-\alpha_1(x_3+x_3')}+A_{12}(k\omega)e^{-\alpha_1x_3-\alpha_2x_3'}]$$
$$-i\frac{c_{44}}{(c_{13}+c_{44})\alpha_2k}\left(\alpha_2^2-\frac{c_{11}}{c_{44}}k^2+\frac{\rho\omega^2}{c_{44}}\right)\frac{1}{D(k\omega)}[A_{21}(k\omega)e^{-\alpha_2x_3-\alpha_1x_3'}+A_{22}(k\omega)e^{-\alpha_2(x_3+x_3')}]+g^{p}_{zx}(k\omega|x_3x_3'). \tag{3.28}$$

In these expressions we have that

$$A_{11}(k\omega)=M_{22}(k\omega)C_{11}(k\omega)-M_{12}(k\omega)C_{21}(k\omega), \tag{3.29a}$$

$$A_{12}(k\omega)=M_{22}(k\omega)C_{12}(k\omega)-M_{12}(k\omega)C_{22}(k\omega), \tag{3.29b}$$

$$A_{21}(k\omega)=-M_{21}(k\omega)C_{11}(k\omega)+M_{11}(k\omega)C_{21}(k\omega), \tag{3.29c}$$

$$A_{22}(k\omega)=-M_{21}(k\omega)C_{12}(k\omega)+M_{11}(k\omega)C_{22}(k\omega); \tag{3.29d}$$

$$D(k\omega)=M_{11}(k\omega)M_{22}(k\omega)-M_{12}(k\omega)M_{21}(k\omega), \tag{3.30}$$

where

$$M_{1(1,2)}(k\omega)=\frac{1}{(c_{13}+c_{44})\alpha_{1,2}}\left[-(c_{13}+c_{44})\alpha_{1,2}^2+c_{44}\left(\alpha_{1,2}^2-\frac{c_{11}}{c_{44}}k^2+\frac{\rho\omega^2}{c_{44}}\right)\right], \tag{3.31a}$$

$$M_{2(1,2)}(k\omega)=\frac{1}{(c_{13}+c_{44})k}\left[(c_{13}+c_{44})k^2+\frac{c_{33}c_{44}}{c_{13}}\left(\alpha_{1,2}^2-\frac{c_{11}}{c_{44}}k^2+\frac{\rho\omega^2}{c_{44}}\right)\right], \tag{3.31b}$$

$$C_{1(1,2)}(k\omega)=\frac{\rho}{2c_{44}}\frac{1}{\alpha_{1,2}^2-\alpha_{2,1}^2}\left(\alpha_{1,2}^2+\frac{c_{13}+c_{44}}{c_{33}}k^2-\frac{c_{44}}{c_{33}}k^2+\frac{\rho\omega^2}{c_{33}}\right), \tag{3.32a}$$

$$C_{2(1,2)}(k\omega)=\frac{\rho k}{2\alpha_{1,2}c_{13}c_{44}}\frac{1}{\alpha_{1,2}^2-\alpha_{2,1}^2}\left[c_{13}\left(\alpha_{1,2}^2-\frac{c_{44}}{c_{33}}k^2+\frac{\rho\omega^2}{c_{33}}\right)-(c_{13}+c_{44})\alpha_{1,2}^2\right]. \tag{3.32b}$$

In the same way we obtain the following results for the Green's functions g_{xz} and g_{zz}:

$$g_{xz}(k\omega|x_3x_3')=\frac{1}{D(k\omega)}[B_{11}(k\omega)e^{-\alpha_1(x_3+x_3')}+B_{12}(k\omega)e^{-\alpha_1x_3-\alpha_2x_3'}+B_{21}(k\omega)e^{-\alpha_2x_3-\alpha_1x_3'}+B_{22}(k\omega)e^{-\alpha_2(x_3+x_3')}]+g^{p}_{xz}(k\omega|x_3x_3'), \tag{3.33}$$

$$g_{zz}(k\omega|x_3x_3')=-i\frac{c_{44}}{(c_{13}+c_{44})k\alpha_1}\left(\alpha_1^2-\frac{c_{11}}{c_{44}}k^2+\frac{\rho\omega^2}{c_{44}}\right)\frac{1}{D(k\omega)}[B_{11}(k\omega)e^{-\alpha_1(x_3+x_3')}+B_{12}(k\omega)e^{-\alpha_1x_3-\alpha_2x_3'}]$$
$$-i\frac{c_{44}}{(c_{13}+c_{44})k\alpha_2}\left(\alpha_2^2-\frac{c_{11}}{c_{44}}k^2+\frac{\rho\omega^2}{c_{44}}\right)\frac{1}{D(k\omega)}[B_{21}(k\omega)e^{-\alpha_2x_3-\alpha_1x_3'}+B_{22}(k\omega)e^{-\alpha_2(x_3+x_3')}]+g^{p}_{zz}(k\omega|x_3x_3'), \tag{3.34}$$

where

$$g^{p}_{xz}(k\omega|x_3x_3')=-\frac{i\rho(c_{13}+c_{44})k}{2c_{33}c_{44}}\frac{1}{\alpha_1^2-\alpha_2^2}(e^{-\alpha_1|x_3-x_3'|}-e^{-\alpha_2|x_3-x_3'|})\,\mathrm{sgn}(x_3-x_3'), \tag{3.35}$$

$$g^{p}_{zz}(k\omega|x_3x_3')=-\frac{\rho}{2\alpha_1c_{33}}\frac{1}{\alpha_1^2-\alpha_2^2}\left(\alpha_1^2-\frac{c_{11}}{c_{44}}k^2+\frac{\rho\omega^2}{c_{44}}\right)e^{-\alpha_1|x_3-x_3'|}+\frac{\rho}{2\alpha_2c_{33}}\frac{1}{\alpha_1^2-\alpha_2^2}\left(\alpha_2^2-\frac{c_{11}}{c_{44}}k^2+\frac{\rho\omega^2}{c_{44}}\right)e^{-\alpha_2|x_3-x_3'|}, \tag{3.36}$$

and

$$B_{11}(k\omega)=M_{22}(k\omega)C_{11}'(k\omega)-M_{12}(k\omega)C_{21}'(k\omega), \tag{3.37a}$$

$$B_{12}(k\omega)=M_{22}(k\omega)C_{12}'(k\omega)-M_{12}(k\omega)C_{22}'(k\omega), \tag{3.37b}$$

$$B_{21}(k\omega)=-M_{21}(k\omega)C_{11}'(k\omega)+M_{11}(k\omega)C_{21}'(k\omega), \tag{3.37c}$$

$$B_{22}(k\omega)=-M_{21}(k\omega)C_{12}'(k\omega)+M_{11}(k\omega)C_{22}'(k\omega); \tag{3.37d}$$

$$C_{1(1,2)}'(k\omega)=\frac{ik\rho}{2\alpha_{1,2}c_{33}c_{44}}\frac{1}{\alpha_{1,2}^2-\alpha_{2,1}^2}\left[c_{44}\left(\alpha_{1,2}^2-\frac{c_{11}}{c_{44}}k^2+\frac{\rho\omega^2}{c_{44}}\right)-(c_{13}+c_{44})\alpha_{1,2}^2\right], \tag{3.38a}$$

$$C_{2(1,2)}'(k\omega)=-\frac{i\rho}{2c_{13}}\frac{1}{\alpha_{1,2}^2-\alpha_{2,1}^2}\left(\alpha_{1,2}^2+c_{13}\frac{c_{13}+c_{44}}{c_{33}c_{44}}k^2-\frac{c_{11}}{c_{44}}k^2+\frac{\rho\omega^2}{c_{44}}\right). \tag{3.38b}$$

The other functions appearing in these expressions have already been defined.

Finally, we write the result for g_{yy}:

$$g_{yy}(k\omega|x_3x_3') = \frac{-\rho}{2c_{44}\alpha_t}e^{-\alpha_t(x_3+x_3')} + g^p_{yy}(k\omega|x_3x_3'), \tag{3.39}$$

$$g^p_{yy}(k\omega|x_3x_3') = \frac{-\rho}{2c_{44}\alpha_t}e^{-\alpha_t|x_3-x_3'|}, \tag{3.40}$$

where

$$\alpha_t = \begin{cases} \left(\dfrac{c_{11}-c_{12}}{2c_{44}}k^2 - \dfrac{\rho\omega^2}{c_{44}}\right)^{1/2}, \\ \tfrac{1}{2}(c_{11}-c_{12})k^2 > \rho\omega^2 \\ \\ -i\left(\dfrac{\rho\omega^2}{c_{44}} - \dfrac{c_{11}-c_{12}}{2c_{44}}k^2\right)^{1/2}, \\ \rho\omega^2 > \tfrac{1}{2}(c_{11}-c_{12})k^2. \end{cases} \tag{3.41}$$

We are now in a position to relate the surface contribution to the low-temperature specific heat of our hexagonal medium to the Green's functions $\{g_{\alpha\beta}(k\omega|x_3x_3')\}$. Let us denote by $U^{(0)}_{\alpha\beta}(\vec{x},\vec{x}';\omega^2)$ the dynamical Green's function for an infinitely extended elastic medium. It is the solution of Eqs. (2.12) with the terms proportional to $\delta(x_3)$ omitted from the left-hand side, subject to exponentially decaying or outgoing wave conditions at infinity. In parallel with Eqs. (3.1) and (3.8), we introduce the Fourier coefficients $\{d^{(0)}_{\alpha\beta}(\vec{k}\omega|x_3x_3')\}$ and $\{g^{(0)}_{\alpha\beta}(k\omega|x_3x_3')\}$ by

$$U^{(0)}_{\alpha\beta}(\vec{x},\vec{x}';\omega) = \int \frac{d^2k}{(2\omega)^2}e^{i\vec{k}\cdot(\vec{x}_\parallel-\vec{x}'_\parallel)}d^{(0)}_{\alpha\beta}(\vec{k}\omega|x_3x_3'), \tag{3.42}$$

and

$$d^{(0)}_{\alpha\beta}(\vec{k}\omega|x_3x_3') = \sum_{\mu\nu} S_{\mu\alpha}(\vec{k})\, S_{\nu\beta}(\vec{k})\, g^{(0)}_{\mu\nu}(k\omega|x_3x_3'), \tag{3.43}$$

where the matrix $\vec{S}(\vec{k})$ is given by Eq. (3.5). It should be clear, from the derivation of the $\{g_{\alpha\beta}(k\omega|x_3x_3')\}$ given in the first part of this section, that the Green's function $g^{(0)}_{\alpha\beta}(k\omega|x_3x_3')$ is just the particular solution $g^p_{\alpha\beta}(k\omega|x_3x_3')$ we have obtained in the process of determining $g_{\alpha\beta}(k\omega|x_3x_3')$, since no reference to the surface of the elastic medium has been made in obtaining these particular solutions.

We now combine Eqs. (2.14), (3.1), and (3.42) to obtain an expression for the function $\Omega(y)$ useful for its asymptotic evaluation

$$\Omega(y) = -S\sum_\alpha \int_0^\infty dx_3 \int \frac{d^2k}{(2\pi)^2}\,[d_{\alpha\alpha}(\vec{k}iy|x_3x_3) - d^{(0)}_{\alpha\alpha}(\vec{k}iy|x_3x_3)], \tag{3.44}$$

where S is the area of the surface of the semi-infinite elastic medium. Since the trace of a matrix is invariant against a similarity transformation, in view of Eqs. (3.8) and (3.43) we can rewrite Eq. (3.44) in the form

$$\Omega(y) = -S\sum_\alpha \int_0^\infty dx_3 \int \frac{d^2k}{(2\pi)^2}\,[g_{\alpha\alpha}(kiy|x_3x_3) - g^p_{\alpha\alpha}(kiy|x_3x_3)]. \tag{3.45}$$

With the use of Eqs. (3.27), (3.34), and (3.39) the integration over x_3 in Eq. (3.45) can be carried out directly, with the result that

$$\begin{aligned}\Omega(y) = &-\frac{S}{2\pi}\int_0^{k_c} dk\,\frac{k}{D(kiy)}\left(\frac{A_{11}(kiy)}{2\beta_1} + \frac{A_{12}(kiy)+A_{21}(kiy)}{\beta_1+\beta_2} + \frac{A_{22}(kiy)}{2\beta_2}\right) + \frac{S}{2\pi}\int_0^{k_c} dk\,\frac{\rho k}{4c_{44}\beta_t^2} \\ &+ i\frac{S}{2\pi}\int_0^{k_c} dk\,\frac{k}{D(kiy)}\left[\frac{c_{44}\beta_1^2 - c_{11}k^2 - \rho y^2}{(c_{13}+c_{44})k\beta_1}\left(\frac{B_{11}(kiy)}{2\beta_1} + \frac{B_{12}(kiy)}{\beta_1+\beta_2}\right) + \frac{c_{44}\beta_2^2 - c_{11}k^2 - \rho y^2}{(c_{13}+c_{44})k\beta_2}\left(\frac{B_{21}(kiy)}{\beta_1+\beta_2} + \frac{B_{22}(kiy)}{2\beta_2}\right)\right].\end{aligned} \tag{3.46}$$

In obtaining this expression we have defined $\beta_1, \beta_2, \beta_t$ as $\alpha_1(kiy)$, $\alpha_2(kiy)$, and $\alpha_t(kiy)$, respectively, subject to the restrictions $\mathrm{Re}\beta_1 > 0$, $\mathrm{Im}\beta_i < 0$, where $i = 1, 2, t$. We have also used the fact that the integrand in Eq. (3.45) is a function of $\vec{k}$ only through its magnitude to carry out the angular integration, which merely yields a factor of 2π. Finally, in evaluating the remaining integral over k in Eq. (3.46), we have cut off the integral at an upper limit $k = k_c$, where k_c is of the order of the reciprocal of a lattice spacing. Such a cutoff arises naturally in a lattice theory, where the allowed values of the wave vector are restricted to lie inside the two-dimensional first Brillouin zone for the semi-infinite crystal, but it must be imposed explicitly in a continuum theory. We will find in Sec. IV. that $\Omega(y)$ has a logarithmic dependence on k_c, in the limit as $|y| \to 0$, so that a precise value of k_c is not needed for our purposes.

We now turn to the determination of the small $|y|$ behavior of $\Omega(y)$, which in view of Eqs. (2.15) and (2.16) is all that is required to obtain the surface contribution to the low-temperature specific heat of our semi-infinite hexagonal elastic medium.

IV. LOCALIZED MODES AND SURFACE SPECIFIC HEAT

The frequency of vibrations localized near the surface can be obtained from the equation

$$D(k\omega)=0, \tag{4.1}$$

when one notes that its satisfaction introduces a new pole in the surface Green's functions.

Using the preceding results for the matrix $\tilde{M}$ [Eqs. (3.31)], and defining

$$\gamma_1^2(k\omega)=\frac{\rho\omega^2-c_{11}k^2}{c_{44}}, \quad \gamma_4^2(k\omega)=\frac{\rho\omega^2-c_{44}k^2}{c_{33}}, \tag{4.2}$$

the determinant $D(k\omega)$ can be expressed as

$$D(k\omega)=\frac{\alpha_1-\alpha_2}{\alpha_1\alpha_2}\frac{1}{k}\frac{1}{c_{13}(c_{13}+c_{44})} \times[-(c_{13}^2k^2+c_{33}c_{44}\gamma_1^2)\gamma_1\gamma_4+c_{44}(c_{33}\gamma_4^2+c_{44}k^2)\gamma_1^2]. \tag{4.3}$$

Defining the speed of localized elastic waves, c_R, by

$$\omega=c_Rk, \tag{4.4}$$

and combining Eqs. (4.1) and (4.3), one finds as the equation for c_R

$$c_{33}\left(c_R^2-\frac{c_{44}}{\rho}\right)\left(c_R^2-\frac{c_{11}}{\rho}+\frac{c_{13}^2}{c_{33}\rho}\right)^2=c_{44}c_R^4\left(c_R^2-\frac{c_{11}}{\rho}\right), \tag{4.5}$$

which is an equation of third degree in c_R^2. The positive and real root of this equation gives the speed of Rayleigh waves on the isotropic surface of an hexagonal crystal (c_R has to be smaller than the speed of bulk waves).

It is interesting to check that in the limit of an isotropic crystal, namely, when

$$c_{13}=c_{12}, \quad c_{33}=c_{11}, \quad c_{44}=\tfrac{1}{2}(c_{11}-c_{12}), \tag{4.6}$$

the result (4.5) reduced to the well-known equation for the speed of Rayleigh waves[16]

$$(2-c_R^2/c_t^2)^4-16(1-c_R^2/c_l^2)(1-c_R^2/c_t^2)=0, \tag{4.7}$$

where the speeds of bulk longitudinal and transverse waves are given, respectively, by

$$c_l^2=c_{11}/\rho, \quad c_t^2=c_{44}/\rho. \tag{4.8}$$

Let us now come back to the calculation of the surface specific heat. Equation (3.46) for the function $\Omega(y)$ can be written compactly as

$$\Omega(y)=-\frac{S}{2\pi}\int_0^{k_c}dk\,k\left(-\frac{\rho}{4c_{44}\beta_t^2}+\frac{1}{D(kiy)}[\mathcal{A}(kiy)+\mathcal{B}(kiy)]\right), \tag{4.9}$$

with

$$\mathcal{A}(kiy)=\frac{A_{11}(kiy)}{2\beta_1}+\frac{A_{12}(kiy)+A_{21}(kiy)}{\beta_1+\beta_2}+\frac{A_{22}(kiy)}{2\beta_2}, \tag{4.10}$$

$$\mathcal{B}(kiy)=\frac{-ic_{44}}{(c_{13}+c_{44})k}\left[\frac{1}{\beta_1}(\beta_1^2+\delta_1^2)\left(\frac{B_{11}(kiy)}{2\beta_1}+\frac{B_{12}(kiy)}{\beta_1+\beta_2}\right)+\frac{1}{\beta_2}(\beta_2^2+\delta_1^2)\left(\frac{B_{21}(kiy)}{\beta_1+\beta_2}+\frac{B_{22}(kiy)}{2\beta_2}\right)\right], \tag{4.11}$$

where we have defined

$$\beta_t(kiy)=\left(\frac{c_{11}-c_{12}}{2c_{44}}k^2+\frac{\rho y^2}{c_{44}}\right)^{1/2}, \tag{4.12}$$

$$\beta_1(kiy)=\alpha_1(kiy), \tag{4.13}$$

$$\beta_2(kiy)=\alpha_2(kiy), \tag{4.14}$$

$$\delta_1^2(kiy)=(-1/c_{44})(\rho y^2+c_{11}k^2). \tag{4.15}$$

Let us also define

$$\delta_4^2(kiy)=(-1/c_{33})(\rho y^2+c_{44}k^2). \tag{4.16}$$

We note from Eqs. (4.13)–(4.16) that

$$\beta_1\beta_2=\delta_1\delta_4>0,$$

$$\beta_1^2+\beta_2^2=-\left(\delta_1^2+\delta_4^2+\frac{(c_{13}+c_{44})^2}{c_{33}c_{44}}k^2\right). \tag{4.17}$$

Making the replacement $\omega\to iy$ in Eq. (4.3), we obtain

$$D(kiy)=\frac{\beta_1-\beta_2}{\delta_1\delta_4}\frac{1}{k}\frac{1}{c_{13}(c_{13}+c_{44})}\times[-(c_{13}^2k^2+c_{33}c_{44}\delta_1^2)\delta_1\delta_4+c_{44}(c_{33}\delta_4^2+c_{44}k^2)\delta_1^2]. \tag{4.18}$$

It is convenient to rewrite the expression (4.10) in the following way. Let us rewrite it as

$$\mathcal{A}=[2\beta_1\beta_2(\beta_1+\beta_2)]^{-1}(\mathcal{A}_1+\mathcal{A}_2), \tag{4.19}$$

where, after use of Eqs. (3.29), $\mathcal{A}_1$ and $\mathcal{A}_2$ can be expressed as

$$\mathcal{A}_1=M_{22}[\beta_1\beta_2(C_{11}+2C_{12})+\beta_2^2C_{11}]-M_{21}[\beta_1\beta_2(C_{12}+2C_{11})+\beta_1^2C_{12}], \tag{4.20}$$

$$\mathfrak{A}_2 = M_{11}[\beta_1\beta_2(C_{22}+2C_{21})+\beta_1^2C_{22}] - M_{12}[\beta_1\beta_2(C_{21}+2C_{22})+\beta_2^2C_{21}]. \qquad (4.21)$$

For simplicity we have omitted indicating explicitly the dependence on k and y of the functions in these expressions. This way or rewriting the expression (4.10) is useful because it enables us to remove a common factor $(\beta_1-\beta_2)^2$ from $\mathfrak{A}_1$ and $\mathfrak{A}_2$. Thus, finally $\mathfrak{A}$ can be written

$$\mathfrak{A} = \frac{\beta_1-\beta_2}{(\beta_1+\beta_2)^2}\frac{\rho}{4(c_{13}+c_{44})}\frac{1}{k}\frac{1}{\delta_1^2\delta_4^2}\left\{\frac{c_{33}}{c_{13}}\delta_1\delta_4^2(\delta_1-\delta_4)^3 + k^2\delta_1\delta_4\left[\left(\frac{3c_{13}}{c_{44}}-2-\frac{2c_{44}}{c_{13}}\right)\delta_4^2+\frac{c_{44}}{c_{13}}\delta_1^2+3\left(2+\frac{c_{44}}{c_{13}}\right)\delta_1\delta_4-\frac{c_{13}}{c_{44}}\frac{\delta_4^3}{\delta_1}\right] - k^4\delta_1\delta_4\frac{(c_{13}+c_{44})^2}{c_{13}c_{33}}\left(1+\frac{c_{13}^2}{c_{44}^2}\frac{\delta_4}{\delta_1}\right)\right\}. \qquad (4.22)$$

For the same reason we write

$$\mathfrak{B} = \frac{-ic_{44}}{2(c_{13}+c_{44})}\frac{1}{k}\frac{1}{\beta_1^2\beta_2^2(\beta_1+\beta_2)}(\mathfrak{B}_1+\mathfrak{B}_2), \qquad (4.23)$$

with

$$\mathfrak{B}_1 = M_{22}\beta_2^2(\beta_1^2+\delta_1^2)[(\beta_1+\beta_2)C'_{11}+2\beta_1C'_{12}] - M_{21}\beta_1^2(\beta_2^2+\delta_1^2)[(\beta_1+\beta_2)C'_{12}+2\beta_2C'_{11}], \qquad (4.24)$$

$$\mathfrak{B}_2 = M_{11}\beta_1^2(\beta_2^2+\delta_1^2)[(\beta_1+\beta_2)C'_{22}+2\beta_2C'_{21}] - M_{12}\beta_2^2(\beta_1^2+\delta_1^2)[(\beta_1+\beta_2)C'_{21}+2\beta_1C'_{22}]. \qquad (4.25)$$

Thus $\mathfrak{B}$ finally can be written

$$\mathfrak{B} = \frac{\beta_1-\beta_2}{(\beta_1+\beta_2)^2}\frac{\rho}{4(c_{13}+c_{44})}\frac{1}{k}\frac{1}{\delta_1^2\delta_4^2}\left\{\frac{c_{44}}{c_{13}}\delta_1^3(\delta_1-\delta_4)^3 + k^2\delta_1^2\left[\left(2\frac{c_{13}}{c_{33}}+\frac{2c_{44}}{c_{33}}-\frac{3c_{44}^2}{c_{13}c_{33}}\right)\delta_1^2-3\left(\frac{2c_{44}}{c_{33}}+\frac{c_{13}}{c_{33}}\right)\delta_1\delta_4 - \frac{c_{13}}{c_{33}}\delta_4^2+\frac{c_{44}^2}{c_{13}c_{33}}\frac{\delta_1^3}{\delta_4}\right] + k^4\delta_1^2\frac{(c_{13}+c_{44})^2}{c_{33}^2}\left(\frac{c_{13}}{c_{44}}+\frac{c_{44}}{c_{13}}\frac{\delta_1}{\delta_4}\right)\right\}. \qquad (4.26)$$

It is convenient to make the change of variable

$$k = |y|(u/c), \qquad (4.27)$$

where c is an arbitrary constant with the dimensions of a speed of sound, in Eqs. (4.9), (4.22), and (4.26). Equation (4.9) thereupon takes the form

$$\Omega(y) = -\frac{S}{2\pi}\int_0^{ck_c/|y|} du\, uF(u), \qquad (4.28)$$

where the expression for $F(u)$ can be deduced from Eqs. (4.9), (4.22), and (4.26). If it were necessary to evaluate this integral exactly, the determination of $\Omega(y)$ would be a difficult problem indeed. Fortunately this is not the case. We require only the dominant term in $\Omega(y)$ in the limit as $|y|\to 0$. From Eq. (4.28) we see that $|y|$ appears only in the upper limit of the integral. This means that the small $|y|$ behavior of $\Omega(y)$ is determined by the behavior of $uF(u)$ for large u. This is most easily seen by breaking up the range of integration $(0, ck_c/|y|)$ into two intervals $(0,t)$ and $(t, ck_c/|y|)$, where t is independent of $|y|$ and large enough that an expansion of $F(u)$ in powers of $1/u^2$ is valid. Thus t should be greater than unity. The only y-dependent contribution to $\Omega(y)$ comes from the upper limit of the integral over the interval $(t, ck_c/|y|)$, and the dominant contribution as $|y|\to 0$ arises from the leading term in the expansion of $F(u)$ in powers of $1/u^2$ for large u. It is straightforward to obtain from Eqs. (4.15)–(4.17) that for large values of u

$$\delta_1^2 = -\frac{c_{11}}{c_{44}}\left(\frac{yu}{c}\right)^2 + O(u^4), \qquad (4.29)$$

$$\delta_4^2 = -\frac{c_{44}}{c_{33}}\left(\frac{yu}{c}\right)^2 + O(u^4), \qquad (4.30)$$

$$\delta_1\delta_4 = +\left(\frac{c_{11}}{c_{33}}\right)^{1/2}\left(\frac{yu}{c}\right)^2 + O(u^4), \qquad (4.31)$$

$$\beta_1^2+\beta_2^2 = \left(\frac{c_{11}}{c_{44}}-\frac{c_{13}^2}{c_{33}c_{44}}-2\frac{c_{13}}{c_{33}}\right)\left(\frac{yu}{c}\right)^2 + O(u^4). \qquad (4.32)$$

With the help of the above expansions and Eqs. (4.9), (4.22), and (4.26) one obtains

$$u^2F(u) = \frac{-\rho}{2(c_{11}-c_{12})} - \frac{\rho}{4(c_{13}-c_{11}c_{33}/c_{13})}\frac{R-P}{\Delta} + O(1/u^2), \qquad (4.33)$$

with

$$R=4\left(\frac{c_{33}}{c_{11}}\right)^{1/2}\left[\frac{c_{13}}{c_{33}}+\frac{c_{11}}{c_{13}}-2\frac{c_{11}}{c_{33}}+\frac{c_{11}}{c_{44}}\left(\frac{c_{11}}{c_{13}}-\frac{c_{13}}{c_{33}}\right)\right], \tag{4.34}$$

$$P=6\left(1-\frac{c_{11}}{c_{13}}\right)-2\frac{c_{13}}{c_{33}}-\frac{c_{11}}{c_{44}}\frac{c_{33}}{c_{13}}\left(1+\frac{c_{11}}{c_{44}}\right)+2\left(1+\frac{c_{13}}{c_{44}}\right)\left[\frac{c_{11}}{c_{44}}+\frac{c_{13}}{c_{33}}\left(\frac{c_{13}}{c_{11}}-\frac{c_{13}}{c_{44}}\right)\right], \tag{4.35}$$

$$\Delta=2\left(\frac{c_{11}}{c_{33}}\right)^{1/2}+\frac{c_{11}}{c_{44}}-\frac{c_{13}}{c_{33}}\left(2+\frac{c_{13}}{c_{44}}\right). \tag{4.36}$$

It follows, therefore, that the dominant term in the small $|y|$ expansion of $\Omega(y)$ is given by

$$\Omega(y)=-\frac{S}{2\pi}\left(\frac{\rho}{2(c_{11}-c_{12})}+\frac{\rho}{4(c_{13}-c_{11}c_{33}/c_{13})}\frac{R-P}{\Delta}\right)\times\ln|y|+o(\ln|y|). \tag{4.37}$$

Comparing Eqs. (2.15) and (4.37) and using Eqs. (2.16), we finally obtain as the surface contribution to the low-temperature specific heat of an hexagonal crystal

$$\Delta C_v(T)=6\pi\frac{k_B^3}{\hbar^2}\zeta(3)\left(\frac{\rho}{c_{11}-c_{12}}+\frac{\rho}{2(c_{13}-c_{11}c_{33}/c_{13})}\frac{R-P}{\Delta}\right)ST^2+o(T^2), \tag{4.38}$$

where R, P, and Δ are given by Eqs. (4.34)–(4.36).

When we specialize this result to the case of an isotropic crystal with the aid of Eqs. (4.6) and Eq. (4.8), we obtain

$$\Delta\tilde{C}_v(T)=3\pi\frac{k_B^3}{\hbar^2}\zeta(3)\frac{2c_t^4-3c_t^2c_l^2+3c_l^4}{c_t^2c_l^2(c_l^2-c_t^2)}ST^2+o(T^2), \tag{4.39}$$

a result which was obtained earlier directly for an isotropic crystal.[3-5,10]

This T^2 law is the analog for the surface specific heat of the "Debye T^3 law" for the low-temperature limit of the specific heat of a three-dimensional crystal. It is given here for the first time for a hexagonal crystal bounded by a stress-free planar surface normal to its sixfold rotation axis. Our result is the analog for hexagonal media of the now classic result (4.39) of Dupuis *et al.*[4] for an isotropic medium. Just as the Debye T^3 law for three-dimensional crystals can be shown to hold only for temperatures below about $0.01\Theta_D$, where Θ_D is the Debye characteristic temperature of the crystal,[17] the same kind of argument shows that one expects the T^2 law for the surface specific heat to hold only for temperatures below about $0.015\Theta_D$. This estimate presupposes that the elastic approximation to the change in the frequency distribution function of an infinitely extended crystal owing to the creation of stress-free surfaces on it coincides with the exact result for frequencies as high as $\frac{1}{10}$ the highest normal-mode frequency of the crystal, and is thus likely to be an upper bound to the temperature range for which the T^2 law obtains.

The principal significance of our result [Eq. (4.38)], is that it is exact, applies to a nontrivial physical situation, and is given by an explicit analytic expression, something that purely numerical calculations are incapable of yielding.

ACKOWLEDGMENTS

One of us (L. D.) would like to thank Professor G. Somorjai (University of California, Berkeley) and Professor A. A. Maradudin, Professor R. F. Wallis, and Professor D. L. Mills (University of California, Irvine) for their hospitality. He benefited also from a NATO travel grant.

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†Research supported in part by AFOSR Grant No. 76-2887. Technical Report No. 75-32.

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