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Vibrational contribution to the low-temperature specific heat of the interface between two different crystals

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We derive for the first time the vibrational contribution to the interface specific heat at low temperatures. The interface is a planar one between two isotropic crystals. Our result is obtained in closed form in the frame of the theory of elasticity.

I. INTRODUCTION

The surface contribution to the specific heat of a crystal has received a great deal of theoretical and experimental interest.[1-5] Dupuis, Mazo, Onsager,[2] and Stratton[3] were the first to give an exact result for the low-temperature surface specific heat of an isotropic elastic continuum. Maradudin and Wallis[4] obtained also this result for the first time from a simple atomic model. Other studies were done, some qualitative only, others on realistic models; some giving exact results in closed form at low temperatures, other using purely numerical approaches.[1] Among the quantitative analytic results valid at low temperatures, only one was obtained for a nonisotropic crystal, namely for an hexagonal crystal.[5]

The interface properties between two crystals are also widely studied.[6] The localized waves which can exist and propagate along a crystalline interface are known as Stonely waves.[7] However to our knowledge the interface specific heat has not been studied, neither theoretically nor experimentally. From the experimental point of view, the measure of the interface specific heat should be possible on a lamellar crystal formed by alternative superpositions of two distinct crystals, or even on a thin powder of one crystal embedded in another. On such samples it should be possible to obtain a non-negligible ratio between the number of interface and bulk atoms. Our hope is that the theoretical result given here will stimulate some experimental work.

We obtain our result by using the method (Sec. II) introduced by Maradudin and Wallis[4] for the calculation of the surface specific heat at low temperatures, but in the present work we calculate the necessary interface Green's function (Sec. III). The knowledge of this interface Green's function enables us to obtain in analytic form the interface specific heat at low temperatures (Sec. IV). The present study is done for two isotropic elastic media.

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

We consider two different elastic media occupying, respectively, the half spaces $x_3>0$ and $x_3<0$. We need to know the Green's function $\overleftrightarrow{U}$ for the two crystals connected by this planar interface. The procedure is similar to the one given[5,8] for the surface. Let us first introduce the bulk Green's function for the crystal at $x_3>0$:

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

where ρ is the mass density, the $C_{\alpha\beta\mu\nu}$ are the position-independent elastic moduli of the material; $\vec{x}(x_1,x_2,x_3)$ the position of a point in the medium, ω the frequency of the time-dependent elastic displacement field in the medium, and α, β, μ, ν the Cartesian indices x, y, or z.

The bulk equation for the other crystal at $x_3<0$ is obtained from the one above by changing ρ and $C_{\alpha\beta\mu\nu}$, respectively, to ρ' and $C'_{\alpha\beta\mu\nu}$:

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

In order to obtain the Green's function $\overleftrightarrow{U}$ for the two crystals connected by a planar interface, we have to solve Eqs. (1) and (1′) subject to the boundary conditions at $x_3=0$:

$$\sum_{\mu\nu} C_{\alpha z\mu\nu} \frac{\partial}{\partial x_\nu} U_{\mu\beta}(\vec{x},\vec{x}\,';\omega)\Big|_{x_3=+0} = \sum_{\mu\nu} C'_{\alpha z\mu\nu} \frac{\partial}{\partial x_\nu} U_{\mu\beta}(\vec{x},\vec{x}\,';\omega)\Big|_{x_3=-0} \tag{2}$$

$$U_{\alpha\beta}(\vec{x},\vec{x}\,')\big|_{x_3=+0} = U_{\alpha\beta}(\vec{x},\vec{x}\,')\big|_{x_3=-0}\,. \tag{2'}$$

The condition (2) comes from the continuity of the stresses across the interface and the condition (2′) from the continuity of the displacements.[7]

Our interest here in the Green's function $\overleftrightarrow{U}$ derives from the following considerations. If we denote by $\overleftrightarrow{U}^{(0)}$ the corresponding bulk Green's function for our two crystals which are the solutions of Eqs. (1) and (1′), respectively, for $x_3 > 0$ and $x_3 < 0$, we can construct a function $\Omega(y)$ according to

$$\Omega(y) = -\sum_\alpha \int dx_1\, dx_2 \int_{-\infty}^{+\infty} dx_3\, [U_{\alpha\alpha}(\vec{x},\vec{x};iy) - U^{(0)}_{\alpha\alpha}(\vec{x},\vec{x};iy)]\,. \tag{3}$$

Maradudin and Wallis[4] introduced such a function in order to calculate the surface contribution to the specific heat of a crystal. We extend their approach to the case of a bicrystal interface. It can be shown in the manner they did[4] 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

$$\Omega(y) \sim -AS \ln|y| + o(\ln|y|), \quad |y| \to 0\,, \tag{4}$$

the interface contribution to the specific heat of the two crystals is given by

$$\Delta C_v(T) = 6AS\,\zeta(3) k_B (k_B T/\hbar)^2 + o(T^2) \tag{5}$$

in the limit of $T \to 0$, where $\zeta(x)$ is the Riemann zeta function, k_B is Boltzmann's constant, and S the interface area.

The problem of calculating the interface contribution to the specific heat of the two crystals is therefore reduced to showing that the function $\Omega(y)$ has the asymptotic form given by Eq. (4) in the limit as $|y| \to 0$, and of determining the coefficient A.

We will show in the following section that it is possible to obtain $\overleftrightarrow{U}$ (and $\overleftrightarrow{U}^{(0)}$) in closed form for isotropic media by solving the partial differential equations (1) and (2) directly. With this result in hand the determination of the interface contribution to the low-temperature specific heat of such media is straightforward, and is carried out in Sec. IV.

III. TRACE OF THE GREEN'S FUNCTION FOR A BICRYSTAL

Thanks to the symmetry of translation parallel to the interface, the Green's function $\overleftrightarrow{U}$ can be Fourier analyzed in the following manner:

$$U_{\alpha\beta}(\vec{x},\vec{x}\,';\omega) = \int \frac{d^2k}{(2\pi)^2}\, e^{i\vec{k}\cdot(\vec{x}_\parallel - \vec{x}\,'_\parallel)}\, g_{\alpha\beta}(\vec{k}\omega\,|x_3 x_3')\,, \tag{6}$$

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. We then use the isotropy of the medium in the plane $x_3 = 0$ and carry out a similarity transformation of our set of equations with respect to a matrix $\overleftrightarrow{S}(\vec{k})$ which rotates the vector $\vec{k}$ into the vector $(k, 0, 0)$. This has as a consequence that the transformed matrix $\overleftrightarrow{d}$ now has the following properties:

$$d_{y\alpha} = d_{\alpha y} = 0 \quad \text{for } \alpha = x \text{ or } z\,, \tag{7}$$

and the calculation of d_{yy} is decoupled from that giving, respectively, d_{xx}, d_{zx} and d_{zz}, d_{xz}. We use this procedure to obtain in closed form the coefficients $d_{\alpha\beta}(k\omega\,|x_3 x_3')$ for the two isotropic elastic media bounded by the plane $x_3 = 0$.

The full derivation of this matrix $\overleftrightarrow{d}$ is given elsewhere,[9] where we use the coefficients $d_{\alpha\beta}(k\omega\,|x_3 x_3')$ to study the correlations functions between two crystal atoms situated in the vicinity of the interface. In the calculation of the interface specific heat we need only to know [Eq. (3)] the trace of $\overleftrightarrow{d} - \overleftrightarrow{d}^{(0)}$, where $\overleftrightarrow{d}^{(0)}$ are the bulk values of $\overleftrightarrow{d}$. Before giving the necessary expressions let us recall that the only nonzero elastic constants for our two isotropic solids are, respectively, c_{11}, c_{12}, c_{44} and c'_{11}, c'_{12}, c'_{44}; the isotropy relations being $2c_{44} = c_{11} - c_{12}$ and $2c'_{44} = c'_{11} - c'_{12}$. Let us also introduce the transverse and longitudinal speeds of sound:

$$\begin{aligned} c_t &= (c_{44}/\rho)^{1/2}; \quad c_l = (c_{11}/\rho)^{1/2}; \\ c_{t'} &= (c'_{44}/\rho')^{1/2}; \quad c_{l'} = (c'_{11}/\rho')^{1/2} \end{aligned} \tag{8}$$

and

$$\begin{aligned} \alpha_t^2 &= k^2 - \omega^2/c_t^2\,; \quad \alpha_l^2 = k^2 - \omega^2/c_l^2\,; \\ \alpha_{t'}^2 &= k^2 - \omega^2/c_{t'}^2; \quad \alpha_{l'}^2 = k^2 - \omega^2/c_{l'}^2\,. \end{aligned} \tag{9}$$

Finally for the two isotropic crystals separated by plane $x_3 = 0$, the solutions[9] of interest here for $x_3 \geqslant 0$ are

$$d_{yy}(x_3 x_3) - d^{(0)}_{yy}(x_3 x_3) = \frac{\rho}{2\alpha_t c_{44}}\, \frac{\alpha_{t'} c'_{44} - \alpha_t c_{44}}{\alpha_{t'} c'_{44} + \alpha_t c_{44}}\, e^{-2\alpha_t |x_3|}\,, \tag{10}$$

$$d_{xx}(x_3x_3) - d_{xx}^{(0)}(x_3x_3) = \frac{1}{|\overleftrightarrow{\mathrm{H}}_A|} \sum_{i=t,l} \sum_{j=t,l,t',l'} |\overleftrightarrow{\mathrm{A}}_{ij}| e^{-(\alpha_i+\alpha_j)|x_3|} , \tag{11}$$

$$d_{zz}(x_3x_3) - d_{zz}^{(0)}(x_3x_3) = \frac{1}{|\overleftrightarrow{\mathrm{H}}_B|} \sum_{i=t,l} \sum_{j=t,l,t',l'} |\overleftrightarrow{\mathrm{B}}_{ij}| e^{-(\alpha_i+\alpha_j)|x_3|} , \tag{12}$$

where

$$\overleftrightarrow{\mathrm{H}}_A = \begin{bmatrix} -(c_{44}/\alpha_t)(k^2+\alpha_t{}^2) & -2c_{44}\alpha_l & -(c'_{44}/\alpha_{t'})(\alpha_{t'}^2+k^2) & -2c'_{44}\alpha_{l'} \\ -2ic_{44}k & -i(c_{44}/k)(\alpha_t^2+k^2) & 2ic'_{44}k & i(c'_{44}/k)(\alpha_{t'}^2+k^2) \\ 1 & 1 & -1 & -1 \\ ik/\alpha_t & i\alpha_l/k & ik/\alpha_{t'} & i\alpha_{l'}/k \end{bmatrix} , \tag{13}$$

$$\overleftrightarrow{\mathrm{H}}_B = \begin{bmatrix} (ic_{44}/k)(\alpha_t^2+k^2) & 2ikc_{44} & -(ic'_{44}/k)(\alpha_{t'}^2+k^2) & -2ic'_{44}k \\ -2c_{44}\alpha_t & -(c_{44}/\alpha_l)(k^2+\alpha_t^2) & -2c'_{44}\alpha_{t'} & (c'_{44}/\alpha_{l'})(k^2+\alpha_{t'}^2) \\ -i\alpha_t/k & -ik/\alpha_l & -i\alpha_{t'}/k & -ik/\alpha_{l'} \\ 1 & 1 & -1 & -1 \end{bmatrix} . \tag{14}$$

The matrices $\overleftrightarrow{\mathrm{A}}_{ij}$ are obtained by substituting the column i in $\overleftrightarrow{\mathrm{H}}_A$ by the column j of the matrix $\overleftrightarrow{\mathrm{K}}_A$ [the columns (or rows) 1 to 4 of each matrix stand, respectively, for t, l, t', l']:

$$\overleftrightarrow{\mathrm{K}}_A = \begin{bmatrix} -c_{44}\frac{k^2+\alpha_t^2}{2\omega^2}\operatorname{sgn}x_3 & c_{44}\frac{k^2}{\omega^2}\operatorname{sgn}x_3 & c'_{44}\frac{k^2+\alpha_{t'}^2}{2\omega^2}\operatorname{sgn}x_3 & -c'_{44}\frac{k^2}{\omega^2}\operatorname{sgn}x_3 \\ ic_{44}\frac{k\alpha_t}{\omega^2} & -ic_{44}\frac{k}{2\alpha_l}\frac{k^2+\alpha_t^2}{\omega^2} & -ic'_{44}\frac{k\alpha_{t'}}{\omega^2} & ic'_{44}\frac{k}{2\alpha_{l'}}\frac{k^2+\alpha_{t'}^2}{\omega^2} \\ -\frac{\alpha_t}{2\omega^2} & \frac{k^2}{2\alpha_l\omega^2} & \frac{\alpha_{t'}}{2\omega^2} & -\frac{k^2}{2\alpha_{l'}\omega^2} \\ \frac{ik}{2\omega^2}\operatorname{sgn}x_3 & -\frac{ik}{2\omega^2}\operatorname{sgn}x_3 & -\frac{ik}{2\omega^2}\operatorname{sgn}x_3 & \frac{ik}{2\omega^2}\operatorname{sgn}x_3 \end{bmatrix} . \tag{15}$$

Similarly the matrices $\overleftrightarrow{\mathrm{B}}_{ij}$ are obtained by substituting the column i of $\overleftrightarrow{\mathrm{H}}_B$ by the column j of the matrix $\overleftrightarrow{\mathrm{K}}_B$:

$$\overleftrightarrow{\mathrm{K}}_B = \begin{bmatrix} ic_{44}\frac{k}{2\alpha_t}\frac{k^2+\alpha_t^2}{\omega^2} & -ic_{44}\frac{k\alpha_l}{\omega^2} & -ic'_{44}\frac{k}{2\alpha_{t'}}\frac{k^2+\alpha_{t'}^2}{\omega^2} & ic'_{44}\frac{k\alpha_{l'}}{\omega^2} \\ c_{44}\frac{k^2}{\omega^2}\operatorname{sgn}x_3 & -c_{44}\frac{k^2+\alpha_t^2}{2\omega^2}\operatorname{sgn}x_3 & -c'_{44}\frac{k^2}{\omega^2}\operatorname{sgn}x_3 & c'_{44}\frac{k^2+\alpha_{t'}^2}{2\omega^2}\operatorname{sgn}x_3 \\ \frac{ik}{2\omega^2}\operatorname{sgn}x_3 & -\frac{ik}{2\omega^2}\operatorname{sgn}x_3 & -\frac{ik}{2\omega^2}\operatorname{sgn}x_3 & \frac{ik}{2\omega^2}\operatorname{sgn}x_3 \\ \frac{k^2}{2\alpha_t\omega^2} & -\frac{\alpha_l}{2\omega^2} & -\frac{k^2}{2\alpha_{t'}\omega^2} & \frac{\alpha_{l'}}{2\omega^2} \end{bmatrix} . \tag{16}$$

The bulk values of $\overleftrightarrow{\mathrm{d}}$ for $x_3 > 0$ are those given by Maradudin and Mills[8]:

$$d_{yy}^{(0)}(x_3x_3) = -1/2\alpha_t c_t^2 , \tag{17}$$

$$d_{xx}^{(0)}(x_3x_3) = -(k^2/2\alpha_l\omega^2)(1-\alpha_t\alpha_l/k^2) , \tag{18}$$

$$d_{zz}^{(0)}(x_3x_3) = -(k^2/2\alpha_t\omega^2)(1-\alpha_t\alpha_l/k^2) . \tag{19}$$

For $x_3 \leqslant 0$, the trace of $\overleftrightarrow{\mathrm{d}} - \overleftrightarrow{\mathrm{d}}^{(0)}$ can be obtained from Eqs. (10)–(16) by interchanging $c_{11}, c_{12}, c_{44}, c_t, c_l, \alpha_t, \alpha_l$ by, respectively, $c'_{11}, c'_{12}, c'_{44}, c_{t'}, c_{l'}, \alpha_{t'}, \alpha_{l'}$ and taking due account of the $\operatorname{sgn}x_3$ appearing in $\overleftrightarrow{\mathrm{K}}_A$ and $\overleftrightarrow{\mathrm{K}}_B$. The bulk Green's function $d^{(0)}$ for $x_3 < 0$, are obtained in the same way from Eqs. (17)–(19).

Let us note that from the relation

$$|\overleftrightarrow{\mathrm{H}}_B| = (\alpha_t \alpha_{t'}/\alpha_l \alpha_{l'})\,|\overleftrightarrow{\mathrm{H}}_A| = 0 \tag{20}$$

one obtains the Stonely[7] waves and their conditions of existence.[10]

IV. INTERFACE SPECIFIC HEAT

Let us now return to the calculation of the interface specific heat. Following the method introduced by Maradudin and Wallis,[4] we can write the interface specific heat in the form given by Eq. (5). The coefficient A appearing in Eq. (5) has to be calculated from the asymptotic evaluation of the function $\Omega(y)$ defined by Eq. (4). With the help of Eq. (6), this expression becomes

$$\Omega(y) = -S\sum_{\alpha}\int_{-\infty}^{+\infty} dx_3 \int \frac{d^2k}{(2\pi)^2}\,[d_{\alpha\alpha}(kiy\,|\,x_3x_3) - d^{(0)}_{\alpha\alpha}(kiy\,|\,x_3x_3)]\,, \tag{21}$$

where S is the interface area.

Substituting the Green's functions (10)–(12) the integration over x_3 in Eq. (21) can be carried out directly. Since the integrand in Eq. (21) is a function of the magnitude of k, it is convenient to carry out the integration on d^2k in polar coordinates. It is also convenient to make the change of variable $k = |y|u/c_t$. This integration thereupon[4,5] can be expressed as

$$\Omega(y) = -\frac{S}{2\pi c_t^2}\int_0^{c_t k_c/|y|} du\, uF(u)\,, \tag{22}$$

where k_c is a cutoff immaterial for our pruposes here. We need only the leading term in the expansion of $F(u)$ in powers of $1/u^2$ for large u. And finally $\Omega(y)$ can be obtained in the following form:

$$\Omega(y) = -As\ln|y| + o(\ln|y|), \quad |y| \to 0\,.$$

We obtain in this manner the coefficient A appearing in Eq. (5). Before giving the result of this calculation, let us introduce the following notations:

$$\begin{aligned}&\nu = c_t^2/c_l^2\,; \quad \nu' = c_{t'}^2/c_{l'}^2\,;\\ &\delta = c_t^2/c_{t'}^2\,; \quad \gamma = c'_{44}/c_{44}\,.\end{aligned} \tag{23}$$

Finally the interface specific heat between two different isotropic crystals is given by

$$\Delta C_v(T) = 3\pi\,\frac{k_B^3}{h^2}\,\frac{\zeta(3)}{c_t^2} \times\left(\frac{-(1-\delta)(\gamma-1)}{\gamma+1} + \frac{2R}{\Delta}\right)ST^2 + o(T^2)\,, \tag{24}$$

with

$$\begin{aligned}R = {} & \gamma^2[-(1+\nu^2)(1-\nu') + \delta(1+\nu)(\nu'^2-\nu'+1)]\\ & -\gamma[\nu'(2\nu^2-\nu+1) + \delta\nu(2\nu'^2-\nu'+1)]\\ & +[(1+\nu')(\nu^2-\nu+1) - \delta(1+\nu'^2)(1-\nu)]\end{aligned} \tag{25}$$

and

$$\Delta = \gamma^2(1+\nu)(1-\nu') + 2\gamma(1+\nu\nu') + (1+\nu')(1-\nu)\,. \tag{26}$$

We have obtained also the low-temperature interface specific heat by a different method on a well defined atomic model[11] for which $c_l^2 = 3c_t^2$ and $c_{l'}^2 = 3c_{t'}^2$. In this limit the two results agree.

One can check also that in the limit of two identical crystals, the T^2 term in Eq. (20) vanishes. This is consistent with the result obtained recently[11] that the leading term in the low-temperature variation of C_v due to a planar defect is of the order of T^3. This result can be obtained only[11] when the frequencies ω are calculated to order k^2 rather than k as done here and in general in the theory of elasticity.

Let us note that we defined the interface specific heat ΔC_v as the difference between the specific heat of two different solids bounded by a planar interface and the specific heat of the same two solids but infinite in extent. One can also define the adhesion specific heat $\Delta C_v^{(a)}$ as the difference in the specific heat between two semi-infinite solids and the same two solids bounded by an interface. These two quantities are obviously related by

$$\Delta C_v^{(a)} = \Delta C_v^{(s)} + \Delta C_v^{(s')} - \Delta C_v\,, \tag{27}$$

where $\Delta C_v^{(s)}$ and $\Delta C_v^{(s')}$ are the surface specific heats of each crystal given by

$$\Delta C_v^{(s)} = 3\pi\,\frac{k_B^3}{h^2}\,\zeta(3)\,\frac{3-3\nu+2\nu^2}{c_t^2(1-\nu)}\,ST^2 + o(T^2)\,, \tag{28}$$

and $\Delta C_v^{(s')}$ is obtained from $\Delta C_v^{(s)}$ by replacing c_t by $c_{t'}$ and ν by ν'.

Let us remark also that this study can be extended to the case of two hexagonal crystals bounded by a planar interface parallel to their basal plane. In particular the interface waves between two hexagonal crystals and their conditions of existence can be obtained in this way. This work is being carried out at present.[12]

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