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Green's-tensor approach in the theory of the surface or interface vibrational contribution to thermodynamic properties of solids

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We present a theory of the surface or interface contribution to vibrational thermodynamic properties of solids. We express the thermodynamic quantities such as the free energy and specific heat in terms of the surface or interface density of vibrational states. We derive a simple analytic expression for this function in terms of a static Green's tensor of the system. We redefine the dynamical Green's tensor compared with some earlier works, requiring that it correspond to a Hermitian differential operator. In order to calculate the free energy, we modify the Debye model to apply it to surface or interface problems. The free energy and specific heat are calculated for the cases of an isotropic solid bounded by a stress-free planar surface and two isotropic solids separated by a flat interface. [S0163-1829(96)04619-X]

I. INTRODUCTION

The thermodynamics of solid surfaces and interfaces has been a subject of theoretical study since the early 1960s. Extensive investigations have been carried out of the problem of obtaining the surface contribution to the low-temperature specific heat of a solid. Dupius, Mazo, and Onsager[1] showed that for an elastically isotropic medium this quantity is proportional to ST^2, where S is the surface area and T is the absolute temperature, and has the form

$$\Delta C_v^{(S)}(T)=3\pi\zeta(3)\,\frac{k_B^3T^2S}{h^2c_s^2}. \tag{1}$$

Here c_l and c_t are the speeds of longitudinal and transverse bulk waves, respectively, $\zeta(z)$ is the Riemann zeta function, h is Planck's constant, k_B is Boltzmann's constant, and

$$c_s^2=\frac{c_l^2c_t^2(c_l^2-c_t^2)}{3c_l^4-3c_l^2c_t^2+2c_t^4}. \tag{2}$$

The result (1) was later confirmed by a number of independent derivations.[2–7] Further investigations yielded $\Delta C_v^{(S)}(T)$ for hexagonal[7,8] and cubic[9,10] crystals whose stress-free surfaces were basal planes of these solids. By the same techniques, $\Delta C_v^{(S)}(T)$ was obtained for different solid interface problems.[11–13]

The majority of the works cited above presented a direct calculation of $\Delta C_v^{(S)}(T)$ and did not consider other thermodynamic properties of solid surfaces and interfaces, such as the zero-point energy. It was noted in a recent work[14] that this quantity can be of interest, in particular, in understanding the phenomenon of the wetting transition on the surfaces of alkali metals.[15]

It is known that the vibrational contribution to the thermodynamic quantities describing a system can be expressed in terms of its density of vibrational states $G(\omega)$, which is defined by

$$G(\omega)=\sum_n \delta(\omega-\omega_n) \tag{3}$$

and is normalized to the total number of degrees of freedom of the system. Here the sum on n runs over all normal modes of the system and ω_n is the frequency of the nth normal mode. Velasco and Garcia-Moliner[6,7] derived this fundamental function for an isotropic solid bounded by a stress-free planar surface. Using this function, they constructed a surface analog of the bulk Debye model. The total number of degrees of freedom was required to be the same in the bounded system as it had been in the unbounded one, although these degrees of freedom were now distributed differently between the bulk and surface vibrations. This led to another Debye cutoff frequency ω_M, which differed from the bulk value ω_D. Finally, the knowledge of $G(\omega)$ and ω_M made it possible to obtain the surface contribution both to the zero-point energy and to the specific heat of an isotropic solid. Their result for the latter contribution agreed with Eq. (1). However, the authors of Refs. 6 and 7 did not extend the Debye model to cover the case of an interface between two solids. It will be apparent from the analysis that follows that this problem is more delicate than the surface case.

Finally, there is one more problem we would like to raise here. We note that $\Delta C_v^{(S)}(T)$ expressed in terms of the density of states in Refs. 6 and 7 is related to the dynamical Green's tensor for a semi-infinite isotropic elastic medium bounded by a planar stress-free surface. On the other hand, Maradudin, Wallis, and Eguiluz[5] showed that it is sufficient to know only the static limit of this tensor to obtain $\Delta C_v^{(S)}(T)$. This fact seems to be mysterious since $\Delta C_v^{(S)}(T)$, in turn, can be expressed uniquely in terms of the density of states. One can hypothesize intuitively that it is the static version of the Green's tensor that determines the surface or interface contribution to the surface density of states, which has not been proven yet.

In this work we present a straightforward analytic method of calculating the surface or interface contribution to the density of vibrational modes $G(\omega)$. We construct a surface or interface analog of the Debye model. Each medium involved in the problem will be characterized by its own density of states $G(\omega)$ and cutoff frequency ω_M. This model will enable us to obtain the surface or interface contribution to the Helmholtz free energy (including the zero-point energy) and the specific heat. We will show that the surface or interface contribution to $G(\omega)$ is completely determined by a static Green's tensor, whose calculation is much simpler than in the dynamical case, which is especially important for anisotropic media (see, e.g., Ref. 9). Finally, we will point out that the conventional definition of the dynamical Green's tensor in the interface problems[11,13] does not correspond to a Hermitian differential operator. The method we present here requires the Hermiticity of the problem. For this reason, the definition of the dynamical Green's tensor we use in the present work is different from the conventional one.

II. THE INTERFACE DENSITY OF VIBRATIONAL STATES

In order to calculate the density of vibrational states $G(\omega)$ for a system of two solids separated by a planar interface we use the elastic continuum theory. The function $G(\omega)$ calculated in the elastic continuum model determines the vibrational contribution to fundamental thermodynamic quantities of the system such as the Helmholtz free energy, including the zero-point energy, and specific heat. The results based on this approach were shown to agree with those obtained in lattice dynamical calculations in the harmonic approximation (see, e.g., the discussions in Refs. 5 and 16).

We consider two different isotropic elastic media 1 and 2 occupying the half spaces $x_3>0$ and $x_3<0$, respectively. Each medium is characterized by its mass density ρ_j and the speeds of longitudinal and transverse bulk waves $c_l^{(j)}$ and $c_t^{(j)}$, respectively. The elastic modulus tensors have the form $C^{(j)}_{\alpha\beta\mu\nu} = \rho_j(c_l^{(j)2}-2c_t^{(j)2})\delta_{\alpha\beta}\delta_{\mu\nu} + \rho_j c_t^{(j)2}(\delta_{\alpha\mu}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\mu})$, $j=1,2$. We begin with a quite formal derivation of the density of vibrational states. In order to calculate this quantity, we need to know the Green's tensor $D_{\alpha\beta}(\mathbf{x},\mathbf{x}'|\omega)$ for two solids in contact along the interface $x_3=0$. We define this tensor as a solution of the equations

$$\left[\rho_j\omega^2\delta_{\alpha\mu}+C^{(j)}_{\alpha\beta\mu\nu}\frac{\partial^2}{\partial x_\beta\partial x_\nu}\right]D_{\mu\gamma}(\mathbf{x},\mathbf{x}'|\omega)=\delta_{\alpha\gamma}\delta(\mathbf{x}-\mathbf{x}') \tag{4}$$

and the boundary conditions

$$D_{\mu\gamma}(\mathbf{x},\mathbf{x}'|\omega)|_{x_3\to0+}=D_{\mu\gamma}(\mathbf{x},\mathbf{x}'|\omega)|_{x_3\to0-}, \tag{5}$$

$$C^{(1)}_{\alpha3\mu\nu}\frac{\partial}{\partial x_\nu}D_{\mu\gamma}(\mathbf{x},\mathbf{x}'|\omega)|_{x_3\to0+} =C^{(2)}_{\alpha3\mu\nu}\frac{\partial}{\partial x_\nu}D_{\mu\gamma}(\mathbf{x},\mathbf{x}'|\omega)|_{x_3\to0-}, \tag{6}$$

which come from the continuity of the displacements and normal stresses across the interface. In addition, we require that $D_{\alpha\beta}(\mathbf{x},\mathbf{x}'|\omega)$ obey the outgoing or exponentially decaying wave conditions as $|x_3|\to\infty$. In Eq. (4) $j=1$ if $x_3>0$ and $j=2$ if $x_3<0$. The greek indices $\alpha,\beta,\ldots$ assume the values 1,2,3 and summation over repeated greek indices is implied throughout the paper.

The partial differential operator appearing on the left-hand side of Eq. (4) supplemented by the boundary conditions (5) and (6) can be shown to be Hermitian. Therefore, the infinite set of eigenfunctions $\{v_\alpha^{(n)}(\mathbf{x})\}$ of the homogeneous version of Eqs. (4)–(6) is complete and orthonormal with a weight $\rho(x_3)=\rho_1\theta(x_3)+\rho_2\theta(-x_3)$, where $\theta(x_3)$ is the Heaviside unit step function,

$$\sum_n v_\alpha^{(n)*}(\mathbf{x})v_\beta^{(n)}(\mathbf{x}')=\delta_{\alpha\beta}\delta(\mathbf{x}-\mathbf{x}'), \tag{7}$$

$$\int_S d^2x_\parallel\int_{-\infty}^{\infty}dx_3\rho(x_3)v_\alpha^{(n)*}(\mathbf{x})v_\alpha^{(n')}(\mathbf{x})=\delta_{nn'}. \tag{8}$$

Here $\mathbf{x}_\parallel=(x_1,x_2,0)$, S is the surface area, and the index $n=1,2,3,\ldots$ labels the eigenfunctions. Then the Green's tensor can be represented in the form

$$D_{\alpha\beta}(\mathbf{x},\mathbf{x}'|\omega)=\sum_n\frac{v_\alpha^{(n)}(\mathbf{x})v_\beta^{(n)*}(\mathbf{x}')}{\omega^2-\omega_n^2}=D^*_{\beta\alpha}(\mathbf{x},\mathbf{x}'|\omega). \tag{9}$$

We next change ω to $\omega-i\eta$ in Eq. (9), where η is a positive infinitesimal, then take the imaginary part of $D_{\alpha\alpha}(\mathbf{x},\mathbf{x}|\omega-i\eta)$, and integrate the result over all $\mathbf{x}$ with a weight $\rho(x_3)$. With the aid of Eq. (8) we obtain the density of states defined in Eq. (3) in the form

$$G(\omega)=\frac{2\omega}{\pi}\int_S d^2x_\parallel\int_{-\infty}^{\infty}dx_3\rho(x_3)\,\mathrm{Im}\,D_{\alpha\alpha}(\mathbf{x},\mathbf{x}|\omega-i\eta). \tag{10}$$

We note here that the definition of the Green's tensor we use differs from the conventional one[11,13] because the differential operator appearing in (4) is greater by a factor of ρ_j than the one in Refs. 11 and 13. However, the operator used in Refs. 11 and 13, together with the boundary conditions (5) and (6), is not Hermitian. As we have seen, the Hermiticity of the operator is essential in deriving the relation (10) between the density of states and the dynamical Green's tensor of the system. Nevertheless, we will show that the method we use here yields the same result for the specific heat as was obtained in Refs. 11 and 13. The point is that if we used the method of Refs. 11 and 13, $\mathrm{Im}\,D_{\alpha\alpha}$ would appear in Eq. (10) without the factor $\rho(x_3)$. However, $D_{\alpha\alpha}$ of Refs. 11 and 13 coincides with $\rho(x_3)D_{\alpha\alpha}$ in our notation, which explains the agreement between the results of the two approaches.

Because the system possesses infinitesimal translational invariance in directions parallel to the interface, it is convenient to introduce the Fourier coefficients $d_{\alpha\beta}(\mathbf{k}_\parallel,\omega|x_3,x_3')$ of the Green's tensor according to

$$D_{\alpha\beta}(\mathbf{x},\mathbf{x}'|\omega)=\int\frac{d^2k_\parallel}{(2\pi)^2}e^{i\mathbf{k}_\parallel\cdot(\mathbf{x}_\parallel-\mathbf{x}_\parallel')}d_{\alpha\beta}(\mathbf{k}_\parallel,\omega|x_3,x_3'), \tag{11}$$

where $\mathbf{k}_\parallel=(k_1,k_2,0)$. Furthermore, the rotational invariance in the plane $x_3=0$ allows one to introduce Green's functions that do not depend on the direction of $\mathbf{k}_\parallel$,[17]

$$g_{\alpha\beta}(k_\parallel,\omega|x_3,x_3')=S_{\alpha\mu}(\hat{\mathbf{k}}_\parallel)d_{\mu\nu}(\mathbf{k}_\parallel,\omega|x_3,x_3')S^{-1}_{\nu\beta}(\hat{\mathbf{k}}_\parallel), \tag{12}$$

where

$$S(\hat{\mathbf{k}}_\parallel)=\frac{1}{k_\parallel}\begin{pmatrix} k_1 & k_2 & 0\\ -k_2 & k_1 & 0\\ 0 & 0 & k_\parallel\end{pmatrix} \tag{13}$$

and $\hat{\mathbf{k}}_\parallel=\mathbf{k}_\parallel/k_\parallel$. It was shown in Ref. 11 that the functions $g_{\alpha\beta}(k_\parallel,\omega|x_3,x_3')$ can be represented in the form

$$\begin{aligned} g_{\alpha\beta}(k_\parallel,\omega|x_3,x_3')={}&\theta(x_3)\{g_{\alpha\beta}^{(B,1)}(k_\parallel,\omega|x_3,x_3')\\ &+g_{\alpha\beta}^{(I,1)}(k_\parallel,\omega|x_3,x_3')\}+\theta(-x_3)\\ &\times\{g_{\alpha\beta}^{(B,2)}(k_\parallel,\omega|x_3,x_3')+g_{\alpha\beta}^{(I,2)}\\ &\times(k_\parallel,\omega|x_3,x_3')\}. \end{aligned} \tag{14}$$

Here $g_{\alpha\beta}^{(B,1)}$ and $g_{\alpha\beta}^{(B,2)}$ are the bulk Green's functions that correspond to the infinite elastic media 1 and 2, respectively. The interface Green's functions $g_{\alpha\beta}^{(I,1)}$ and $g_{\alpha\beta}^{(I,2)}$ appear as a result of the presence of the interface and provide the satisfaction of the boundary conditions.

We next use Eqs. (11)–(14) in Eq. (10) to obtain

$$G(\omega)=G^{(B,1)}(\omega)+G^{(I,1)}(\omega)+G^{(B,2)}(\omega)+G^{(I,2)}(\omega). \tag{15}$$

The density of states $G^{(B,j)}(\omega)$ in the unbounded jth medium is given by[16]

$$G^{(B,j)}(\omega)=\frac{3\omega^2V^{(j)}}{2\pi^2c_B^{(j)3}}, \tag{16}$$

where $V^{(j)}$ is the volume occupied by the jth medium and

$$\frac{3}{c_B^{(j)3}}=\frac{2}{c_t^{(j)3}}+\frac{1}{c_l^{(j)3}}. \tag{17}$$

The interface contributions to the density of states are given by

$$\begin{aligned} G^{(I,1)}(\omega)={}&\frac{2\omega S\rho_1}{\pi}\int_0^\infty dx_3\int\frac{d^2k_\parallel}{(2\pi)^2}\\ &\times\operatorname{Im} g_{\alpha\alpha}^{(I,1)}(k_\parallel,\omega-i\eta|x_3,x_3), \end{aligned} \tag{18}$$

$$\begin{aligned} G^{(I,2)}(\omega)={}&\frac{2\omega S\rho_2}{\pi}\int_{-\infty}^0 dx_3\int\frac{d^2k_\parallel}{(2\pi)^2}\\ &\times\operatorname{Im} g_{\alpha\alpha}^{(I,2)}(k_\parallel,\omega-i\eta|x_3,x_3). \end{aligned} \tag{19}$$

We will show that all the integrals in Eqs. (18) and (19) can be evaluated analytically and can be expressed in terms of the trace of the static Green's tensor $g_{\alpha\beta}^{(I,j)}(k_\parallel,0|x_3,x_3')$. We start with the simplest case, when the second medium is a vacuum and the plane $x_3=0$ represents a stress-free surface.

III. DENSITY OF STATES AND THERMODYNAMIC QUANTITIES FOR A SEMI-INFINITE SOLID BOUNDED BY A STRESS-FREE SURFACE

Because we are dealing with only one elastic medium, we will drop the index j in this section. The Green's tensor satisfies the equation

$$\begin{aligned} &\left[\rho\omega^2\delta_{\alpha\mu}+C_{\alpha\beta\mu\nu}\frac{\partial^2}{\partial x_\beta\partial x_\nu}\right]D_{\mu\gamma}(\mathbf{x},\mathbf{x}'|\omega)\\ &\quad=\delta_{\alpha\gamma}\delta(\mathbf{x}-\mathbf{x}'),\quad x_3,x_3'>0, \end{aligned} \tag{20}$$

and the stress-free boundary conditions

$$C_{\alpha3\mu\nu}\frac{\partial}{\partial x_\nu}D_{\mu\gamma}(\mathbf{x},\mathbf{x}'|\omega)\big|_{x_3=0}=0. \tag{21}$$

Repeating the derivation of the preceding section, we obtain the density of states as a sum of bulk and surface contributions

$$G(\omega)=G^{(B)}(\omega)+G^{(S)}(\omega), \tag{22}$$

where $G^{(B)}$ is given by Eq. (16) with the index j dropped. The function $G^{(S)}$, which we will call the surface density of states, has the form

$$\begin{aligned} G^{(S)}(\omega)={}&\frac{2\omega S\rho}{\pi}\int_0^\infty dx_3\int\frac{d^2k_\parallel}{(2\pi)^2}\\ &\times\operatorname{Im} g_{\alpha\alpha}^{(S)}(k_\parallel,\omega-i\eta|x_3,x_3). \end{aligned} \tag{23}$$

The elements of the surface Green's tensor $g_{\alpha\beta}^{(S)}(k_\parallel,\omega|x_3,x_3')$ are derived in Ref. 17; here we only have to divide them by ρ to conform to the definition of the Green's tensor we use in this work:

$$\begin{aligned} g_{11}^{(S)}(k_\parallel,\omega|x_3,x_3)={}&-\frac{k_\parallel^2}{2\alpha_l\omega^2r_+\rho}\Bigg[r_-e^{-2\alpha_lx_3}+2e^{-(\alpha_l+\alpha_t)x_3}\\ &+\frac{r_-k_\parallel^2}{\alpha_l\alpha_t}e^{-2\alpha_tx_3}\Bigg], \end{aligned} \tag{24a}$$

$$g_{22}^{(S)}(k_\parallel,\omega|x_3,x_3)=-\frac{1}{2\alpha_tc_t^2\rho}e^{-2\alpha_tx_3}, \tag{24b}$$

$$\begin{aligned} g_{33}^{(S)}(k_\parallel,\omega|x_3,x_3)={}&-\frac{k_\parallel^2}{2\alpha_t\omega^2r_+\rho}\Bigg[\frac{\alpha_l\alpha_tr_-}{k_\parallel^2}e^{-2\alpha_lx_3}\\ &+2e^{-(\alpha_l+\alpha_t)x_3}+r_-e^{-(\alpha_l+\alpha_t)x_3}\Bigg], \end{aligned} \tag{24c}$$

with

$$\alpha_{l,t}(k_\parallel,\omega)=\left(k_\parallel^2-\frac{\omega^2}{c_{l,t}^2}\right)^{1/2} \tag{25}$$

and

$$r_\pm=\frac{-4k_\parallel^2\alpha_l\alpha_t\pm(k_\parallel^2+\alpha_t^2)^2}{4\alpha_l\alpha_t(k_\parallel^2+\alpha_t^2)}. \tag{26}$$

We next introduce the function

$$f(k_\parallel,\omega)=\frac{\rho S}{8\pi^3}\int_0^\infty dx_3\int_0^{2\pi}d\theta\, g_{\alpha\alpha}^{(S)}(k_\parallel,\omega|x_3,x_3), \tag{27}$$

where θ is the polar angle in the (k_1,k_2) plane. We see that because of the simple exponential dependence of

$g^{(S)}_{\alpha\alpha}(k_\parallel,\omega|x_3,x_3)$ on x_3, we can immediately evaluate the integral over this variable in Eq. (27). We note also that the integral over θ is trivial and gives 2π since the integrand does not depend on the direction of $\mathbf{k}_\parallel$.

Thus we know the explicit expression for $f(k_\parallel,\omega)$, which we will not write down explicitly because of its cumbersome form. The surface density of states is given by

$$G^{(S)}(\omega)=4\omega\int_0^\infty dk_\parallel k_\parallel \ \mathrm{Im}\ f(k_\parallel,\omega-i\eta). \tag{28}$$

It turns out that we can evaluate this integral analytically by means of complex analysis. First, we note that $g^{(S)}_{\alpha\alpha}(k_\parallel,\omega|x_3,x_3)$ depends on $k_\parallel$ and ω only through $k_\parallel^2$ and ω^2. Therefore, the same is true for $f(k_\parallel,\omega)$. This fact enables us to introduce the variables

$$p=k_\parallel^2,\quad \Omega=\omega^2, \tag{29}$$

which we will use later on as the arguments of f. Since

$$G^{(S)}(\omega)=2\omega\tilde{G}^{(S)}(\omega^2)=2\omega\tilde{G}^{(S)}(\Omega), \tag{30}$$

where $\tilde{G}^{(S)}(\omega^2)$ is the surface contribution to $\tilde{G}(\omega^2)=\Sigma_n\delta(\omega^2-\omega_n^2)$, we obtain that

$$\tilde{G}^{(S)}(\Omega)=\int_0^\infty dp\ \mathrm{Im}\ f(p,\Omega-i\eta). \tag{31}$$

This integral can be reduced to a contour one as follows:

$$\begin{aligned}\int_0^\infty dp\ \mathrm{Im}\ f(p,\Omega-i\eta)\\ &=\frac{1}{2i}\int_0^\infty dp[f(p,\Omega-i\eta)-f(p,\Omega+i\eta)]\\ &=\frac{1}{2i}\int_0^\infty dp[f(p+i\eta,\Omega)-f(p-i\eta,\Omega)]\\ &=\frac{1}{2i}\int_{C_1} dp\ f(p,\Omega),\end{aligned} \tag{32}$$

where the contour C_1 is shown in Fig. 1 by the solid line. Here we have used the fact that it is immaterial whether we subtract the infinitesimal $i\eta$ from p or add it to Ω, since this imaginary infinitesimal is important only in the terms containing $\sqrt{p-\Omega/c_{l,t}^2}$. We consider f as a function of complex p and real Ω. Due to the presence of the functions $\alpha_{l,t}$ defined in Eq. (25), the Riemann surface on which $f(p,\Omega)$ is single valued consists of four sheets, each of which is defined by a combination of the sheets of $\sqrt{p-\Omega/c_l^2}$ and $\sqrt{p-\Omega/c_t^2}$. The branch cuts associated with these square roots are shown in Fig. 1. We next note that the singularities of $f(p,\Omega)$ come only from the singularities of the functions $g^{(S)}_{\alpha\alpha}(k_\parallel,\omega|x_3,x_3)$ given in Eqs. (24). In particular, the pole $p=\Omega/c_R^2$, where c_R is the speed of Rayleigh waves in the solid, is associated with the Rayleigh root of the function r_+ and lies to the right of $p=\Omega/c_t^2$ on the real p axis.

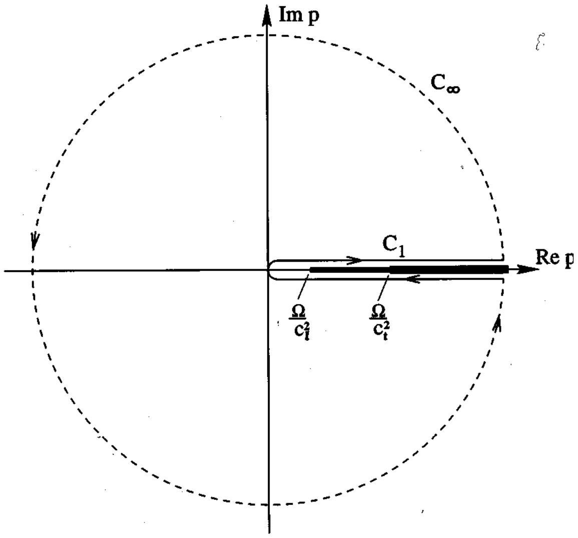

FIG. 1. Complex p plane and the integration contours C_1 and C_∞ used in the evaluation of the integral in Eq. (31).

The other singular points correspond to leaky surface waves and do not lie on the first (physical) Riemann sheet.[18] Thus, if we close the contour C_1 by a circle C_∞ of an infinitely large radius, as shown in Fig. 1, we can claim that $f(p,\Omega)$ is regular and has no singularities inside the closed contour $C=C_1+C_\infty$. As a simple consequence of the Cauchy theorem, we obtain

$$\tilde{G}^{(S)}(\Omega)=-\frac{1}{2i}\int_{C_\infty} dp\ f(p,\Omega). \tag{33}$$

The analysis of the behavior of $f(p,\Omega)$ for large $|p|$ shows that this function decreases as const/$|p|$ as $|p|\to\infty$. Since $|p|\gg\Omega/c_{t,l}^2$ Ω can be set equal to zero and $\tilde{G}^{(S)}(\Omega)$ does not depend on Ω at all:

$$\tilde{G}^{(S)}(\Omega)=-\pi\{pf(p,0)\}. \tag{34}$$

We point out that the expression in curly brackets does not depend on p.

Thus $\tilde{G}^{(S)}(\Omega)$ is completely determined by the static limit ($\Omega\to 0$) of $f(p,\Omega)$. This is the reason why we did not calculate the explicit form of this function. We could have used the static Green's functions $g^{(S)}_{\alpha\beta}(k_\parallel,0|x_3,x_3')$ from the very beginning. These functions are much easier to calculate than their dynamical analogs, especially in the case of anisotropic media.[9]

Using Eqs. (27), (28), (30), and (34), we obtain

$$G^{(S)}(\omega)=-\frac{\rho S\omega}{2\pi}\int_0^\infty dx_3\{k_\parallel^2 g^{(S)}_{\alpha\alpha}(k_\parallel,0|x_3,x_3)\}. \tag{35}$$

Again, we stress that the function in curly brackets does not depend on $k_\parallel$. Substituting Eqs. (24) into Eq. (35) in the limit $\omega=0$ results in

$$G^{(S)}(\omega)=\frac{S\omega}{8\pi c_s^2}, \tag{36}$$

with c_s^2 defined in Eq. (2). Now we know both terms in Eq. (22). This enables us to construct a surface analog of the Debye model. For an infinite monatomic crystal, which we macroscopically treat as an isotropic elastic medium, we require that the total number of degrees of freedom be $3N$, where N is the number of atoms in the volume V. Hence we have the normalization condition

$$\int_0^{\omega_D} d\omega\; G^{(B)}(\omega)=3N, \tag{37}$$

which determines the bulk Debye cutoff frequency ω_D,

$$\omega_D=(6\pi^2)^{1/3}\left(\frac{N}{V}\right)^{1/3} c_B\,, \tag{38}$$

where c_B is defined in Eq. (17) with the index j dropped. When we are dealing with a semi-infinite medium, the *same number* of degrees of freedom is distributed differently between bulk and surface vibrations, which leads to a new maximum (cutoff) frequency ω_M defined by the relation

$$\int_0^{\omega_M} d\omega[G^{(B)}(\omega)+G^{(S)}(\omega)]=3N. \tag{39}$$

Finally, we obtain that ω_M differs from ω_D by a small negative correction appearing as a result of the perturbation introduced by the stress-free surface:

$$\omega_M=\omega_D\left[1-\frac{S}{V}\,\frac{(6\pi^2)^{2/3}c_B^2}{144\pi c_s^2}\left(\frac{V}{N}\right)^{1/3}\right]. \tag{40}$$

The surface zero-point energy has the form

$$\begin{aligned}\Delta F^{(S)}(0)&=\int_0^{\omega_M} d\omega\,\frac{\hbar\omega}{2}\,[G^{(B)}(\omega)+G^{(S)}(\omega)]\\&\quad-\int_0^{\omega_D} d\omega\,\frac{\hbar\omega}{2}\,G^{(B)}(\omega)\\&=-S\,\frac{\hbar\omega_D^3}{96\pi c_s^2}.\end{aligned} \tag{41}$$

The temperature-dependent part of the surface free energy in the limit $k_BT\ll\hbar\omega_D$ is given by

$$\Delta F^{(S)}(T)=\left(\frac{k_BT}{\hbar}\right)^3\frac{\hbar S}{8\pi c_s^2}\,\zeta(3). \tag{42}$$

The low-temperature surface specific heat $\Delta C_v^{(S)}(T)$ that is obtained from Eq. (42) coincides with Eq. (1). In addition, the results for ω_M and $\Delta F^{(S)}(0)$ given in Eqs. (40) and (41) agree with those obtained in Ref. 7, where the surface analog of the Debye model was developed. The important point of our derivation is that we have shown that the density of vibrational states of a semi-infinite solid is completely determined by the static Green's tensor of this system, and so are the free energy and specific heat.

IV. THE INTERFACE DEBYE MODEL

We now return to the system of two isotropic solids in contact considered in Sec. II. We are going to construct an interface Debye model for it, which, to our knowledge, has not been developed yet. The interface contributions to the density of vibrational states are given by Eqs. (18) and (19). It turns out that we can apply exactly the same technique to evaluate these integrals that we used in solving the surface problem. The analytic properties of the integrands seem to be more complicated since the Riemann surface now consist of 16 sheets due to the presence of 4 different square roots: $\sqrt{k_\parallel^2-(\omega^2/c_{l,t}^{(1)2})}$ and $\sqrt{k_\parallel^2-(\omega^2/c_{l,t}^{(2)2})}$. However, there are still no singularities inside the contour $C=C_1+C_\infty$ shown in Fig. 1. Thus the interface density of states is determined by the static interface Green's tensor and we obtain the analogs of Eq. (35),

$$G^{(I,1)}(\omega)=-\frac{\rho_1 S\omega}{2\pi}\int_0^\infty dx_3\{k_\parallel^2 g_{\alpha\alpha}^{(I,1)}(k_\parallel,0|x_3,x_3)\}, \tag{43}$$

$$G^{(I,2)}(\omega)=-\frac{\rho_2 S\omega}{2\pi}\int_{-\infty}^0 dx_3\{k_\parallel^2 g_{\alpha\alpha}^{(I,2)}(k_\parallel,0|x_3,x_3)\}. \tag{44}$$

We next use the explicit expressions for the functions $g_{\alpha\alpha}^{(I,j)}(k_\parallel,0|x_3,x_3)$ derived in Ref. 13. The result of the integration over x_3 then leads to

$$G^{(I,1)}(\omega)=\frac{S\omega\beta_{12}}{8\pi c_t^{(1)2}}, \tag{45}$$

where

$$\begin{aligned}\beta_{12}=\frac{4}{\Delta}\Bigg\{&(1+\nu_1^2)(1+\nu_2)-\gamma_{12}^2(1-\nu_2)(1+\nu_1)^2\\&-2\gamma_{12}\nu_1\nu_2(1+\nu_1)-(1-\nu_1)^2[\gamma_{12}^2(1-\nu_2)+2\gamma_{12}\nu_2\\&-(1+\nu_2)]+\frac{\Delta}{4}\,\frac{1-\gamma_{12}}{1+\gamma_{12}}\Bigg\},\end{aligned} \tag{46a}$$

$$\gamma_{12}=\rho_2c_t^{(2)2}/\rho_1c_t^{(1)2},\qquad \nu_j=c_t^{(j)2}/c_l^{(j)2}, \tag{46b}$$

$$\begin{aligned}\Delta=4[&\gamma_{12}^2(1+\nu_1)(1-\nu_2)+2\gamma_{12}(1+\nu_1\nu_2)\\&+(1-\nu_1)(1+\nu_2)].\end{aligned} \tag{46c}$$

The expression for $G^{(I,2)}(\omega)$ has the form

$$G^{(I,2)}(\omega)=\frac{S\omega\beta_{21}}{8\pi c_t^{(2)2}}, \tag{47}$$

where β_{21} can be obtained from the expression for β_{12} by interchanging the indices 1 and 2. To check the correctness of Eqs. (45) and (47) we can assume that the two solids we consider are not distinct. In this case we see that $G^{(I,1)}(\omega)=G^{(I,2)}(\omega)\equiv 0$, which indicates the absence of the interface. We also point out that the simple frequency dependence of $G^{(I,j)}(\omega)$ is a consequence of the general law that the density of states is proportional to ω^{d-1}, where d is the dimensionality of the system. In our case $d=2$, since we are dealing with an interface contribution.

It seems that in order to construct the interface Debye model we can repeat the procedure we followed in the case of a surface. However, if we require that the total density of states (15) be normalized to the total number of degrees of freedom $3(N_1+N_2)$, while $G^{(B,j)}(\omega)$ are normalized to $3N_j$, we obtain an unphysical result for the cutoff frequency ω_M: the number of atoms N_j in the jth medium does not enter the expression for ω_M in the combination (N_j/V_j), as it clearly should. Fortunately, this difficulty can be removed. We claim that the interface perturbs the vibrational spectrum of each solid and require that *each* medium be described by its own density of states

$$G^{(j)}(\omega)=G^{(B,j)}(\omega)+G^{(I,j)}(\omega) \tag{48}$$

and its own cutoff frequency $\omega_M^{(j)}$. Then we normalize $G^{(j)}(\omega)$ to $3N_j$.

The justification for this requirement can be provided by a simple example. Let us consider the same two solids occupying the half spaces $x_3>0$ and $x_3<0$, but now separated by a very thin gap, so that we have two stress-free surfaces instead of the interface. Even if we consider these two solids as an entire system, we see that it is meaningless to describe the density of states of the system by the function (15). At the same time, the separate description (48) leads to the established result (40) for each medium.

Thus, returning to our interface problem, we obtain the following cutoff frequency for the jth medium:

$$\omega_M^{(j)}=\omega_D^{(j)}\left[1-\frac{S}{V_j}\,\frac{(6\pi^2)^{2/3}c_B^{(j)2}\beta_{jj'}}{144\pi c_t^{(j)2}}\left(\frac{V_j}{N_j}\right)^{1/3}\right]. \tag{49}$$

Here $j'=2$ for $j=1$ and $j'=1$ for $j=2$; $\omega_D^{(j)}=(6\pi^2N_j/V_j)^{1/3}c_B^{(j)}$ is the Debye frequency of the jth solid. The interface contribution to the zero-point energy is

$$\Delta F^{(I)}(0)=-\frac{\hbar S}{96}\left[\frac{\omega_D^{(1)3}}{c_t^{(1)2}}\,\beta_{12}+\frac{\omega_D^{(2)3}}{c_t^{(2)2}}\,\beta_{21}\right], \tag{50}$$

while the temperature-dependent part in the low-T limit has the form

$$\Delta F^{(I)}(T)=\left(\frac{k_BT}{\hbar}\right)^3\frac{\hbar S\zeta(3)}{8\pi}\left[\frac{\beta_{12}}{c_t^{(1)2}}+\frac{\beta_{21}}{c_t^{(2)2}}\right]. \tag{51}$$

Finally, we can obtain the interface contribution to the specific heat

$$\Delta C_v^{(I)}(T)=3\pi\zeta(3)\,\frac{k_B^3T^2S}{h^2}\left[\frac{\beta_{12}}{c_t^{(1)2}}+\frac{\beta_{21}}{c_t^{(2)2}}\right]. \tag{52}$$

This expression can be reduced to the result of Ref. 11.

V. CONCLUSION

In this paper we have studied the thermodynamic properties of solid surfaces and interfaces. The main goal of this work was to develop a simple analytic approach for calculating the surface or interface density of vibrational states, since this function plays a fundamental role in the thermodynamics of vibrations. We have related this function to the static Green's tensor of the system [Eqs. (35), (43), and (44)]. This is a generalization of the result obtained in Ref. 5, namely, that the static Green's tensor determines the surface or interface contribution to the specific heat. The density of states we have derived for an isotropic elastic medium bounded by a stress-free surface coincides with the result of Ref. 7 and gives the established expressions for the specific heat[1–7] and free energy.[7]

In the case of two different isotropic solids in contact across a planar interface we have constructed the interface analog of the Debye model. We have shown that it is necessary to describe each medium by its own density of states, which should be normalized to the total number of vibrational degrees of freedom in this medium. This requirement gives rise to new cutoff frequencies for both media. We have obtained the interface free energy and specific heat for this system and have found that the latter result agrees with the one obtained in Ref. 11.

The approach we have developed in this work seems to be quite straightforward and can be applied to different surface or interface problems. In particular, it can be useful in further studies of thermodynamic properties of anisotropic media, whose static Green's tensor is much easier to calculate than its dynamical analog. This method is also applicable to the determination of the thermodynamic properties of solid-liquid interfaces, which is a problem of considerable current experimental interest.[15] This work is being carried out at the present time and the results are planned to published elsewhere.

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