Low-temperature specific heat of a thin film

Paul Mazur*
Department of Physics, University of California, Irvine, 92717
(Received 16 September 1980)

On the basis of a simple model of a simple cubic crystal, calculations are carried out of the low-temperature specific heat of a thin film of L layers bounded by two free (001) surfaces. The specific heat is given as the sum of four terms, namely: $C^{(B)}(T)$, $C^{(s)}(T)$, $C^{(s')}(T)$, and $C^{(ss')}(T)$, corresponding, respectively, to the bulk specific heat, the two surface specific heats, and a term which depends on the proximity of the two surfaces.

I. INTRODUCTION

There has been a great deal of interest in recent years in studying, both theoretically and experimentally, the thermodynamic and electromagnetic properties of thin films. The great interest, no doubt, has been stimulated by the enormous variety of technological applications of thin films. On the basis of a simple model of a simple cubic crystal, calculations are carried out of the low-temperature specific heat of a thin film of L layers bounded by two free (001) surfaces. The specific heat is determined as the sum of four terms, namely, $C^{(B)}(T)$, $C^{(s)}(T)$, $C^{(s')}(T)$, and $C^{(ss')}(T)$ corresponding, respectively, to the bulk specific heat, the two surface specific heats, and a term which depends on the proximity of the two surfaces. The lattice model which we have chosen to use is the so-called Montroll-Potts model of a simple cubic crystal with nearest-neighbor, central- and noncentral-force interactions between atoms.[1] It is well known that this model does not satisfy the conditions imposed by the requirements of infinitesimal rotational invariance[2]; it does not give rise to Rayleigh surface waves; a film based on it also does not possess the plate modes in the long-wavelength limit predicted both by continuum theory[3] and by lattice theory.[4] These deficiencies of the model notwithstanding, exact calculations on this model and ones similar to it have predicted many interesting characteristics of the lattice vibration frequency spectrum which have pointed a way to the understanding of the frequency spectra to be expected from more realistic models. An outstanding example of this is Montroll's[5] calculation of the frequency spectrum of a square lattice where he demonstrated exactly that the frequency spectrum contains singularities. Van Hove[6] later showed, using a theorem of Morse, that the singularities were a consequence of the periodic nature of the dispersion relation $\omega(q)$. Although much work has been done[7] on calculating the surface specific heat on the continuum level and numerically on lattice-dynamical models we are not aware of any attempt to calculate analytically the specific heat of a thin film for a lattice even as simple as the Montroll-Potts model.

Our method is first to obtain the dynamical Green's function for a thin film of a Montroll-Potts crystal, bounded by a pair of (001) free surfaces. This result is then used directly to calculate the specific heat of a thin film.

Note added in proof. The Montroll-Potts model does give rise to Rayleigh waves if the interlayer bonds are not normal to the surface, as in the case of a (110) surface. See S. L. Cunningham, Surf. Sci. 33, 139 (1972).

II. DYNAMICAL GREEN'S FUNCTION FOR A CRYSTAL FILM

The dynamical Green's function for a crystal film has been obtained by Maradudin.[8] The derivation is described in detail in Ref. 9. For completeness, we describe the model of the film being used.

We construct the film in the following way. We begin with an infinitely extended simple cubic crystal whose lattice translation vectors are given by

$$\vec{x}(l) = a_0(l_1, l_2, l_3),$$

where a_0 is the lattice parameter, and l_1, l_2, l_3 are any three integers, positive, negative, or zero, which we denote collectively by l. We then excise a film of L layers by equating to zero all interactions between atoms in the plane $l_3=0$ and atoms in the plane $l_3=1$ and between atoms in the plane $l_3=L$ and atoms in the plane $l_3=L+1$, and then restricting l_3 to assume only the values $1 \leq l_3 \leq L$.

The time-independent equations of motion of the infinite crystal perturbed by the annulment of the interactions between the layers $l_3=0$ and $l_3=1$ and between the layers $l_3=L$ and $l_3=L+1$ can be written in the form

$$(\overleftrightarrow{L}^{(0)} - \delta\overleftrightarrow{L}^{(1)} - \delta\overleftrightarrow{L}^{(2)})\vec{u} = 0,$$

where the elements of the matrices $\overleftrightarrow{L}^{(0)}$, $\delta\overleftrightarrow{L}^{(1)}$, and $\delta\overleftrightarrow{L}^{(2)}$ are given by

$$L^{(0)}_{\alpha\beta}(ll';\omega^2)=\delta_{\alpha\beta}[M\omega^2\delta_{l_1l_1'}\delta_{l_2l_2'}\delta_{l_3l_3'} +\gamma(\delta_{l_1l_1'-1}\delta_{l_2l_2'}\delta_{l_3l_3'}+\delta_{l_1l_1'+1}\delta_{l_2l_2'}\delta_{l_3l_3'}+\delta_{l_1l_1'}\delta_{l_2l_2'-1}\delta_{l_3l_3'} +\delta_{l_1l_2'}\delta_{l_2l_2'+1}\delta_{l_3l_3'}+\delta_{l_1l_1'}\delta_{l_2l_2'}\delta_{l_3l_3'-1}+\delta_{l_1l_1'}\delta_{l_2l_2'}\delta_{l_3l_3'+1}-6\delta_{l_1l_1'}\delta_{l_2l_2'}\delta_{l_3l_3'})],$$

$$\delta L^{(1)}_{\alpha\beta}(ll')=-\delta_{\alpha\beta}\gamma\delta_{l_1l_1'}\delta_{l_2l_2'}(\delta_{l_30}-\delta_{l_31})(\delta_{l_3'0}-\delta_{l_3'1}),$$

$$\delta L^{(2)}_{\alpha\beta}(ll')=-\delta_{\alpha\beta}\gamma\delta_{l_1l_1'}\delta_{l_2l_2'}(\delta_{l_3L}-\delta_{l_3L+1})(\delta_{l_3'L}-\delta_{l_3'L+1}),$$

where M is the mass of an atom in the crystal, and γ is the nearest-neighbor force constant. To simplify the Montroll-Potts model further, we have assumed that the central- and non-central-force constants are all equal. In these expressions α and β label the Cartesian axes. The matrix $\overleftrightarrow{L}^{(0)}$ describes the vibrations of the infinitely extended crystal, $\delta\overleftrightarrow{L}^{(1)}$ subtracts the interactions between the planes $l_3=0$ and $l_3=1$, and $\delta\overleftrightarrow{L}^{(2)}$ subtracts the interactions between the planes $l_3=L$ and $l_3=L+1$.

We now define the Green's function $G_{\alpha\beta}$ and $U_{\alpha\beta}(ll';\omega^2)$ as the solution of the equation

$$(\overleftrightarrow{L}^{(0)}-\delta\overleftrightarrow{L}^{(1)}-\delta\overleftrightarrow{L}^{(2)})\overleftrightarrow{U}=\overleftrightarrow{I}. \quad (1)$$

Equation (1) is solved by assuming that

$$U_{\alpha\beta}(ll';\omega^2)=\frac{\delta_{\alpha\beta}}{N^2}\sum_{\vec{k}_\parallel}U(\vec{k}_\parallel\omega\,|\,l_3l_3')e^{i\vec{k}_\parallel\cdot[\vec{x}_\parallel(l)-\vec{x}_\parallel(l')]}, \quad (2)$$

where $\vec{k}_\parallel=\hat{x}_1k_1+\hat{x}_2k_2$ is a two-dimensional wave vector parallel to the surface, and where $\hat{x}_1$ and $\hat{x}_2$ are unit vectors in the 1 and 2 directions. We assume periodic boundary conditions in the 1 and 2 directions, with the periodicity element being a square with edges of length Na_0 along each of these directions. The N^2 allowed values of the wave vector $\vec{k}_\parallel$ are therefore given by

$$\vec{k}_\parallel=\frac{2\pi}{Na_0}(m_1,m_2,0),\quad -\frac{N}{2}+1\le m_1;\quad m_2\le\frac{N}{2}, \quad (3)$$

where m_1 and m_2 are integers. The area swept out by the allowed values of $\vec{k}_\parallel$ is the two-dimensional first Brillouin zone for this problem.

It is shown in Ref. 9 that

$$U(\vec{k}_\parallel\omega\,|\,l_3l_3')=\frac{1}{\gamma}\frac{t^{|l_3-l_3'|+1}}{t^2-1}+\frac{1}{\gamma}\frac{t^{l_3+l_3'}}{t^2-1}+\frac{1}{\gamma}\frac{t}{t^2-1}\frac{t^{2L}}{1-t^{2L}}(t^{-l_3-l_3'+1}+t^{-l_3+l_3'}+t^{l_3-l_3'}+t^{l_3+l_3'-1}), \quad (4)$$

where

$$t=\begin{cases}\zeta-(\zeta^2-1)^{1/2}, & \zeta>1 \quad (5a)\\ \zeta+i(1-\zeta^2)^{1/2}, & -1<\zeta<1 \quad (5b)\\ \zeta+(\zeta^2-1)^{1/2}, & \zeta<-1 \quad (5c)\end{cases}$$

and

$$\zeta=3-\cos k_1a_0-\cos k_2a_0-\frac{M}{2\gamma}\omega^2. \quad (5d)$$

III. THE LOW-TEMPERATURE SPECIFIC HEAT OF A THIN FILM

In this section we utilize the results of Sec. II to obtain the low-temperature specific heat of a thin film. What is meant by low temperature will emerge in the course of this discussion.

In the harmonic approximation the specific heat of a crystal is given by

$$C_v(T)=k_B\sum_s\frac{(\frac{1}{2}\beta\hbar\omega_s)^2}{\sinh^2\frac{1}{2}\beta\hbar\omega_s}, \quad (6)$$

where $\beta=(k_BT)^{-1}$, with T the absolute temperature and k_B Boltzmann's constant, ω_s is the frequency of the sth normal mode, and the sum on s runs over all the normal modes of the crystal. In the limit of low temperatures, when β is large, it is convenient to expand the summand on the right-hand side of Eq. (6) in powers of $\exp(-\beta\hbar\omega_s)$, in which case we obtain

$$C_v(T)=k_B\sum_{n=1}^{\infty}n\sum_s(\beta\hbar\omega_s)^2e^{-n\beta\hbar\omega_s}. \quad (7)$$

To evaluate the sum on s in the expression we introduce the function $F(z)$ of the complex variable z by

$$F(z)=\sum_s\frac{1}{z^2-\omega_s^2}. \quad (8)$$

This function has simple poles at $z=\pm\omega_s$, with residues $\pm1/(2\omega_s)$, respectively. Because only positive values of the $\{\omega_s\}$ appear on the right-hand side of Eq. (7) we can rewrite the sum on s in this equation in the form of a contour integral involving the function $F(z)$,

$$C_v(T)=\frac{k_B(\beta\hbar)^2}{\pi i}\sum_{n=1}^{\infty}n\int_{C_1}z^3e^{-n\beta\hbar z}F(z)dz, \quad (9)$$

where the integration contour is shown in Fig. 1(a).

The presence of the descending exponential in the integrand in Eq. (9) means that we may deform the integration contour into the contour C_2 shown in Fig. 1(b), and we know that the contribution from the infinite semicircle vanishes, so that we are left with an integral down the imaginary axis. With the change of variable $z = iy$ we obtain for the specific heat the result

$$C_v(T) = \frac{k_B(\beta\hbar)^2}{\pi} \sum_{n=1}^{\infty} n \int_{-\infty}^{\infty} y^3 F(iy) \sin n\beta\hbar y \, dy \,. \quad (10)$$

In obtaining this result we have used the fact, evident from Eq. (8), that $F(iy)$ is an even function of y.

Since n in Eq. (10) is always greater than or equal to unity, and since β is large at low temperature for the calculation of $C_v(T)$ at low temperatures we require the asymptotic behavior of the integral

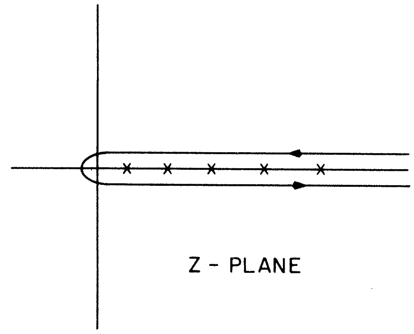
$$J = \int_{-\infty}^{\infty} y^3 F(iy) \sin n\beta\hbar y \, dy \quad (11)$$

in the limit as $n\beta\hbar \to +\infty$. The theory of the asymptotic behavior of Fourier integrals[10] yields the result that the large-$n\beta\hbar$ behavior of the integral J is determined by the singularities of the function $y^3F(iy)$. It can be shown easily[11] that the function $F(iy)$ can have its only singularity at the point $y = 0$. Our task, therefore is to determine the nature of the singularity in $F(iy)$ at $y = 0$, from which the asymptotic behavior of the integral J can be inferred from tabulated results.

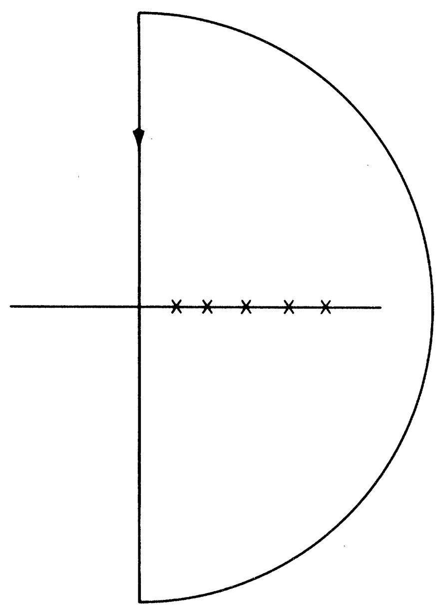
We are aided in this task by the observation that it is a general result from the theory of the effects of defects on the vibrations of crystal lattices that[12]

$$\sum_s \frac{1}{\omega^2 - \omega_s^2} = F(\omega) = M \sum_{l\alpha} U_{\alpha\alpha}(ll \,|\, \omega^2) \,, \quad (12)$$

in the case of a Bravais crystal in the presence of a defect that changes none of the masses of the constituent atoms. This result, together with Eqs. (4) and (5) enables us to write



(a)



(b)

FIG. 1. (a) Path of integration for the line integral in Eq. (9) which encompasses all of the positive poles of $F(z)$. (b) Deformed semicircular path along which the line integral in Eq. (9) is actually calculated.

$$F(iy) = \frac{3M}{N^2} \sum_{l_1=1}^{N} \sum_{l_2=1}^{N} \sum_{l_3=1}^{L} \sum_{\vec{k}_\parallel} U(\vec{k}_\parallel iy \,|\, l_3 l_3)$$

$$= \frac{3M}{\gamma} \sum_{\vec{k}_\parallel} \sum_{l_3=1}^{L} \left(\frac{t}{t^2-1} + \frac{t^{2l_3}}{t^2-1} + \frac{t}{t^2-1} \frac{t^{2L}}{1-t^{2L}} (t^{-2l_3+1} + 2 + t^{2l_3-1}) \right), \quad (13)$$

where now

$$t = \zeta - (\zeta^2 - 1)^{1/2} \quad (14)$$

because

$$\zeta = \frac{My^2}{2\gamma} + 3 - \cos k_1 a_0 - \cos k_2 a_0 > 1 \,. \tag{15}$$

We carry out the sums on l_3 and replace summation on $\vec{k}$ by integration over θ_1 and θ_2 according to

$$k_1 a_0 = \theta_1 , \quad k_2 a_0 = \theta_2 , \quad -\pi \le \theta_1, \theta_2 \le \pi , \tag{16}$$

to obtain

$$F(iy) = -\frac{3M}{\pi^2\gamma} N^2 L \int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \frac{t}{1-t^2} - \frac{3M}{\pi^2\gamma} N^2 \int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \frac{t^2}{(1-t^2)^2} - \frac{3M}{\pi^2\gamma} N^2 \int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \frac{t^2}{(1-t^2)^2}$$
$$- \frac{6M}{\pi^2\gamma} N^2 L \int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \frac{t}{1-t^2} \frac{t^{2L}}{1-t^{2L}} , \tag{17}$$

where ζ is now given by

$$\zeta = \frac{My^2}{2\gamma} + 3 - \cos\theta_1 - \cos\theta_2 \,. \tag{18}$$

The first term in Eq. (17), $F^{(B)}(iy)$, is the bulk contribution; the second and third terms, $F^{(s)}(iy)$, are equal to each other, each representing the contribution associated with the presence of a single, bounding surface on the crystal, i.e., it gives the surface contribution for a semi-infinite crystal; the contribution given by the last term, $F^{(2s)}(iy)$, has its origin in the presence of the second surface, and describes the effects of the interference between the contributions associated with each surface separately. We will see that this term vanishes as the number of layers in the film, L, increases without limit.

We consider each of these several contributions in turn. The function $F^{(B)}(iy)$ is given by

$$F^{(B)}(iy) = -\frac{3M}{\pi^2\gamma} N^2 L \int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \frac{t}{1-t^2} = -\frac{3M}{2\pi^2\gamma} N^2 L \int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \frac{1}{(\zeta^2-1)^{1/2}}$$
$$= -\frac{3}{2}\frac{M}{\gamma}\frac{N^2 L}{\pi^3} \int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \int_0^\pi d\theta_3 \frac{1}{My^2/2\gamma + 3 - \cos\theta_1 - \cos\theta_2 - \cos\theta_3} , \tag{19}$$

where we have used successively the fact that

$$\frac{t}{1-t^2} = \frac{1}{2(\zeta^2-1)^{1/2}} \tag{20}$$

and

$$\frac{1}{\pi}\int_0^\pi d\theta_3 \frac{\cos l\theta_3}{\zeta - \cos\theta_3} = \frac{[\zeta - (\zeta^2-1)^{1/2}]^{|l|}}{(\zeta^2-1)^{1/2}} . \tag{21}$$

The first few terms in the expansion of the three-dimensional integral of Eq. (19) have been obtained in Ref. 13. The result is

$$F^{(B)}(iy) \sim -\frac{3}{2}\frac{M}{\gamma} N^2 L \left[0.505\,46 - \frac{1}{\sqrt{2}\,\pi}\left(\frac{M}{2\gamma}\right)^{1/2} |y| - 0.014\,625\left(\frac{M}{2\gamma}\right) y^2 + \frac{1}{4\sqrt{2}\,\pi}\left(\frac{M}{2\gamma}\right)^{3/2} |y|^3 + O(y^4) \right] . \tag{22}$$

The singular terms in this expansion are those containing $|y|$, $|y|^3, \ldots$. With the aid of the results of Ref. 10, we find that the leading terms in the large $n\beta\hbar$ expansion of the integral J, Eq. (11), associated with the function $F^{(B)}(iy)$ are given by

$$J^{(B)} \sim N^2 L \left[\frac{36}{\pi}\left(\frac{M}{\gamma}\right)^{3/2} \frac{1}{(n\beta\hbar)^5} + \frac{135}{\pi}\left(\frac{M}{\gamma}\right)^{5/2} \frac{1}{(n\beta\hbar)^7} + \cdots \right] . \tag{23}$$

Substitution of this result into Eq. (10) yields the first two terms in the low-temperature expansion of the bulk specific heat of the Montroll-Potts model,

$$C_v^{(B)}(T) \sim 3N^2 L k_B \left[\frac{2\pi^2}{15}\left(\frac{k_B T}{\hbar\omega_0}\right)^3 + \frac{\pi^4}{21}\left(\frac{k_B T}{\hbar\omega_0}\right)^5 + \cdots \right] , \tag{24}$$

where the frequency ω_0 is defined by

$$\omega_0^2 = \frac{\gamma}{M} = \tfrac{1}{12}\omega_L^2 , \tag{25}$$

and ω_L is the largest normal-mode frequency of the Montroll-Potts model. We note that $3N^2L$ is the total number of degrees of freedom in the film.

We turn now to the determination of the small-$|y|$ behavior of the function $F^{(s)}(iy)$, or more precisely the singular part of this behavior. We have that

$$F^{(s)}(iy) = -\frac{3}{\pi^2}\frac{N^2}{\omega_0^2}\int_0^\pi d\theta_1\int_0^\pi d\theta_2\frac{t^2}{(1-t^2)^2} = -\frac{3}{4\pi^2}\frac{N^2}{\omega_0^2}\int_0^\pi d\theta_1\int_0^\pi d\theta_2\frac{1}{\zeta^2-1}$$
$$= -\frac{3}{8\pi^2}\frac{N^2}{\omega_0^2}\int_0^\pi d\theta_1\int_0^\pi d\theta_2\left(\frac{1}{y^2/2\omega_0^2+2-\cos\theta_1-\cos\theta_2}-\frac{1}{y^2/2\omega_0^2+4-\cos\theta_1-\cos\theta_2}\right). \quad (26)$$

It is clear that the function defined by the second integral has derivatives of all orders at $y=0$. The singular part of $F^{(s)}(iy)$ can arise only from the first integral, which we rewrite as

$$F^{(s)}(iy)_{\text{sing}} = -\frac{3}{8}\frac{N^2}{\omega_0^2}\frac{1}{\pi^2}\int_0^\pi d\theta_1\int_0^\pi d\theta_2\int_0^\infty dt\exp\left[-t\left(\frac{y^2}{2\omega_0^2}+2-\cos\theta_1-\cos\theta_2\right)\right]$$
$$= -\frac{3}{8}\frac{N^2}{\omega_0^2}\int_0^\infty dt\exp\left[-\left(\frac{y^2}{2\omega_0^2}+2\right)t\right]I_0^2(t) = -\frac{3}{8\pi}\frac{N^2}{\omega_0^2}\frac{1}{1+y^2/4\omega_0^2}K\left(\frac{1}{1+y^2/4\omega_0^2}\right), \quad (27)$$

here $K(k)$ is the complete elliptic integral of the first kind.

We now use the fact that $K(k)$ has the following expansion in the vicinity of $k\approx 1$ (Ref. 14):

$$K(k)\sim -\left(1+\tfrac{1}{4}k'^2+\tfrac{9}{64}k'^4+\tfrac{25}{256}k'^6+\cdots\right)\ln\frac{k'}{4}$$
$$-\left(\tfrac{1}{4}k'^2+\tfrac{21}{128}k'^4+\tfrac{185}{1536}k'^6+\cdots\right), \quad (28)$$

where

$$k'=(1-k^2)^{1/2}.$$

In the present case

$$k'^2=\frac{y^2}{2\omega_0^2}\frac{1+y^2/8\omega_0^2}{(1+y^2/4\omega_0^2)^2},$$
$$k'=\frac{|y|}{2^{1/2}\omega_0}\left(1-\frac{3y^2}{16\omega_0^2}+\frac{23y^4}{512\omega_0^4}-\cdots\right). \quad (29)$$

The singular part of $F^{(s)}(iy)$ can come only from the terms in the first line of Eq. (28). Combining Eqs. (27), (28), and (29) we obtain finally that

$$F^{(s)}(iy)_{\text{sing}}=\frac{3N^2}{8\pi\omega_0^2}\left(1-\frac{y^2}{8\omega_0^2}+\frac{y^4}{8\omega_0^4}-\cdots\right)\ln|y|.$$

It follows from the results of Ref. 10 that the leading terms in the large-$n\beta\hbar$ expansion of the integral J, Eq. (11), corresponding to the function $F^{(s)}(iy)$ are given by

$$J^{(s)}\sim 3N^2\frac{\omega_0^2}{8\pi}\left(\frac{6\pi}{(n\beta\hbar\omega_0)^4}+\frac{15\pi}{(n\beta\hbar\omega_0)^6}+\frac{630\pi}{(n\beta\hbar\omega_0)^8}+\cdots\right). \quad (30)$$

When we substitute this result into Eq. (10) we obtain as the surface contribution to the low-temperature specific heat of the semi-infinite Montroll-Potts model,

$$C_v^{(s)}(T)\sim 3N^2\frac{k_B}{8\pi}\left[6\zeta(3)\left(\frac{k_BT}{\hbar\omega_0}\right)^2+15\zeta(5)\left(\frac{k_BT}{\hbar\omega_0}\right)^4+630\zeta(7)\left(\frac{k_BT}{\hbar\omega_0}\right)^6+\cdots\right]. \quad (31)$$

The leading term in this expansion had been obtained previously by Dobrzynski and Leman.[15]

We come finally to the contribution to the specific heat rising from the presence of a second surface. The function $F^{(2s)}(iy)$ is given by

$$F^{(2s)}(iy)=-\frac{3N^2L}{4\pi^2\omega_0^2}\int_{-\pi}^{+\pi}d\theta_1\int_{-\pi}^{+\pi}d\theta_2\frac{1}{(-1+t^{-2L})(\zeta^2-1)^{1/2}}. \quad (32)$$

We look for the singular part of $F^{(2s)}(iy)$. Since it does not appear possible to calculate the integral in Eq. (32) by straightforward analytical methods, we resort to an approximate procedure. We note first that t lies between 0 and 1, no matter what the value of y, and is equal to 1 only when $y=\theta_1=\theta_2=0$. The minimum value of ζ occurs at $\theta_1=\theta_2=0$. Consequently we see that the integrand in Eq. (32) is strongly peaked at the origin ($y=\theta_1=\theta_2=0$) and decreases exponentially with L as one moves away from the origin. It would appear legitimate, therefore, for large L, to expand the integrand around $\theta_1=\theta_2=0$.

Letting $\theta_1=r\sin\theta$ and $\theta_2=r\cos\theta$, we expand t and ζ around $\theta_1=\theta_2=0$ to get

$$\zeta\approx 1+b+\frac{r^2}{2}+R_1(r,\theta),$$
$$\zeta^2-1=b^2+2b+(b+1)r^2+R_2(r,\theta), \quad (33)$$

with

$$R_1(r,\theta)\sim O(r^4),$$
$$R_2(r,\theta)\sim O(r^4),$$

and

$$t\approx 1+b+\frac{r^2}{2}+R_1(r,\theta)$$
$$-[b^2+2b+(b+1)r^2+R_2]^{1/2}, \quad (34)$$

where

$$b = \frac{y^2}{2\omega_0^2}.$$

We need further to substitute for t^{-2L} in the integrand of Eq. (32) which we rewrite as

$$t^{-2L} = e^{-2L\ \ln t}. \tag{35}$$

Since we are interested in the singular behavior of $F^{(2s)}(iy)$ which occurs at $y=0$, we expand ln to give

$$\ln t \approx -[b^2 + 2b + (b+1)r^2] - \frac{b^2}{2} - \frac{br^2}{2} + O(r^4). \tag{36}$$

Substituting for ln$t$ from Eq. (36) and for $\zeta^2 - 1$ from Eq. (33) into Eq. (32) we obtain

$$F^{(2s)}(iy) = -\frac{3N^2L}{4\pi^2\omega_0^2}\iint \frac{r\,dr\,d\theta}{(\exp\{-2L[-u^{1/2} - \frac{1}{2}b^2 - \frac{1}{2}br^2 + O(r^4)]\} - 1)u^{1/2}}, \tag{37}$$

where

$$u = [b^2 + 2b + (b+1)r^2 + O(r^4)].$$

Since to order r^2, the integrand in Eq. (37) is independent of θ, we can integrate over θ (0 to 2π) and extend the integration over r to infinity since $L \gg 1$.

We now expand the term in bold parentheses in the denominator of Eq. (37) as follows:

$$(e^{b^2L}e^{2Lu^{1/2}}e^{2L[br^2/2+O(r^4)]} - 1)^{-1} = (e^{b^2L}e^{2Lu^{1/2}} - 1)^{-1}\left(1 - \frac{br^2Le^{b^2L}e^{2Lu^{1/2}} + O(r^4)}{(e^{b^2L}e^{2Lu^{1/2}} - 1)}\right). \tag{38}$$

Substituting Eq. (38) into Eq. (37) we obtain

$$F^{(2s)}(iy) = -\frac{3N^2L}{2\pi\omega_0^2}\int_0^\infty \frac{rdr}{(e^{b^2L}e^{2Lu^{1/2}} - 1)u^{1/2}} + \frac{3N^2L}{2\pi\omega_0^2}\int \frac{dr\,br^3Le^{b^2L}e^{2Lu^{1/2}}}{(e^{b^2L}e^{2Lu^{1/2}} - 1)^2u^{1/2}} + \cdots. \tag{39}$$

Note that the first integral $F_1^{(2s)}(iy)$ in Eq. (39) is singular at $y=0$ while the second integral $F_2^{(2s)}(iy)$ and, therefore, the rest of the terms in the series of Eq. (39) are zero at $y=0$. We now treat these integrals with $y \neq 0$.

In $F_1^{(2s)}(iy)$, we make the change of variables

$$Z = [b^2 + 2b + (b+1)r^2]^{1/2}, \quad dZ = \frac{(b+1)rdr}{Z}, \tag{40}$$

to obtain

$$\begin{aligned} F_1^{(2s)}(iy) &= -\frac{3N^2L}{2\pi\omega_0^2}\int_{(b^2+2b)^{1/2}}^\infty \frac{dZ}{e^{b^2L}e^{2LZ} - 1} \\ &= \frac{3N^2}{4\pi\omega_0^2}[2LZ - \ln(e^{b^2L}e^{2LZ} - 1)]\Big|_{Z=(b^2+2b)^{1/2}}^{\infty} \\ &= \frac{3N^2}{4\pi\omega_0^2}\ln(1 - \exp\{-2L[(b^2+2b)^{1/2} + \tfrac{1}{2}b^2]\}). \end{aligned} \tag{41}$$

Substituting the above expression for $F_1^{(2s)}(iy)$ into Eq. (10) we obtain

$$C_{v(1)}^{(2s)} = \frac{k_B(\beta\hbar)^2 3N^2}{4\pi^2\omega_0^2}\sum_{n=1}^\infty n\int_{-\infty}^\infty y^3\ln(1 - \exp\{-2L[(b^2+2b)^{1/2} + \tfrac{1}{2}b^2]\})\sin n\beta\hbar y\,dy. \tag{42}$$

We now expand the ln in Eq. (42):

$$\ln(1 - \exp\{-2L[(b^2+2b)^{1/2} + \tfrac{1}{2}b^2]\}) = \ln(1 - e^{-2L\sqrt{2b}}) + \ln\left(1 + \frac{e^{-2L\sqrt{2b}}\{1 - \exp[-2L\sqrt{2b}\,(\sqrt{1+b/2} - 1 + b^2/2\sqrt{2b})]\}}{1 - e^{-2L\sqrt{2b}}}\right). \tag{43}$$

Note that the first ln in Eq. (43) is singular at $y=0$, while the second ln vanishes at $y=0$.

Substitute Eq. (43) into Eq. (42) to obtain

$$\begin{aligned} C_{v(1)}^{(2s)} &= \frac{3k_B(\beta\hbar)^2N^2}{4\pi^2\omega_0^2}\sum_{n=1}^\infty n\int_{-\infty}^{+\infty} y^3\ln(1 - e^{2L\sqrt{2b}})\sin n\beta\hbar y\,dy \\ &+ \frac{3k_B(\beta\hbar)^2N^2}{4\pi^2\omega_0^2}\sum_{n=1}^\infty n\int_{-\infty}^{+\infty} y^3\ln\left(1 + \frac{e^{-2L\sqrt{2b}}\{1 - \exp[-2L\sqrt{2b}\,(\sqrt{1+b/2} - 1 + b^2/2\sqrt{2b})]\}}{1 - e^{-2L\sqrt{2b}}}\right)\sin n\beta\hbar y\,dy. \end{aligned} \tag{44}$$

The integral in the first sum of Eq. (44) can be done exactly. The integrand in the second sum is analytic at $y=0$ and, according to Lighthill,[10] gives no contribution to the low-temperature specific heat.

Before proceeding with the exact calculation of the first sum of Eq. (44), we show that $F_2^{(2s)}(iy)$ from Eq. (39) gives no contribution to the specific heat at low temperature. We have

$$F_2^{(2s)}(iy) = +\frac{3N^2L}{2\pi\omega_0^2}\int_0^\infty \frac{dr\, b r^3 L\, e^{b^2L} e^{2Lu^{1/2}}}{(e^{b^2L}e^{2Lu^{1/2}}-1)^2 u^{1/2}}. \tag{45}$$

Again we let $z=(b^2+2b+(b+1)r^2)^{1/2}$. Then

$$F_2^{(2s)}(iy) = \frac{3N^2L}{2\pi\omega_0^2}\int_{(b^2+2b)^{1/2}}^\infty b e^{b^2L}\frac{(z^2-b^2-2b)e^{2Lz}dz}{(e^{b^2L}e^{2LZ}-1)^2(1+b)^2}. \tag{46}$$

We integrate by parts to obtain

$$F_2^{(2s)}(iy) = +\frac{3N^2L^2b}{\pi\omega_0^2}\int_{(b^2+2b)^{1/2}}^\infty \frac{2z\,dz}{e^{b^2L}e^{2Lz}-1}\frac{1}{(1+b)^2}. \tag{47}$$

The integrated part vanishes.

Since the integrand in Eq. (47) is finite at $Z=0$, we can set the lower limit on the integral to zero. The integral can be evaluated as a power series to give

$$F_2^{(2s)}(iy) = \frac{3N^2b}{8\pi\omega_0^2 e^{b^2L}}\left(1+\tfrac{1}{4}e^{-b^2L}+\tfrac{1}{9}e^{-2b^2L}+\cdots\right). \tag{48}$$

Substituting Eq. (48) into Eq. (10) we obtain

$$C_{v(2)}^{(2s)} = \frac{3N^2k_B(\beta\hbar)^2}{8\pi\omega_0^2}\sum_{n=1}^\infty n\int_{-\infty}^{+\infty} y^3 b\, e^{-b^2L}\left(1+\tfrac{1}{4}e^{-b^2L}+\tfrac{1}{9}e^{-2b^2L}+\cdots\right)\sin n\beta\hbar y\, dy. \tag{49}$$

According to Lighthill,[10] the asymptotic expansion of

$$\int_0^\infty F(y)\sin 2\pi x y\, dy \underset{x\to\infty}{\sim} \frac{F(0)}{2\pi x}-\frac{F''(0)}{(2\pi x)^3}+\frac{F''''(0)}{(2\pi x)^5}-+\cdots. \tag{50}$$

Comparing Eq. (49) with Eq. (50) we see that

$$F(y)\sim y^5 e^{-my^2}$$

and that all even derivatives of $F(y)$ evaluated at $y=0$ are zero. Consequently, $C_{v(2)}^{(2s)}=0$ in the low-temperature limit.

We have, therefore, that $C_v^{(2s)}(T)$ reduces to the first sum in Eq. (44), which is

$$C_v^{(2s)}(T)\sim\frac{3k_B(\beta\hbar)^2N^2}{4\pi^2\omega_0^2}\sum_{n=1}^\infty nF_n, \tag{51}$$

where

$$\begin{aligned}F_n &= \int_{-\infty}^{+\infty} y^3\ln(1-e^{-2L\sqrt{2b}})\sin n\beta\hbar y\, dy\\ &= -2\left(\frac{\omega_0}{2L\sqrt{2}}\right)^4\left[\frac{12}{\epsilon_n^5}-\frac{\pi^4}{\epsilon_n}\left(\frac{1}{\sinh^4\epsilon_n\pi}+\frac{2\cosh^2\epsilon_n\pi}{\sinh^4\epsilon_n\pi}\right)\right.\\ &\quad -\frac{3\pi^2}{\epsilon_n^3\sinh^2\epsilon_n\pi}-\frac{3\pi^3\cosh\epsilon_n\pi}{\epsilon_n^2\sinh^3\epsilon_n\pi}\\ &\quad\left.-\frac{3\pi\cosh\epsilon_n\pi}{\epsilon_n^4\sinh\epsilon_n\pi}\right],\end{aligned} \tag{52}$$

with

$$\epsilon_n=\frac{n\hbar\omega_0}{2k_BTL\sqrt{2}}=n\epsilon_0.$$

It is interesting to observe that as $\epsilon_0\to\infty$ or $T\to 0$ that

$$F_n\to 2\left(\frac{\omega_0}{2L\sqrt{2}}\right)^4\left(\frac{12}{\epsilon_n^5}\right)+6\pi\left(\frac{\omega_0}{2L\sqrt{2}}\right)^4\frac{1}{\epsilon_n^4}.$$

which gives, in this limit, a contribution to the specific heat given by

$$C_v^{(2s)}(T) = -\frac{6\sqrt{2}}{15}N^2Lk_B\pi^2\left(\frac{k_BT}{\hbar\omega_0}\right)^3 + \frac{3N^2k_B}{4\pi}\left[6\zeta(3)\left(\frac{k_BT}{\hbar\omega_0}\right)^2\right]. \tag{53}$$

Equation (53) is not valid for large L since ϵ_0 must be large. In the limit of large L, the sum in Eq. (51) can be converted to an integral which can be shown to be

$$C_v^{(2s)}(T)\underset{L\to\infty}{\sim}-\frac{3}{16\pi^2}\frac{N^2}{L^2}k_B\int_0^\infty \epsilon F(\epsilon)d\epsilon,$$

where $F(\epsilon)$ is $F_m(\epsilon)$ given by Eq. (52), dropping the subscript n.

The first term in Eq. (53) (more than) cancels all of the leading term in the bulk contribution [see Eq. (24)] while the second term is exactly equal to the leading term in the surface contribution, given by $2C_v^{(s)}(T)$.

We have finally for the total specific heat of a thin film at low temperature,

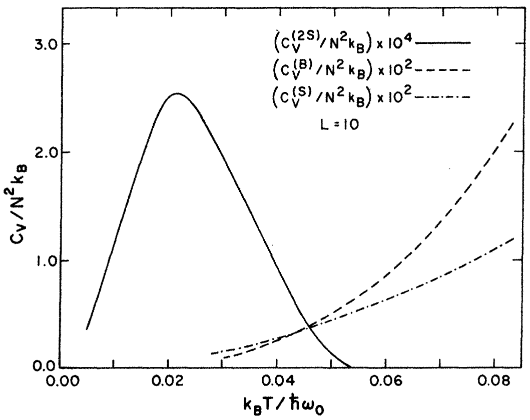


FIG. 2. Separate contributions to the total specific heat for a thin film of ten layers. Note that the interactive contribution $C_v^{(2s)}$ is magnified 100 times compared to the bulk and surface contributions.

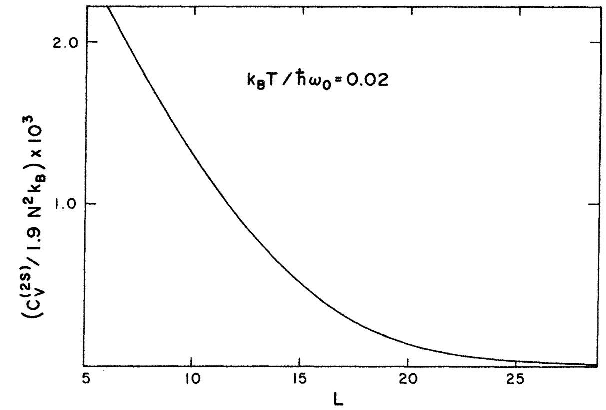


FIG. 4. Plot of the interactive contribution $C_v^{(2s)}$ to the specific heat for a fixed temperature as a function of film thickness showing the expected vanishing of this term as L increases.

$$C_v(T) \sim C_v^{(B)}(T) + 2C_v^{(s)}(T) + C_v^{(2s)}(T)$$
$$= 3N^2Lk_B\left[\frac{2\pi^2}{15}\left(\frac{k_BT}{\hbar\omega_0}\right)^3 + \frac{\pi^4}{21}\left(\frac{k_BT}{\hbar\omega_0}\right)^5 + \cdots\right] + \frac{3N^2k_B}{4\pi}\left[6\zeta(3)\left(\frac{k_BT}{\hbar\omega_0}\right)^2 + 15\zeta(5)\left(\frac{k_BT}{\hbar\omega_0}\right)^4 + 630\zeta(7)\left(\frac{k_BT}{\hbar\omega_0}\right)^6 + \cdots\right]$$
$$- \frac{6N^2Lk_B}{15}\sqrt{2}\left(\frac{k_BT}{\hbar\omega_0}\right)^3\pi^2 + \frac{3}{16}\frac{N^2k_B}{\pi^2L^2}\sum_{n=1}^{\infty}\left[\frac{\pi^4\epsilon_n}{n}\left(\frac{1}{\sinh^4\epsilon_n\pi} + \frac{2\cosh^2\epsilon_n\pi}{\sinh^4\epsilon_n\pi}\right) + \frac{3\pi^2}{\epsilon_n\sinh^2\epsilon_n\pi} + \frac{3\pi^3\cosh\epsilon_n\pi}{\sinh^3\epsilon_n\pi} + \frac{3\pi\cosh\epsilon_n\pi}{\epsilon_n^2\sinh\epsilon_n\pi}\right]. \tag{53}$$

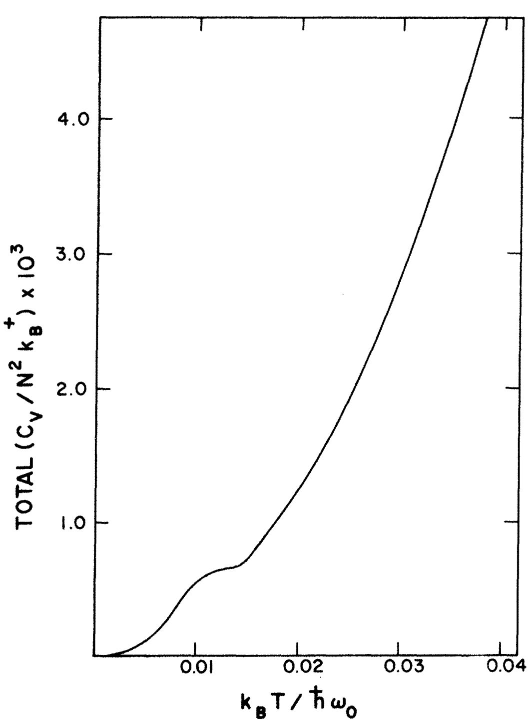


FIG. 3. Total specific heat C_v which is the sum of the contributions plotted in Fig. 2 for the same ten-layered film.

In Fig. 2 we have plotted $C_v^{(B)}$, $2C_v^{(s)}$, and $C_v^{(2s)}$ as a function of the temperature for a thin film of ten layers. Note particularly the maximum in $C_v^{(2s)}$. In Fig. 3 is plotted the total specific heat, C_v $(=C_v^{(B)}+2C_v^{(s)}+C_v^{(2s)})$ as a function of temperature for the same thin film. The maximum in $C_v^{(2s)}$ leads to a bump in the total specific heat which should be observable with available experimental techniques. For an insulating layer whose Debye temperature is 100 K, the bump should be observable in the temperature range of one to two degrees Kelvin.

In Fig. 4 is plotted $C_v^{(2s)}$ versus the thickness of the film for a fixed temperature. The contribution to the specific heat of the term becomes negligible for a film of the order of 30 layers.

There is no reason to expect that the bump is related to the model crystal which has been investigated here. Such an interference term between the two surfaces of the film represented by $C_v^{(2s)}$ should certainly be present in more realistic models.

ACKNOWLEDGMENTS

The author would like to thank Professor A. A. Maradudin, Professor D. L. Mills, and Professor

R. F. Wallis for their hospitality and many enlightening discussions during my association with them at U. C. Irvine. This work was supported in part by the Army Research Office under Grant No. DAAG-29-78-G0108.

---

*Permanent address: Department of Physics, Rutgers University, Camden, N. J. 08102.

[1]A. A. Maradudin, E. W. Montroll, G. H. Weiss, and I. P. Ipatova, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic, New York, 1971), p. 139ff.

[2]See, for example, Ref. 1, p. 580.

[3]See, for example, L. D. Landau and E. M. Lifshitz, *Theory of Elasticisty* (Pergamon, Oxford, 1970), p. 113.

[4]G. P. Alldredge, Phys. Lett. 42A, 281 (1972).

[5]E. W. Montroll, J. Chem. Phys. 15, 575 (1947).

[6]L. Van Hove, Phys. Rev. 89, 1189 (1953).

[7]A. A. Maradudin, R. F. Wallis, and A. Eguiluz, *Statistical Mechanics and Statistical Methods in Theory and Applications,* edited by U. Landman (Plenum, New York, 1977), p. 371 and references therein.

[8]A. A. Maradudin (unpublished).

[9]P. Mazur and A. A. Maradudin, Phys. Rev. B (in press).

[10]M. J. Lighthill, *Introduction to Fourier Analysis and Generalized Functions* (Cambridge University Press, Cambridge, 1958), Chapt. IV.

[11]See Ref. 1, p. 587.

[12]See Ref. 1, p. 397.

[13]A. A. Maradudin, *et al., Green's Functions For Monatomic Simple Cubic Lattices* (Académie Royale de Beligique, Brussels, 1960).

[14]I. S. Gradohteyn and I. W. Ryzhik, *Table of Integrals Series and Products* (Academic, New York, 1965), p. 905.

[15]L. Dobrzynski and G. Leman, J. Phys. (Paris) 30. 116 (1969).