Calculation of the heat capacity of a thin membrane at very low temperature

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We calculate the dependence of heat capacity of a freestanding thin membrane on its thickness and temperature. A remarkable fact is that for a given temperature, there exists a minimum in the dependence of the heat capacity on the thickness. The ratio of the heat capacity to its minimal value for a given temperature is a universal function of the ratio of the thickness to its value corresponding to the minimum. The minimal value of the heat capacitance for a given temperature is proportional to the temperature squared. Our analysis can be used, in particular, for optimizing support membranes for microbolometers.

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I. INTRODUCTION

Thin freestanding membranes are extensively used for sensing and detecting, in particular, for mounting of microbolometers.1 Thermal and heat transport properties of such membranes are very important for the sensitivity of such bolometers and their time response. At low temperatures, the wavelength of thermal phonons responsible for the heat capacity and conductance can exceed the membrane thickness, b. In this case, the vibrational modes significantly differ from those in bulk materials.2 In particular, the lowest vibrational mode (the bending mode) has a quadratic rather than a linear dispersion law.3 The finite-size effects,4 as well as the role of bending modes for membranes2 and long molecules in polymer crystals,5 were discussed. However, the dependence on thickness of the heat capacity of membranes was not explicitly considered.

The contributions of the low-energy modes to the low-frequency density of vibrational states increase with decrease of the membrane thickness. As a result, the low-temperature heat capacity also increases. As the thickness increases, the heat capacity is determined by higher modes having an essentially linear dispersion law. Consequently, the heat capacity crosses over to that of a bulk material. As a result, the thickness dependence of the heat capacity of thin membranes is nonmonotonous, having a sharp minimum at some optimal, temperature-dependent thickness. This minimum is similar to the minimum in thickness dependence of the ballistic heat transfer (power radiation) predicted in Ref. 6. However, the concrete values of the optimal thickness for the heat capacity and the ballistic heat transfer are different. Consequently, a proper choice of the membrane thickness can be used for optimizing the time response of microbolometers mounted on thin freestanding membranes. The present Brief Report is aimed at the theory of low-temperature heat capacity of thin freestanding membranes.

II. VIBRATIONAL SPECTRUM

The vibrational modes of a thin membrane are superpositions of bulk longitudinal and transverse modes, their relative weights being determined by boundary conditions—both normal and tangential stresses should vanish. The eigenmodes are classified as symmetric (SM) and antisymmetric (AM). Both are superpositions of the longitudinal and transverse bulk modes with wave vectors \( k^l \) and \( k^t \), respectively. The relations between \( k^l \) and \( k^t \) are

\[
\begin{align*}
\tan(bk'^t/2) & = - \frac{4k^l}{(k^l)^2 - (k^t)^2}, \\
\tan(bk'^l/2) & = - \frac{4k^t}{(k^l)^2 - (k^t)^2},
\end{align*}
\]

for SM and AM, respectively. Here \( k^l \) and \( k^t \) denote perpendicular and parallel components of the wave vectors with respect to the membrane. Inserting the dispersion laws of the bulk modes, \( k^l = \omega/c_l \) and \( k^t = \omega/c_t \), where \( c_l \) and \( c_t \) are speeds of transversal and longitudinal sound, into Eqs. (1) and (2), one obtains transcendental equations for the dispersion laws, \( \omega_{s,n}(k) \), of different vibrational branches. Here the subscript \( s \) stands for the branch type, while \( n \) stands for its number.

In addition to AM and SM, there exists a horizontal shear mode (HS), which is a transversal wave with both displacement and wave vector parallel to the plane of the membrane. The HS mode dispersion law is

\[
\omega_{HS,n} = c_i\sqrt{(n\pi/b)^2 + k_i^2},
\]

where \( n \) is an integer number. SM, AM, and HS modes are the only vibrations that can exist in a membrane. The modes possess a very important property: as follows from Eqs. (1)–(3), the frequencies of all modes scale as

\[
\omega_{s,n} = 2c_i b^{-1} w_{s,n}(bk_i).
\]

Figure 1 shows the six lowest branches. Only the three lowest branches are gapless; consequently, only they contribute to the heat capacity of a membrane at \( k_B T \ll \hbar \omega_{HS,1}(0) \). The lowest HS and SM are linear at \( k \ll b^{-1} \), while the AM dispersion law can be approximated at small \( k_i \) as

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we obtain the dispersion law for flexural waves:

\[ \omega_{\text{AM},0}(k_b) = \frac{\lambda}{2m} k_{b/2}^2, \quad m^* = \frac{hc_i^3}{2c_i b \sqrt{c_i^2 - c_s^2}}. \]  

(5)

The lowest AM branch is a flexural wave and the dispersion law of this branch can be obtained from the two-dimensional (2D) analog of the Bernoulli-Euler theory.\(^1\) We will reproduce the derivation here since we will need it for the analysis of the applicability range of our theory. Choosing the \(z\) axis perpendicular to the membrane, we have\(^7\)

\[ \rho \frac{\partial^2 u}{\partial t^2} + \frac{D}{b} \Delta^2 u = 0, \quad D = \frac{b^3 E}{12(1 - \sigma^2)}. \]  

(6)

where \(u\) is the displacement perpendicular to the membrane, \(\rho\) is the density of the membrane material, \(E\) is the Young modulus, \(\sigma\) is the Poisson ratio, and \(\Delta\) is the 2D Laplace operator. Searching for a solution in the form \(u \sim e^{i(k_b x - \omega t)}\), we obtain the dispersion law for flexural waves:

\[ \omega_{\text{AM}} = k_{b/2}^2 (D/\rho b)^{1/2}. \]  

(7)

Substituting the conventional expressions for the Young modulus and Poisson ratio through the sound velocities \(c_i\) and \(c_s\) and density \(\rho\), we arrive at the same dispersion law as given by Eq. (5). This equation is valid only in the long wavelength approximation, \(\lambda \gg b\).

III. HEAT CAPACITY OF A FREESTANDING MEMBRANE

We compute the heat capacity per unit area from the general equation

\[ C = \frac{1}{A} \sum_{b, n, k_b} \frac{(\beta \omega_{\text{AM},0}(k_b))^2 e^{\beta \omega_{\text{AM},0}(k_b)} - 1}{[e^{\beta \omega_{\text{AM},0}(k_b)} - 1]^2}, \quad \beta = \frac{1}{k_B T}, \]  

(8)

where \(A\) is the area of the membrane.

The heat capacity per unit area \(C\) of a thick membrane \((b \gg \lambda \pi b\epsilon)\) increases linearly with the thickness \(b\) as it should for a three-dimensional body. But for a thin membrane \((b \ll \lambda \pi b\epsilon)\), there is a minimum of heat capacity. The position of this minimum depends not only on the properties of the membrane material but also on temperature. It is important to underline that we calculated the heat capacity of a membrane per unit area. To find the specific heat capacity \(c_v\), we should divide the heat capacity per unit area \(C\) by the thickness \(b\).

For temperature \(T \ll \hbar \pi c_i / k_B b\), the heat capacity of a membrane is dominated by the contribution of the lowest AM branch. So we can find a crude estimate for the position of the minimum, \(b_{\text{min}}\), by equating the heat capacity per unit area of a bulk sample to the contribution of the lowest AM branch to the heat capacity per unit area of a thin film.

We find the total heat capacity per unit area of a bulk sample by multiplying the thickness \(b\) of the membrane and its specific heat capacity \(c_v\) by

\[ c_v \approx \frac{2 \pi^2}{5} \left( \frac{k_B T}{\hbar c_i} \right)^3, \quad \frac{1}{c_v} = \frac{2}{3} \left( \frac{2}{c_i} + \frac{1}{c_s} \right). \]  

(9)

The contribution of the lowest AM with the dispersion law (5) can be easily calculated from Eq. (8) as

\[ \frac{C_{\text{AM},0}}{k_B} = \frac{k_B T m^2(2)}{\pi \hbar^2}. \]  

(10)

From the equality \(c_i b = C_{\text{AM},0}\), we obtain

\[ b_{\text{min}} = a = \frac{c_i b^2 c_i^2}{k_B^2 c_i^2 \sqrt{c_i^2 - c_s^2}} \approx \frac{5 \sqrt{3}(2)}{4 \pi^3} = 0.11. \]  

(11)

For the temperature 0.1 K, the estimated position of the heat capacity minimum \(b_{\text{min}} \approx 400 \text{ nm}\).

A more accurate procedure is based on the exact expression (8). Making use of the scaling relation (4), one can cast this equation in the form

\[ C = \frac{k_B}{2 \pi b^2} \mathcal{F}(\xi), \]  

(12)

\[ \mathcal{F}(\xi) = \sum_{s, n} \int_0^\infty \xi d\xi \frac{[z_w'(\xi)]^2}{[z_w'(\xi)]^2}, \]  

(13)

Here \(\xi = b k_b\) and we assume that the temperature is well below the Debye temperature so that we can integrate from 0 to infinity. One sees that the heat capacity per unit area is a nonmonotonous function of the film thickness, \(b\). Its minimum can be determined by equating the derivative \(\partial C/\partial b\) to zero. It leads to the relation

\[ b_{\text{min}} = \frac{b c_i}{k_B c_i}, \]  

(14)

where \(z^*\) is determined from the equation \(\mathcal{F}' (z^*)z^* = -2\mathcal{F}(z^*)\). The value of \(z^*\) depends on the ratio \(c_s/c_i\), and for \(c_s/c_i = 1.6, z^* = 1.9\).

Numerical calculations including the 30 lowest branches give the value \(b_{\text{min}} \approx 240 \text{ for } T = 0.1 \text{ K}\), which is not far from the crude estimate obtained using only the lowest mode. Substituting Eq. (14) into Eq. (12), we obtain

FIG. 1. The six lowest branches of vibrations in a membrane. The lowest AM branch is quadratic around zero.
The result can be summarized in the universal form

\[ \frac{C_{\min}}{C} = \left( \frac{b_{\min}}{b} \right)^2 \frac{F(z')}{F(z)} \cdot \frac{\tau_{\min}}{\tau}, \]

where \( b_{\min}(T) \) is given by Eq. (14). This is shown in Fig. 2.

**IV. APPLICABILITY RANGE OF THE THEORY**

There are several phenomena limiting the increase of the heat capacity with the decrease of the film thickness. The obvious limit is that the elasticity theory is not applicable when the thickness is comparable with interatomic distance. Below we will discuss another limit posed by anharmonic effects. The amplitude of thermal vibrations increases with decreasing thickness. As a result, in a very thin membrane the harmonic approximation used in this Brief Report becomes invalid.

To make an estimate, let us assume for simplicity that the thickness of the membrane \( b \ll b_{\min} \) and take into account only the AM,0 branch. Due to the thermal vibrations, the membrane will not be perfectly flat but have a shape described by some function \( f(x,y) \). The resulting increase in the area of the membrane corresponds to some average tension \( T \) of the membrane. Let us therefore first study the membrane in the presence of an external tension, and later insert the thermal value of this tension. In this case, in the equation of motion (6) an additional term appears:

\[ \rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = \frac{E_b^2}{12(1-\sigma^2)} \frac{\partial^4 \mathbf{u}}{\partial x^4} + \frac{T}{c^2}, \]

the dispersion law being

\[ \omega = \sqrt{\frac{E_b^2}{12\rho(1-\sigma^2)} k^4 + \frac{T}{\rho k^2}}. \]

When the second term in Eq. (17) becomes greater than the first one, the dispersion law changes to linear and the heat capacity of the membrane approaches some limiting value. Since thermal vibration produce an average strain, they will change the dispersion law. So, for a crude estimate, we will evaluate the average strain produced by the thermal vibrations and compare its contribution with the first item \( E_b^2 k^4 / 12\rho(1-\sigma^2) \). We can express the variation of the membrane area as \( \Delta A \approx 1/2 \int_{A} \nabla f^2 dx \). Substituting for \( f \) thermal modes of a square membrane and performing thermal average, one obtains an estimate for the typical elongation:

\[ \frac{\Delta L}{L} \approx \frac{k_b T_0}{\rho b^3 (c_1^2 - c_r^2) c_1^2} \ln \frac{L}{L_T}, \]

This relative elongation strongly depends on the membrane thickness. Substituting \( T = E(\Delta L/L) \) in Eq. (17) and comparing its contribution with the first item for thermal wave vectors, we obtain an estimate of the critical thickness below which our theory is not applicable:

\[ b_{\text{cl}} = \left( \frac{12 h c_l}{c_1 \sqrt{3(c_1^2 - c_r^2) \rho}} \ln \frac{L}{L_T} \right)^{1/4}. \]

Numerically, this estimate gives the thickness of several atomic layers, so it does not pose additional limitations as compared to the general range of applicability of the elasticity theory.

**V. SENSITIVITY AND RESPONSE TIME OF THE BOLOMETER**

Suppose we use a thin freestanding membrane with a detector on it as a sensitive element of a bolometer. In the presence of an incident flow of energy, \( P_i \) (see Fig. 3), we can obtain the temperature of a membrane as a function of time:

\[ \frac{C_{\min}}{C} = \left( \frac{b_{\min}}{b} \right)^2 \frac{F(z')}{F(z)} \cdot \frac{\tau_{\min}}{\tau}, \]
where $C_{\text{mem}}$ is the heat capacity of the membrane under the detector, $P_2(T_0)$ is the heat flow from surrounding media to the membrane under the detector, $P_1(T)$ is the heat flow from the membrane under the detector, and $T_0$ is the temperature of surrounding media. We assume that phonons are ballistic, i.e., the mean free path of the phonons is much longer than the size of the detector. Usually the relative temperature difference is less than 0.01, so we can expand the radiation power $P_1(T)$ around $T_0$ and use heat capacity as a constant. In this case, we obtain a response time \( \tau = C/(\partial P/\partial T) \). In Eq. (12), the part that depends only on $bT$ can be separated,

\[
P_1(t) = P_1(T) - P_2(T_0) + C_{\text{mem}}(T)(dT/dt),
\]

independent, the rate of temperature increase depends only on the heat capacity of the membrane under the detector, and \( T_0 \) is the temperature of surrounding media. We assume that phonons are ballistic, i.e., the mean free path of the phonons is much longer than the size of the detector. Usually the relative temperature difference is less than 0.01, so we can expand the radiation power $P_1(T)$ around $T_0$ and use heat capacity as a constant. In this case, we obtain a response time \( \tau = C/(\partial P/\partial T) \). In Eq. (12), the part that depends only on $bT$ can be separated,

\[
P = T^3 \tilde{P}(bT).
\]

From this we obtain response time as a function only of $bT$,

\[
\tau = \frac{\tilde{C}(bT)}{3\tilde{P}(bT) + bT\tilde{P}'(bT)}.
\]

From this we immediately obtain that the minimal response time $\tau_{\text{min}}$ as a function of membrane thickness does not depend on temperature. The dependence of the response time $\tau$ versus the membrane thickness is shown in Fig. 2. The position of $\tau_{\text{min}}$ is close to the position of $C_{\text{min}}$. In Fig. 2, this difference is difficult to see because it is only 5%. If we measure pulses of energy shorter than $\tau$, the rate of temperature increase depends only on the heat capacity of the membrane. In the opposite case, when pulses are longer than $\tau$, the final temperature difference depends only on $p = (\partial P/\partial T)$. The dependence of $p$ on the ratio $b/b_{\text{min}}$ is also presented in Fig. 2. From this picture we can see that the heat capacity $C$, the derivative of the radiation power with temperature $p$, and response time $\tau$ reach their minimal values at different thicknesses. This difference is about 10%. If one wants to construct a detector, one has to obtain either the shortest response time or the greatest temperature difference. Our calculations demonstrate that the best sensitivity and the shortest response time can be obtained by choosing the supporting membrane with thickness $b_{\text{min}}$.

VI. DISCUSSION AND CONCLUSIONS

We have studied the heat capacity of a thin membrane at low temperatures such that the typical wavelength of thermal phonons is of the order or smaller than the thickness of the membrane. Because of the quadratic dispersion law of the lowest vibrational branch, the heat capacity per area will increase with decreasing thickness below a certain thickness $b_{\text{min}}$. The thickness of minimal heat capacity is temperature dependent, $b_{\text{min}} \approx 1/T$. The shape of the curve $C(b)$ has the universal form (15). If we want to use the membrane for the support of microbolometers, the reduction of the heat capacity is important for the sensitivity of the detector for short pulses and the thickness should be chosen equal to $b_{\text{min}}$ at the operating temperature of the bolometer.

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