Supersolidity and the Thermodynamics of Solid Helium

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*The specific heat of solid helium in the temperature range below about 1.2 K has been found to contain a term varying as T^7, in addition to the usual T^3 contribution always found in a crystalline dielectric solid. It has been proposed by Anderson, Brinkman and Huse, (Science **310**, 1164 (2005)) that the existence of this T^7 term supports their theory of supersolidity. However, in this paper we show that corrections to the phonon specific heat arising from phonon dispersion are much larger than expected based on simple order of magnitude estimates and, as a consequence, it is very unlikely that the existence of this T^7 term can be considered as evidence for supersolidity.*

1. INTRODUCTION

Recently, a number of experiments have reported evidence that suggests that solid helium becomes a superfluid when cooled below a critical temperature T_c. Kim and Chan[1–3] have performed torsional oscillator experiments with solid helium over a wide range of pressure and temperature. They found that below T_c the period of the oscillator decreases indicating that a fraction of the mass of the solid helium has become decoupled from the torsional oscillator. This is referred to as non-classical rotational inertia (NCRI). At the time of writing this article, however, the experimental situation is not entirely clear. Rittner and Reppy[4] have also detected a decoupling of mass in a torsional oscillator experiment but report that the effect can be greatly reduced by annealing the solid helium sample at high temperature. This suggests that the effect is associated with some sort

of defect. Initial attempts to detect a steady state superflow, i.e., a dc flow of mass through a solid helium crystal were unsuccessful.[5,6] However, a recent experiment by Sasaki et al.[7] was able to detect a flow of mass which occurs when a crystal contains grain boundaries. This flow had the characteristics of a superflow, i.e., the rate of transport of mass was essentially independent of the driving force and appeared to be limited by a critical velocity.

There have been a number of theoretical papers that argue that a supersolid state does not occur in solid helium that is free of defects.[8,9] In contrast, Anderson, Brinkman and Huse[10] have presented a theory based on the idea that solid helium is "incommensurate". In this context, incommensurate means that in the ground state the number of lattice sites is greater than the number of atoms. One of the interesting predictions of their theory is that there should be a correction to the low temperature specific heat that varies as T^7. This would be in addition to the normal T^3 term arising from phonons in a dielectric solid at low temperatures. They point out that measurements of the specific heat by Gardner, Hoffer and Phillips[11] provide evidence for such a term. Furthermore, they claim that a term with this temperature dependence and magnitude is unlikely to arise from corrections to the low temperature limiting form of the phonon specific heat. Such corrections can arise from two independent mechanisms. Anharmonicity of the phonons does lead to a T^7 contribution but should be very small. The deviation of the phonon dispersion relation from linearity gives a contribution which in lowest order goes as T^5. Anderson et al.[10] point out that such terms are smaller than the T^3 contribution by powers of the parameter $(T/\Theta_D)^2$, where Θ_D is the Debye temperature. Since for solid helium Θ_D is 25 K, they expected that the corrections to the specific heat arising from phonon dispersion should be negligible in the temperature range around 1 K. In this paper we examine this question more closely and show that, in fact, the corrections due to dispersion are very unlikely to be small.

2. SPECIFIC HEAT OF PHONONS

The specific heat of solid helium has been investigated by a number of authors.[11–14] Here, we concentrate attention on the data of Gardner et al.[11] which are for pressures close to the melting curve and cover the temperature range 0.35 to around 1.2 K. The data for a molar volume of 20.96 cm^3 are shown in Fig. 1. It can be seen from the figure that these data can be fit very well by the sum of the usual T^3 term expected in a dielectric solid at low temperature together with an extra contribution going as T^7. Can the existence of this T^7 term be understood in terms of
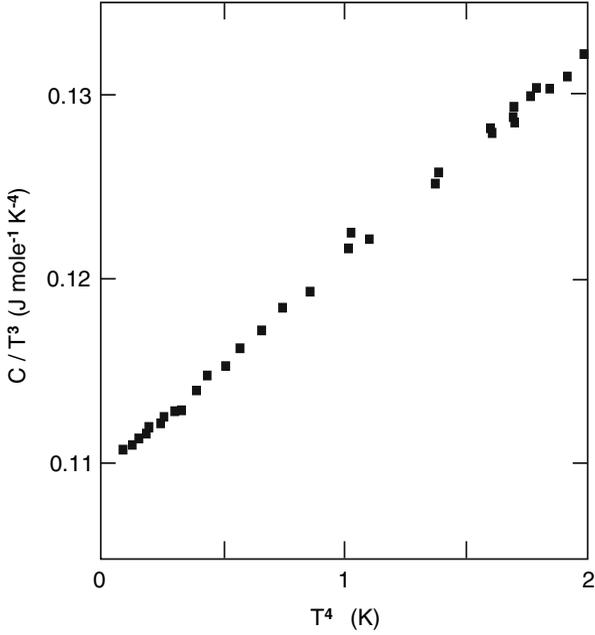
Fig. 1. Specific heat at constant volume of solid helium-4 per mole at a molar volume of $20.96\,\mathrm{cm}^3\,\mathrm{mole}^{-1}$ plotted as C/T^3 as a function of T^4. This is taken from Fig. 7 of Ref. 11. Some of the data points in the range below $T^4 = 0.1$ have not been included in this plot.

a phonon contribution or does it mean that there must be an extra effect associated with superfluidity?

For a dielectric solid at very low temperatures the specific heat per unit volume is given by the formula

$$C_{\mathrm{D}}(T) \approx \frac{2\pi^2 k^4 T^3}{5 v_{\mathrm{D}}^3 \hbar^3} = \frac{12\pi^4}{5} nk \left(\frac{T}{\Theta_{\mathrm{D}}} \right)^3, \tag{1}$$

where n is the number of atoms per unit volume and v_{D} is the Debye velocity, defined as

$$\frac{1}{v_{\mathrm{D}}^3} = \left\langle \frac{1}{v_j(\theta, \phi)^3} \right\rangle, \tag{2}$$

with $v_j(\theta, \phi)$ being the velocity of the j-th phonon branch in the direction θ, ϕ. The Debye temperature is

$$\Theta_{\mathrm{D}} = \left(\frac{6\pi^2}{V_{\mathrm{atom}}}\right)^{1/3} \frac{\hbar v_{\mathrm{D}}}{k}, \tag{3}$$

where V_{atom} is the volume per atom. The Debye temperature of solid helium at the melting pressure and as $T \to 0$ is $26\,\mathrm{K}$.[11] This corresponds to a Debye velocity of $2.85 \times 10^4\,\mathrm{cm\,s^{-1}}$.

Here, we investigate whether the effect of phonon dispersion results in an appreciable deviation of the specific heat from the T^3 law in the temperature range of interest, i.e., the range in which Gardner et al. have noticed that there is an excess heat capacity that can be fit by a T^7 term. This range extends from roughly $0.6\,\mathrm{K}$ to $1.2\,\mathrm{K}$. At $1.2\,\mathrm{K}$, for example, the specific heat was found to be approximately 20% above the T^3 value.

The general expression for the phonon specific heat neglecting anharmonicity is

$$C(T) = \frac{\hbar^2}{kT^2} \int \frac{\omega^2 g(\omega)\exp(\beta\hbar\omega)}{[\exp(\beta\hbar\omega) - 1]^2} d\omega, \tag{4}$$

where $g(\omega)$ is the density of phonon states per unit volume and frequency. The density of states can be calculated from the phonon dispersion curve $\omega_j(\vec{q})$ if this is known for all wave vectors and polarizations. Unfortunately, detailed measurements of the phonon dispersion in solid helium have not been made and so it is not possible to determine $g(\omega)$ reliably in this way.[15]

To get some idea of the corrections to the specific heat from dispersion consider first a simplified model in which the dispersion relation is isotropic, and the transverse and longitudinal sound velocities are the same and therefore equal to v_{D}. Suppose that the first correction to linear dispersion is of the form[16]

$$\omega = v_{\mathrm{D}} q(1 - \gamma_3 q^2 + \cdots). \tag{5}$$

Then it is straightforward to show that the lowest order correction to the specific heat is

$$C_3 = \frac{40\pi^4}{7} \gamma_3 \frac{k^6 T^5}{\hbar^5 v_{\mathrm{D}}^5}. \tag{6}$$

Thus, the correction relative to the Debye specific heat C_{D} is

$$\frac{C_3}{C_{\mathrm{D}}} = \frac{100\pi^2}{7} \gamma_3 \left(\frac{kT}{\hbar v_{\mathrm{D}}}\right)^2. \tag{7}$$

Is this correction appreciable at 1 K? To answer this, an estimate of the parameter γ_3 is needed. We can get an approximate idea of the magnitude of γ_3 from the known values of this parameter in liquid helium. Very accurate measurements have been made by Rugar and Foster.[16] They find values that are of the order of $1\,\text{Å}^2$. The value is negative at low pressures but it is known from other experiments and analysis to become positive at higher pressures and to have a value of around $2.2\,\text{Å}^2$ close to the freezing pressure.[17] If we take $1\,\text{Å}^2$ as a representative value we obtain the result

$$\frac{C_3}{C_D} \approx 0.3T^2 \approx 200 \left(\frac{T}{\Theta_D} \right)^2 . \tag{8}$$

Thus, based on this estimate at least, two things are clear. The magnitude of the correction to the specific heat due to non-linear phonon dispersion is significant at 1 K, i.e., of the order of 30%, and in the same general range as found by Gardner et al. Second, the correction to the specific heat is much larger than the simple order of magnitude estimate of $(T/\Theta_D)^2$.

As a next step, we consider higher order terms in the dispersion. At first sight one might expect that the frequency ω would be a power series containing only odd powers of q. However, in a remarkable paper Kemoklidze and Pitaevski (KP)[18] have shown that because of the long range part of the van der Waals force the series contains a q^4 term, i.e.,

$$\omega = v_D q (1 - \gamma_3 q^2 - \gamma_4 q^3 + \cdots). \tag{9}$$

They derive an explicit result for the coefficient γ_4

$$\gamma_4 = \frac{\pi^2}{24} \frac{\rho \phi}{v_L^2 m^2}, \tag{10}$$

where ρ is the mass density, v_L is the longitudinal sound velocity and m is the atomic mass. ϕ is the coefficient of the van der Waals force at long distance, i.e., the potential energy associated with the van der Waals force between two atoms is $V(r) = -\phi/r^6$. As far as we can see, the KP effect should only apply to longitudinal phonons. Putting in values appropriate for solid helium at the melting pressure[19] ($\rho = 0.1908\,\text{g cm}^{-3}$, $v_L = 4.88 \times 10^4\,\text{cm s}^{-1}$, and $\phi = 1.57 \times 10^{-60}\,\text{erg cm}^6$) gives $\gamma_4 = 1.2\,\text{Å}^3$. If this were the only correction term in the dispersion relation, i.e., if $\gamma_3 = \gamma_5 = \cdots = 0$, then the lowest order correction can be calculated to be

$$C_4 = \frac{15\,120\zeta(7)}{\pi^2} \gamma_4 \frac{k^7 T^6}{\hbar^6 v_L^6}. \tag{11}$$

To compare this with the T^3 specific heat, note that in an isotropic approximation the Debye velocity is related to the longitudinal v_{L} and transverse v_{T} sound velocities by the formula

$$v_{\mathrm{D}}^{-3} = (v_{\mathrm{L}}^{-3} + 2v_{\mathrm{T}}^{-3})/3. \tag{12}$$

Then we find that

$$\frac{C_4}{C_1} = \frac{113\,400\zeta(7)}{\pi^4}\gamma_4\frac{1}{1+2v_L^3/v_T^3}\frac{k^3T^3}{\hbar^3v_L^3} = 1.6 \times 10^{-3}T^3. \tag{13}$$

Thus in the temperature range up to $1.2\,\mathrm{K}$, this amounts to a small correction. Consequently we will not further consider effects arising from the KP term γ_4.

Now let us consider how a phonon contribution to the specific heat that goes as T^7 might arise. There appear to be two possibilities. The first is to propose that the corrections to the phonon dispersion relation are of the form

$$\omega = v_D q(1 - \gamma_3 q^2 - \gamma_5 q^4), \tag{14}$$

with negligible higher order terms, and with the coefficient γ_3 much smaller than expected. If γ_3 is zero, it is straightforward to show that the correction to the specific heat arising from γ_5 is C_5 where

$$\frac{C_5}{C_1} = 112\pi^4\gamma_5\frac{k^4T^4}{\hbar^4v_{\mathrm{D}}^4}. \tag{15}$$

To get a T^7 term of the magnitude found by Gardner $et\ al$ would require that $\gamma_5 = 2.0\,\text{Å}^4$. This is not unreasonably large since it is of the order of the square of the values of γ_3 that have been measured in liquid helium.

A second possibility that we consider as more likely is that the cubic dispersion term γ_3 is positive for some propagation directions and polarizations and negative for others. We note that calculations of the phonon dispersion in solid helium give anomalous dispersion (i.e., negative γ_3) for some directions and polarizations.[20] Then when considering all polarizations and directions, the T^5 term could happen to be small. A T^7 term could arise either from the γ_5 term already discussed or from the γ_3 term in second order. For a single branch with velocity v_{D}, the correction to the specific heat arising from the γ_3 term in second order is

$$C_{3,2} = \frac{896\pi^6}{15}\gamma_3^2\frac{k^8T^7}{\hbar^7v_{\mathrm{D}}^7}. \tag{16}$$

The total correction coming from all polarizations and directions would then be given by the same expression but with an average value $\langle \gamma_3^2 \rangle$ replacing γ_3^2. To get agreement with the data of Gardner *et al.* requires $\langle \gamma_3^2 \rangle^{1/2} = 0.7 \text{Å}^2$, which is a reasonable value.

We can also investigate the corrections to the T^3 law in a simple model crystal. Consider as an example a face-centered cubic crystal with central forces between nearest neighbors described by a spring constant K. Let the atomic mass be M. For this model the Debye temperature is [21]

$$\Theta_D = \frac{2.965 \hbar}{k} \sqrt{\frac{K}{M}}. \tag{17}$$

A straightforward numerical calculation of the phonon density of states followed by an evaluation of the specific heat gives the result

$$\frac{C}{C_D} = 1 + 60 \left(\frac{T}{\Theta_D} \right)^2 + \cdots \tag{18}$$

Thus, again the correction to the specific heat is much larger than the rough estimate of $(T/\Theta_D)^2$. In Fig. 2 we show the specific heat of the fcc crystal as a function of T/Θ_D. The measurements of Gardner et al. cover
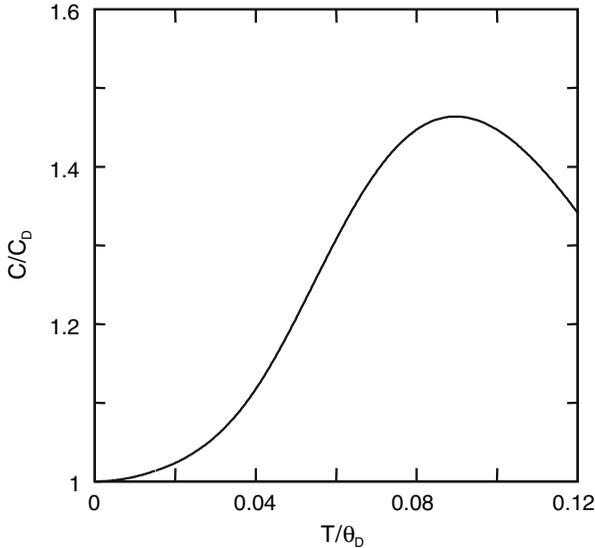

Fig. 2. Specific heat $C(T)$ of a fcc crystal plotted as $C(T)/C_D$ versus T/Θ_D. C_D is the low temperature Debye specific heat proportional to T^3.

the temperature range up to $T/\Theta_D : 0.05$. It can be seen that for the fcc model C/C_D varies by 20 % over this temperature range.

3. DISCUSSION

The above estimates show that one cannot conclude that the excess specific heat seen by Gardner et al.[11] is evidence that there is a T^7 contribution to the specific heat that results from the zero-point vacancies in an incommensurate solid. Phonon dispersion should lead to a contribution to the specific heat that has a magnitude roughly the same as the T^7 term that has been found experimentally, but at the present time there is no way to calculate the precise magnitude and temperature dependence of this contribution. For example, while the simple model of the fcc crystal that we have considered gives a correction to the phonon specific heat that is positive, if the phonon dispersion is anomalous as it is in liquid helium at low pressure,[16,17] the correction will be negative. An accurate measurement of the phonon dispersion curves by neutron scattering, for example, would make it possible to estimate the phonon contribution.

Finally, we emphasize that in this paper we have addressed only the phonon contribution to the specific heat. There may also be a significant contribution from thermally- excited vacancies. Through X-ray studies,[22] the lattice parameter of solid helium has been measured as a function of temperature for samples maintained under conditions of nearly constant volume. The lattice parameter is found to decrease as the temperature is raised and it is assumed that this decrease occurs because vacancies are thermally excited. From the experimental data, an activation energy E_v for vacancy formation can be found. It is then possible to use this value of E_v to calculate the vacancy contribution C_{vac} to the specific heat. Surprisingly, the predicted value of C_{vac} appears to be too large to be consistent with the measured specific heat.[22] One possible explanation for this discrepancy is that the vacancies are not localized and that as a result they form a band of energies.[23–25] It is also possible that in fact the phonon specific heat is less than has been believed and that as a consequence more of the specific heat that is experimentally measured arises from vacancies.

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