Thermodynamics of an incommensurate quantum crystal

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Abstract

We present a simple theory of the thermodynamics of an incommensurate quantum solid. The ground state of the solid is assumed to be an incommensurate crystal, with quantum zero-point vacancies and interstitials and thus a non-integer number of atoms per unit cell. We show that the low temperature variation of the net vacancy concentration should be as $T^4$, and that the first correction to the specific heat due to this varies as $T^7$; these are quite consistent with experiments on solid $^4$He. We also make some observations about the recent experimental reports of “supersolidity” in solid $^4$He that motivate a renewed interest in quantum crystals.
Recent experiments showing a marked low temperature reduction in the rotational moment of inertia of crystals of solid $^4$He have rekindled interest in this highly quantum-mechanical solid. The proposed “supersolid” phase is believed to occur due to the quantum behavior of point defects, namely vacancies and interstitials, in this crystal of bosons. Over the past twenty years various experiments have been performed to measure the temperature dependence of the vacancy concentration in solid $^4$He. Although there are considerable differences in the results, the most accurate data comes from x-ray measurements of the lattice constant as a function of temperature at fixed density. These data have usually been interpreted in terms of a classical theory of vacancies involving an activation energy and a configurational entropy for their creation. However, this theory implies a corresponding vacancy contribution to the specific heat that is as large as the phonon contribution near 1 Kelvin. Such a classical vacancy contribution to the specific heat has not been seen; the specific heat is instead well explained almost entirely in terms of the $T^3$ term from the phonon spectrum, and the leading correction to this fits very well to a $T^7$ term. There have been various attempts to explain this discrepancy but none have been satisfactory and the problem has remained open.

Here we propose a simple phenomenological thermodynamic description of a low-temperature incommensurate quantum solid. We note that the ground state of a quantum solid need not be commensurate, i.e. it need not have an integer number of atoms per unit cell. One description of the quantum solid is as a density wave that has formed in the quantum fluid. The periodicity of this density wave need not match precisely to the particle density, so that the ground state may be incommensurate, with unequal densities of vacancies and interstitials. The x-ray measurements on solid hcp $^4$He show that the density of vacancies increases faster than that of interstitials with increasing temperature, indicating that thermal fluctuations favor vacancies more than interstitials. Whether or not the same is true for quantum fluctuations is not clear at this point. We develop a simple thermodynamic theory of the low temperature behavior of an incommensurate quantum solid, finding that the low temperature net change in vacancy density at fixed particle density follows a $T^4$ power law behavior. The x-ray data are quite consistent with such a temperature dependence, as we show below. In addition, we show that this simple model produces a $T^7$ correction to the specific heat, as has been observed. Such a scenario could apply to any highly quantum solid and is not specific to bosons, so solid $^3$He should and does show
similar phenomena \[7, 8\]; perhaps hydrogen might, also.

It has been argued by one of us based on Jastrow-type wave functions that it is expected that there will be vacancies in the ground state of a highly quantum fluctuating solid such as $^4$He, and that such a ground state may be superfluid \[9\]. The vacancies are an integral feature of the ground state and carry no entropy or energy. These vacancies may be sufficiently mobile that they never behave as classical particle-like objects at the temperatures where the solid is present. Thus we will assume that the vacancies and interstitials in solid $^4$He remain in a strongly-correlated quantum state up to temperatures in the vicinity of 1 Kelvin, so they do not make a large contribution to the specific heat other than the incommensurability effect that we describe below.

For an hcp lattice of volume $V$ and lattice constant $a$, the number of lattice sites is $N_s = \sqrt{2}/a^3$. If the ground state crystal is incommensurate, then its number $N$ of atoms differs from its number of sites: $N \neq N_s$. Recent data on the possible superfluid nature of these solids \[2\] suggests that these two numbers could differ by up to 1%, although it seems quite possible that the 1% effect in the apparent superfluid density could arise from a much smaller (or even zero) net density of defects. Such a small difference between the number of atoms and the number of lattice sites may have escaped detection in simulations \[10, 11, 12\] of the ground state of solid $^4$He. Direct comparisons of experimental measurements of the density of $^4$He atoms to the x-ray density of sites do not appear to have been published for the low pressure hcp phase where the apparent supersolidity has been seen, although Simmons \[13\] tells us that the difference appears to be well under 1%. We thus strongly urge that more simultaneously precise density and lattice constant measurements be done for the quantum solids to learn how incommensurate their ground states really are, especially at the lowest densities where quantum fluctuations should be strongest.

Given that a crystal may be incommensurate, one needs to develop a theory in which the lattice constant and the density can change independently. In the temperature range we consider, the vacancies and interstitials are assumed to be incorporated in a highly-correlated quantum state of the system and the only low frequency modes giving large contributions to the temperature dependence of the free energy are the phonons. In the standard treatment of the low temperature thermal expansion of a crystal it is the density dependence of the phonon velocities (the Gruneisen parameters) that determine the expansion. Here we will instead work at fixed particle density, but allow the lattice constant and thus the incommensurability
to vary, driven by the dependence of the phonon velocities on the incommensurability. Thus we consider the free energy for a given mass of helium at a fixed volume, so that we do not need to include the overall density as a variable. Let the incommensurability

\[ \epsilon = \frac{N_s - N}{N_s} = \epsilon_0 + \delta \]  

be the net fractional vacancy number (i.e., the fraction of vacancies minus the fraction of interstitials). We will ask about the crystal’s behavior as a function of its incommensurability, although this is not a variable that is under ready experimental control. Here \( \epsilon_0 \) is the incommensurability at absolute zero temperature. Thus we obtain the following expression for the free energy as an expansion at low temperature and low deviation \( \delta \) of the incommensurability from the ground state value:

\[ F = -E_0 + \frac{E_2}{2} \delta^2 - (D_0 + D_1 \delta + ...) T^4 + ... . \]  

\( -E_0 \) is the ground state energy and \( E_2 \) gives the harmonic increase of the crystal’s energy when, staying at \( T = 0 \), the incommensurability is changed away from its ground state value by changing the number of lattice sites and thus the lattice constant. The \( T^4 \) term in the free energy is simply that due to acoustic phonons, and possibly also the acoustic superfluid mode that is expected to be present in a supersolid. The velocities of these acoustic modes in general vary with the incommensurability and are not at an extremum at the ground state incommensurability (which is \( \delta = 0 \)). Thus there is a term that is linear in \( \delta \) in the prefactor of this \( T^4 \) term, from its lowest-order linear variation with the incommensurability \( \epsilon \). The parameter \( D_1 \) plays the role of the Gruneisen parameter in driving the change in the lattice constant with temperature, but here this change is happening at fixed particle density. Next we simply find the value of the incommensurability that minimizes this free energy (2) at a given low temperature, obtaining to lowest order the temperature dependence

\[ \delta \approx \frac{D_1}{E_2} T^4, \]  

instead of the classical thermally-activated form \( (\delta \sim \exp (-\Delta/k_B T)) \) that one obtains in the classical vacancy theory. Figure 1 shows that the x-ray data [4] fits about as well to our proposed \( T^4 \) temperature dependence as it does to the classical theory. Clearly, when similar measurements are made more precisely and/or carried to lower temperatures, a discrimination between these two simple theories will be made; again, we encourage such
FIG. 1: The percentage net density of vacancies in a solid $^4$He crystal of molar volume 20.9 cm$^3$, as measured using x-rays via the change $\Delta a$ in the lattice constant from a reference value. Filled circles are the data from Ref. [4]. The solid line is a thermally-activated (classical) fit, while the dashed line is a fit to the $a \approx a_0 + bT^4$ behavior we expect if the ground state is incommensurate. The zero on the vertical axis is free and was chosen so that the classical fit goes to that value in the low $T$ limit. Figure courtesy of Ralph Simmons.

Efforts. Note that here $\delta$ is the increase in the fractional net density of vacancies above the possibly nonzero value it already has in the ground state. Also, the strong quantum fluctuations might mean that the ground state concentrations of vacancies and interstitials are both rather larger than $\epsilon_0$, but it is only the difference between these densities (that we are calling the net density) that is readily measurable and that enters as a thermodynamic parameter.

If instead the ground state is commensurate ($\epsilon_0 = 0$) and is locked in to a Mott “insulating” state with exactly one atom per lattice site, then the energy as a function of the change in the incommensurability $\delta$ is linear ($\sim |\delta|$) rather than quadratic. This results in the classical, thermally-activated behavior (it can be viewed as activation of atomic “carriers” across the Mott gap of this insulator). Another possibility is that the quantum fluctuations are strong enough to put the system out of the Mott insulating phase, but the ground state remains commensurate with $\epsilon_0 = 0$ due to an approximate (one might say “coincidental”) vacancy-interstitial symmetry of the ground state. In this latter case, the $\delta \sim T^4$ behavior will occur, provided the thermal excitations break that approximate symmetry, as they
certainly appear to from the x-ray data (Fig. 1) [4].

A second known anomaly follows from (2). The specific heat of solid $^4$He in the temperature range near 1 Kelvin was shown to fit nearly exactly (see [6], Fig. 7) to the sum of two power laws:

$$C = AT^3 + BT^7 .$$  \hfill (4)

The phonons give corrections to the $T^3$ specific heat due to their anharmonicity and dispersion, but these are expected to be down from the leading $T^3$ by powers of $(T/\Theta_D)$, where the Debye temperature $\Theta_D \cong 25$ K for helium. The observed $T^7$ correction is orders of magnitude larger than this [6]. Minimizing (2) with respect to $\delta$, the free energy as a function of temperature behaves as

$$F = -E_0 - D_0 T^4 - D_1^2 T^8/2E_2 + ... .$$  \hfill (5)

Thus the incommensurate crystal shows a positive $T^7$ leading correction to the phonon specific heat, due to its change of incommensurability with temperature. This is quite consistent with the experimental specific heat measurement [6]. The x-ray and specific heat experiments together give rough estimates of $E_2 \cong 80$ K/atom, $D_0 \cong 0.013$ (K$^3$-atom)$^{-1}$ and $D_1 \cong 0.06$ (K$^3$-atom)$^{-1}$ for the parameters in our free energy (taking $k_B = 1$). The new parameters $E_2$ and $D_1$ are of the same order as but larger than $E_0$ and $D_0$, respectively, all of which seems quite reasonable to us.

It should be noted that nowhere in the present argument did we invoke the boson nature of $^4$He. In fact, the discrepancies found in $^4$He between the temperature dependent x-ray vacancy data and the specific heat data within a classical vacancy model are also there in solid $^3$He [7]. There are quantitative differences between the isotopes, however, in that the corrections to the leading $T^3$ in the specific heat are much larger in $^3$He [8]. In fact, for $^3$He the correction to the leading $T^3$ term becomes larger than the $T^3$ term itself, and does not fit well to a simple $T^7$ correction [8]. But when the correction is that large, it should be expected that terms beyond $T^7$ cannot be neglected. Of course, the difference between bosons and fermions is essential when considering supersolidity, but it is not crucial for the thermodynamic issues we have discussed above.

Before concluding, we make a few comments about the recent experimental indications [2] of “supersolid” behavior in solid $^4$He: First we note the strong dissipation feature seen in the amplitude of their oscillator vs. temperature in Fig. 2A of Ref. [2]. This dissipation
should be significant only when the rate of damping of the superflow is of the same order as the frequency of the oscillator, which is about 1 kHz. The broad (on the temperature axis) dissipation feature implies that this damping rate is decreasing rather gradually with decreasing temperature, and passes through 1 kHz near the maximum damping, around $T = 60 \text{ mK}$. The appearance of a detectable apparently supersolid signal at much higher temperature should not be viewed as a possible supersolid phase transition at those higher temperatures, but instead possibly as the temperature where the precursors to supersolidity (the critical fluctuations) first become detectable in this experiment. This very broad regime with precursors to the apparent supersolidity suggests to us two possibilities: first, that perhaps these experiments are near a supersolid quantum critical point, where the quantum fluctuations destroy supersolid order in the ground state, replacing it with some sort of quantum vortex liquid ground state; or second, that the superflow is being damped by some temperature-dependent mechanism other than vortices (transverse phonons and umklapp are two possibilities that are not present in the liquid phase) and this damping only vanishes at zero temperature. Note that here we are always discussing the damping at linear order in the apparent superfluid velocity, thus in linear response to the solid’s motion. The actual supersolid transition is where this rate of damping vanishes, so one can have a true superflow in linear response. From these recent experiments at just the one frequency \[2\], we cannot determine where this transition actually happens, or even whether it does happen even at zero temperature, although we should conclude from their data that the supersolid transition temperature must be below the dissipation feature, which puts it below 50 mK \[14\]. The results of similar experiments at other frequencies that are “in the works” should be very informative. \[15\]

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