

Properties of Metastable Quantum Solids

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Abstract We consider the properties of quantum solids at pressures below the pressure range in which the solid is the stable phase. We estimate the spinodal pressure and determine how this pressure varies as a function of the de Boer parameter.

Keywords Solid helium

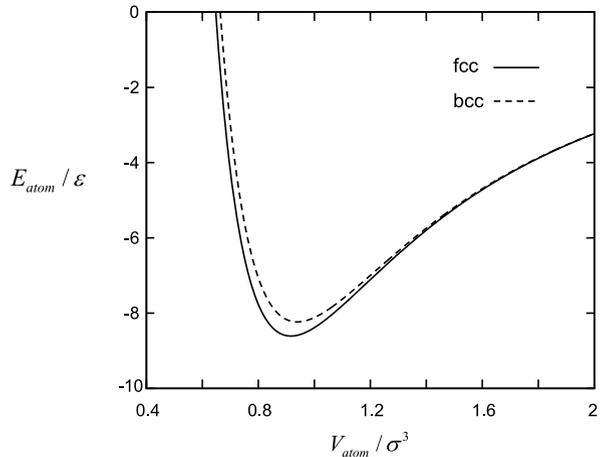
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During the past few years extensive investigations have been made of the properties of liquid helium at negative pressures [1, 2].¹ The equation of state of liquid helium-3 and -4 has been measured very accurately in the pressure range where the liquid is stable [3, 4]. This equation of state can be extrapolated into the pressure range in which the liquid is metastable. This extrapolation gives an estimate of the spinodal pressure, i.e., the pressure at which the bulk modulus and sound velocity go to zero and the liquid becomes unstable against long wavelength density fluctuations. For helium-3 this pressure P_s is -3.2 bars [5] and for helium-4 it is -9.6 bars [6]. Using the extrapolation of the equation of state, it is also possible to calculate the rate at which vapor bubbles will nucleate when the liquid is under negative pressure [5, 7–12]. These theoretical predictions have been tested and confirmed in a number of experiments [13, 14]. In a recent paper [15], we performed analogous calculations for metastable solid helium at pressures below the normal melting pressure. In this article, we first summarize the conclusions of that paper and then extend the work to present a more general view of the properties of quantum and classical solids at

¹ For a short review of early work on cavitation in liquid helium, see [1].

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Fig. 1 Energy per atom as a function of the volume per atom for fcc and bcc structures



pressures below the pressure range in which the solid is the thermodynamically stable phase.

Consider first a classical solid made up of atoms which interact through a Lennard–Jones potential

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1)$$

where r is the spacing between a pair of atoms. For any crystal structure it is straightforward to calculate the total energy per atom as a function of the volume per atom. For fcc and bcc crystals the results are shown in Fig. 1; we have not performed this calculation for hcp but it is reasonable to assume that the result would be very close to the result for fcc. The spinodal is at the volume per atom V_s where the second derivative of the energy goes to zero; this is at $1.183\sigma^3$ for fcc and $1.212\sigma^3$ for bcc. The spinodal pressure is found to be $-6.988\epsilon/\sigma^3$ for fcc and $-6.520\epsilon/\sigma^3$ for bcc. Near to the spinodal volume, the energy per atom is in the form of a power series in $(V - V_s)$ with the term $(V - V_s)^2$ absent. It is straightforward to show that as a consequence, the sound velocity goes to zero according to the law $c \propto (P - P_s)^{1/4}$. It is clear that this law should hold for any form of the potential provided the total energy of the solid comes from the potential energy, i.e., if the phonon zero-point energy is neglected.

In liquid helium, the pressure-dependence of the sound velocity for positive pressures has been measured extremely accurately (a precision of $\sim 10^{-4}$ for helium-4) [3, 4]. Analysis of the sound velocity in both helium-3 and -4 shows that the sound velocity varies with pressure as $(P - P_s)^\gamma$ with the exponent γ close to $1/3$, rather than $1/4$. A theory that allows for the effect of the phonon zero-point energy when the pressure is close to the spinodal has been proposed [16]. This successfully explains why γ is $1/3$, but it is not understood why the sound velocity should vary as $(P - P_s)^{1/3}$ even for pressures as much as 30 bars above P_s .

For solid helium, accurate measurements of the sound velocity over a wide pressure range are not available. However, very accurate measurements of the Debye

Fig. 2 Plot of $\Theta_D^3 V_m$ versus pressure for solid helium-4 taken from Ref. [15]. Θ_D is the Debye temperature and V_m is the molar volume. The open squares are from the measurements of Ahlers (Refs. [17–21]). The solid line is a least squares fit to the data. The intercept on the horizontal axis gives the spinodal pressure of -10.1 bars

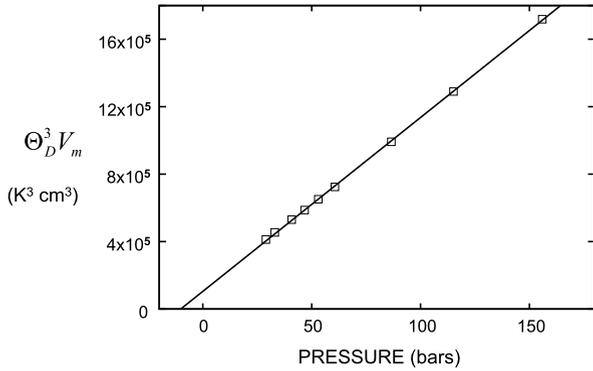


Table 1 Comparison of the spinodal pressure P_s with the value P_s^{cl} based on classical mechanics. The values for Ne, Ar, Kr and Xe are from the Monte Carlo calculations of Herrero (Ref. [22]) using the parameters in columns 2 and 3. The values for helium are from Ref. [15]. The spinodal pressure for H_2 was obtained from the fit shown in Fig. 4

Element	σ (Å)	ε (K)	Λ	P_s^{cl} (bars)	P_s (bars)
^3He	2.56	10.2	3.08	-587	-2.7
^4He	2.56	10.2	2.68	-587	-10.1
H_2	2.93	37.0	1.73	-1420	-340
Ne	2.782	35.9	0.584	-1600	-910
Ar	3.404	120.1	0.186	-2930	-2460
Kr	3.638	164.9	0.102	-3300	-3000
Xe	3.961	231.8	0.0633	-3590	-3380

temperature Θ_D have been made [17–21] and, in the low temperature limit Θ_D is related to the sound velocity by $c \propto \Theta_D V_m^{1/3}$, where c is now an appropriate average of the transverse and longitudinal sound velocities and V_m is the molar volume. In Fig. 2 we show plots of $\Theta_D^3 V_m$ versus pressure for solid ^4He [15]. The data are fit extremely well by a straight line thus indicating that $c \propto (P - P_s)^{1/3}$. A similar fit is found for helium-3 [15]. By extrapolation of the fit into the region below the melting pressure, it was estimated that the spinodal pressure is -10.1 bars for ^4He and -2.7 bars for ^3He . These values are remarkably close to the spinodal pressures for the liquid.

It is interesting to consider these results for the spinodal pressures in terms of the de Boer parameter $\Lambda \equiv h/\sigma\sqrt{m\varepsilon}$ where m is the atomic mass. Herrero [22] has used Monte Carlo simulations to calculate the spinodal pressures of noble gas solids (Ne, Ar, Kr, Xe). His results for P_s are listed in Table 1 along with the pressure P_s^{cl} obtained from the formula $-6.988\varepsilon/\sigma^3$ based on classical mechanics. In Fig. 3 we plot the ratio P_s/P_s^{cl} as a function of Λ , including both Herrero’s results and the values we have obtained for solid helium. To add to this plot it is of interest to investigate the properties of solid hydrogen since this has a value of Λ that is between that of helium and neon. Accurate measurements of the specific heat of solid hydrogen have

Fig. 3 Plot of the ratio of the spinodal pressure P_s to the classical spinodal pressure P_s^{cl} versus the de Boer parameter Λ . The values for Xe, Kr, Ar and Ne are taken from Ref. [15], ^4He and ^3He from Ref. [15], and H_2 as calculated in this paper

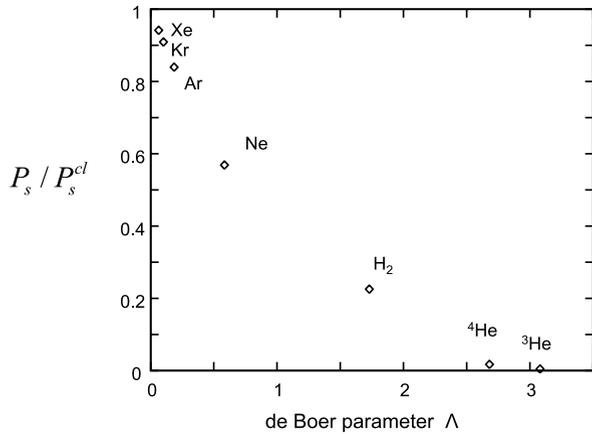
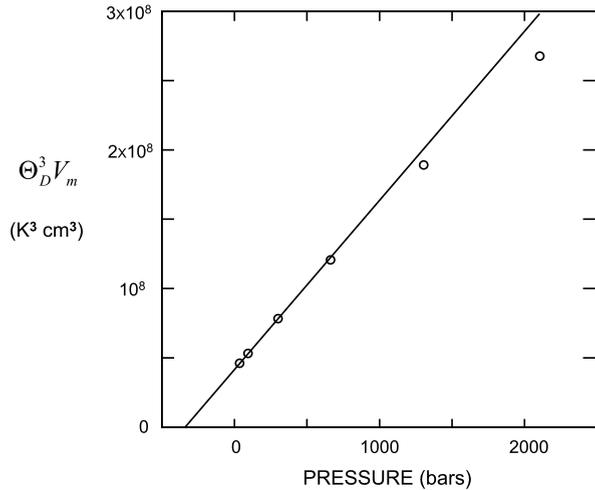


Fig. 4 Plot of $\Theta_D^3 V_m$ versus pressure for solid hydrogen. Θ_D is the Debye temperature and V_m is the molar volume



been made by Krause and Swenson [23] and the low temperature limiting value of the Debye temperature has been obtained.

In Fig. 4, we show a plot of $\Theta_D^3 V_m$ versus pressure. The solid line in the figure is a linear fit to the data for the three lowest pressures. This fit indicates that the spinodal pressure is -340 bars. This result is included in the summary graph of Fig. 3. We note that for hydrogen the $(P - P_s)^{1/3}$ law appears to hold only for low pressures. This suggests the following picture. The $c \propto (P - P_s)^{1/3}$ law that results from the zero-point energy contribution to the total energy holds in the pressure range close to P_s . For highly quantum solids the zero-point energy is large and so the pressure range “close to P_s ” is much larger than in classical solids with Λ small.

For liquid helium it has been possible to make experimental measurements in a pressure range that extends almost to the spinodal. These measurements have been made using a focused sound wave to produce a large pressure swing within a small volume of the liquid close to an acoustic focus [13, 14]. It is more difficult to perform

this type of measurement in a solid because the sound velocity depends on the crystallographic direction, and so it is harder to achieve strong acoustic focusing. However, for hcp solids such as helium-4 and hydrogen the sound velocity is isotropic around the c -axis and so it should be possible to use a cylindrical sound transducer provided that a crystal can be grown with c -axis along the axis of the transducer. Other experimental issues include the possible production of a large number of vacancies before the spinodal is reached and the thermal or quantum nucleation of bubbles. A preliminary discussion of these topics has been given in the previous article (Ref. [15]).

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