

# Properties of Metastable Solid Helium Below the Normal Melting Pressure

Humphrey J. Maris

Received: 26 February 2009 / Accepted: 3 April 2009 / Published online: 21 April 2009  
© Springer Science+Business Media, LLC 2009

**Abstract** In this note we report on simple estimates of the properties of metastable solid helium that is at a pressure below the normal melting pressure. We calculate the nucleation rate for formation of the liquid phase and estimate the “spinodal” pressure at which the solid becomes macroscopically unstable.

**Keywords** Solid helium · Nucleation · Supersolid

**PACS** 67.80

## 1 Introduction

In the past few years there have been many studies of the properties of liquid helium at temperatures and pressures such that the liquid is metastable. These studies have included investigations of the nucleation of vapor bubbles in liquid under tension,<sup>1</sup> [2] nucleation in superheated liquid [3] and nucleation of the solid in over pressurized liquid [4–11]. Helium is an ideal material for such studies of nucleation because it can be made very pure. In addition, it is possible to study the effect of quantum tunneling on the nucleation process [4, 5, 12, 13]. Although the nucleation of the solid from the liquid has been investigated by a number of workers, it appears that the nucleation of the liquid from the solid has not been studied. In this paper we consider the properties that may be expected for metastable solid helium at pressures below the normal melting pressure  $P_m$ , and discuss the rate at which the liquid phase is nucleated.

---

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

H.J. Maris (✉)  
Department of Physics, Brown University, Providence, RI 02912, USA  
e-mail: [Humphrey\\_Maris@Brown.edu](mailto:Humphrey_Maris@Brown.edu)

We want to emphasize that as far as we know, this is the first investigation of this topic and the results we obtain have to be regarded as tentative.

## 2 Estimate of the Spinodal Pressure

One approach to the investigation of metastable solid helium would be to perform some sort of a microscopic calculation starting from first principles. However, for liquid helium a much simpler approach has been successfully used which we now describe. The sound velocity in liquid helium has been measured extremely accurately at positive pressures. It has been possible to extrapolate the equation of state into the negative pressure range leading to several interesting results [14]. In a first attempt, the sound velocity was expanded as a power series in the pressure. It was found that for densities  $\rho$  in the range below the equilibrium density  $\rho_0$  at zero pressure the power series converged very slowly indicating that there must be some sort of singularity at negative pressure. It was then realized (this was rather obvious in retrospect) that this was because there is a “spinodal” pressure  $P_c$  at which the sound velocity goes to zero and the liquid becomes macroscopically unstable. To make an estimate of the value of  $P_c$  a Padé approximant scheme was used. This led to  $P_c = -8.87$  bars [14]. Subsequently, it was noticed that the sound velocity  $c$  for positive pressures could be fit remarkably well by the equation

$$c^3 = b(P - P_c), \quad (1)$$

where  $b$  is a constant. This gives the value  $P_c = -9.624$  bars [15].<sup>2</sup> There is a theory that explains why the sound velocity varies with pressure as in (1) when the pressure is close the spinodal [16]. However, (1) gives a remarkably good fit to the variation of the sound velocity with pressure even for pressures up to the freezing pressure of 25 bars. As far as we know, there is absolutely no understanding of this surprising result.

Using the estimated properties of liquid helium it is possible to construct a theory of the rate at which bubbles nucleate and the cavitation threshold. Bubble nucleation occurs via thermal activation or quantum tunneling. At temperatures below 0.2 K, only quantum tunneling is important and cavitation cannot occur until the liquid is subjected to a pressure that is within a few tenths of a bar of the spinodal pressure [12, 13]. Thus, an experimental measurement of the pressure that is required to produce cavitation provides a test of the calculation of the spinodal pressure. Cavitation measurements of Caupin and Balibar [17] gave good agreement with the spinodal estimates mentioned. Furthermore, subsequent microscopic calculations by Solis and Navarro [18] also gave good agreement with the estimate of the spinodal pressure. This provides substantial support for the extrapolation methods that have been used.

<sup>2</sup>Note that, of course, this result for  $P_c$  is the numerical value obtained from the fit. This value is used in calculating the equation of state, as plotted in Fig. 5, for example. Based on the errors in the data and because of the uncertainty about how to extrapolate to the spinodal, the value of  $P_c$  is probably uncertain by several tenths of a bar.

There are a number of complications that have to be dealt with in applying the same approach to solid helium. The first problem, of course, is that it is possible that solid helium becomes unstable in way that is not related to the vanishing of the sound velocity. For example, there could be a transition to another phase or an instability associated with the production of vacancies, as we will discuss later. If for the moment we ignore this possibility and follow a similar approach to that used for liquid helium, the next complication is that in solid helium there are three different sound modes (longitudinal L, fast transverse T1, and slow transverse T2), and the velocity of these modes varies with propagation direction. Ideally, we would like to estimate how the velocity of each of these modes changes as the pressure is reduced below the  $P_m$ . The stability limit of the solid will be reached when the velocity of any one of the modes propagating in any direction becomes zero.<sup>3</sup> In addition, the velocity of these waves is not accurately known and, in fact, measured values on single crystals of known orientation are available for only a few molar volumes  $V_m$ . Specifically, Franck and Wanner have made measurements for  $V_m$  of 19.28 and 20.32 cm<sup>3</sup> [19, 20], Greywall for 4 values of  $V_m$  between 19.0 and 20.5 cm<sup>3</sup> [21, 22], and Crepeau et al. for 21 cm<sup>3</sup> [23, 24]. The accuracy of the results varies greatly between the different elastic constants. For example, at  $V_m = 20.5$  cm<sup>3</sup>, Greywall has an uncertainty of 0.5% for  $C_{11}$ ,  $C_{44}$  and  $C_{66}$  but 6% for  $C_{33}$ . These errors are much larger than the errors of measurements for liquid helium-4 where the uncertainty is better than 0.1% [25]. These errors and the limited amount of data make it difficult to extrapolate the sound velocity into the metastable regime. In addition, the measurements were made at different temperatures.<sup>4</sup>

Because of the lack of accurate sound velocity data, as an alternate method we have used the Debye temperature to make an extrapolation and estimate the spinodal pressure. The Debye temperature is given by the formula

$$\Theta_D = \frac{\hbar v_D}{k} \left( \frac{6\pi^2 N_A}{V_m} \right)^{1/3}, \quad (2)$$

where  $N_A$  is Avogadro's number, and  $v_D$  is the Debye velocity. This velocity is given by

$$\frac{1}{v_D^3} = \frac{1}{3} \left\{ \frac{1}{(\bar{v}_l)^3} + 2 \frac{1}{(\bar{v}_t)^3} \right\}, \quad (3)$$

where the average velocities  $\bar{v}_l$  and  $\bar{v}_t$  are defined by

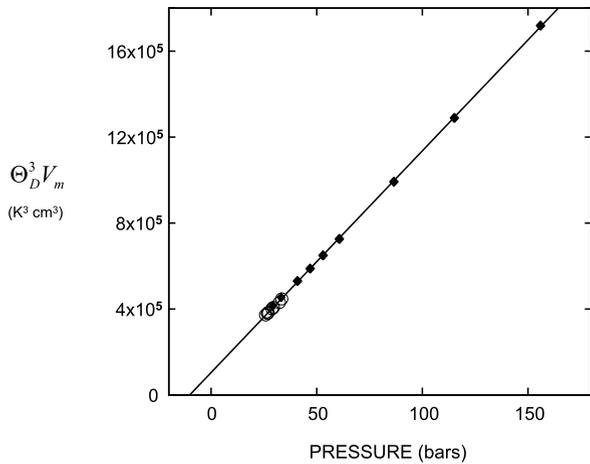
$$\frac{1}{\bar{v}_l} = \left\langle \frac{1}{v_l^3} \right\rangle^{1/3}, \quad \frac{1}{\bar{v}_t} = \left\langle \frac{1}{v_t^3} \right\rangle^{1/3}, \quad (4)$$

where the  $\langle \dots \rangle$  brackets denote angular averages of the longitudinal and transverse velocities. Then, if the cube of the sound velocity varies linearly with pressure as it

<sup>3</sup>The stability limit can also be expressed as a condition on the elastic constants.

<sup>4</sup>The temperature dependence of the sound velocity in helium-3 has been measured by [26].

**Fig. 1** Plot of the cube of the Debye temperature  $\Theta_D$  times the molar volume  $V_m$  as a function of pressure for solid helium-4. The *solid diamonds* are the data of Ahlers (ref. [27]), and the open circles from Gardner et al. (ref. [28]). The *solid line* is based on (5) as described in the text



does in liquid helium (see (1)) it should be true that

$$V_m \Theta_D^3 = \tilde{b}(P - P_c), \tag{5}$$

where  $\tilde{b}$  is a constant. The advantage of this formula is that the Debye temperature has been very accurately determined in experiments performed by Ahlers [27], and by Gardner, Hoffer and Phillips [28]. Ahlers’ data extends over a broad range of pressures (up to 156 bars), while those of Gardner et al. are restricted to a range close to the melting pressure. The authors present their results as tables of  $\Theta_D$  as a function of molar volume; to determine the pressure we have used the pressure-volume relation for zero temperature obtained by Edwards and Pandorf [29]. In Fig. 1 we show the results of a fit to the experimental data using (5). All 9 data points of Ahlers and all 9 of Gardner et al. have been plotted and used with equal weight in the fit. It can be seen that the data are fit extremely well. The fit gives  $\tilde{b} = 1.0315 \times 10^{-2} \text{ g}^{-1} \text{ cm}^4 \text{ s}^2 \text{ K}^3$  and a spinodal pressure of  $-10.14$  bars. If only points for pressure below 60 bars are included,  $P_c$  changes to  $-10.39$  bars. Use of all of the data of Ahlers and none of the Gardner data gives  $P_c = -10.47$  bars. One cannot obtain useful results from the Gardner data alone because these data cover only a very small range of pressures.

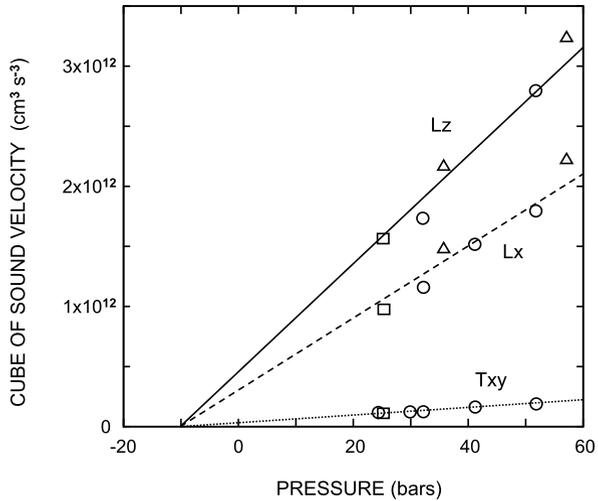
Just as for liquid helium, there is no understanding of why (5) gives such a good fit to the experimental data over a wide pressure range. If the exponent in (5) is allowed to vary from the value 3, we find that the best fit is obtained with an exponent of 2.94.<sup>5</sup>

It is interesting to note that these values for the spinodal pressure are remarkably close to the spinodal for liquid helium (see estimate of  $-9.624$  bars already mentioned).

In Fig. 2 we show plots of the cube of the sound velocity as a function of pressure. Plots are shown for the three sound modes for which there is most data. The

<sup>5</sup>This choice minimizes the sum of the squares of  $e_n$ , where  $e_n$  is the fractional error of the fit relative to the  $n$ -th data point.

**Fig. 2** Plot of the cube of the sound velocity as a function of pressure for solid helium-4. Circles are from Greywall (ref. [21]), squares from Crepeau et al. (ref. [23, 24]), and triangles from Wanner and Franck (ref. [19, 20]). The sound velocities are for longitudinal waves propagating in the  $z$ -direction ( $Lz$ ) and  $x$ -direction ( $Lx$ ), and transverse waves propagating in the  $x$ -direction and polarized along  $y$ . The solid lines are based on (1) as described in the text



linear fits that are shown are based on the spinodal pressure  $P_c = -10.14$  bars as just found. It can be seen that this value of  $P_c$  gives a good fit to the experimental data. Thus, although it appears reasonable to expect that the pressure at which the sound velocity goes to zero will depend on the propagation direction and polarization, this plot provides no strong evidence for this.

In the next section we will consider the nucleation of the liquid phase from the metastable solid at pressures below the melting pressure. To do this, we need the bulk modulus  $B$  and the shear modulus  $\mu$  for the solid. For helium-4 the bulk modulus at melting has been measured by Grilly [30] with result  $B_m = 268$  bars. If all sound velocities vary with pressure as given by (1), then it should be true that

$$\left(\frac{B}{\rho}\right)^{3/2} = \tilde{b}(P - P_c), \tag{6}$$

where  $\tilde{b}$  is a constant. Hence,

$$\tilde{b} = \frac{1}{P_m - P_c} \left(\frac{B_m}{\rho_m}\right)^{3/2}. \tag{7}$$

Using  $P_c = -10.14$  bars,  $P_m = 25.32$  bars, and  $\rho_m = 0.1908 \text{ g cm}^{-3}$  this gives<sup>6</sup>

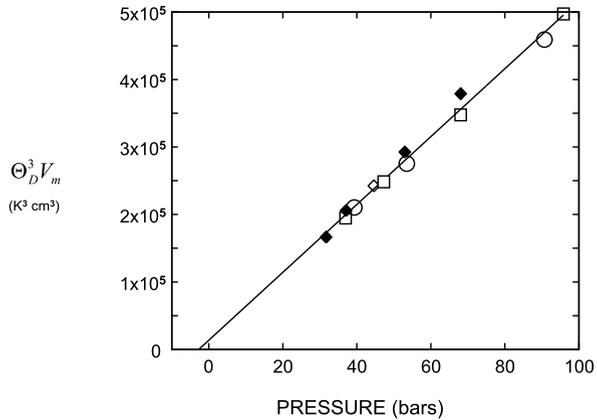
$$\tilde{b} = 1.485 \times 10^6 \text{ g}^{-1} \text{ cm}^4 \text{ s}^{-1}. \tag{8}$$

It follows from (6) that the density at the spinodal is

$$\rho_c = \rho_m - \frac{3}{\tilde{b}^{2/3}} (P_m - P_c)^{1/3} = 0.1151 \text{ g cm}^{-3}. \tag{9}$$

<sup>6</sup>Equation (6) with  $\tilde{b}$  given by (8) gives values of the bulk modulus that are within a few % of the values obtained by Edwards and Pandorf (ref. [29]) for pressures between 32 and 78 bars.

**Fig. 3** Plot of the cube of the Debye temperature  $\Theta_D$  times the molar volume  $V_m$  as a function of pressure for solid helium-3. The *open squares* are the data of Sample and Swenson (ref. [31]), the *solid diamonds* are from Greywall (ref. [32]), and the *open circles* are from Pandorf and Edwards (ref. [33]). The *solid line* is based on (5) as described in the text



This compares with the estimated density of the liquid at its spinodal of  $0.0943 \text{ g cm}^{-3}$  [15].

To estimate the shear modulus we note that in helium-4, the transverse sound velocity is roughly half of the longitudinal velocity. Thus, the contribution to the right hand side of (3) from the transverse waves is about 16 times larger than the contribution from the longitudinal waves. (Of course, we have no way to know if this remains true when the pressure is reduced into the metastable regime). Thus

$$\bar{v}_t \approx \left( \frac{V_m}{9\pi^2 N_A} \right)^{1/3} \left( 1 + \frac{1}{16} \right)^{1/3} \frac{k\Theta_D}{\hbar}, \tag{10}$$

and the shear modulus (averaged over direction) is

$$\mu = \rho \bar{v}_t^2 \approx b_\mu \frac{(P - P_c)^{2/3}}{V_m}, \tag{11}$$

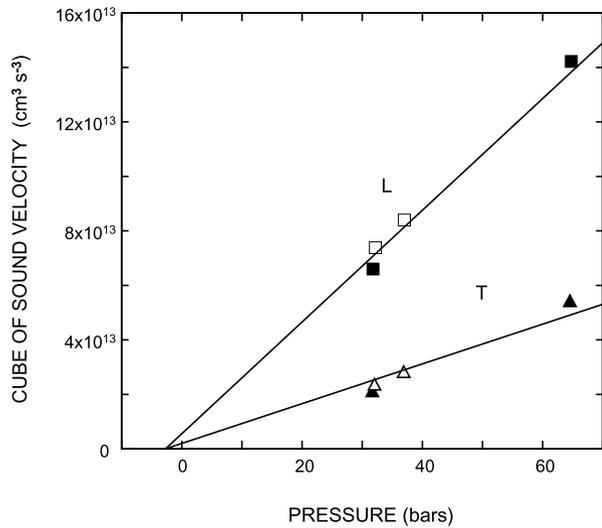
where from (5),  $b_\mu = 2.390 \times 10^4 \text{ g}^{1/3} \text{ cm}^{8/3} \text{ s}^{-2/3}$ .

For helium-3 the Debye temperature has been determined in experiments by Sample and Swenson [31], Greywall [32], and Pandorf and Edwards [33]. These papers again present results for  $\Theta_D$  as a function of the molar volume  $V_m$ . We have used the measurements of Pandorf and Edwards to obtain the pressure and have plotted  $\Theta_D^3 V_m$  vs.  $P$  in Fig. 3. The best fit to (5) is obtained with  $\tilde{b} = 5.0296 \times 10^{-3} \text{ g}^{-1} \text{ cm}^4 \text{ s}^2 \text{ K}^3$  and  $P_c = -2.71$  bars. This is based on giving each measurement of  $\Theta_D$  the same weight. Again, the fit is very good. As for helium-4, the value obtained for  $P_c$  is surprisingly close to the spinodal pressure in the liquid, i.e., the value  $-3.14$  bars.<sup>7</sup>

The elastic constants of bcc helium-3 have been measured by Wanner [35] and Greywall [21, 36]. We have used these to calculate the longitudinal and transverse sound velocity in the [100] direction as a function of pressure and a plot of velocity

<sup>7</sup>This is the value found in [34] corrected for a small error coming from confusion over bars and atmospheres.

**Fig. 4** Plot of the cube of the sound velocity as a function of pressure for helium-3. The *open symbols* are from Greywall (ref. [21] and [36]), and the *solid symbols* from Wanner (ref. [35]). The sound velocities are for longitudinal waves *L* and transverse waves *T* propagating in the [100] direction



cubed versus pressure is shown in Fig. 4.<sup>8</sup> The solid line is based on (6) with the same spinodal pressure of  $-2.71$  bars as found above. It is clear that a better fit to the transverse velocity data would be obtained with a somewhat larger (i.e., more positive) spinodal pressure.

In bcc helium-3 there is a transverse mode that propagates in the [110] direction with a very low velocity  $[(C_{11} - C_{12})/2\rho]^{1/2}$ . For example, at a molar volume of  $21.66 \text{ cm}^3$ , this velocity is only  $1.12 \times 10^4 \text{ cm s}^{-1}$ , whereas the other transverse wave has a velocity of  $3.77 \times 10^4 \text{ cm s}^{-1}$ . At first sight, one might guess that since this velocity is so low, when the pressure is reduced it will be this slow transverse mode which will be the first to become unstable. However, this idea is incorrect since the measurements of Greywall<sup>9</sup> show that in fact the velocity of this mode changes by only a small amount when the pressure is decreased from 65 bars to 32 bars.

For helium-3, the bulk modulus has been measured by Grilly [37], and an analysis similar to that described above for helium-4 gives

$$\tilde{b} = 1.497 \times 10^6 \text{ g}^{-1} \text{ cm}^4 \text{ s}^{-1}, \tag{12}$$

$$\rho_c = 0.0481 \text{ g cm}^{-3}. \tag{13}$$

This is to be compared with the spinodal density of the liquid which is  $0.0546 \text{ g cm}^{-3}$  [34]. The shear modulus is found to be given by  $\mu = b_\mu \frac{(P - P_c)^{2/3}}{V_m}$  with  $b_\mu = 1.113 \times 10^4 \text{ g}^{1/3} \text{ cm}^{8/3} \text{ s}^{-2/3}$ .

<sup>8</sup>We include the data from only the lowest and highest molar volumes that were studied by Wanner.

<sup>9</sup>See, Fig. 9 of ref. [32].

### 3 Nucleation of the Liquid from the Solid

Here we consider the extent to which it may be possible to investigate experimentally the properties of metastable solid helium at pressures below the freezing pressure. The general theory of the nucleation of a new phase from a metastable phase is discussed in Landau and Lifshitz [38] and in Lifshitz and Kagan [39]. For thermally-activated nucleation, the rate of nucleation per unit volume and per unit time is

$$\Gamma = \Gamma_0 \exp(-\Delta E/kT), \tag{14}$$

where  $\Delta E$  is the energy barrier and  $\Gamma_0$  is the attempt rate per unit volume and time. The energy barrier is the minimum amount of work needed to form a critical nucleus of the new phase. There is no complete theory of the attempt rate  $\Gamma_0$  [39, 40], but on physical grounds it is expected be of the order of the thermal frequency  $kT/\hbar$  multiplied by the inverse of the volume of the critical nucleus. If the temperature is very low so that  $\Delta E/kT \gg 1$ , nucleation can still occur as a result of quantum tunneling [39, 41]. However, this is important only if the energy barrier is very small.

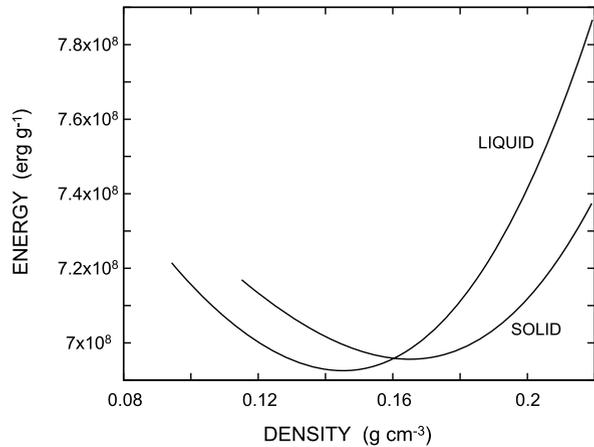
There have been many studies of the nucleation of bubbles in liquids under reduced pressure, the formation of liquid from supersaturated vapor, and the freezing of supercooled liquid. These studies have included many experiments with helium [1, 4–11]. However, there has been very limited study of the nucleation of the liquid from the solid.<sup>10</sup> In part, this is because if a solid with a free surface is heated, melting will normally first occur at the surface of the solid. This makes it difficult to significantly superheat a solid unless a means is found to heat just the interior of the solid without heating the surface. For solid helium, there is the possibility to reach the region of the phase diagram where the solid is metastable by lowering the pressure within the interior of the solid. This can be achieved by generating high amplitude sound with an ultrasonic transducer and bringing this sound to a focus in the interior. Care must be taken with the focusing because of the elastic anisotropy of the solid. Solid helium-4 is elastically isotropic about the *c*-axis. It should be possible to use a cylindrical transducer (rather than hemispherical as used in most of the experiments with liquid) and grow a helium crystal with the *c*-axis along the axis of the cylinder. In this way, strong focusing can be achieved. For solid helium-3 the longitudinal sound velocity varies with direction by about  $\pm 10\%$ . This amount of anisotropy is sufficiently small that it should be possible to achieve a reasonable degree of focusing with a hemispherical or spherical transducer. In what follows we will consider the possible nucleation of the liquid in this type of experiment.

To calculate the energy barrier, suppose that a spherical volume of radius  $R_0$  of solid is converted into liquid, and the region occupied by this liquid then changes to become a sphere of radius  $R$ . As a result of the change in the volume, the solid around the volume will be strained elastically and have an elastic energy  $\delta E_{elastic}$ . Thus the energy change is the sum of four terms

$$\delta E = -\frac{4\pi}{3} R_0^3 \rho_s e_s(\rho_s) + \frac{4\pi}{3} R^3 \rho_l e_l(\rho_l) + \delta E_{elastic} + 4\pi R^2 \alpha_{ls}. \tag{15}$$

<sup>10</sup>For recent work, see [42–44].

**Fig. 5** Energy per unit mass of liquid and solid helium-4 as a function of density. The lower limit of each plot is at the spinodal density



In this expression  $e_s$  and  $e_l$  are the energies per unit mass of the solid and liquid, with density  $\rho_s$  and  $\rho_l$ , respectively. The surface energy is  $4\pi\alpha_{ls}$  where  $\alpha_{ls}$  is the energy of the liquid-solid interface per unit area. From conservation of mass, the density of the liquid must be

$$\rho_l = \rho_s \frac{R_0^3}{R^3}. \quad (16)$$

It is straightforward to calculate the elastic energy with the result<sup>11</sup>

$$\delta E_{elastic} = 8\pi\mu(R - R_0)^2 R_0. \quad (17)$$

This formula is based on linear elasticity and thus assumes that  $(R - R_0)/R_0$  is a small quantity. Note that (15) is an example of what is called the “thin wall approximation” in nucleation theory [41]. This amounts to the assumption that the radius of the nucleus is large compared to the width of the interface between the two phases. This approximation breaks down as the spinodal is approached [39, 41].

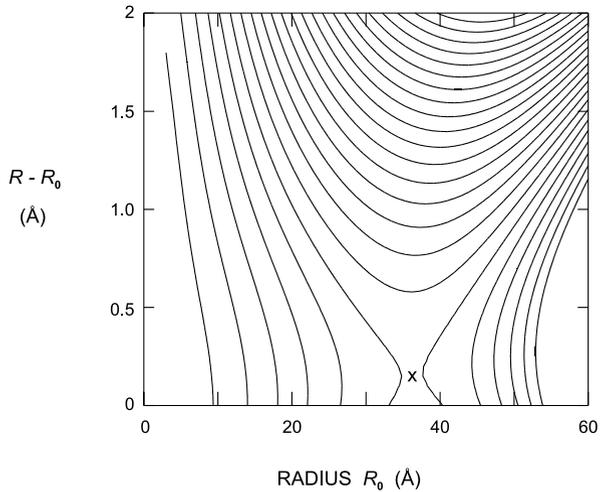
We have used the results derived in the previous section to determine  $e_s(\rho_s)$  and can take  $e_l(\rho_l)$  as given in ref. [15]. These quantities are plotted in Fig. 5. One can see from this plot that whenever the density is above about  $0.16 \text{ g cm}^{-3}$ , the liquid has more energy than the solid when the densities of the liquid and solid are the same. Thus, in this density range nucleation of the liquid is impossible unless  $R > R_0$ .

To investigate nucleation in more detail we have performed a series of calculations of  $\delta E$  as a function of  $R_0$  and  $R - R_0$ . An example is shown in Fig. 6, which is based on a value of  $0.15 \text{ erg cm}^{-2}$  for the surface energy  $\alpha_{ls}$ <sup>12</sup>. From this type of plot we can find the location of the saddle point that corresponds to the energy barrier  $\Delta E$ . In Fig. 7 we show the energy barrier as a function of pressure. The three curves are for values of the surface tension of 0.05, 0.1 and  $0.15 \text{ erg cm}^{-2}$ . Above a pressure

<sup>11</sup>A closely related problem is considered in [45], p. 20.

<sup>12</sup>The surface energy of solid helium is anisotropic. See [46, 47].

**Fig. 6** Contour plot of the energy as a function of the parameters  $R_0$  and  $R$  as defined in the text. The pressure is  $-6.96$  bars. The contour lines have an energy spacing of  $100$  K. The position of the saddle point corresponding to the energy barrier  $\Delta E$  is marked by  $x$



of about  $3.31$  bars, the energy barrier becomes infinite, regardless of the value of the surface tension, even if the surface tension is zero. This means that above this pressure no matter the values of  $R_0$  and  $R$  the energy is always increased when solid is converted to liquid. One can understand this based on (15). We introduce the “radial strain” defined by

$$\eta \equiv (R - R_0)/R_0. \tag{18}$$

Equation (15) then becomes

$$\delta E = \frac{4\pi}{3} R_0^3 \left\{ -\rho_s e_s(\rho_s) + \rho_l e_l(\tilde{\rho}_l) + 6\mu\eta^2 + \frac{3(1 + \eta)^2 \alpha_{ls}}{R_0} \right\}, \tag{19}$$

where  $\tilde{\rho}_l = \rho_s/(1 + \eta)^3$ . The contribution from the surface energy is always positive. Consequently, for nucleation to occur, i.e., to have  $\delta E < 0$ , the density of the solid has to be such that there is a value of  $\eta$  that makes the quantity

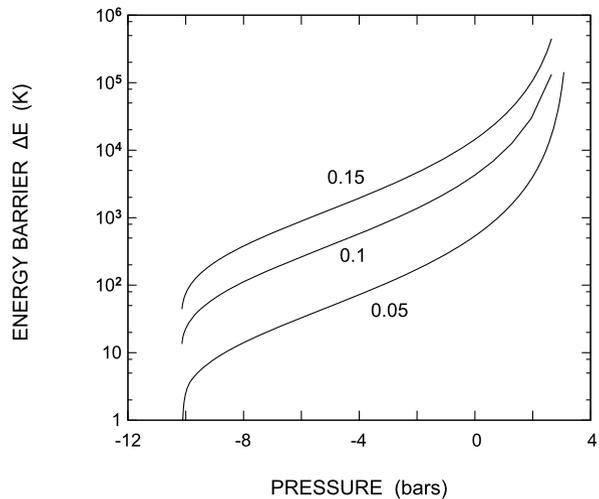
$$-\rho_s e_s(\rho_s) + \rho_l e_l(\tilde{\rho}_l) + 6\mu\eta^2 \tag{20}$$

less than zero. This sets the upper value of the density and pressure at which nucleation can occur.

The general order of magnitude of the prefactor  $\Gamma_0$  is in the range  $10^{25}$  to  $10^{30} \text{ cm}^{-3} \text{ s}^{-1}$  [39]. Thus in order for there to be an appreciable probability of nucleation of the liquid at  $1$  K, for example, the energy barrier has to lie in the range below  $100$  K. One can see from Fig. 7, that this only happens close to the spinodal pressure of  $-10.14$  bars. Note, however, that in this pressure range there are several difficulties with making an accurate calculation of the energy barrier:

- 1) As already mentioned, near to the spinodal the thin wall approximation used in (15) must break down.
- 2) The surface tension varies with pressure and may become small as the spinodal is approached.

**Fig. 7** The energy barrier for nucleation of the liquid from the solid as a function of pressure. The different curves are labeled by the liquid-solid surface energy  $\alpha_{ls}$  in units of  $\text{erg cm}^{-2}$



- 3) There are uncertainties in the equation of state of the solid near to the spinodal and the spinodal pressure itself is uncertain.<sup>13</sup>

It is interesting that of these difficulties, 1) and 2) do not affect the result that nucleation cannot occur above a pressure of 3.31 bars.

Finally, we consider other possible effects that might occur as the pressure is lowered:

- 1) One can see that the elastic energy term has the effect of raising  $\delta E$  and thereby suppressing the nucleation of the liquid. If the solid could undergo plastic flow while the critical nucleus of liquid was growing, the energy barrier  $\Delta E$  would be decreased and the nucleation rate would increase.
- 2) The liquid could possibly form as a result of the production of vacancies. In this scenario, as the pressure is lowered the activation energy for vacancies should decrease resulting in a large increase in the number of mobile thermally-activated vacancies. The activation energy for vacancy formation decreases as the density is lowered [48] and may become zero. One could consider a process in which a small liquid drop nucleus is formed and the strain energy  $\delta E_{elastic}$  is lowered by the diffusion of vacancies toward the drop. To determine whether this mechanism could make it easier for nucleation of the liquid to occur in a nucleation experiment using the ultrasonic technique requires knowledge of vacancy energies and mobility. Alternatively, if the activation energy for vacancies became sufficiently small liquid could form not via the initial formation of a small liquid nucleus but instead by the production of a large vacancy concentration throughout the solid. This would lower the density of the solid to a value close to the liquid density. Jung and Franck [49] have studied the effect of rapidly superheating high pressure solid helium (pressure in the range 240 to 1700 bars) and have seen effects

<sup>13</sup>There is also the uncertainty associated with the different spinodal pressures for different elastic constants of the solid.

that they attribute to the production of a high density of thermal vacancies. The melting mechanism has also been discussed by Fecht and Johnson [50] and by Forsblom and Grimvall [51].

- 3) If nucleation of the liquid cannot occur there could be a transition to the bcc phase. In principle, the nucleation of bcc from hcp could be calculated by a method similar to that used here; however, since the stable bcc phase exists over such a small region of the  $P$ – $T$  plane it would be hard to extrapolate to estimate the properties of this phase at lower pressures.

## 4 Summary

We have considered the properties of metastable solid helium-4 and helium-3 at pressures below the normal melting pressure and have estimated the spinodal pressure. The estimates are based on what are hopefully reasonable extrapolations of the properties of solid helium into the metastable regime; the techniques are similar to those used with success for liquid helium. We have found the remarkable result that for both helium-3 and helium-4 the spinodal pressures are very close to the spinodal pressures for the liquid. We have also considered the possible nucleation of the liquid phase from the solid, and find that because of the elastic strain energy resulting from the formation of a liquid nucleus, the nucleation rate is greatly suppressed and may not occur until close to the spinodal. From the discussion in the previous section, it would appear that measurements of the nucleation of the liquid can be made using ultrasonic techniques. This is currently being attempted by J. Dupont-Roc.

**Acknowledgements** We thank S. Balibar, D.O. Edwards and J. Dupont-Roc for helpful discussions. This work was supported in part by the National Science Foundation through Grant No. DMR-0605355.

## References

1. H.J. Maris, S. Balibar, M.S. Pettersen, *J. Low Temp. Phys.* **93**, 1069 (1993)
2. J.A. Nissen, E. Bodegom, L.C. Brodie, J.S. Semura, *Phys. Rev. B* **40**, 6617 (1989)
3. D. Lezak, L.C. Brodie, J.S. Semura, E. Bodegom, *Phys. Rev. B* **37**, 150 (1988)
4. V.L. Tsymbalenko, *J. Low Temp. Phys.* **88**, 55 (1991)
5. J.P. Ruutu, P.J. Hakonen, J.S. Penttila, A.V. Babkin, J.P. Saramaki, E.B. Sonin, *Phys. Rev. Lett.* **77**, 2514 (1996)
6. Y. Sasaki, T. Mizusaki, *J. Low Temp. Phys.* **110**, 491 (1998)
7. X. Chavanne, S. Balibar, F. Caupin, *Phys. Rev. Lett.* **85**, 5506 (2001)
8. F. Werner, G. Beaume, A. Hobeika, S. Nascimbene, C. Herrmann, F. Caupin, S. Balibar, *J. Low Temp. Phys.* **136**, 93 (2004)
9. S. Kimura, F. Ogasawara, R. Nomura, Y. Okuda, *J. Low Temp. Phys.* **134**, 145 (2004)
10. R. Ishiguro, F. Caupin, S. Balibar, *Europhys. Lett.* **75**, 91 (2006)
11. R. Ishiguro, F. Caupin, S. Balibar, *J. Low Temp. Phys.* **148**, 645 (2007)
12. H.J. Maris, *J. Low Temp. Phys.* **98**, 403 (1995)
13. M. Guilleumas, M. Barranco, D.M. Jezek, R.J. Lombard, M. Pi, *Phys. Rev. B* **54**, 16135 (1996)
14. Q. Xiong, H.J. Maris, *J. Low Temp. Phys.* **77**, 347 (1989)
15. H.J. Maris, D.O. Edwards, *J. Low Temp. Phys.* **129**, 1 (2002)
16. H.J. Maris, *Phys. Rev. Lett.* **66**, 45 (1991)
17. F. Caupin, S. Balibar, *Phys. Rev. B* **64**, 064507 (2001)
18. M.A. Solis, J. Navarro, *Phys. Rev. B* **45**, 13080 (1992)

19. R. Wanner, J.P. Franck, Phys. Rev. Lett. **24**, 365 (1970)
20. J.P. Franck, R. Wanner, Phys. Rev. Lett. **25**, 345 (1970)
21. D.S. Greywall, Phys. Rev. A **3**, 2106 (1971)
22. D.S. Greywall, Phys. Rev. B **16**, 5127 (1977)
23. R.H. Crepeau, O. Heybey, D.M. Lee, S.A. Strauss, Phys. Rev. A **3**, 1162 (1971)
24. R.H. Crepeau, D.M. Lee, Phys. Rev. A **6**, 516 (1972)
25. B.M. Abraham, Y. Eckstein, J.B. Ketterson, M. Kuchnir, P.R. Roach, Phys. Rev. A **1**, 250 (1970)
26. R. Wanner, K.H. Mueller, H.A. Fairbank, J. Low Temp. Phys. **13**, 153 (1973)
27. G. Ahlers, Phys. Rev. A **2**, 1505 (1970)
28. W.R. Gardner, J.K. Hoffer, N.E. Phillips, Phys. Rev. A **7**, 1029 (1973)
29. D.O. Edwards, R.C. Pandorf, Phys. Rev. A **140**, 816 (1965)
30. E.R. Grilly, J. Low Temp. Phys. **11**, 33 (1973)
31. H.H. Sample, C.A. Swenson, Phys. Rev. **158**, 188 (1967)
32. D.S. Greywall, Phys. Rev. B **15**, 2604 (1977)
33. R.C. Pandorf, D.O. Edwards, Phys. Rev. **169**, 222 (1968)
34. H.J. Maris, J. Low Temp. Phys. **98**, 403 (1995)
35. R. Wanner, Phys. Rev. A **3**, 448 (1971)
36. D.S. Greywall, Phys. Rev. B **11**, 1070 (1975)
37. E.R. Grilly, J. Low Temp. Phys. **4**, 615 (1971)
38. L.D. Landau, E.M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1969), Sect. 150
39. I.M. Lifshitz, Y. Kagan, Sov. Phys. JETP **35**, 206 (1972)
40. D.W. Oxtoby, J. Phys. Condens. Matter. **4**, 7629 (1992)
41. H.J. Maris, C. R. Phys. **7**, 946 (2006)
42. K. Lu, Y. Li, Phys. Rev. Lett. **80**, 4474 (1998)
43. X.-M. Bai, M. Li, Phys. Rev. B **72**, 052108 (2005)
44. S.-N. Luo, L. Zheng, A. Strachan, D.C. Swift, J. Chem. Phys. **126**, 034505 (2007)
45. L.D. Landau, I.M. Lifshitz, *Theory of Elasticity* (Pergamon, Oxford, 1970)
46. O.A. Andreeva, K.S. Keshishev, JETP Lett. **46**, 200 (1987)
47. O.A. Andreeva, K.S. Keshishev, S.Y. Osipyan, JETP Lett. **49**, 759 (1989)
48. L. Pollet, M. Boninsegni, A.B. Kuklov, N.V. Prokofiev, B.V. Svistunov, M. Troyer, Phys. Rev. Lett. **101**, 097202 (2008)
49. J. Jung, J.P. Franck, Jpn. J. Appl. Phys. **26**(Suppl 26-3m), A115 (1987)
50. H.J. Fecht, W.L. Johnson, Nature **334**, 50 (1988)
51. M. Forsblum, G. Grimvall, Nat. Mater. **4**, 388 (2005)