

# Nucleation of Solid Helium from Liquid Under High Pressure

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*We consider the homogenous nucleation of solid helium from the liquid phase at pressures above the normal freezing pressure. We find that if the liquid-solid surface energy  $\alpha$  is assumed to be independent of pressure, then at 1 K nucleation should occur at a liquid pressure in the range 60 to 70 bars. Allowance for the variation of  $\alpha$  with pressure is found to result in a very large reduction in the nucleation rate.*

## 1. INTRODUCTION

Recently, there have been a number of studies of the nucleation of bubbles in liquid helium at negative pressures.<sup>1</sup> Helium is of especial interest for nucleation studies because it can be made highly pure. In addition, because helium can remain liquid even at absolute zero temperature, it is possible to investigate bubble nucleation via quantum tunneling.<sup>2,3</sup> However, the nucleation of the solid phase from liquid held at a pressure above the normal freezing pressure has been studied in much less detail.<sup>4-11</sup> It is believed<sup>12</sup> that in the studies that have so far been made of this process, the nucleation has always occurred at the walls of the container, rather than in bulk liquid, i.e., it is thought that heterogeneous nucleation has taken place. Attempts have been made to observe homogeneous nucleation, but these have been unsuccessful.<sup>13,14</sup> In these experiments, a transient high pressure is produced away from the walls of the experimental cell by using a focused sound beam. It is not easy to make an accurate estimate of the liquid pressure in these experiments. In the region of the acoustic focus, the fluctuation in density is large and it is important to

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allow for the non-linearity of the relation between density change and pressure. Consider, for example, an experiment in which the static pressure in the experimental cell is close to the freezing pressure of 25 bars. If the sound produces a density fluctuation of amplitude  $0.04 \text{ g}\cdot\text{cm}^{-3}$ , the pressure will decrease to  $-5.5$  bars on the negative swing and go up to 110 bars on the positive part of the cycle. Thus, the positive pressure swing is much larger than the negative pressure swing. It appears likely that pressures as great as 100 bars have been produced in the experiments.<sup>13,14</sup>

In this paper, we will present calculations of the rate of nucleation of solid from pressurized liquid helium. The basic formulation of the problem is given in Sec. 2, and numerical results for the energy barrier and the nucleation rate are given in Sec. 3.

## 2. NUCLEATION THEORY

We review here the theory of thermally-activated nucleation based on the "thin wall" approximation.<sup>15,16</sup> Let the Helmholtz free energy of the liquid and the solid per unit volume be  $f_L(\rho_L)$  and  $f_S(\rho_S)$ , respectively. Consider a large container of liquid helium with a uniform density  $\rho_L$ . The pressure is

$$P_L = -f_L + \rho_L \frac{\partial f_L}{\partial \rho_L} \quad (1)$$

If we form a small sphere of solid of radius  $R$  while keeping the density of the surrounding liquid constant, the increase in free energy is

$$\Delta F = \frac{4\pi}{3} R^3 [f_S(\rho_S) - f_L(\rho_L) + (\rho_L - \rho_S) f'_L(\rho_L)] + 4\pi R^2 \alpha, \quad (2)$$

where  $f'_L \equiv \partial f_L / \partial \rho_L$ , and  $\alpha$  is the liquid-solid surface energy per unit area. If we choose the density of the solid so that for a given radius  $R$  the value of  $\Delta F$  is a minimum, we find the condition

$$f'_S(\rho_S) = f'_L(\rho_L), \quad (3)$$

which is equivalent to the requirement that the Gibbs' energy per unit mass is equal for the liquid and solid. Using Eqs. (1) and (3), we can write Eq. (2) in the form

$$\Delta F = \frac{4\pi}{3} R^3 [P_S(\rho_S) - P_L(\rho_L)] + 4\pi R^2 \alpha, \quad (4)$$

where it is to be understood that the densities are related through Eq. (3). The barrier has a maximum when

$$R_c = \frac{2\alpha}{P_S(\rho_S) - P_L(\rho_L)}. \quad (5)$$

The height of the barrier is then<sup>15, 16</sup>

$$\Delta F_{\max} = \frac{16\pi\alpha^3}{3[P_S(\rho_S) - P_L(\rho_L)]^2}. \quad (6)$$

If the liquid pressure exceeds the equilibrium freezing pressure by a small amount  $\Delta P$ , the barrier height reduces to the expression

$$\Delta F_{\max} = \frac{16\pi\alpha^3 \rho_L^{f2}}{3(\rho_S^f - \rho_L^f)^2 (\Delta P)^2}, \quad (7)$$

where  $\rho_S^f$  and  $\rho_L^f$  are the density of the solid and liquid at the freezing pressure.

The results given above are based on a "thin wall approximation" because it is implicitly assumed that the width of the interface between the liquid and the solid is small compared to the radius  $R$  of the solid nucleus. Minoguchi<sup>17</sup> has constructed a more general theory that does not rely on this approximation. He takes the energy density to include terms proportional to  $|\nabla\rho|^2$  and also to  $|\nabla\eta|^2$ , where  $\eta$  is the "translational symmetry breaking parameter."  $\eta$  measures the amplitude of the short range density oscillations that are characteristic of the solid phase. Unfortunately, in this approach it is necessary to make a number of approximations and also to make assumptions about the values of the new parameters that are introduced. The width of the liquid-solid interface has been estimated<sup>18</sup> to be roughly 4-5 interatomic spacing, i.e., 10 to 13 Å. Whether or not it is in fact necessary to go beyond the thin wall approximation is dependent on the size of the critical nucleus, and this we now calculate.

### 3. NUMERICAL CALCULATIONS

To obtain numerical results, we first need an estimate of the free energies  $f_L(\rho_L)$  and  $f_S(\rho_S)$ . We will estimate these quantities using experimental data for  $T = 0$  K, since the change in the equation of state of liquid and solid helium up to at least 1 K is small. For the liquid, we use the equation of state proposed by Abraham *et al.*<sup>19</sup> This takes the pressure to

vary as a third order polynomial in the density. They determined the coefficients of the polynomial from their measurements of the sound velocity. The pressure as a function of density is shown in Fig. 1. Of course, we are making an extrapolation of the equation of state of Abraham *et al.* into a range of pressures in which measurements have not been made. However, in the range of pressure that we are considering, extrapolations of other fits that have been made to the measured equation of state give curves of pressure versus density that differ from what is shown in Fig. 1 by only a small amount.<sup>20</sup>

For the solid, we have used the data of Edwards and Pandorf<sup>21</sup> who determined the internal energy and pressure for a series of molar volumes. We have made a fit to their data using a fourth order polynomial in the molar volume. The pressure of the solid as a function of density is included in Fig. 1.

To calculate the nucleation barrier, we choose a liquid density and calculate the Gibbs' energy per unit mass for the liquid. We then find the density of the solid at which the Gibbs' energy of the solid matches that of the liquid (see Eq. (3)). The difference between the pressure of the liquid and the solid is then calculated and the energy barrier can then be determined from Eq. (6). For the liquid-solid surface energy  $\alpha$  we use  $0.17 \text{ erg} \cdot \text{cm}^{-2}$ .<sup>22</sup> The results for the radius of the critical nucleus are shown

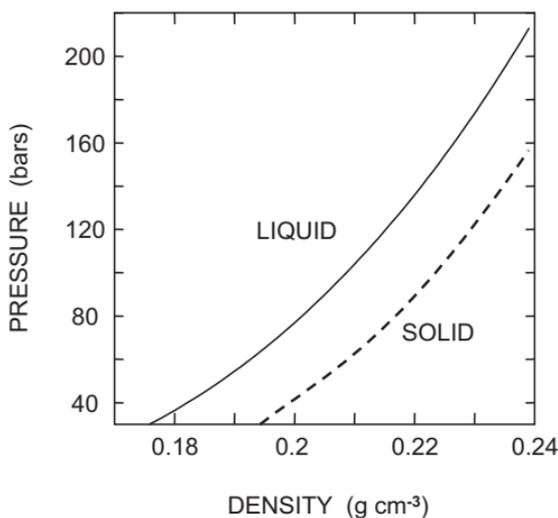


Fig. 1. The pressure in the liquid and in the solid as a function of the density. The calculation of the pressure is described in the text.

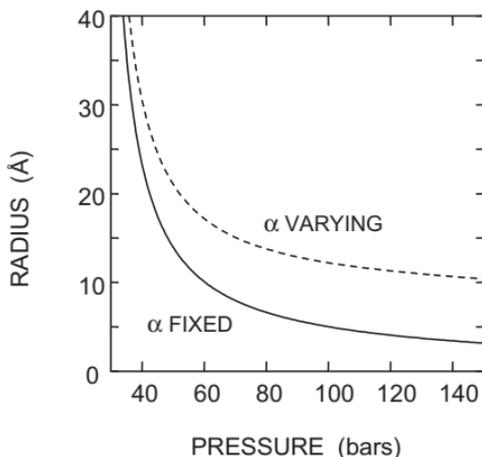


Fig. 2. The radius of the critical nucleus as a function of the pressure. Results are shown for a constant liquid-solid surface energy  $0.17 \text{ erg} \cdot \text{cm}^{-3}$  and for a surface energy that varies with pressure according to Eq. (9).

in Fig. 2 and the energy barrier is in Fig. 3. It can be seen that the energy barrier drops rapidly with increasing pressure. The nucleation rate  $\Gamma$  by thermal activation per unit volume and unit time is given by

$$\Gamma = \Gamma_0 \exp(-\Delta F_{\max}/kT), \quad (8)$$

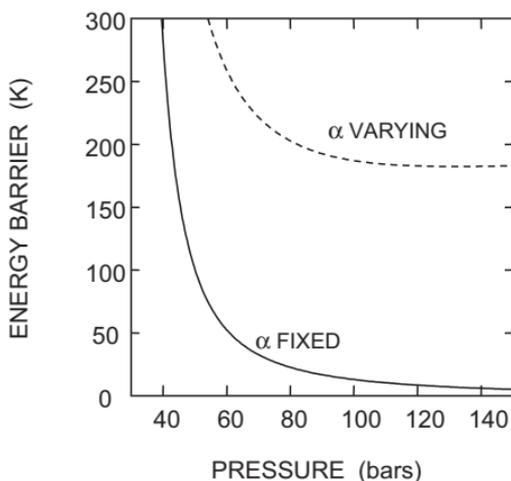


Fig. 3. The nucleation barrier for formation of the solid phase as a function of pressure. The solid curve shows the barrier for a constant liquid-solid surface energy  $\alpha$  of  $0.17 \text{ erg} \cdot \text{cm}^{-3}$ . The dotted curve is based on the assumption that  $\alpha$  varies with pressure according to Eq. (9).

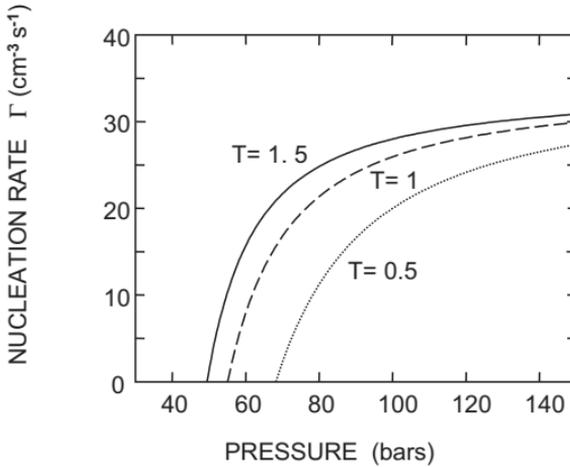


Fig. 4. Nucleation rate as a function of pressure at temperatures of 0.5, 1 and 1.5 K. The liquid-solid surface energy is assumed to have a constant value of  $0.17 \text{ erg} \cdot \text{cm}^{-3}$ .

where the prefactor  $\Gamma_0$  is usually taken to be of the order of an attempt frequency  $\nu$  divided by the volume  $V_c$  of the critical nucleus. We take  $V_c = 4\pi R_c^3/3$  and  $\nu = kT/h$ . Results for  $\Gamma$  are shown in Fig. 4 for temperatures of 0.5, 1 and 1.5 K.

Nucleation is likely to be seen when the product of  $\Gamma$  with the experimental volume  $V_{\text{exp}}$  and the experimental time  $\tau_{\text{exp}}$  is of the order of unity. In an ultrasonic experiment it is hard to give precise values for  $V_{\text{exp}}$  and  $\tau_{\text{exp}}$  because the pressure is varying in both space and time. Thus the maximum pressure is achieved only within a distance from the center of the acoustic focus which is a fraction of the sound wavelength, and this maximum pressure exists for only a fraction of each cycle. For a 1 MHz sound wave applied for a few cycles we take  $10^{-14} \text{ cm}^3 \cdot \text{s}$  as a rough estimate for  $V_{\text{exp}}\tau_{\text{exp}}$ . Thus, nucleation is likely to be seen when  $\Gamma$  has a value exceeding  $\sim 10^{14} \text{ cm}^{-3} \cdot \text{s}^{-1}$ . Hence, the calculation predicts that nucleation will occur at pressures of 85, 66, and 58 bars for temperatures of 0.5, 1, and 1.5 K respectively. This is in disagreement with experiment; no nucleation of the solid has been detected even at pressures as high as 100 bars.

To investigate the reason for this, we consider some of the assumptions of the nucleation theory. The calculation uses the thin wall model. As can be seen from Fig. 2, the radius of the critical nucleus is comparable to the interatomic spacing when the pressure becomes large. Thus the thin wall approximation becomes suspect. For nucleation of bubbles at negative pressure, it is known that the use of the thin wall approximation gives an

overestimate of the barrier height;<sup>23</sup> it is not obvious that this also happens for nucleation of the solid.

Another important question is how the liquid-solid surface energy varies with pressure. We do not know of any theory of this variation. As a simple model, we can consider that this energy arises because at the interface some number of atoms are forced to exist in a local configuration that has a higher energy than the configurations that exist in the liquid or in the solid. The number of such atoms per unit area of the interface is of the order of  $a^{-2}$ , where  $a$  is the interatomic spacing. In these local configurations, the extra energy arises because atoms are displaced some distance from their ideal positions. Hence, we can take the extra energy per unit area to be of the order of  $\frac{1}{2} \beta (\delta x)^2 / a^2$ , where  $\beta$  is an effective spring constant between atoms and  $\delta x$  is the displacement of the atom. If we suppose that the arrangement of the atoms in the interfacial layer does not change with pressure, then  $\delta x$  will remain a constant fraction of the interatomic spacing. Then the surface energy will vary with pressure in the same way as  $\beta$ . But the bulk modulus  $B$  is proportional to  $\beta/a$ , and hence it appears reasonable to take the surface energy as proportional to the product  $Ba$ , i.e., to vary in the same way as  $B\rho^{-1/3}$ . Specifically, we will assume that

$$\alpha(P) = \alpha(P_F) \frac{B_L(P) \rho_L(P_F)^{1/3}}{B_L(P_F) \rho_L(P)^{1/3}}, \quad (9)$$

where  $P_F$  is the freezing pressure of 25.3 bars,  $\rho_L(P_F) = 0.1725 \text{ g} \cdot \text{cm}^{-3}$  is the density at the freezing pressure, and  $\alpha(P_F)$  is the surface tension at the normal freezing pressure ( $0.17 \text{ erg} \cdot \text{cm}^{-2}$ ). This gives a surface energy that varies with pressure as shown in Fig. 5. Of course, one could consider a number of other possible ways to estimate the variation of  $\alpha$  with  $P$ . For example, the parameters in Eq. (9) that refer to the liquid could be replaced by parameters for the solid.

Results for the critical radius, energy barrier, and nucleation rate based on the use of a surface energy that varies with pressure according to Eq. (9) are shown in Figs. 2, 3, and 6. It can be seen that this modification has a profound effect on the calculated results. The size of the critical nucleus is increased and thus the thin wall approximation is more likely to be accurate. The nucleation barrier is found to decrease rapidly while the pressure is increased in the range immediately above  $P_F$  just as happens when  $\alpha$  is constant. However, above a pressure of about 80 bars the barrier becomes almost constant. Thus, we have the surprising result that going further into the metastable phase does not increase the probability of nucleation. We are not aware of any comparable example. Furthermore, the barrier never decreases to a value small enough to give an appreciable

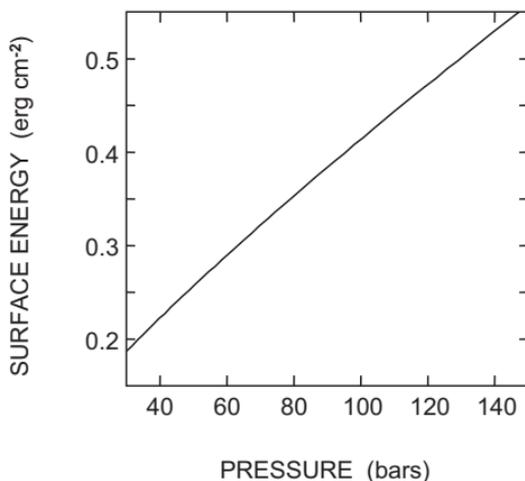


Fig. 5. The liquid-solid surface energy  $\alpha$  as a function of pressure as calculated from Eq. (9).

probability of nucleation on the time scale and volume scale of typical ultrasonic experiments. It seems that this may provide an explanation of the failure to observe nucleation in ultrasonic experiments.

Of course, since the radius of the critical nucleus is approximately equal to the width of the interface, to construct a more quantitative theory it would be necessary to go beyond the thin wall approximation. Also we have not attempted to calculate the rate of quantum tunneling through

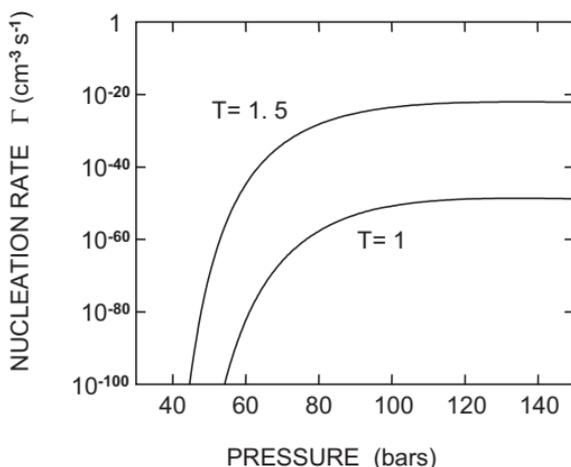


Fig. 6. Nucleation rate as a function of pressure at temperatures of 0.5, 1, and 1.5 K. The liquid-solid surface energy is assumed to vary with pressure according to Eq. (9).

the nucleation barrier. An excellent discussion of the theory of quantum nucleation has been given by Lifshitz and Kagan.<sup>24</sup> For pressures only slightly above the freezing pressure they are able to show that the nucleation rate  $\Gamma_Q$  varies as

$$\Gamma_Q = \Gamma_{Q0} \exp(-B), \quad (10)$$

where  $\Gamma_{Q0}$  is a prefactor, and  $B$  is proportional to the 4th power of the surface energy and varies with pressure as  $(P - P_F)^{-7/2}$ . In this range of pressure where the critical nucleus is large, they show that it is permissible to treat the liquid as incompressible. This makes the calculation of the kinetic energy of the system during the tunneling process straightforward. However, examination of their result shows that the tunneling rate in this pressure range is totally negligible. At higher pressures (e.g., 50 bars above  $P_F$ ) where Eq. (10) does give a significant tunneling rate, tunneling occurs on a short time scale, and the incompressible approximation breaks down. Thus, it does not appear to be practical to attempt a serious calculation at this time.

It is possible that at some high pressure nucleation occurs via a totally different mechanism. A number of authors have discussed the possibility that there is a "spinodal" for the high pressure liquid at which the liquid becomes unstable in some way. For example, it is possible that the energy at the roton minimum becomes zero and that the solid can form via this instability.<sup>25</sup>

We have not attempted to estimate how the barrier height changes with temperature. Regardless of the details of this variation, the nucleation rate presumably increases simply because there is more thermal energy available to overcome the barrier. However, at high temperatures the growth rate of the solid is small. As a consequence, it may be difficult to detect nucleation in an ultrasonic experiment because the solid will grow to only a very small size during the time scale of the experiment (1 to 10  $\mu$ s).

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### REFERENCES

1. For recent reviews of this work, see F. Caupin, S. Balibar, and H. J. Maris, in *Proceedings of the 23rd International Conference on Low Temperature Physics*, Hiroshima, August 2002, to be published in *Phys. B*; and S. Balibar and F. Caupin, in *NATO Advanced*

- Research Workshop on Liquids Under Negative Pressure*, A. Imre, H. J. Maris, and P. R. Williams (ed), Kluwer, Dordrecht (2002), to appear.
2. H. Lambaré, P. Roche, S. Balibar, H. J. Maris, O. A. Andreeva, C. Guthmann, K. O. Keshishev, and E. Rolley, *Eur. Phys. J.* **2**, 381 (1998).
  3. F. Caupin and S. Balibar, *Phys. Rev. B* **64**, 064507-1 (2001).
  4. S. Balibar, B. Castaing, and C. Laroche, *J. Phys. (Paris)* **41**, 283 (1980).
  5. V. L. Tsymbalenko, *J. Low Temp. Phys.* **88**, 55 (1992).
  6. J. P. Ruutu, P. J. Hakonen, J. S. Penttilä, A. V. Babkin, J. P. Saramaki, and E. B. Sonin, *Phys. Rev. Lett.* **77**, 2514 (1996).
  7. Y. Sasaki and T. Mizusaki, *J. Low Temp. Phys.* **110**, 491 (1998).
  8. T. A. Johnson and C. Elbaum, *Phys. Rev. E* **62**, 975, (2000).
  9. R. Nomura, H. H. Hensley, T. Matsushita, and T. Mizusaki, *J. Low Temp. Phys.* **94**, 377 (1994).
  10. V. Tsepelin, H. Alles, A. Babkin, J. P. H. Harme, R. Jochemsen, A. Y. Parshin, and G. Tvalashvili, *Phys. B* **284–288**, 351 (2000).
  11. X. Chavanne, S. Balibar, and F. Caupin, *Phys. Rev. Lett.* **86**, 5506 (2001).
  12. S. Balibar, T. Mizusaki, and Y. Sasaki, *J. Low Temp. Phys.* **120**, 293 (2000).
  13. D. Konstantinov and H. J. Maris, unpublished.
  14. G. Beaume, S. Nascimbene, F. Caupin, and S. Balibar, unpublished results and private communication, July 2002.
  15. See, for example, L. D. Landau and I. M. Lifshitz, *Statistical Physics*, Pergamon, Oxford, (1969), p. 471.
  16. M. Uwaha, *J. Low Temp. Phys.* **52**, 15 (1983).
  17. T. Minoguchi, *J. Low Temp. Phys.* **126**, 627 (2002).
  18. F. Pederiva, A. Ferrante, S. Fantoni, and L. Reatto, *Phys. Rev. Lett.* **72**, 2589 (1994).
  19. B. M. Abraham, Y. Eckstein, J. B. Ketterson, M. Kuchnir, and P. R. Roach, *Phys. Rev A* **1**, 250 (1970). See Eq. (12) of this paper.
  20. This includes, for example, the fit used by F. Dalfovo, A. Latri, L. Pricauptenko, S. Stringari, and J. Treiner, *Phys. Rev. B* **52**, 1193 (1995).
  21. D. O. Edwards and R. C. Pandorf, *Phys. Rev. A* **140**, 816 (1965).
  22. D. O. Edwards, M. S. Pettersen, and H. Baddar, in *Excitations in 2D and 3D Quantum Fluids*, A. F. G. Wyatt and H. J. Lauter, (ed.), Plenum Press, New York, (1991), p. 361.
  23. H. J. Maris, *J. Low Temp. Phys.* **77**, 347 (1989).
  24. I. M. Lifshitz and Y. Kagan, *Sov. Phys. JETP* **35**, 206 (1972).
  25. T. Schneider and C. P. Enz, *Phys. Rev. Lett.* **27**, 1186 (1971).