Liquid Helium at Negative Pressures: Nucleation of Bubbles and Anomalous Phonon Dispersion

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We calculate the rate at which bubbles nucleate in ^{4}He when the liquid is at negative pressure. Previous calculations have predicted that at low temperatures ($T \leq 0.3$ K) the nucleation rate remains low until a pressure of roughly -15 bar is reached. We show that this result is incorrect, and that at a critical pressure P_c (≈ -9 bar) the liquid becomes macroscopically unstable. We have made a calculation of the nucleation rate allowing for this effect. It is shown that the effect of quantum nucleation is small and probably hard to observe experimentally. Finally, we demonstrate that one can understand the pressure dependence of the phonon dispersion relation by a simple model. This model uses a parameter which also enters into the nucleation calculation.

1. INTRODUCTION

In this paper we discuss the physical properties of liquid helium at low temperatures and negative pressures. This work was stimulated by the experimental and theoretical investigations that have been made of the nucleation of bubbles in helium under tension (for a review of cavitation in quantum liquids, see Ref. 1). In general, one expects that the nucleation rate Γ (per unit volume and time) is a very rapidly increasing function of the tension applied to the liquid. Consequently, in any particular experiment which studies a certain volume V of liquid for a length of time τ, one can determine a fairly definite negative pressure P_n at which bubbles first

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nucleate. The nucleation rate at P_n must be such that there is an appreciable probability that a bubble will nucleate in V in time τ. Thus

$$\Gamma(P_n)V\tau \simeq 1 \tag{1}$$

When only homogeneous nucleation is considered, previous calculations of Γ have predicted that a large negative pressure is required to produce nucleation.[2] For example, if V is 10^{-3} cm^3 and τ is 10^{-5} sec, P_n should be -6 bar at 2 K and -17 bar at 0 K. (We describe these calculations in the next section.) In most experimental studies, nucleation has been found to occur at much smaller negative pressures.[1,3] This discrepancy has been explained in terms of heterogeneous nucleation at electron bubbles or vortices. Very recently, careful measurements by Nissen et al.[4] in the temperature range 1.6 K to the lambda point have given much larger values of P_n, and the values are in reasonable agreement with the predictions of the homogeneous nucleation theory. In these experiments a very small volume is studied, which greatly reduces the chance of heterogeneous nucleation.

If heterogeneous nucleation can indeed be avoided, it should be possible to study the homogeneous nucleation rate over a wide range of temperature. Of particular interest would be the rate at very low temperature (below $\simeq 0.3$ K) where the nucleation has been predicted to proceed via quantum tunneling, rather than thermal activation. In this paper we reexamine the theory of homogeneous nucleation in helium. We find that the earlier theories are incorrect in that they take no account of the equation of state of liquid helium in the negative pressure regime. For example, we determine that liquid helium-4 becomes *macroscopically unstable* before a negative pressure of -10 bar is reached. Thus there is no possibility that P_n can rise at low temperatures to a value as large as -17 bar, as predicted by Akulichev and Bulanov.[2] In the next section, we give a brief review of previous theories, and in Sec. 3 we make an estimate of the equation of state for negative pressures. The calculation of the nucleation rates is in Sec. 4. Finally, in Sec. 5 we show that the behavior of the liquid at negative pressures gives an interesting insight into the seemingly unrelated phenomenon of anomalous phonon dispersion.

2. NUCLEATION THEORY

The standard theory of the nucleation of bubbles[2,3] proceeds as follows. To form a bubble of radius R in the liquid requires a free energy

$$F(R) = 4\pi R^2 \alpha - \tfrac{4}{3}\pi R^3 |P| \tag{2}$$

where α is the liquid-gas surface free energy and $|P|$ is the magnitude of

the (negative) applied pressure. There is thus an energy barrier

$$\Delta F = \frac{16\pi\alpha^3}{3|P|^2} \tag{3}$$

which occurs at a radius R_0 given by

$$R_0 = \frac{2\alpha}{|P|} \tag{4}$$

The rate of nucleation by thermal activation over this barrier is thus

$$\Gamma_t = \Gamma_t^0 \exp(-16\pi\alpha^3/|P|^2 kT) \tag{5}$$

where Γ_t^0 is the attempt frequency. To calculate the rate of nucleation by quantum tunneling in the WKB approximation, one has to evaluate the integral

$$I = \int_0^{R_1} (2m^*F/\hbar^2)^{1/2}\, dR \tag{6}$$

where R_1 is the radius at which F becomes zero. From (2)

$$R_1 = 3\alpha/|P| \tag{7}$$

where m^* is the effective mass. Lifshitz and Kagan[5] show that

$$m^* = 4\pi R^3 \rho \tag{8}$$

where ρ is the density of the liquid.* Then

$$I = \frac{135\pi^2 6^{1/2} \rho^{1/2} \alpha^4}{32\hbar|P|^{7/2}} \tag{9}$$

and the nucleation rate is

$$\Gamma_Q = \Gamma_Q^0 \exp(-2I) \tag{10}$$

where Γ_Q^0 is a prefactor.

The prefactors Γ_T^0 and Γ_Q^0 are discussed in Refs. 2, 3, and 5. We have used the results given in Ref. 2 to find the total nucleation rate (we used the surface energy measured by Eckardt et al.[6]). We then calculated the pressure P_n at which nucleation will occur for three different values of $V\tau$ (V = volume, τ = duration of experiment). The result is shown in Fig. 1.

In this calculation there are several assumptions. There are, for example, uncertainties about the prefactors and the possible effect of dissipation on the nucleation rate. In addition, it is important to recognize that the formulas for the barrier ΔF for classical nucleation and the WKB integral I are not

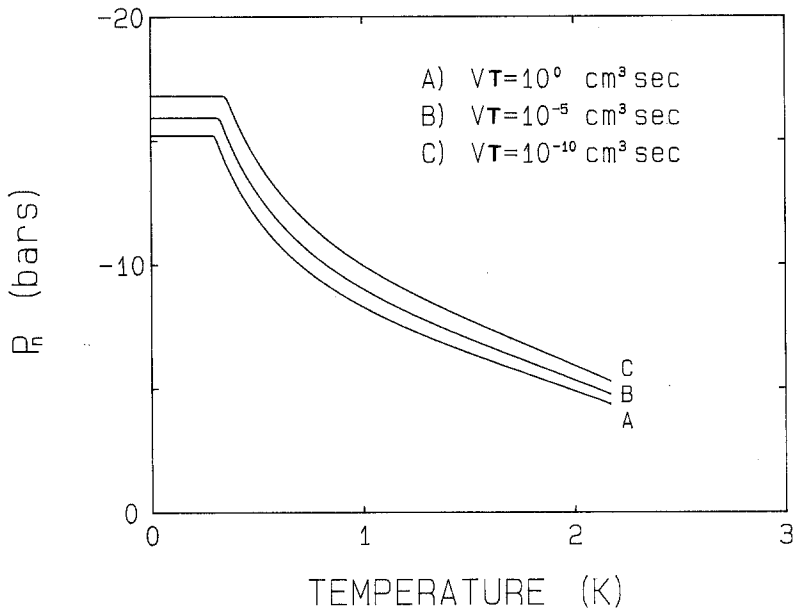*The density of the gas is considered to be negligible.

Fig. 1. Calculated pressure at which nucleation of bubbles occurs as a function of temperature. The three curves are for different values of the product $V\tau$ ($V =$ experimental volume, $\tau =$ duration of experiment). Calculation is based on Eqs. (5) and (10) using prefactors given in Ref. 2.

of completely general validity. For example, the derivation of ΔF is based on the assumption that nucleation proceeds via the formation and growth of an "ideal bubble," i.e., a spherical volume containing a region of essentially zero density (gas). This assumption is not necessarily true; it may be energetically favorable for the "bubble" to contain helium at a density intermediate between the liquid and gas densities since this lowers the surface energy. To consider such possibilities, we first estimate the properties of liquid helium under conditions of negative pressure.

3. EQUATION OF STATE FOR NEGATIVE PRESSURE

For positive pressures the most accurate data that relate to the equation of state are the sound velocity measurements of Abraham et al.[7] They measured for $T < 0.1$ K the quantity

$$\Delta c(P) = c(P) - c(0) \tag{11}$$

where $c(P)$ is the sound velocity at pressure P, for 39 values of pressure in the range up to the freezing pressure. They then used an earlier estimate

of $c(0)$ by Whitney and Chase[8] to calculate values of $c(P)$ itself. The fractional uncertainty in $c(0)$ is estimated to be $\pm 4 \times 10^{-4}$; random errors in $c(P)$ are roughly $\pm 3 \times 10^{-5}$. From $c(P)$ one can obtain the equation of state from the relations

$$\rho(P) = \rho(0) + \int_0^P \frac{dP}{c^2(P)} \tag{12}$$

$$E(\rho) = E(\rho_0) + \int_0^\rho \frac{P(\rho')}{\rho'^2} \, d\rho' \tag{13}$$

where $E(\rho)$ is the energy per unit mass. Thus, to find the equation of state for negative P, it is sufficient to estimate $c(P)$.

To do this we have used several methods, and the results are summarized in Fig. 2. In Fig. 2a we show the results of least squares fits of the form

$$c(P) = a_0 + a_1 P + \cdots + a_m P^m \tag{14}$$

with $m = 2$ to 7. Because there are many points near to $P = 0$, we weighted each point by the spacing to its neighbors. The series of fits converges very slowly and suggests that there may be some form of singularity for negative pressure. To investigate this further, we have also fit the data to Padé approximations of the form*

$$c(P) = \frac{A_0 + A_1 P + \cdots + A_m P^m}{1 + B_1 P + \cdots + B_m P^m} \tag{15}$$

with $m = 1$ to 3 (Fig. 2b). These fits again suggest that some sort of singularity occurs for negative pressure, i.e., they suggest that at pressure P_c ($P_c < 0$) c goes to zero, possibly as

$$c(P) \propto (P - P)_c^\nu \tag{16}$$

where $\nu < 1$. To understand why such behavior should occur, consider the dependence of the energy E per unit mass on the molar volume V. We expect this to look qualitatively similar to a plot of interatomic potential versus atomic separation, i.e., as sketched in Fig. 3. Thus, for some $V = V_c$ there is an inflection point (assuming for the moment that E is an analytic function of V) at which dE/dV has a maximum value. Hence, at V_c the pressure reaches a minimum value P_c and the bulk modulus B becomes zero. Thus, near V_c

$$B \propto V_c - V \tag{17}$$

$$P - P_c \propto (V_c - V)^2 \tag{18}$$

*This is an estimate based on the error in the time delay and on the point to point fluctuations in the fit of the data to a smooth curve (see Fig. 2b or Ref. 8).
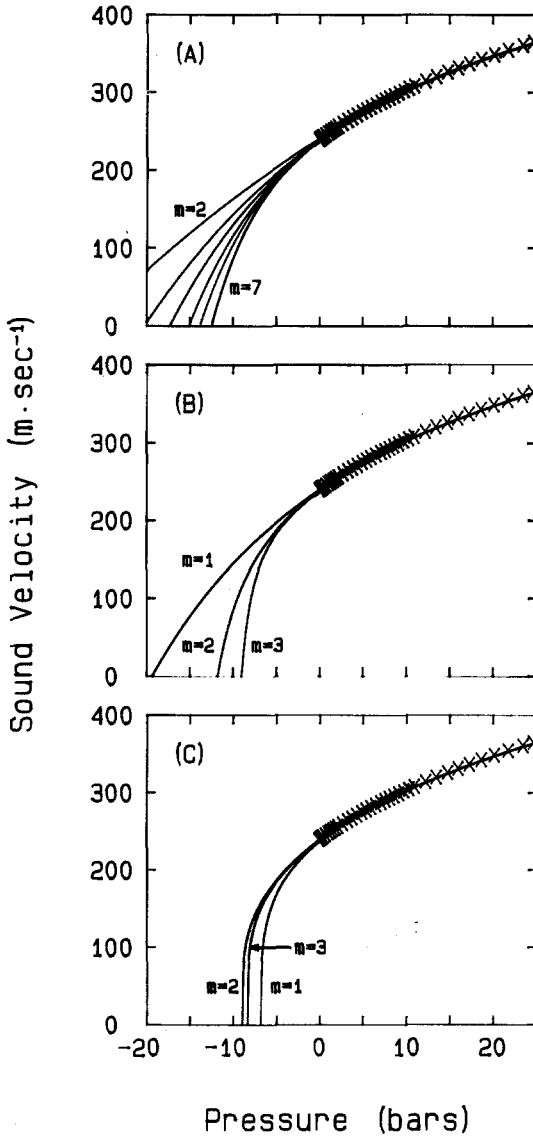
Fig. 2. Fits to sound velocity as a function of pressure. X denotes experimental data of Abraham *et al.*[7] (A) Polynomial fits (Eq. (14)) for $m = 1$ to 7. These form a monotonic sequence. (B) Padé approximant fits of c to P (Eq. (15)) for $m = 1, 2, 3$. (C) Padé fits of c^4 to P (Eq. (20)) for $m = 1, 2, 3$.
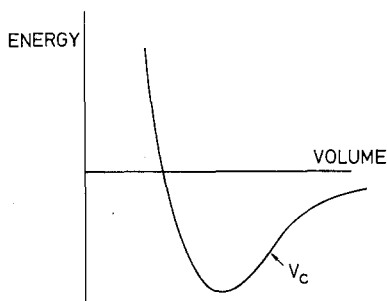
Fig. 3. Qualitative form of the energy as a function of volume. V_c is the volume at which the pressure has its maximum negative values.

Thus, since the density remains finite

$$c \propto (V_c - V)^{1/2}$$

$$\propto (P - P_c)^{1/4} \tag{19}$$

This suggests that we could make a better fit to the data using

$$c^4(P) = c^4(0)\left\{\frac{C_0 + C_1 P + \cdots + C_m P^m}{1 + D_1 P + \cdots + D_m P^m}\right\} \tag{20}$$

This is shown in Fig. 2c for $m = 1$ to 3. For $m = 2$ the value of P_c is -8.87 bar, and for $m = 3$ it is -8.37 bar. The rms deviation of the data from the fit decreases by a factor of 15 going from $m = 1$ to $m = 2$, but by only 45% on going from $m = 2$ to $m = 3$. Thus, we will use Eq. (20) with $m = 2$ as our estimate of $c(P)$ for $P < 0$. The values of the parameters in the fit are (in cgs units):

$$C_0 = 1.000624$$

$$C_1 = 1.626051 \times 10^{-7} \qquad D_1 = 2.30240 \times 10^{-8}$$

$$C_2 = 5.617522 \times 10^{-15} \qquad D_2 = -6.27846 \times 10^{-17} \tag{21}$$

The value of V_c is found to be 36.3 cm^3 mole^{-1}.

The sound velocity in ^{3}He has also been measured as a function of pressure[9] but the data are not as accurate. We have made several fits to the data and it appears that P_c lies between -2 and -4 bar.

For helium-4 we have tried to examine the assumption that E has a simple inflection point, i,e., the form near V_c

$$E(V) \simeq E(V_c) + (V - V_c)E_1 + (V_c - V)^3 E_3 + \cdots \tag{22}$$

where E_1 and E_3 are constants. If the cubic term is replaced by a factor $(V_c - V)^\gamma$ with $\gamma > 2$ one finds that near P_c
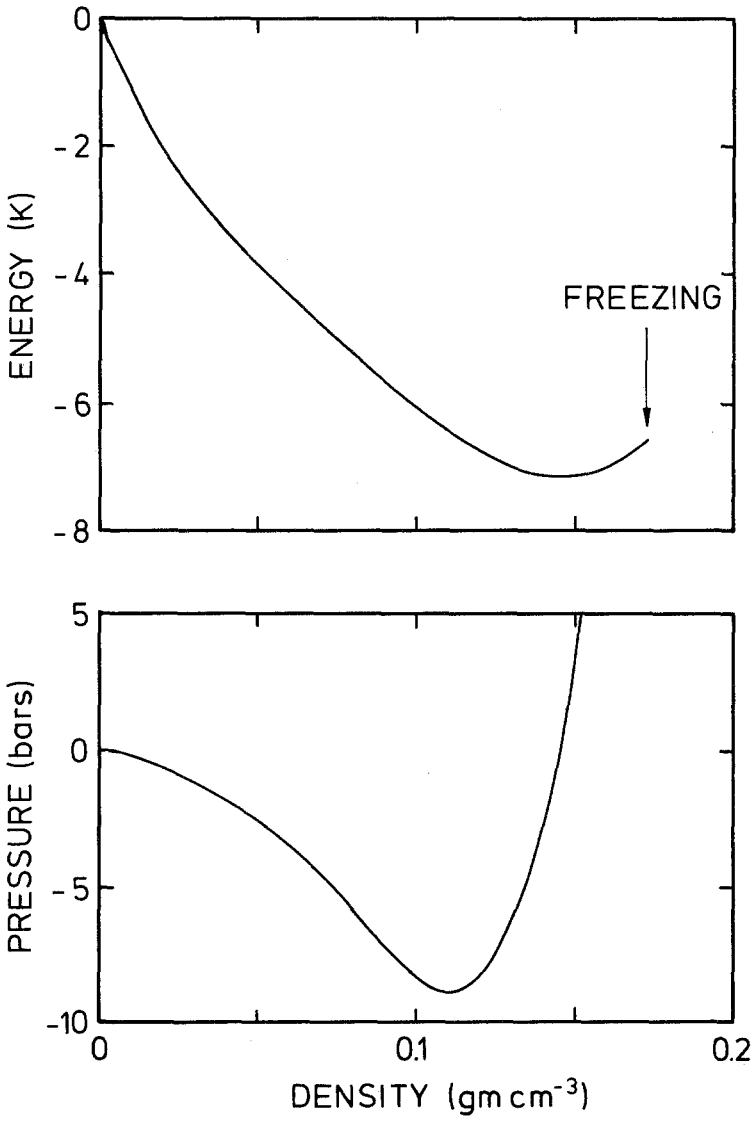
$$c \propto (P - P_c)^\nu \tag{23}$$

Fig. 4. Equation of state of liquid helium as estimated by the method described in the text.

with $\nu = (\gamma/2 - 1)/(\gamma - 1)$. To try to determine ν from the experimental data we use a method described by Baker.[10] We make a Padé fit of the form

$$\frac{d \log c(P)}{dP} = \frac{c_0 + c_1 P + \cdots + c_m P^m}{1 + d_1 P + \cdots d_m P^m} \tag{24}$$

This will have a pole at P_c and the residue at the pole is the exponent ν. For $m = 1$ we find $P_c = -9.49$ bar and $\nu = 0.331$; for $m = 2$ the values are $P_c = -9.24$ bar and $\nu = 0.312$. The sum of the squares of the errors changes by only 0.03% on going from $m = 1$ to 2. These fits are thus in reasonable agreement with the earlier estimate (8.87 bar) for P_c. The value of ν differs appreciably from 1/4. If ν is actually 0.312, then the exponent γ in the energy must be 3.66 instead of 3. It is not clear whether these differences are significant, and we are not aware of any theory of nonanalytic terms in the energy of a quantum system at low temperatures near to an instability point.

Finally, we construct a simple model for the equation of state for $V > V_c$. To do this we use a method similar to that employed by Ebner and Saam.[11] We consider the energy per unit volume f as a function of the mass density ρ, and approximate this by a power series

$$f = A\rho^2 + B\rho^3 + C\rho^4 + D\rho^5 \tag{25}$$

Constant and linear terms do not appear because the energy density and chemical potential should vanish for $\rho = 0$. We then fix the constants A, B, C, and D by the requirement that f and its first three derivatives be continuous at the critical density ρ_c ($\rho_c = 4.00260/V_c = 0.11031$ g.cm^{-3}). This gives (in cgs units)

$$A = -2.6323 \times 10^9 \tag{26a}$$

$$B = 3.18040 \times 10^{10} \tag{26b}$$

$$C = -2.67989 \times 10^{11} \tag{26c}$$

$$D = 8.69650 \times 10^{11} \tag{26d}$$

The results for the energy per atom and the pressure are shown in Fig. 4.

4. NUCLEATION THEORY REVISITED

The standard theory of nucleation described in Sec. 2 predicts that at low T, nucleation does not occur until pressures in the range -15 to -17 bar are reached. However, our estimate of the equation of state predicts that the liquid becomes unstable at a pressure of -9 bar. It is clear that the simple theory of nucleation must be incorrect and that the nucleation rate

has to become very large as P_c is approached. In this section we will calculate how this happens.

The theory of nucleation processes at low temperatures has been discussed by Lifshitz and Kagan.[5] Let $f(\rho)$ be the free energy density per unit volume when the system has a uniform density ρ. They assume that in a nonuniform system, the total free energy can be approximated by

$$F\{\rho\} = \int dV[f(\rho) + \lambda(\nabla\rho)^2] \tag{27}$$

where λ is a constant. Let ρ_1 be the density in the initial metastable liquid. Then the change in free energy relative to this state can be written

$$\delta F\{\rho\} = \int dV[\phi(\rho, \rho_1) + \lambda(\nabla\rho)^2] \tag{28}$$

where

$$\phi(\rho, \rho_1) = f(\rho) - f(\rho_1) - (\rho - \rho_1)f'(\rho_1) \tag{29}$$

The inclusion of the last term in Eq. (29) means that one can calculate δF from (28) without having to take account of the condition

$$\int (\rho - \rho_1) \, dV = 0 \tag{30}$$

We can imagine that initially the system is in the state of uniform density ρ_1. The density distribution $\{\rho(\mathbf{r})\}$ is then changed in a continuous way until a state is reached in which δF is negative. It is clear from (28) that the first change in the density from the uniform state must give a positive δF. Thus, before $\delta F < 0$ is reached δF will pass through a maximum value δF_{max}. One can now imagine considering all possible ways of going from the uniform state to a state with $\delta F < 0$. Each way will have some value for δF_{max}, and there will be a minimum value for this quantity which we call δF_{minmax}. This quantity is the nucleation barrier ΔF.

In the "standard" theory of nucleation, one assumes that the density distribution $\rho(\mathbf{r})$ at the saddle point (where the free energy is δF_{minmax}) has the form of a bubble of radius R_0 (see Eq. (4)) with a thin wall, i.e., wall thickness $\ll R_0$. The interior of the bubble has density zero, and the profile of the wall is the same as that of a planar interface. Given these assumptions the nucleation barrier calculated from Eq. (28) agrees with the result (3) given earlier. It is clear, however, that this result is not general. It is a good approximation when the negative pressure is small so that the radius R_0 is very large. If the pressure is sufficiently large, the radius of the bubble at the saddle point configuration will become comparable to the thickness of the bubble wall and the standard theory for ΔF (Eq. (3)) will not apply. (Note, however, the comments we make on this point in what follows).

4.1. Nucleation near to the Critical Pressure

Lifshitz and Kagan[5] (LK) have calculated ΔF (i.e., δF_{minmax}) in the limit of pressures very close to the instability point P_c. In this range we can expand $\phi(\rho, \rho_1)$ as a power series in which the first two nonzero terms are

$$\phi(\rho, \rho_1) \cong \tfrac{1}{2} f''(\rho_1)(\rho - \rho_1)^2 + \tfrac{1}{6} f'''(\rho_1)(\rho - \rho_1)^3$$

$$\cong \tfrac{1}{6} f'''(\rho_c)[3(\rho_1 - \rho_c)(\rho - \rho_1)^2 + (\rho - \rho_1)^3] \tag{31}$$

where ρ_c is the density at pressure P_c. LK showed that in this limit the size of the critical nucleus is of the order of

$$\frac{\lambda^{1/2}}{(\rho_1 - \rho_c)^{1/2} f'''(\rho_c)^{1/2}} \tag{32}$$

i.e., the nucleus becomes very large as $\rho_1 \to \rho_c$. The change in density at the center of the nucleus (relative to bulk liquid) is of order of $\rho_1 - \rho_c$, i.e., a small fraction of the mean density. This nucleus is favored because the large size and small density variation give a very low value for the part of the energy involving the gradient term λ. The result of LK can be expressed in the form

$$\Delta F = \frac{J_0 \cdot 9 \cdot 2^{1/2} \lambda^{3/2} (\rho_1 - \rho_c)^{3/2}}{f'''(\rho_c)^{1/2}} \tag{33}$$

$$= \frac{J_0 \cdot 9 \cdot 2^{5/4} \lambda^{3/2} (P - P_c)^{3/4}}{f'''(\rho_c)^{5/4} \rho_c^{3/4}} \tag{34}$$

J_0 is a numerical constant which LK estimate to be $\simeq 40$. The quantity $f'''(\rho_c)$ can be determined from the dependence of c on P near to P_c, since it is straightforward to show that in this regime

$$c^4 \approx 2\rho_c f'''(\rho_c)(P - P_c) \tag{35}$$

4.2. Estimation of the Parameter λ

To evaluate the barrier height and the nucleation rate just calculated, we need to make an estimate of λ. We want to do this in such a way that the theory of Lifshitz and Kagan goes over into the standard theory of nucleation in the case that the negative pressure is small and the bubble radius is large compared to the wall thickness. To achieve this it is sufficient to make sure that the value of λ is consistent with the surface tension of liquid in the following sense. Consider a free plane surface of liquid helium normal to the z axis. From Eq. (28) we have that in equilibrium

$$\lambda \frac{d^2 \rho}{dz^2} = 2 \frac{\partial \phi}{\partial \rho} \tag{36}$$

For $z \to -\infty$, $\rho \to 0$, and for $z \to \infty$, $\rho \to \rho_1$ with ρ_1 here the density of bulk liquid helium at $P = 0$. The density profile of the interface is given by[5]

$$z(\rho) = \int^{\rho} (\lambda/\phi)^{1/2} \, d\rho \tag{37}$$

and the surface tension α is

$$\alpha = 2 \int_{0}^{\rho_1} (\lambda\phi)^{1/2} \, d\rho \tag{38}$$

Thus, if we know ϕ we can fix a definite value for λ by the requirement that Eq. (38) gives the correct value for α, which at $T = 0$ is 0.378 erg $\cdot$ cm^{-2}. In this way we obtain

$$\lambda = 9.13 \times 10^{-7} \quad \text{(cgs)} \tag{39}$$

As a test of the calculation we show in Fig. 5 the density profile for the planar interface, plotted as density divided by bulk density versus position. The shape and width of the interface are in close agreement with the calculations of Ebner and Saam.[11,*] For example, the width (distance between points of reduced density 0.1 and 0.9) is 7.7 Å whereas their result is 7.8 Å. A distinction between the results occurs on the low density side of the interface. In the Ebner and Saam calculation, the density decreases
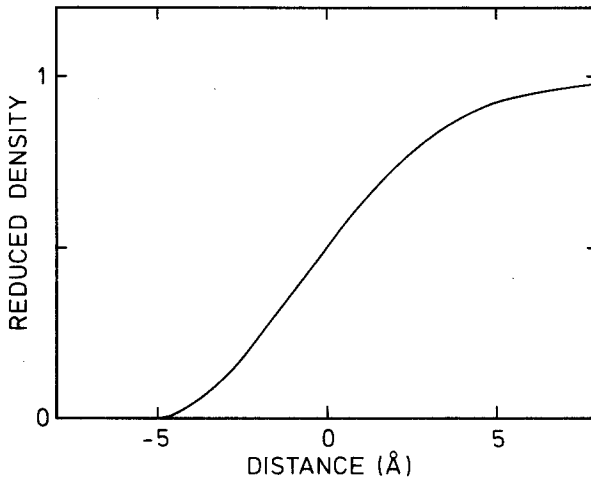

Fig. 5. Reduced density (density divided by the density in bulk liquid) as a function of distance perpendicular to a planar interface.

*We compare to their results for the "renormalized surface density" including the effect of zero-point surface modes.

exponentially in this regime. In our model the density instead goes to zero according to

$$\rho(z) \propto (z - z_0)^2$$

as $z \to z_0$ for $z > z_0$. This unphysical result is a consequence of the simple form we have taken for the density functional (Eq. (27)). As far as we can see, it should not affect the main conclusions of this paper.

4.3. Calculation of Barrier Height in the General Case

Using the value of ξ just determined, we obtain from Eq. (34) the height of the barrier for P close to P_c as

$$\Delta F = 13.2(P - P_c)^{0.75} \qquad K \qquad (40)$$

where P is measured in bars. For P very small, we have argued that the "standard theory" for the barrier should be correct. From Eq. (3) we then obtain

$$\Delta F = \frac{6550}{P^2} \qquad K \qquad (41)$$

In Fig. 6 we have plotted these two limiting expressions (dashed lines) as a function of P. It is clear that there is no obvious way to interpolate between these two limits. Consequently, we have calculated numerically the barrier height as a function of P. It is straightforward to show from Eq. (28) that in the critical nucleus the density must vary with radius r according to

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\rho}{dr} \right) = \frac{1}{2\lambda} \frac{d\phi}{d\rho} \qquad (42)$$

with the boundary conditions

$$\frac{d\rho}{dr} = 0, \qquad r = 0$$

$$\rho \to \rho_1, \qquad r \to \infty \qquad (43)$$

Numerical solutions of this equation for several pressures are shown in Fig. 7. These results confirm the previous discussion. At low pressures the nucleus has a core of low density (zero density in our simplified model) and a wall thickness small compared to the radius. When P is close to P_c, the nucleus consists of a small decrease in density below ρ_c. These solutions can then be used to calculate the energy barrier ΔF using Eq. (28), and this is shown as the solid line in Fig. 6.

One can see from these results that except for very low pressures (where nucleation is very unlikely to occur) or very close to P_c, the exact value for
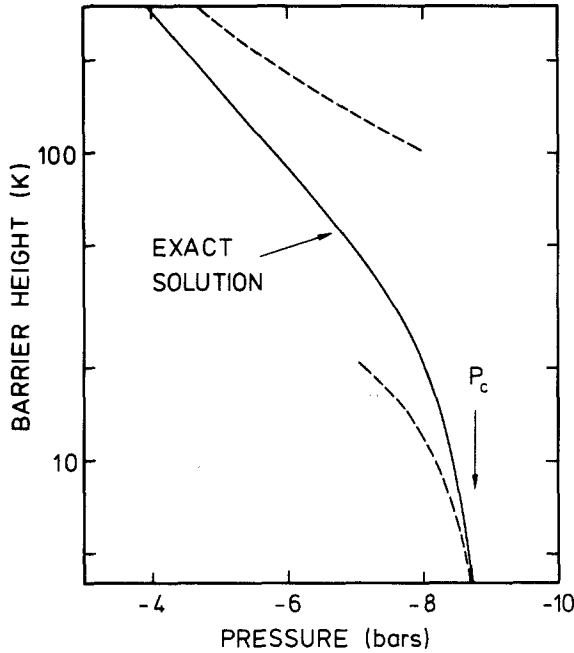
Fig. 6. Energy barrier ΔF as a function of pressure. The dashed lines show the results calculated using the analytical expressions (Eqs. (40) and (41)) for P close to 0 and P_c. The solid line is the exact solution.

(Eqs. (40) and (41)). Thus, a calculation of tensile strength or nucleation rates based on these formulas is very uncertain. The point is that over the range of experimental interest where the barrier height lies in the range 10 to 100 K the radius of the critical nucleus is only a few times the thickness of the planar liquid-solid interface.

4.4. Calculation of Classical Nucleation Rates

To calculate the nucleation rate Γ_T as a function of T and P, we have

$$\Gamma_T = \Gamma_T^0 \exp(-\Delta F/kT) \qquad (44)$$

The general order of magnitude of Γ_T^0 is given by

$$\Gamma_T^0 \sim \frac{\nu}{V_N} \qquad (45)$$

where ν is the attempt frequency and V_N is the volume of the critical nucleus.[5] For simplicity, we take $\nu = kT/h$, and use for V_N the volume of a sphere of radius 10 Å (the size range of the critical nuclei as shown in
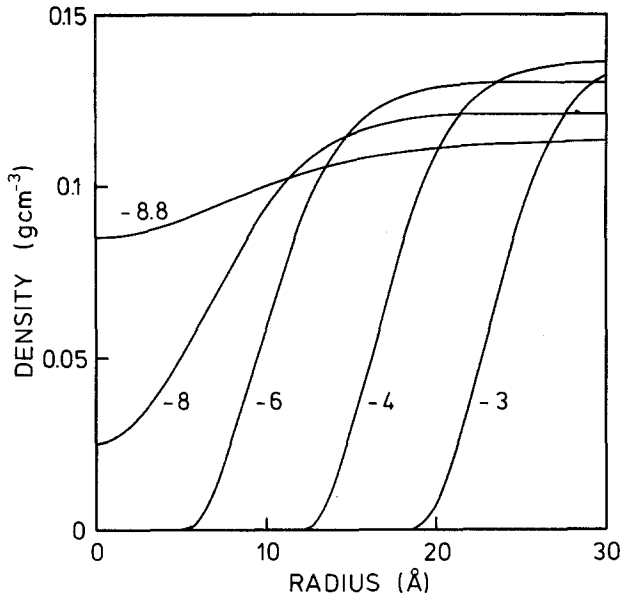
Fig. 7. Density as a function of radius for a series of critical nuclei.
The curves are labelled by the pressures in bars.

Fig. 7). As an additional simplification we neglect the effect of temperature on ΔF, i.e., we are assuming that the surface energy and the equation of state are temperature independent.

The results of this calculation are shown in Fig. 8 for a set of temperatures between 0.2 and 2 K. From these results we can find the effective tensile strength as a function of temperature, i.e., the magnitude P_n of the negative pressure required to produce nucleation in a given volume and time. This is shown in Fig. 9. At high temperatures (≥ 1.5 K) the results are only slightly smaller* than the results of the previous theories (see Fig. 1). At lower temperature P_n rises much less rapidly and, of course, can never become larger than $|P_c|$. Thus, in this range P_n is much smaller than previous theories have predicted.

4.5. Effect of Quantum Tunneling

The calculations described so far ignore the possibility of quantum tunneling through the nucleation barrier. This tunneling must provide a

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*Note that in Fig. 1 the calculations allow for the temperature dependence of the surface energy, whereas in Fig. 9 they do not. In addition, the prefactors are not the same. If it were not for these differences, the disagreement between the new calculation and former theories in the high temperature regime would be larger.
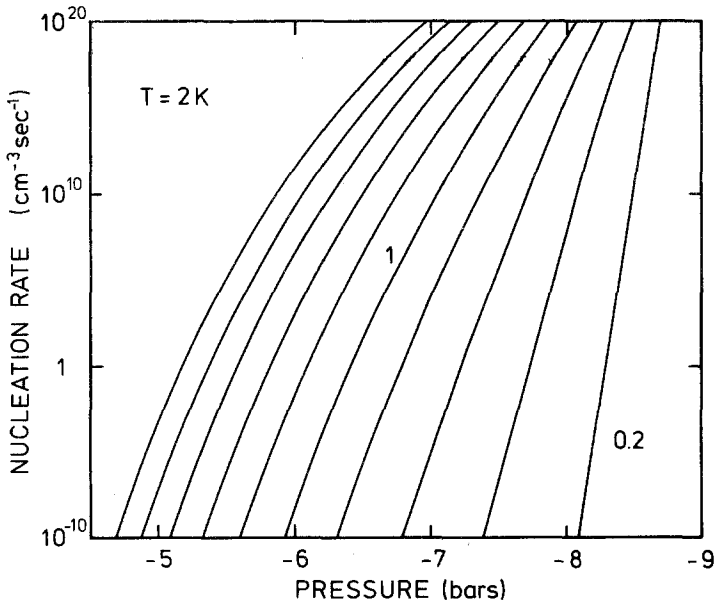
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Fig. 8. Nucleation rate due to thermal fluctuations as a function of pressure. The different curves are for temperatures from 0.2 to 2 K at 0.2 K intervals.

finite nucleation rate even at $T = 0$ K, and in previous theories led to the temperature-independent nucleation rate at low temperature (see Fig. 1). The form of the nucleation rate is given by Eq. (10). For P small the value of the WKB integral through the barrier is given by Eq. (9). For P close
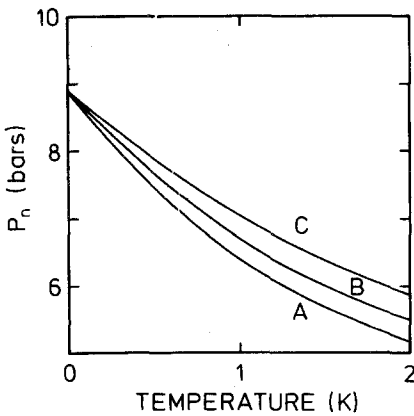

Fig. 9. Magnitude of the pressure required to cause nucleation as a function of temperature. The curves A, B, and C correspond to products of experimental volume and time of 1, 10^{-5}, and 10^{-10} cm^3 sec, respectively.

to P_c one can use results of Lifshitz and Kagan to show that*

$$2I \approx \frac{36 \cdot 2^{3/4} s_0 \lambda^2 (P - P_c)^{1/4}}{\hbar f'''(\rho_c)^{7/4} \rho_c^{3/4}} \tag{46}$$

where the constant s_0 is estimated to be ~ 100. Thus

$$2I \approx 1.50 \times 10^6 |P|^{-7/2}, \qquad P \approx 0 \tag{47}$$

$$\approx 34.1 (P - P_c)^{1/4}, \qquad P \approx P_c \tag{48}$$

For the prefactors we take the same approach as in the previous section, but use a temperature-independent attempt frequency of 10^{11} sec^{-1}. This gives $\Gamma_Q^0 = 2.4 \times 10^{31}$ sec^{-1}.

Evaluation of the nucleation rates using the formulas (47) and (48) reveals the same sort of difficulty as was found in the thermal nucleation problem. The two limiting formulas give results which differ by a very large amount at intermediate pressures. For example, at 5 bar the small P result gives a quantum nucleation rate of 10^{-2300} cm^{-3} sec^{-1}, whereas the $P \approx P_c$ result is 4×4^{10} cm^{-3} sec^{-1}. In the case of thermal nucleation, we were able to find an exact numerical solution for the barrier height as a function of pressure. This height was found to lie in between the two limiting formulas, and to be well-approximated by neither of these formulas over essentially the entire range of pressures of experimental interest. In the quantum case, it is a very hard problem to find an exact numerical solution for the WKB integral I, and we have not attempted to do this. In addition, there is no obvious way to guess a formula that interpolates between Eqs. (47) and (48) because of the very different dependences on P in the two expressions.

To get around this difficulty to some extent, we have used the following method. We try to estimate the temperature T^* at which quantum and thermal nucleation rates are equal. Thus T^* is given by†

$$kT^* = \Delta F / 2I \tag{49}$$

We now calculate T^* using the limiting forms for ΔF and I. The result is

$$kT^* = \frac{256 \hbar |P|^{3/2}}{405 \cdot 6^{1/2} \pi \alpha \rho^{1/2}}, \qquad P \approx 0 \tag{50}$$

$$= \frac{J_0}{2^{3/2} s_0} \frac{(P - P_c)^{1/2} \hbar f'''(\rho)_c^{1/2}}{\lambda^{1/2}}, \qquad P \approx P_c \tag{51}$$

These are plotted as the solid curves A and B in Fig. 10. Although it is still not certain how to interpolate between these two limiting forms, these results do suggest that T^* is always small. For example, if we write

$$kT^* = a|P|^{3/2}(P - P_c)^{1/2}(1 + bP) \tag{52}$$

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*Note that there is a mistake in Eq. (4.4) of Lifshitz and Kagan's paper which relates their parameter ξ_0 to $P - P_c$.
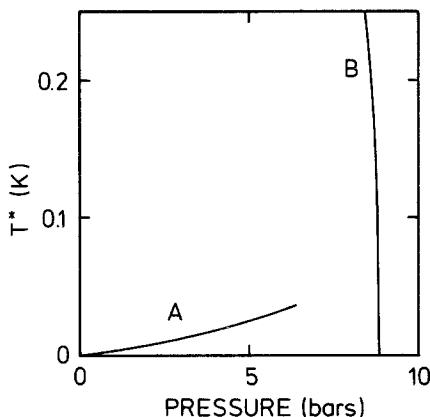
†We ignore the difference in the prefactors.

Fig. 10. Temperature T^* at which nucleation rates due to thermal fluctuations and quantum tunneling are equal. Curve A is for P close to zero (Eq. (50)), and B is for $P \approx P_c$ (Eq. (51)).

and choose a and b so that this reduces to (50) or (51) in the limiting cases, we find that the maximum value of T^* is 0.3 K at a pressure of -7.3 bar.

If this rough estimate of T^* is correct, it means that very careful experiments will be required to study quantum tunneling. Suppose, for example that T^* is, in fact, 0.3 K (for all pressures). Then, quantum nucleation (QN) is unimportant above this temperature. Hence, we see from Fig. 9 that QN can be neglected until the applied negative pressure exceeds 8 bar. Thus, QN is important only in a very small region of the P-T plane, i.e., between $P = -8$ and -8.87 bar and for $T < 0.3$ K. Production of controlled and known pressures in this range close to P_c is a difficult experimental problem.

5. PHONON DISPERSION

In this paper we have assumed that at the pressure P_c liquid helium becomes macroscopically unstable, i.e., unstable at long wavelengths. This seems to be a reasonable assumption based on what is known about the pressure dependence of the dispersion curve for elementary excitations. Short-wavelength excitations (in the roton region) have energies which increase as the pressure is lowered,[12] and thus it is unlikely that an instability occurs in this region.

Given this picture, the dispersion curve in the phonon region should look as shown in Fig. 11. For small momentum we can write

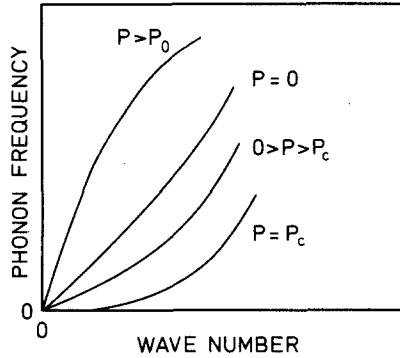$$\omega_k = ck(1 + \alpha_2 k^2 + \cdots) \tag{53}$$

Fig. 11. Qualitative form of the phonon dispersion curve for various pressures. P_c is the pressure at which the liquid becomes unstable. P_o is the pressure at which α_2 vanishes.

For P in the range 0 to 10 bar, very accurate measurements of α_2 have been made by Rugar and Foster.[13] (We have used these data even though they cover a limited pressure range because of their accuracy.) In this range α_2 is positive. At a pressure P_0 of around 20 bar,[14] α_2 changes sign, and above this pressure the dispersion curve changes to concave upwards (see Fig. 11). For negative pressure the sound velocity decreases, and finally becomes zero at P_c.

Lifshitz and Kagan[5] remark that the parameter λ determines the spatial dispersion of sound. If one takes the usual equations of continuum elasticity and adds the term $\lambda |\nabla \rho|^2$ into the energy density one obtains the result*

$$\omega_k^2 = k^2(c^2 + 2\rho\lambda k^2 + \cdots) \tag{54}$$

Thus,

$$\alpha_2 = \lambda \rho / c^2 \tag{55}$$

To have α_2 change sign at P_0, one would then need that λ also change sign. This seems unlikely but is not impossible. One can have λ negative provided that the uniform liquid is kept stable due to the presence of positive terms in the energy proportional to squares of higher derivatives of ρ. However, we consider that a much more likely explanation of the sign change of α_2 is as follows. The dispersion included in Eq. (54) is just the spatial dispersion, i.e., the dispersion due to the finite k. There is also the possibility of dispersion due to the time-response of the liquid. For low frequencies we may consider this to arise from the presence of a term in the energy per unit volume of the form

$$E_1 = \tfrac{1}{2}\beta\dot{\rho}^2 \tag{56}$$

*There is a mistake of a factor of 2 in the paper by Lifshitz and Kagan.

We discuss below the microscopic origin of such a term. One then obtains the result

$$\alpha_2 = \frac{\lambda\rho}{c^2} - \frac{\beta\rho}{2}$$

(57)

Our idea is that, whereas c goes to zero at P_c, λ and β are fairly slowly varying functions of P. (We have, in fact, already implicitly assumed that λ is independent of P in the calculation of nucleation barriers). To test this we plot α_2/ρ as a function of $1/c^2$ in Fig. 12. This gives a linear plot as predicted by Eq. (57), and a least-squares fit to the data points leads to the values

$$\lambda = 10.5 \times 10^{-7} \quad \text{(cgs)}$$

(58)

$$\beta = 1.55 \times 10^{-15} \quad \text{(cgs)}$$

(59)

The value for λ is only 15% larger than the value (9.13×10^{-7}) determined in Sec. 4.2 by the fit to the experimental value of the surface tension, and this agreement gives strong support to the model of phonon dispersion we have presented. Of course, the determination of both λ and β from the single function $\alpha_2(\rho)$ depends entirely on the assumption that λ and β vary with ρ much more slowly than does the sound velocity.

Finally, consider the physical origin and magnitude of the term involving β. To do this we take a "single-particle" view of liquid helium. We
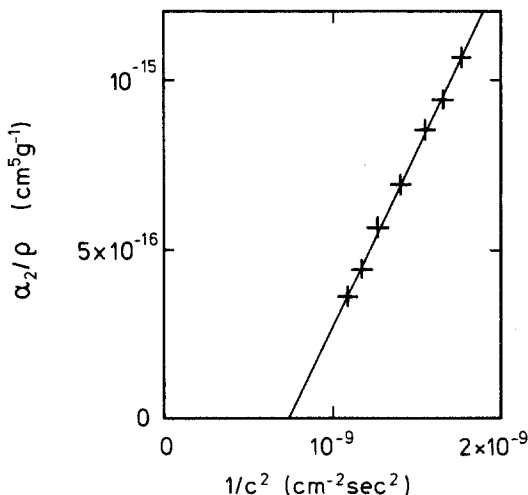

Fig. 12. Plot of α_2/ρ versus inverse square of sound velocity to determine the parameters λ and β.

imagine that each helium atom sits in a potential well V determined by the average position of its neighbors. When the density changes, the depth and shape of this potential will vary, and the wave function of the helium atom will be deformed. If the density (and hence the potential) are slowly varying in time, it is clear that to a good approximation the wave function will always be the ground state for the instantaneous value of the potential energy function. It is straightforward to show that the first correction to the wave function due to the time variation of V is

$$\delta\psi = -i\hbar \sum_{n \neq 0} \frac{\dot{V}_{n0}}{E_{n0}^2} \psi_n \tag{60}$$

where $\dot{V}_{n0}$ is the matrix element of $\dot{V}$ between the ground state ψ_0 and ψ_n, and $E_{n0} = E_n - E_0$. Terms in $\delta\psi$ proportional to second and higher time derivatives of V have been neglected. Thus, the energy of the atom is equal to the ground state energy in the instantaneous potential, plus an excess energy

$$\delta E = \hbar^2 \sum_n \frac{|\dot{V}_{n0}|^2}{E_{n0}^3} \tag{61}$$

Note that this excess energy can be appreciable even though the rate of change in density is sufficiently slow that the wave function is deformed adiabatically. The probability of real transitions occurring is proportional to $\exp(-\text{constant}/\omega)$ where ω is the frequency of the density oscillations, and hence is extremely small at low frequency.

Since the number of atoms per unit volume is ρ/M ($M = $ atomic mass), we find from (56) that

$$\beta = \frac{2\hbar^2\rho}{M} \sum \frac{1}{E_{n0}^3} \left| \frac{dV_{n0}}{d\rho} \right|^2 \tag{62}$$

To make a very rough estimate of β, we take each atom to be a three-dimensional Einstein oscillator of frequency ω_0, i.e. we take V proportional to r^2. For each oscillator the only possible transitions are to the $n = 2$ excited state. If the variation of the oscillation frequency is

$$\frac{d\omega_0}{d\rho} = \frac{\gamma\omega_0}{\rho} \tag{63}$$

where γ is the Gruneisen constant, then

$$\frac{dV}{d\rho} = \frac{M\omega_0^2\gamma r^2}{\rho} \tag{64}$$

Hence, evaluating the matrix element and setting $E_{n0} = E_{20} = 2\hbar\omega_0$, we have

$$\beta = \frac{3\hbar\gamma^2}{8M\omega_0\rho} \tag{65}$$

If we arbitrarily choose the phonon frequency ω_0 to correspond to a phonon energy of 10 K, we obtain

$$\beta = 0.32 \times 10^{-15} \gamma^2 \quad (\text{cgs}) \tag{66}$$

Thus, the value of β from experimental data $(1.55 \times 10^{-15} \, \text{cgs})$ requires $|\gamma| = 2.2$ which is very reasonable.

The existence of the term $\frac{1}{2}\beta\dot{\rho}^2$ is the energy density has no effect on the calculation of the energy barrier for classical nucleation since this is a calculation in statics. However, it must decrease the rate of quantum tunneling. For $|P|$ small it is straightforward to show that this decrease is small, but this may not be true for P approaching P_c. We have not attempted this calculation.

6. SUMMARY

Previous theories[1,2] have predicted that the pressure P_n to produce bubbles in liquid helium-4 should rise to very large values (≈ -15 bar) at low temperatures. We have shown that this is not true, and that helium becomes macroscopically unstable at a pressure P_c which is approximately -9 bar. We have made an estimate of the equation of state of helium in the range $0 > P > P_c$. We then calculated the energy barrier and nucleation rate for the creation of bubbles by thermal fluctuations. The results demonstrate that the form and energy of the critical nucleus are, at all pressures of experimental interest, poorly approximated by previous analytical results. We then show that the nucleation of bubbles by quantum tunneling is important only at very low temperatures and for pressures close to P_c. Finally, we demonstrate that one can understand the pressure-dependence of the phonon dispersion relation by a simple model in which the energy density contains extra terms involving time and space derivatives of the density.

A specific prediction of the theory is that at temperatures below 2 K the tensile strength of helium should rise only slowly as the temperature is decreased (see Fig. 9), and should reach a maximum value at low temperatures of less than 9 bar. We are presently constructing an experiment to test this prediction.

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REFERENCES

1. V. A. Akulichev, *Ultrasonics* **26**, 8 (1986).
2. V. A. Akulichev and V. A. Bulanov, *Sov. Phys. Acoust.* **20**, 501 (1975).
3. P. L. Marston, *J. Low Temp. Phys.* **25**, 383 (1976).
4. J. A. Nissen, E. Bodegom, L. C. Brodie, and I. S. Semura, *Adv. Cryog. Eng.* **33**, 999 (1988).
5. I. M. Lifshitz and Y. Kagan, *Sov. Phys.-JETP* **35**, 206 (1972).
6. J. R. Eckardt, D. O. Edwards, S. Y. Shen, and F. M. Gasparini, *Phys. Rev. B* **16**, 1944 (1977).
7. B. M. Abraham, Y. Eckstein, J. B. Ketterson, M. Kuchnir, and P. R. Roach, *Phys. Rev. A* **1**, 250 (1970).
8. W. M. Whitney and C. E. Chase, *Phys. Rev. Lett.* **9**, 243 (1962).
9. B. M. Abraham, D. Chung, Y. Eckstein, J. B. Ketterson, and P. R. Roach, *J. Low Temp. Phys.* **6**, 521 (1972).
10. G. A. Baker, in *The Padé Approximant in Theoretical Physics*, G. A. Baker and J. L. Gammel, eds. (Academic, New York, 1970), p. 1.
11. C. Ebner and W. F. Saam, *Phys. Rev. B* **12**, 923 (1975).
12. R. A. Cowley and A. D. B. Woods, *Can. J. Phys.* **49**, 177 (1971).
13. D. Rugar and J. S. Foster, *Phys. Rev. B* **30**, 2595 (1984).
14. R. C. Dynes and V. Narayanamurti, *Phys. Rev. B* **12**, 1729 (1975).