The expansion coefficient of liquid helium 3 and the shape of its stability limit

Frédéric Caupin, Sébastien Balibar and Humphrey J. Maris*

Laboratoire de Physique Statistique de l'Ecole Normale Supérieure
associé aux Universités Paris 6 et Paris 7 et au CNRS
24 rue Lhomond 75231 Paris Cedex 05, France
**Department of Physics, Brown University, Providence, Rhode Island 02912*

We propose the existence of a new feature in the phase diagram of liquid helium 3. Instead of being monotonic in temperature, the liquid-gas spinodal line should present a minimum at 0.4 K. In analogy with cold water where this was proposed by Speedy, we explain that such a minimum is a consequence of the thermal expansion coefficient being negative down to the spinodal line. We justify this from a comparison with our recent measurements of the temperature dependence of cavitation in liquid helium 3 and from new theoretical arguments.

PACS numbers: 67.55.Cx, 64.60.Qb, 65.20.+w

The high purity of liquid helium makes it an ideal material in which to study homogeneous nucleation. During the past years, cavitation, that is the gas nucleation in the stretched liquid, has been extensively studied. The negative pressure at which cavitation occurs is obtained by focusing a high amplitude sound wave in a small region far from any wall, thus making heterogeneous nucleation unlikely. In this contribution, we present a detailed analysis of results recently obtained in helium 3 [1]. We show that these results disagree to some extent with existing theoretical descriptions of the liquid at negative pressure. We then propose an estimation of the stability limit for liquid ^{3}He based on sound velocity measurements by Roach *et al.*[2]. The new spinodal line $P_s(T)$ we obtain exhibits a minimum at 0.4 K and gives a temperature dependence of the cavitation pressure which is now consistent with our measurements. For water, Speedy[3] previously proposed a spinodal $P_s(T)$ with a minimum and showed that this behavior was linked to the change in sign of the isobaric expansion coefficient α. This change in sign corresponds to a line of density maxima, and also occurs in liquid ^{3}He at positive pressure. We give an extrapolation of the line of density maxima at negative pressure and finally present theoretical arguments about the sign of α near the spinodal line.

In any substance below its saturated vapor pressure, the liquid phase can be metastable since an energy barrier E_b must be overcome for liquid-gas separation to occur, that is for a bubble to nucleate in the liquid. The experiments in liquid helium reported in Ref. 1 measure the probability of these cavitation events. For a given experiment performed in an experimental volume V and during an experimental time τ, this probability is, at a pressure P and a temperature T:

$$\Sigma(P,T) = 1 - \exp\left[-\Gamma_0 V\tau \exp\left(-\frac{E_\mathrm{b}(P,T)}{k_\mathrm{B}T}\right)\right] , \tag{1}$$

where Γ_0 is a prefactor discussed below. The experimental measurements are reproduced by the asymmetric S-curve formula of Eq. (1) with great accuracy[4]. Γ_0 has the dimensions of frequency times an inverse volume. It is natural to estimate Γ_0 as an attempt frequency ν at which the fluctuations try to overcome the nucleation barrier multiplied by the density of the critical nuclei which can be taken to be spheres of radius R_c [5–7]. Typically, R_c is around 1 nm and the attempt frequency varies from $k_\mathrm{B}T/h$ to E_b/h; all the different estimates thus lie between $5\times 10^{36}\,T$ and $1.5\times 10^{38}\,T\,\mathrm{m}^{-3}\,\mathrm{s}^{-1}$ with T in K. Pettersen *et al.*[7] have calculated V and τ for the experimental method which uses an acoustic wave to produce a negative pressure swing in the liquid. For ^{3}He and for a 1 MHz acoustic wave as in Ref. 1, this gives $V\tau = 1.2\times 10^{-22}\,\mathrm{m}^3\,\mathrm{s}$ [8]. The theoretical estimates of the factor $\Gamma_0 V\tau$ thus vary from $6\times 10^{14}\,T$ to $1.8\times 10^{16}\,T$. Although this range extends over two orders of magnitude, it does not significantly affect the value of the energy barrier: for $\Sigma = 0.5$, all estimates give $E_\mathrm{b} = (34\pm 3)k_\mathrm{B}T$.

Recently, Caupin and Balibar[1] have given experimental limits for the pressure at which the cavitation probability is one half (the cavitation line $P_\mathrm{cav}(T)$) in liquid ^{3}He and liquid ^{4}He. They made a comparison with the spinodal pressure at which the nucleation barrier vanishes as calculated by Maris at low temperature: $P_\mathrm{s} = -3.15$ bar for ^{3}He [9]. In fact, because of thermal or quantum fluctuations in the liquid, the cavitation pressure is always higher than the spinodal pressure, and the difference can be calculated from Eq. (1) if the expression of $E_\mathrm{b}(P,T)$ is known.

Maris[9] has calculated $E_\mathrm{b}(P)$ at low temperature by a density functional method; close to the spinodal, his results are well represented by a power law:

$$\frac{E_\mathrm{b}}{k_\mathrm{B}} = \beta(P-P_\mathrm{s})^\delta , \tag{2}$$

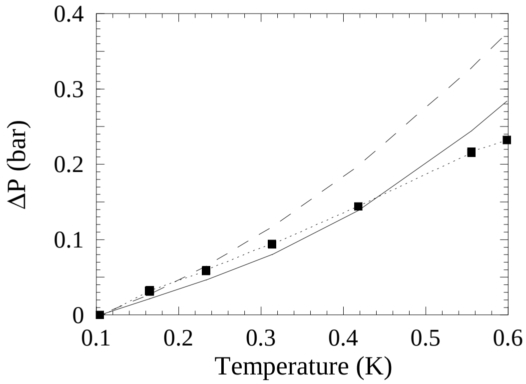

Fig. 1. Comparison between experimental and theoretical temperature variation $\Delta P = P_{\mathrm{cav}}(T) - P_{\mathrm{cav}}(0.1\,\mathrm{K})$ of the cavitation pressure. The experimental ΔP is given by full squares ; the dotted line is a guide to the eye. Other lines are the theoretical ΔP calculated with $\Gamma_0 V\tau = 6 \times 10^{14}\,T$ using two different sources for the spinodal pressure (see Fig. 2): Guilleumas *et al.*[6] (dashed line) and this work (solid line).

with $\beta = 47.13$ and $\delta = 3/4$, when $E_{\mathrm{b}}/k_{\mathrm{B}}$ is expressed in K and P in bar. However, to calculate the cavitation pressure up to 0.6 K, we need to know the temperature dependence of E_{b}. The strongest source of this dependence is that the spinodal pressure varies with temperature; therefore we write $E_{\mathrm{b}}(P,T) = E_{\mathrm{b}}(P - P_{\mathrm{s}}(T))$ and assume that Eq. (2) remains valid at higher temperature with parameters β and δ held constant. The temperature dependence of the cavitation pressure follows from Eq. (1):

$$P_{\mathrm{cav}}(T) = P_{\mathrm{s}}(T) + \left[\frac{T}{\beta}\ln\left(\frac{\Gamma_0 V\tau}{\ln 2}\right)\right]^{1/\delta} \quad . \tag{3}$$

Fig. 1 displays the quantity $\Delta P = P_{\mathrm{cav}}(T) - P_{\mathrm{cav}}(0.1\,\mathrm{K})$: the squares correspond to experimental data[1]; the two other lines are theoretical ΔP calculated with Eq. (3) for the lowest possible value of the prefactor, namely $\Gamma_0 V\tau = 6 \times 10^{14}\,T$. For $P_{\mathrm{s}}(T)$ we first use the curve calculated by Guilleumas *et al.*[6], which leads to the dashed line for ΔP; we notice that the temperature variation of ΔP thus obtained is stronger than the experimental one. How can we explain this discrepancy? Of course one can assume that the theory fails in estimating the value of Γ_0. However, to reproduce the experimental temperature dependence of P_{cav} would require $\Gamma_0 V\tau$ to be at least 3 orders of magnitude smaller than expected. We do not see any reasons to support this hypothesis. Instead, we think that the experimental measurements question the shape of the spinodal limit.

Before proceeding further, we need to recall how the spinodal pressure

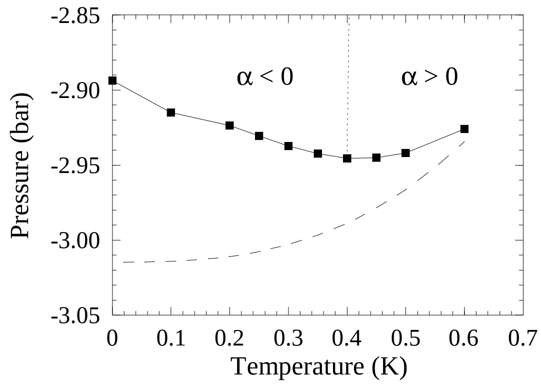

Fig. 2. Comparison between two theoretical estimates of the spinodal line: Guilleumas *et al.*[6] (dashed line) and this work (full squares). The spinodal found in this work shows a minimum at 0.4 K. The dotted line is a linear extrapolation of the line of density maxima as measured by Boghosian *et al.*[10] between 0 and 11 bar.

P_s can be obtained: Maris' method[9] consists in extrapolating measurements of the sound velocity c at positive pressure with a law of the form $c = [b\,(P - P_s)]^{1/3}$. Maris used for c the measurements of Abraham *et al.* at low temperature[11]. We used the same method with a set of data from Roach *et al.*[2]: they measured the first sound velocity along isochores at starting pressures from 1.6 to 28.1 bar and as a function of temperature from 0.01 to 0.6 K. The spinodal line we obtained is shown in Fig. 2: the spinodal pressure reaches a minimum of -2.9 bar around $T = 0.4$ K [14]. We would like to emphasize that none of the previous estimates of the spinodal pressure in liquid ^{3}He [6,9,12,13] has mentioned the possible existence of a minimum in the spinodal line. The new shape of the spinodal curve we propose is sufficient to remove the discrepancy stated above: using again Eq. (3) with the value $\Gamma_0 V\tau = 6 \times 10^{14}\,T$, we find a cavitation line whose temperature dependence is consistent with the experimental results (see Fig. 1, solid line).

We shall now turn to the physical origin of such a minimum in the spinodal. A similar behavior was first proposed by Speedy in the case of water[3]. This was the basis of the stability limit conjecture introduced to explain anomalies of supercooled water: in his theory, the liquid-gas spinodal was assumed to be reentrant at temperatures below 35°C. A review of this topic also describing alternative theories can be found in Ref. 15. Speedy shows that close to the spinodal the sign of the isobaric thermal expansion coefficient α of the liquid is the same as the sign of $\mathrm{d}P_s/\mathrm{d}T$. Therefore, if the locus of points such that $\alpha(P, T) = 0$ intersects the spinodal, this results in an extremum in the curve $P_s(T)$. Water and ^{3}He have in common that both liquids exhibit a line of density maxima: in some temperature range, they expand when cooled. Therefore they may exhibit such a minimum in the spinodal. We have tried to adapt Speedy's conjecture to the case of ^{3}He. The measurements of Roach *et al.* give the expansion coefficient, but unfortunately they are made in a region of the phase diagram where α is always negative; to obtain the line of density maxima in ^{3}He, we need to know the temperature where α vanishes. Therefore we used measurements by Boghosian *et al.*[10], which extend to higher temperatures and agree well with Roach values in the region where both sets overlap. A simple linear extrapolation of the line of density maxima for pressures below 11 bar extends down to the minimum in the spinodal as shown in Fig. 2.

We now give some theoretical arguments concerning the sign of α. The negative sign of α in ^{3}He at low temperature is related to the variation of the effective mass with density[16]. Indeed, using a Maxwell relation, we can write:

$$\alpha = -\frac{1}{V}\left(\frac{\partial S}{\partial P}\right)_T \ . \tag{4}$$

In the Fermi liquid region, the heat capacity C_{V} is linear in T and we have $S = C_{\mathrm{V}} = (m^*/m)\, C_{\mathrm{F}}$ where C_{F} is the heat capacity of the Fermi gas. Using Greywall's measurements of the effective mass[17] and extrapolating them at negative pressure as we did before[18], we find that α given by Eq. (4) remains negative down to the spinodal. Of course we should consider the corrections to the linear regime of the heat capacity and their evolution close to the spinodal. We see two sources of corrections. The first one is the contribution of phonons to the heat capacity, which varies as $(T/c)^3$, where c is the sound velocity; this term could become important near the spinodal where the isothermal sound velocity vanishes. However, this is relevant only for the long wavelength phonons: as stated by Lifshitz and Kagan[19], the first correction to the linear dispersion gives for small momentum:

$$\omega_k{}^2 = k^2(c^2 + 2\rho\lambda k^2)\ , \tag{5}$$

where λ is a constant. As the spinodal is approached, the dispersion relation thus becomes quadratic. A calculation shows that the correction to α remains negligible at temperatures of interest here. We also note that, if the sound remains adiabatic at small k close to the spinodal, the use of c_{S}, which does not vanish at P_{s}, instead of c_{T} would further reduce the phonon contribution. The second correction is due to the coupling of the quasiparticles to the incoherent spin fluctuations and varies as $T^3 \ln T$. This effect has been studied by Greywall[20], who has shown that its amplitude decreases when pressure decreases; it is not clear to us if this is the case until the spinodal is reached, and this point requires further investigation.

Frédéric Caupin, Sébastien Balibar and Humphrey J. Maris

We have studied the temperature dependence of the cavitation pressure in liquid ^{3}He. We have shown that recent measurements disagree with existing theories. We then proposed a new picture for liquid ^{3}He at negative pressure. From the pressure and temperature dependence of the sound velocity in ^{3}He, we obtained a liquid-gas spinodal different from what was previously predicted: this new spinodal is reentrant, that is to say that the curve $P_{\mathrm{s}}(T)$ exhibits a minimum of $-2.9\,\mathrm{bar}$ at $T = 0.4\,\mathrm{K}$. This new feature in the phase diagram of liquid ^{3}He agrees with our measurements of the temperature dependence of the cavitation pressure. Following an analysis by Speedy in the case of water, we have emphasized the relationship between this behavior and the negative expansion coefficient in ^{3}He. Finally we have given theoretical arguments to estimate this expansion coefficient at negative pressures.

REFERENCES

1. F. Caupin and S. Balibar, *Phys. Rev. B* **64**, 064507 (2001).
2. P. R. Roach *et al.*, *J. Low Temp. Phys.* **52**, 433 (1983).
3. R. J. Speedy, *J. Phys. Chem.* **86**, 3002 (1982).
4. F. Caupin *et al.*, *J. Low Temp. Phys.* **113**, 473 (1998).
5. Q. Xiong and H. J. Maris, *J. Low Temp. Phys.* **77**, 347 (1989).
6. M. Guilleumas *et al.*, *Phys. Rev. B* **47**, 9116 (1993).
7. M. S. Pettersen, S. Balibar and H. J. Maris, *Phys. Rev. B* **49**, 12062, (1994).
8. The expression of $V\tau$ obtained in Ref. 7 actually depends on the minimum pressure reached, but we have checked that this does not affect our conclusions.
9. H. J. Maris, *J. Low Temp. Phys.* **98**, 403 (1995).
10. C. Boghosian, H. Meyer and J. E. Rives, *Phys. Rev.* **146**, 110 (1966).
11. B. M. Abraham *et al.*, *J. Low Temp. Phys.* **6**, 521 (1972).
12. M. A. Solís and J. Navarro, *Phys. Rev. B* **45**, 13080 (1992).
13. J. Casulleras and J. Boronat, *Phys. Rev. Lett.* **84**, 3121 (2000).
14. Thermodynamically, the spinodal line is derived from the isothermal sound velocity rather than from the adiabatic one. Both velocities lead to spinodal lines showing a minimum and their difference is less than 30 mbar. We have actually plotted the spinodal obtained with the isothermal data in Fig. 2, and we used it in the above reasoning.
15. P. G. Debenedetti, *Metastable liquids* (Princeton University Press, Princeton, 1996).
16. K. A. Brueckner and K. R. Atkins, *Phys. Rev. Lett.* **1**, 315 (1958).
17. D. S. Greywall, *Phys. Rev. B* **33**, 7520 (1986).
18. S. Balibar *et al.*, *J. Low Temp. Phys.* **113**, 459 (1998).
19. I. M. Lifshitz and Y. Kagan, *Zh. Eksp. Teor. Fiz.* **62**, 385 (1972) [*Sov. Phys. JETP* **35**, 206 (1972)]. See also Ref. 5.
20. D. S. Greywall, *Phys. Rev. B* **27**, 2747 (1983).