Limits of metastability of liquid helium

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Abstract

Helium can remain in a metastable liquid state at a pressure below its saturated vapour pressure or above its melting pressure. This metastability can reach high degrees in helium because of its purity. We review the present knowledge of the stretched liquid state; experiments on cavitation are interpreted in relation to the existence of a liquid-gas spinodal limit. In view of recent experiments, we also consider overpressurized liquid helium 4 and address the question of the stability of the superfluid phase against the solid.

Key words: helium; nucleation; cavitation; crystallization

Any liquid can exist during a limited time at pressures below its boiling pressure P_b or above its freezing pressure P_f. It stays in a metastable state, because an energy barrier E_b must be overcome for the gas or solid phase to nucleate. This barrier results from the competition between the volume energy reflecting the stability of the new phase, and the energy needed to create an interface. Nucleation can be favoured by impurities or walls, or triggered by cosmic rays; this type of nucleation is called heterogeneous. It is possible to avoid nucleation on walls. Because helium is the only substance to remain liquid down to the absolute zero, it can be prepared free from impurities; consequently, it is an attractive system in which to study homogeneous nucleation which is a test of the intrinsic cohesion of the liquid. In this paper, we review experiments and theories about metastable liquid ^{3}He and ^{4}He.

1. Stretched liquid helium

Let us start with the liquid below its freezing pressure. The main goal of nucleation theories is to determine the barrier E_b and calculate the nucleation rate of the gas. The thin wall approximation (TWA) considers a spherical nucleus with a sharp interface between the gaseous core and the surrounding liquid. The barrier corresponds to a critical radius R_c. At a temperature T, thermal fluctuations overcome E_b when the system reaches a sufficiently negative pressure; bubbles appear at the cavitation pressure P_cav [1]:

$$P_\mathrm{cav} = P_\mathrm{b} + \frac{\rho}{\rho' - \rho}\left(\frac{16\,\pi\,\sigma^3}{3\,k_\mathrm{B}T\ln(\Gamma_0 V\tau)}\right)^{1/2} \qquad (1)$$

where ρ and ρ' are the respective densities of the liquid and of the vapour at equilibrium, σ is the bulk surface tension, Γ_0 is the product of an attempt frequency to overcome the barrier by the density of independent nucleation sites (roughly $1/{R_\mathrm{c}}^3$), and V and τ are the experimental volume and time.

The TWA ceases to be valid when R_c approaches the width of the liquid-gas interface at a flat free surface, measured to be 0.76 nm [2]. In this regime, E_b can be lowered by using a smoothly varying density profile; this is successfully described within the density functional theory (DFT) [3]. We compare TWA and DFT in the following, along with experiments.

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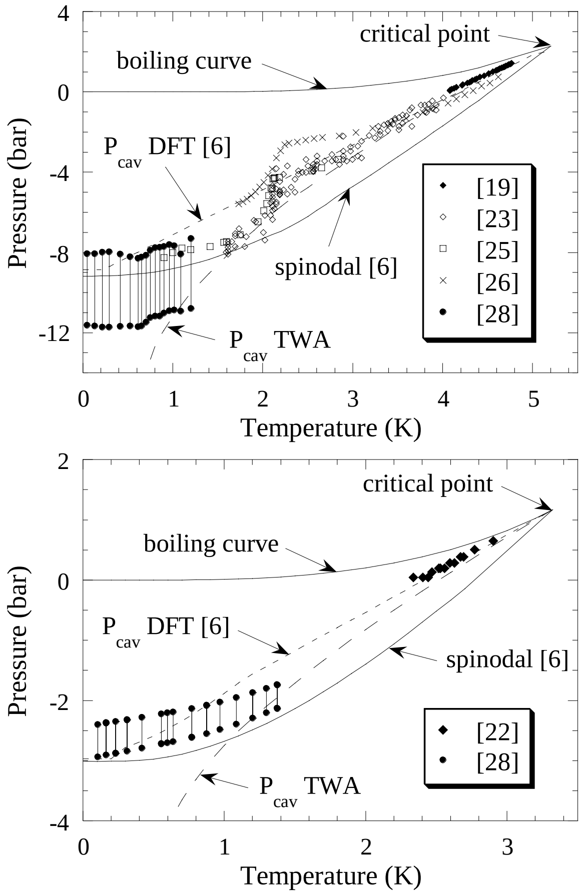

Fig. 1. Compilation of theoretical (dashed lines) and experimental (data points) values of $P_{\rm cav}$ in ^{4}He (top) and ^{3}He (bottom). Theoretical curves for $P_{\rm cav}$ were plotted using for $\Gamma_0 V \tau$ the value of the acoustic experiment (around 10^{17}).

The DFT also account for the existence of an extreme boundary for the metastability of the liquid [4–7]. There is a negative pressure $P_{\rm s}$, called the spinodal pressure, at which the liquid has a vanishing sound velocity (that is a diverging compressibility); $E_{\rm b}$ vanishes at $P_{\rm s}$, and the liquid becomes macroscopically unstable even at zero temperature. This again shows the failure of the TWA which predicts a diverging $P_{\rm cav}$ at low temperature. This spinodal limit can also be found by extrapolating sound velocity measurements obtained at positive pressure [8,9], and by microscopic calculations [10–14]. In the case of superfluid ^{4}He, the roton liquid theory was recently used to obtain $P_{\rm s}(T)$ along with other thermodynamical properties at negative pressure (superfluid transition temperature T_λ, isentropic lines and line of density minima) [15,16]. All methods give close estimates of $P_{\rm s}$: at $T = 0\,$K, $P_{\rm s} \simeq -9.4\,$bar in ^{4}He and $-3.1\,$bar in ^{3}He.

At low temperature, there is a more efficient nucleation process than thermal activation: quantum tunneling through the barrier. Both TWA and DFT predict that a crossover should take place at a temperature T^*, below which $P_{\rm cav}$ becomes temperature independent [3,9,17]. DFT predictions for T^* are around 220 mK for ^{4}He, and 120 mK for ^{3}He [9,17].

Let us now turn to the experiments. Attempts have been made to measure the tensile strength of liquid ^{4}He as far back as in 1956. It was found that cavitation occurred at much less negative values than theoretically expected, presumably because of heterogeneous nucleation; for a review of these early experiments, see Ref. [18]. During the last two decades, experiments have reached the homogenous nucleation limit. A first category of experiments consists in measuring the maximum superheating attainable in liquid helium. They were first performed by the Portland State University (PSU) group, using a transient superheating technique on a single crystal of bismuth [19]; continuous isobaric heating [20] and the mean lifetimes method in a bubble chamber [21] were later used. The second category of experiments consists in depressing the liquid during a fraction of a microsecond, in a small region far from any wall. This is done with an ultrasonic wave, focused at the center of a hemispherical transducer. This method, designed by the PSU group [23], suppresses the influence of heterogeneous nucleation. It also allows one to investigate the negative pressure region. Measurements were repeated and extended by several groups [24–28]. Fig. 1 shows a choice of the available experimental and theoretical work for both isotopes. They are all fairly consistent with each other. In fact, the quantity directly measured in acoustic experiments is the driving voltage of the transducer $V_{\rm cav}$ corresponding to $P_{\rm cav}$. The pressure was calibrated by different methods: light scattering [23], dependence of $V_{\rm cav}$ on the static pressure and calculation from the electrical characteristics of the transducer [28]; the last two methods lead respectively to upper and lower bounds on $P_{\rm cav}$, as displayed in Fig. 1 for the low temperature data.

The low temperature region is of special interest. First because it discriminates between the TWA and theories accounting for the existence of a spinodal limit (like DFT): measurements below 1 K agree with the latter. The other issue is a check of the predicted crossover from thermal to quantum nucleation, the signature of which is the levelling of $P_{\rm cav}$. Evidence for this phenomenon was reported in ^{4}He [27,28] at a temperature consistent with the theory. In ^{3}He, such a plateau is lacking: instead of levelling, the amplitude of $P_{\rm cav}$ even increases sharply when the temperature is decreased below 80 mK [28] (not shown in Fig. 1); this was attributed to the Fermi degeneracy of the liquid [29].

The experimental temperature dependence of $P_{\rm cav}$ in the thermal regime can also be compared with the theory. This is complicated by the fact that the acoustic wave follows isentropic lines; after correcting the temperature accordingly using Ref. [15], we found a good agreement for ^{4}He. In ^{3}He, $P_{\rm cav}$ was found to increase more slowly than expected. This made us question the shape of the spinodal curve, and we found experimental and theoretical evidence for an anomaly: $P_{\rm s}(T)$ reaches a minimum around 0.4 K, and this is related to the existence of a line of density maxima in liquid ^{3}He [30].

An interesting observation concerns the behaviour of $P_{\rm cav}$ near T_λ: $P_{\rm cav}$ exhibits a change in slope; it also lies below the predicted value between 1 and 2 K. It was suggested to relate this to the increase in the vortex density near T_λ [25].

Finally let us mention the study of cavitation on electron bubbles, which act like calibrated impurities in liquid helium [31]. The corresponding $P_{\rm cav}$ is less negative, as expected; interestingly, it does not show any peculiar behaviour near T_λ.

2. Overpressurized liquid helium

Liquid helium can also be metastable with respect to the solid phase. A number of groups have studied this metastability by pressurizing or cooling a cell filled with liquid ^{4}He across the equilibrium freezing curve: they have reported nucleation overpressures between 3.5 and 100 mbar [32–36]. In ^{3}He, to our knowledge, measurements of metastability are available in the superfluid phase only : they correspond to overpressures between 2.5 and 11 mbar [37,38]. The same ultrasonic method as for the study of cavitation has been used in ^{4}He. Far from any wall, even an overpressure estimated to be larger than 17 bar did not lead to the nucleation of the solid phase. More recently, the hemispherical transducer was put on a glass plate; by measuring the reflectivity of the glass/helium interface, Chavanne *et al.* obtained an instantaneous measurement of the density at the focus, and they observed nucleation of hcp solid at an overpressure as large as 4.3 bar [39]. In both types of experiment, the nucleation threshold becomes temperature independent at low temperature; it was proposed that this was due to a crossover to a quantum regime of nucleation [33–35,39].

The TWA may be used to study nucleation of the solid in the overpressurized liquid. The nucleus is now a solid sphere. In Eq. 1, $P_{\rm cav}$ must be replaced by the nucleation pressure $P_{\rm n}$, $P_{\rm b}$ by the equilibrium freezing pressure $P_{\rm f}$, and ρ' by the density of the solid at equilibrium. The density factor, which was close to -1 for cavitation, is now around 10. Calculated values of $P_{\rm n}$ are plotted as a function of temperature in Fig. 2 with typical experimental values of $\Gamma_0 V\tau$. We have neglected the small temperature variation of the parameters appearing in Eq. 1. We have also represented the crossover from thermal to quantum nucleation using

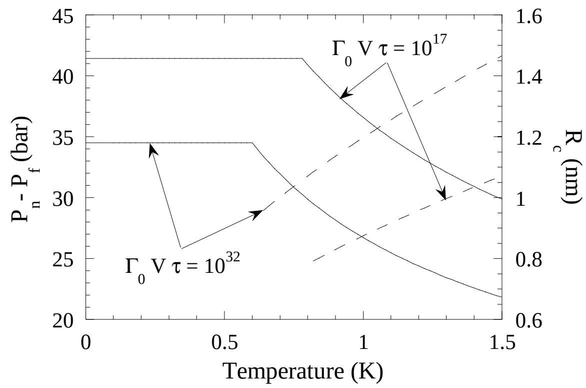

Fig. 2. Nucleation pressure of the solid as obtained from the TWA (solid lines, left scale). The radius of the critical nucleus is also shown (dashed lines, right scale). Two typical values of $\Gamma_0 V\tau$ were used: 10^{32} (corresponding to the large cell experiment) and 10^{17} (corresponding to the ultrasonic experiment).

Uwaha's calculation in the TWA (after reintroducing the density factor forgotten in his expression of $E_{\rm b}$ in the thermal regime) [40]. The corresponding critical radius $R_{\rm c}$ is also shown; as the liquid-solid free interface is calculated to be 4-5 atomic layers wide (1 to 1.3 nm) [41], one can see that the TWA is not really applicable. An additional problem of this standard theory is that it does not take into account the compressibility of both phases, although at such high overpressures as calculated for $P_{\rm n}$, the density of the metastable liquid approaches the one of the stable solid. It would be interesting to go beyond the TWA, with building a DFT-like theory; but such a theory would have to account in some way for the spatial ordering of the solid. Dalfovo *et al.* have tried to describe the equilibrium freezing pressure at low temperature within a DFT [42], and more recently Minoguchi has proposed an approach to the nucleation problem with an effective free energy involving two parameters, the density and a translational symmetry breaking parameter [43].

A puzzling question is the possibility of the existence of an absolute limit to the metastability of the liquid against the solid, as the spinodal discussed above is a limit to the metastability of the liquid against the gas. This idea was first proposed by Schneider and Enz, who associated it with the softening of the roton mode: the roton gap decreases with increasing pressure, and they proposed that it would eventually vanish, leading to spontaneous appearance of the solid [44]. However, up to now the only arguments for a vanishing roton gap are extrapolations of values measured in the stable liquid. The use of the roton liquid theory to describe the metastable superfluid also shows another possible instability [16]; it is also a way to locate the metastable superfluid transition line, to which experiments might be sensitive.

Let us now discuss the experimental results. The measured nucleation pressure is far below the value calculated in the TWA. As the measured P_{n} is close to P_{f}, the TWA provides a good estimate of what would be the homogeneous nucleation energy: at 4 bar, one finds $R_{\mathrm{c}} = 10\,\mathrm{nm}$ and $E_{\mathrm{b}} = 3000\,\mathrm{K}$. This is far too large to be overcome by thermal or quantum fluctuations in the experiments. A detailed analysis of the acoustic experiment rather leads to $E_{\mathrm{b}} = 10 \times T$ with T expressed in K; the difference is attributed to heterogeneous nucleation, taking place on one most favorable nucleation site on the glass plate [39]. In the previous experiments, nucleation at overpressures of a few millibars is presumably due to even more favorable impurities, more easily found because of the large surface of the cell involved. The geometrical effect of the walls has been investigated by Uwaha [40], but it is not sufficient to explain the large discrepancy with homogeneous nucleation [34,45]. Chemical defects like graphite particles have been proposed to reduce E_{b} to the depinning energy of a crystal seed from the defect [45]. Influence of quantized vortices in the superfluid has also been considered [46]. The experimental effort is now turned towards reaching the homogeneous nucleation limit of the solid, by using the transducer without any glass plate at larger driving voltages.

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