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Metastable Liquids

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Abstract. How far can one supercool a liquid before it crystallizes? How much can one stretch it before cavitation occurs ? In order to answer such questions, we have studied liquid helium, a model system. In this review, we show the limitations of the elementary "standard nucleation theory". We then show that the existence of "spinodal" limits need to be considered in the frame of "density functional" methods. We also shortly consider the possibility of nucleation by quantum tunneling. The main emphasis is on cavitation and crystallization in liquid helium, but we also mention several connections with more classical systems, in particular water.

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Introduction: Metastable liquids and negative pressures

For a certain time, a liquid can stay in a metastable state, outside of the stability region in its phase diagram. For example liquid water can be supercooled down to about - 40 °C (233 K) [1]. Water has also been stretched to - 1400 bar, a remarkably large negative pressure [2]. Such a metastablility is possible because the liquid-solid and the liquid-gas transitions are discontinuous, i.e. first order. As a result interfaces between a liquid and its vapor or solid phase have a finite surface tension. For a more stable phase (solid or gas) to appear in a less stable one (the metastable liquid), an interface has to be created somehow, and there is an energy cost for that. As a consequence, there is an energy barrier against the nucleation of the stable phase, and metastability is possible.

Nucleation is called "heterogeneous" when it is influenced by the presence of defects, impurities, walls or radiation. This is the most common case in nature. For example, water droplets in clouds freeze around -20 °C, and this temperature depends on the pollution by dust particles and various chemicals. In the absence of defects, walls etc., nucleation is an intrinsic property of the system, it usually takes place very far from equilibrium conditions and it is called "homogeneous". In this review, we mostly consider homogeneous nucleation, which is simpler to describe quantitatively.

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Some people find it difficult to consider negative pressures, although they are present in every day life, for example at the top of high tries[4]. The pressure of a gas cannot be negative. Suppose that a gas is contained in a chamber closed by a piston. If one pulls the piston, the pressure P of the gas vanishes linearly with the density ρ inside according to the equation of state $P(\rho)$. Condensed matter is different: at zero pressure, liquids and solids have a finite density due to attractive intermolecular interactions. Stretching a liquid or a solid means applying a positive stress to it, that is a negative pressure.

If our chamber had very clean, smooth and hydrophilic walls, and if it was filled with very pure water instead of a gas, we could pull the piston and reach a moderate negative pressure before vapor bubbles would nucleate. The pressure would follow an extension of the equation of state $P(\rho)$ in a metastable region at negative pressure. In 1850, Berthelot held the world record for negative pressures by cooling down a very clean glass ampoule which he had first filled with water at high temperature and pressure and sealed. When cooled down, the water evolved along an isochore and the pressure decreased. Below a certain temperature depending on initial conditions, the water was under stress. Berthelot reached - 50 bar. In 1991, Zheng et al.[2] used the same method and reached - 1400 bar with small water inclusions in quartz crystals.

Finally, since an acoustic wave is an oscillation in density and pressure, it can induce negative pressures if its amplitude is larger than the static pressure in the medium where it propagates. A liquid can be taken far away from its stability region on the path of a large amplitude acoustic wave. This is the method we use for the study of homogeneous cavitation or crystallization in pure liquids.

1. Cavitation in helium 4, helium 3 and water.

1.1. Helium 3

Helium being the coldest liquid, all impurities can be frozen out. If a large amplitude acoustic wave is focused away from any walls, homogeneous cavitation can be studied. Fig. 1 shows a comparison with theory of experimental measurements of the cavitation threshold pressure in ^{4}He. All the measurements[5, 6, 7, 8] were done with acoustic waves except the one by Sinha et al.[9] who used heat pulses. As we shall see, Fig. 1 shows the limitations of the "standard theory" of cavitation at low temperature, and the necessary consideration of a spinodal limit within "density functional theories".

The standard theory [10] assumes that, in the liquid at a negative pressure P, cavitation results from the nucleation of a spherical bubble which has a radius R and a thin wall whose energy equals the macroscopic surface tension γ. The free energy of this bubble (the "nucleus") is

$$F(R) = 4\pi R^2\gamma + \frac{4}{3}\pi R^3 P \tag{1}$$

where the first term is a surface cost and the second one, being negative, is a gain in volume energy. According to Eq.1, $F(R)$ reaches a maximum value E for a "critical radius" $R_c = \frac{2\gamma}{|P|}$, and this maximum value is the energy barrier against nucleation, given by

$$E = \frac{16\pi\gamma^3}{3P^2}. \tag{2}$$

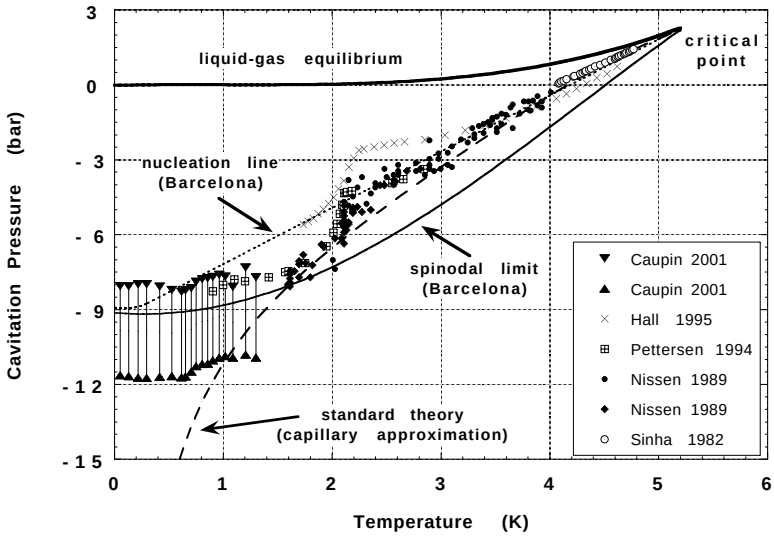

Figure 1. Summary of cavitation results in helium 4. Comparison with theory. The experiments by Caupin et al. [5] confirm that the cavitation pressure deviates from the predictions of the standard theory at low temperature. Agreement is found with the density functional theory of Guilleumas et al. [13] in Barcelona.

Within this "standard theory", one proceeds by writing a nucleation rate per unit volume and per unit time as

$$\Gamma = \Gamma_0 \exp -(E/k_B T) \tag{3}$$

In front of the Arrhenius exponential, the "prefactor" Γ_0 is the product of an attempt frequency by a density of independent sites. Indeed, one counts in how many places (per unit volume) the system can try to pass the energy barrier, and how often it can do it per unit time.

Finally, if the experiment is done in a volume V during a time τ, the nucleation probability is an integral of the rate and writes

$$\Sigma = 1 - \exp\left[-\Gamma_0 V \tau \exp\left(-E/k_B T\right)\right], \tag{4}$$

It varies exponentially with $V\tau$, and as a double exponential of the departure from equilibrium. In a short range of pressure or temperature, it increases from completely negligible to almost equal to one. The "nucleation threshold" P_c corresponds to the probability Σ being one half. From Eqs. 2 to 4, the nucleation line $P_c(T)$ is:

$$P_c(T) = \left(\frac{16\pi\gamma^3}{3T\ln(\Gamma_0 V\tau/\ln 2)}\right)^{1/2} \tag{5}$$

Eq. 5 shows that homogeneous nucleation occurs at a pressure (or a temperature) which depends weakly on the prefactor Γ_0, the volume V and the time τ of the experiment.

As shown by Fig. 1, the standard theory agrees with experiments at high enough temperature. This is because the critical radius R_c is larger than 10 Å, the typical thickness of the liquid-gas interface. However, Eq. 5 predicts that the cavitation threshold P_c should diverge as T tends to zero. If true, this would imply that R_c would tend to zero, which is unphysical. In fact, the experimental measurements show that P_c tends to a large but finite negative pressure, of order -10 bar. This is what was predicted by several theories which used the "density functional" method in order to account for the existence of a "spinodal limit".

Just like a solid, a liquid cannot be stretched up to infinite stress without breaking. This is what the existence of a "spinodal limit" means. The existence of such an instability is already present in the van der Waals equation of fluids. In the case of liquid helium near $T = 0$, H.J. Maris showed [11] that the equation of state has the simple form

$$P - P_{sp} = \frac{b^2}{27}(\rho - \rho_{sp})^3 \tag{6}$$

As a consequence, the cube of the sound velcity $c = \sqrt{dP/d\rho}$ varies linearly with P. At the spinodal limit, the compressibility is infinite and the sound velocity equals zero. Our latest fit with experimental measurements gives $b = 1.4030\ 10^6\ \mathrm{g}^{-1}\mathrm{cm}^4\mathrm{s}^{-1}$, a spinodal pressure $P_{sp}(0)$ = -9.6435 bar and a spinodal density $\rho_{sp}(0) = 0.094175$ $\mathrm{g.cm}^{-3}$. As temperature increases, the spinodal pressure increases up to the critical point. Several calculations have have been performed with rather different methods and good general agreement with each other [12, 13, 14, 15, 11, 16, 17, 18, 19].

In order to treat nucleation at low temperature, not only the spinodal limit needs to be considered, it is also necessary to optimize the density field which corresponds to a critical nucleus with minimal energy. This is a saddle point in configuration space. The energy of each configuration can be calculated by using a "density functional theory". The simplest form is the one used by H.J. Maris [16], where

$$F = \int [f(\rho) + \lambda(\nabla\rho)^2] d^3r \tag{7}$$

In this expression, $f(\rho)$ is the Helmholtz free energy per unit volume for a system with homogeneous density ρ. It is closely related to the equatin of state. Thanks to the coefficient λ, the energy of the interface γ can be calculated by looking for the particular density profile which minimizes it. It is adjusted from a comparison with experimental measurements of γ.

The Barcelona group [13] used a more elaborate form which includes temperature dependent terms. They obtained the "nucleation line" on Fig. 1 with Eq. 4 after calculating the density field optimizing the activation energy E at each pressure and temperature. With this more elaborate theory, the agreement with experiments is satisfactory, although the temperature dependence is not well reproduced at very low T, and the theory does not reproduce the apparent cusp which appears in the data near 2K.

The cusp occurs near the superfluid transition temperature T_λ. It has been shown recently [12] that the extension of the lambda line is nearly vertical in the $P - T$ plane at negative pressure. Bubbles might nucleate on microscopic vortices which proliferate near T_λ, but there has been no attempt to calculate such an effect yet. As for the behavior at very low T, its understanding asks for the consideration of quantum effects. As thermal fluctuations become very small, it becomes more probable that the liquid tunnels through the energy barrier into the gas state than pass over

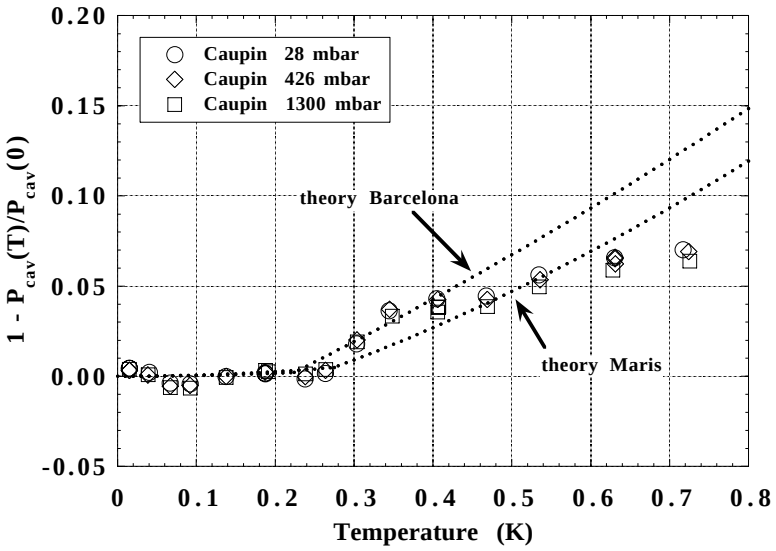

Figure 2. Comparison of the temperature dependence of cavitation in helium 4 with quantum cavitation theories. The experimental temperature has been corrected for the adiabatic cooling in the acoustic wave (see text).

it. This tunneling occurs in configuration space and concerns a region of the liquid with nanometric size. The calculation of this remarkable quantum effect has been performed by Maris [17] and the Barcelona group [13]. They used different methods but arrived to similar results. They had to calculate the action corresponding to the tunneling from a homogeneous configuration at reduced density to an inhomogeneous configuration where a "bubble" has appeared. In fact, the "bubble" is a local density field which had to be optimized in order to minimize the corresponding action. As shown on Fig. 2, they both predict a quantum plateau where the cavitation pressure is temperature independent. This plateau ends at a crossover temperature $T^* \approx$ 240 mK, above which nucleation is classical, i.e. thermally activated. Agreement with experiments was found in ^{4}He after a correction was applied to the experimentally measured temperature. In the acoustic cavitation experiments by Caupin et al. [5], the thermometer measures the static temperature in the cell. However, since the sound wave is adiabatic and its amplitude is large, a significant adiabatic cooling occurs inside the negative swings of the wave so that the local, instantaneous temperature in the wave was reduced by a factor as large as about 3. The data points on Fig. 1 are not yet corrected for this effect. The correction was applied for Fig. 2 which shows reasonable agreement with the theories of quantum cavitation.

1.2. Helium 3 and water

Helium has two stable isotopes. The one we considered above was ^{4}He. Being lighter, 3He has larger quantum fluctuations, so that the molar volume of the liquid is larger and its cohesion smaller. This means that the spinodal pressure should be less negative, and that is in fact what has been predicted [11, 13]: -3.1 bar instead of -9.6 bar for

^{4}He near $T = 0$. Our experiments have confirmed this prediction [5]. Moreover, a careful study of the temperature dependence of the cavitation pressure [20] led us to the conclusion that the spinodal line is non-monotonic as a function of temperature in ^{3}He. The origin of this effect is an anomaly in the thermal expansion of liquid ^{3}He, which connects the physics of this quantum liquid to that of water.

For very different reasons, cold liquid ^{3}He and cold liquid water show a similar anomaly: when heated up they contract instead of expanding. In the first case this is a quantum property which can be understood in the frame of Landau's "Fermi liquid theory" [20]. In the case of water, breaking H-bonds allows a denser packing of water molecules because H-bonds impose local tetrahedral arrangements which take space. Debenedetti showed [21] that the thermal expansion coefficient $\alpha = (1/V)(\partial V/\partial T)$ and the slope of the spinodal line dP_{sp}/dT have the same sign. This led R. Speedy [22] to his "stability conjecture" for water. He predicted that the spinodal line should have a minimum at -35 °C and -1400 bar, where it meets the line of density maxima which separates a region with negative α from the one with positive α at higher T. This line passes through the well established point at 4 °C and +1 bar, but its exact shape at negative pressure is still a matter of controversy [23].

In ^{3}He, we obtained some experimental evidence of the existence of a very shallow minimum in the spinodal line. If one could generate acoustic waves with an amplitude as large as 1400 bar in liquid water, it should be possible to test Speedy's prediction. This experiment is in progress in our laboratory. Homogeneous cavitation in liquid freon and liquid ethanol has already been observed around -200 bar [24].

2. Crystallization

The same acoustic technique can be used to study the nucleation of a solid phase from an overpressurized liquid phase. One has to use the positive swings of the wave instead of the negative ones. Such a study is also in progress in our laboratory. In a preliminary experiment [25], a sound wave was focused onto a clean glass plate in order to measure directly the amplitude of the wave from the reflectivity of light at the glass/helium interface. As shown by Fig. 3, it was necessary to reach a pressure 4.3 bar above the liquid-solid equilibrium pressure $P_m = 25.3$ bar to nucleate solid helium from liquid helium at low temeprature.

This overpressure is much larger than what had been observed previously - a few mbar only [26]- and this was attributed to the glass plate being locally clean compared to ordinary cells which are likely to contain dust particles which nucleate the solid phase much more easily. However, 4.3 bar is much less than what one would expect for homogeneous nucleation of solid helium at low temperature. If one uses the standard theory, i.e. equations similar to the ones in the first Section, one finds that the nucleation threshold is around 60 bar at low T. It is possible to excite acoustic waves with the necessary amplitude and this study is in progress in our laboratory. It calls for a few remarks.

An accurate prediction of this nucleation threshold is difficult because the free energy depends on density and on the order parameter of the crystal, so that the usual density functional method has to be significantly improved. Minoguchi has undertaken such an improved theory [27]. Furthermore, the possible existence of a spinodal line for the liquid-solid transition is an open question. Is there a limiting pressure at which the liquid phase is totally unstable against the spontaneous appearance of a crystalline phase, that is a long range periodic order? The particular case of liquid helium offers

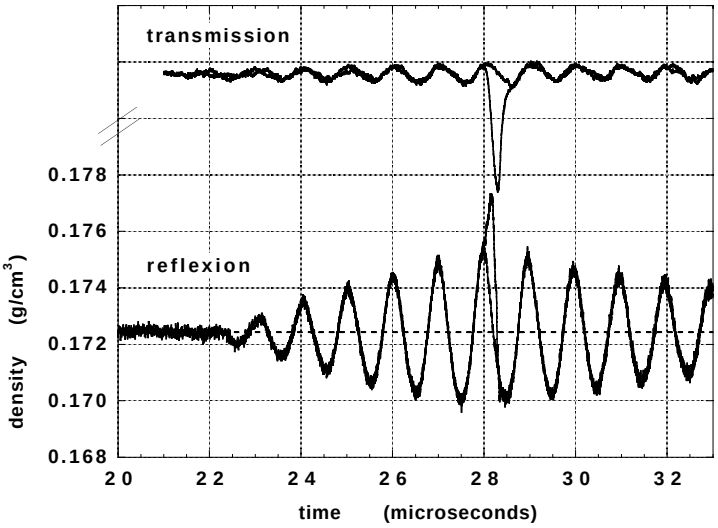

Figure 3. Some nucleation signals obtained by X. Chavanne et al. [25] in their study of acoustic crystallization. Two pairs of recordings are superimposed on top (transmission) as on the bottom (reflexion) of this figure. Chavanne et al. used sound bursts with a width of 6 cycles. Nucleation of solid helium was observed when the sound amplitude exceeded a threshold density of order 0.003 g/cm^3 corresponding to a pressure 4.3 bar above the liquid-solid equilibrium line. The two signals in transmission were recorded with the same excitation level corresponding to this nucleation threshold; the probability of nucleation was 0.45 in this case.

a possible answer to this question. Since the historical work of L. Landau, it is well known that the elementary excitations in the liquid are phonons and rotons [28]. Rotons have a finite wave vector and a minimum energy Δ which decreases with pressure. There must be a critical pressure P_r at which Δ vanishes, i.e. rotons become soft. If one could reach P_r, a density modulation would spontaneously appear in the liquid, with a wavelength of order the atomic spacing. This was proposed by Schneider and Enz [29] in 1971 and it was recently predicted that P_r is about 200 bar [30]. In analogy with instabilites of charged liquid surfaces [31], we believe that the softening of rotons can trigger the liquid-solid transition. Here, liquid helium shows an additional advantage. Its physics is so accurately known that it offers unique opportunities to investigate the possible existence of a liquid-solid spinodal limit. Another advantage is of course that the properties of the liquid-solid interface are very well known as well [32], in particular the liquid-solid interfacial tension. This is an exceptional situation since, in usual systems, it is very difficult to measure the surface tension of a solid. In fact, the standard theory of nucleation has often been used to determine an approximate value of this quantity, for example in the case of ice [1] or hydrogen crystals [33].

With this short review, we have tried to summarize the interest of helium as

model system to study nucleation in metastable liquids, a research field which has considerably progressed in the recent years. We are grateful to H.J. Maris for a long and regular collaboration on this subject since more than ten years.

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