The limit of metastability of water under tension: theories and experiments

The limit of metastability of water under tension: theories and experiments

Eric Herbert and Frédéric Caupin[1]

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

E-mail: frederic.caupin@ens.fr

Abstract
Two scenarios are proposed for explaining the thermodynamic anomalies of supercooled water, but they cannot be directly tested in this region because of the onset of homogeneous crystallization. They also give two distinct temperature dependences of the limit of metastability of water stretched beyond its boiling curve: either monotonic, as in simple liquids, or exhibiting a minimum. Therefore cavitation experiments could allow one to distinguish between the competing pictures. We review previous experiments and describe our preliminary results.

When a liquid is depressed below its saturated vapour pressure P_{sat}, it is expected to transform into its vapour, which is more stable. However, if care is taken to use a very pure liquid in a very clean vessel, this transformation (also called cavitation) may occur only far beyond the line of thermodynamical equilibrium; in such systems, the pressure may even be negative, which means that the liquid is subjected to a mechanical tension. We first recall the theoretical framework for addressing this issue, before pointing out its relevance in the debate about the phase diagram of water. We then review cavitation experiments, including our ongoing work. We finally discuss the possible origin of the large discrepancy observed between two sets of experiments.

1. Theoretical background

1.1. Nucleation in the capillary approximation

In the capillary approximation (CA) [1], the nucleating bubble is treated as a sphere filled with vapour, separated from the metastable liquid by abrupt walls. At a pressure P, its energy results from a competition between the surface tension σ and the volume energy, and leads

---

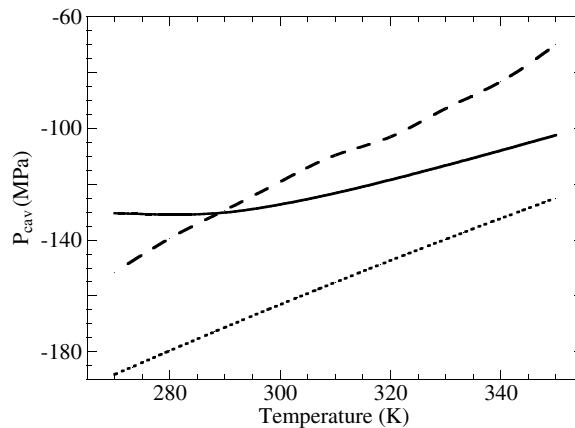[1] Author to whom any correspondence should be addressed.

Figure 1. Cavitation pressure versus temperature. The dotted line shows the prediction from the CA. The solid line was calculated with a DFT [10] using Speedy's SL, and the dashed line using a SL from Stanley's group [7].

to an energy barrier $E_B = (16\pi\sigma^3)/[3\,(P_{sat} - P)^2]$ at a critical radius $R_c = 2\sigma/(P_{sat} - P)$. The nucleation rate of the vapour phase follows an Arrhenius law, $\Gamma = \Gamma_0 \exp[-E_B/(k_B T)]$, where Γ_0 is a kinetic prefactor. Cavitation becomes likely when the thermal fluctuations have an energy comparable to E_B. In the capillary model, the cavitation probability in a volume V and during a time τ is $\Sigma = 1 - \exp(-\Gamma V \tau)$, and reaches $\frac{1}{2}$ at the cavitation pressure $P_{cav} = \{(16\pi\sigma^3)/[3\,k_B T \ln(\Gamma_0 V \tau / \ln 2)]\}^{\frac{1}{2}}$.

The result obtained for water is shown as a dotted line in figure 1.

1.2. Existence of a spinodal limit

The CA misses an important feature of the liquid–gas transition. It predicts that E_B should decrease with decreasing pressure but should never reach zero. However, it does at the spinodal limit (SL) $P_s(T)$ where the compressibility of the liquid diverges so that it becomes unstable against long wavelength fluctuations [2]. The limitation of the CA comes from its treatment of the bubble boundary as a sharp wall: for large negative pressures, when R_c becomes of the order of the liquid–interface thickness, this approximation fails, and may lead to unphysical P_{cav} beyond P_s. In other words, there is a lower energy path for nucleation, connecting the liquid to the gas phase by expansion of a smoothly varying density profile. To take this into account, one may use density functional theory (DFT), as proposed by Cahn and Hilliard [3]. Such a theory is able to relate the cavitation line (where E_B is of the order of $k_B T$) to the SL (where E_B vanishes).

1.3. The case of water

Every liquid possesses a SL, but for water it may have a peculiar temperature behaviour. Speedy [4] has shown that $P_s(T)$ could present a minimum, whereas it is positively sloped for common liquids. This feature is made possible by the existence of a line of density maxima (LDM) in water. For example, at 1 bar, if water is cooled starting from a temperature below $4\,°C$, it expands instead of contracting as other liquids do. This LDM still exists in the stretched liquid; it has even been located at moderate negative pressures [5]. If the LDM reaches the SL, thermodynamics implies that $P_s(T)$ should change slope [4].

How can we estimate $P_s(T)$? One may extrapolate the compressibility measured in the stable region to find where it diverges. Doing this, Speedy found a minimum of -212 MPa at $30\,°C$ [4]. On the other hand, Stanley and his group, using molecular dynamics simulations (MDS) based on several microscopic interparticle potentials, found that the LDM avoids $P_s(T)$ which keeps a positive slope [6, 7].

These two scenarios were in fact proposed in a broader picture for water. The concern was mainly to explain the numerous anomalies observed in supercooled water: many thermodynamical properties exhibit a large increase in the supercooled region (SR). Speedy's idea was that at low temperature, after reaching the minimum, the liquid–gas SL was retracing to positive pressure in the SR. This would give an explanation for the anomalies, because many quantities are singular on a SL. However, it has now been understood [8] that the liquid–gas SL could not retrace to positive pressure in the SR; otherwise this would imply a second, metastable, critical point for the liquid–gas transition. Still, the question is open about the fate of the liquid–gas SL at low temperature, because it could retrace and then end at negative pressure, by reaching a liquid–solid SL (see references 187 to 189 of [8]) or a glass transition line [9].

On the other hand, the MDS from Stanley and his group suggest another explanation for water anomalies in the SR. They show a first-order transition line in the SR between two metastable liquids (low and high density liquids); it ends in the SR with a new (liquid–liquid) critical point. The anomalies of supercooled water would thus reflect the vicinity of this metastable critical point.

The problem is that no experiment can be performed at low enough temperature in the SR to verify this, because spontaneous crystallization occurs. The existence of two liquids is only indirectly supported by water polyamorphism. This is why we propose, as an additional test of the scenarios, to check the prediction of the cavitation pressure and to compare it with experiments. Indeed, it was recently shown, with a density functional method, that the qualitative behaviour of $P_s(T)$ (with or without a minimum) reflected itself in $P_{cav}(T)$ [10]. Both estimates of $P_{cav}(T)$ are shown on figure 1. We now turn to the experimental attempts to measure $P_{cav}(T)$.

2. Experiments

2.1. A brief review

To stress water to negative pressure, several methods have been employed. The first to be used was the Berthelot tube technique: a vessel is filled with liquid water at high temperature and positive pressure, then sealed and cooled down at constant volume. The liquid sample follows an isochore and is brought to negative pressure. Attempts using macroscopic vessels [5, 11–13] give cavitation pressures in the range -4.6 to -20 MPa at room temperature. P_{cav} is calculated from an extrapolation of the equation of state (EOS) measured in the stable region and the known density and cavitation temperature of the sample, or measured with a pressure gauge.

Another method was designed by Briggs [14]: by spinning a glass capillary filled with water, he obtained $P_{cav}(T)$ with a minimum value of -27.7 MPa at $10\,°C$; the tension falls to a much smaller value at lower temperature (down to -2 MPa at $0\,°C$).

Shock tube and bullet piston experiments generate negative pressure by reflection of a compression wave travelling in water at an appropriate boundary; their analysis has been reconsidered several times and the presently accepted results are around -9.6 MPa [15]. These approaches may fail to obtain homogeneous nucleation because of the presence of walls or the contact of the sample with air; on the other hand, acoustic methods can produce a large

pressure swing focused in a closed container away from the walls. This is the method we use and we will describe its details in the next subsection. For the moment, let us just state here that the previous acoustic experiments used a wide variety of frequencies and pulse shapes; the most negative cavitation pressures were around -20 MPa at room temperature [16, 17]. This pressure was measured with a hydrophone, or estimated by the static pressure method (see section 2.2).

Zheng *et al* returned to the static Berthelot method, but improved on it by using synthetic water inclusions in quartz [18]. A quartz crystal with cracks is autoclaved in the presence of liquid water. Water fills the cracks which then heal at high temperature, thus providing low density water in a small Berthelot tube (around 20 μm^3). Zheng *et al* reported a maximum tension of -140 MPa at 43 °C. They were able to cool other inclusions further without observing cavitation. They concluded that the isochore was retracing to less negative pressure, and interpreted this as evidence that the LDM extends down to the SL, which supports Speedy's model. Other inclusion experiments (on water or solutions) support values of P_{cav} comparable to the one from Zheng *et al*; let us call this set of experiments group A.

To have a more direct check of Speedy's conjecture, we chose to use an acoustic method, because it is able to obtain P_{cav} at low temperature, in contrast with the inclusion technique [18].

2.2. Acoustic cavitation

To study water, we have adapted a set-up previously used for liquid helium [19]. A hemispherical piezoelectric transducer immersed in the liquid focuses a few cycles of a 1.3 MHz sound wave, generating a large pressure swing in a small region (100 μm^3) during a short time (100 ns). The ultrapure and degassed water sample is contained in a thermostated stainless steel cell where the static pressure P_{stat} can be varied. Among several methods of detection of the cavitation events [20], we have chosen the echo method as the most flexible. When a bubble appears at the focus, it reflects part of the incoming sound wave back to the hemisphere, which converts it back into voltage; this gives a large change in the transducer voltage, at a time corresponding to twice the time of flight over the sphere radius. To measure the cavitation probability Σ, we repeat many bursts (from 400 to 10 000) under the same conditions (T, P_{stat}, excitation voltage V); when V is increased, Σ changes smoothly from 0 to 1 in a narrow range, and we define the cavitation voltage V_{cav} as the value of V at which $\Sigma = \frac{1}{2}$.

We have estimated the corresponding pressure by the static pressure method (already employed for water [17] and helium [19]). When P_{stat} is increased, V_{cav} increases accordingly, so the pressure swing still reaches a minimum pressure equal to P_{cav}. The relation we measured is linear and we assume that it extrapolates to P_{cav} at zero voltage. Figure 2 shows the temperature dependence of P_{cav}.

3. Discussion

In our preliminary results, we obtain cavitation pressures far from the theoretical value [10], and from the measurement by Zheng *et al* [18]. However, they are consistent with many of the other values reported in the literature [5, 14, 16, 17] (let us call this set of experiments group B), and there seems to be a large gap between groups A and B. We see three possible reasons for this:

- Our pressure calibration is wrong. This could be due to non-linearities in the focusing of the sound wave. Their effect (as seen in simulations on liquid helium [21]) would be the
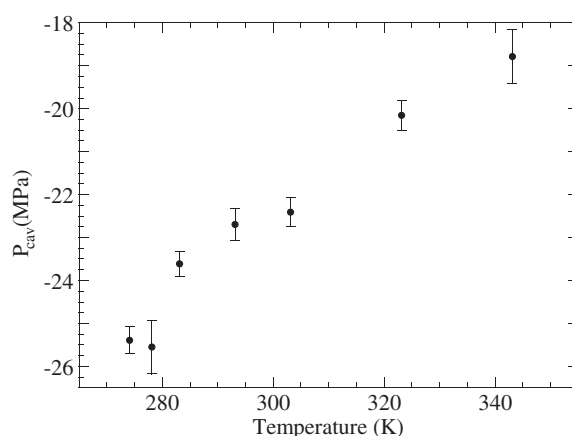
Figure 2. Cavitation pressure versus temperature, as obtained from the static pressure method in our experiment.

static pressure method giving an overestimate of the actual P_{cav}, which would go in the right direction. However, non-linearities are smaller in the hemispherical geometry than in the spherical one [21]; furthermore, a recent calibration we made with an hydrophone and the calibrations based on various methods used in group B seem to confirm that $P_{cav} \simeq -25$ MPa.

- We observe heterogeneous cavitation on impurities. However, the accurate statistical study of our results seems to support homogeneous nucleation. Furthermore, care was taken to use pure and degassed water in group B; we should then find impurities with a cavitation threshold common to all experiments of group B and absent from group A, even if the presence of walls and the large experimental time in this case were to favour heterogeneous nucleation. Such an impurity could be an organic cluster, destroyed by the autoclaving technique used for group A (see p 830 of [18]).

- The estimate of P_{cav} for group A is wrong. Group A measures a cavitation temperature and converts it into pressure thanks to an extrapolated EOS, assuming that the volume of the inclusions remains constant. Alvarenga *et al* showed this assumption to be approximate in some cases [22], but they still estimated that pressures of -100 MPa were reached in their inclusions. One could also question the extrapolation used for the EOS, but it would have to be really wrong to make group A and group B consistent, and this is not expected to be the case from MDS.

To investigate this further, we plan a more detailed pressure study, the use of autoclaved water in our experiments and a direct measurement of the EOS at negative pressure using optical methods.

References

[1] Fisher J C 1948 *J. Appl. Phys.* **19** 1062
[2] Debenedetti P G 1996 *Metastable Liquids* (Princeton, NJ: Princeton University Press)
[3] Cahn J W and Hilliard J E 1959 *J. Chem. Phys.* **31** 688
[4] Speedy R J 1982 *J. Phys. Chem.* **86** 3002
[5] Henderson S J and Speedy R J 1987 *J. Phys. Chem.* **91** 3062
[6] Poole P H, Sciortino F, Essmann U and Stanley H E 1992 *Nature* **360** 324

[7] Yamada M, Mossa S, Stanley H E and Sciortino F 2002 *Phys. Rev. Lett.* **88** 195701
[8] Debenedetti P G 2003 *J. Phys.: Condens. Matter* **15** R1669
      See, however, Speedy R J 2004 *J. Phys.: Condens. Matter* **16** 6811
      Debendetti P G 2004 *J. Phys.: Condens. Matter* **16** 6815
[9] Speedy R J 2004 *J. Chem. Phys.* **120** 10182
[10] Caupin F 2005 *Phys. Rev.* E **71** 051605
[11] Berthelot M 1850 *Ann. Chim. Phys.* **30** 232
[12] Jones W M, Overton G D N and Trevena D H 1981 *J. Phys. D: Appl. Phys.* **14** 1283
[13] Hiro K, Ohde Y and Tanzawa Y 2003 *J. Phys. D: Appl. Phys.* **36** 592
[14] Briggs L J 1950 *J. Appl. Phys.* **21** 721
[15] Williams P R and Williams R L 2000 *Proc. R. Soc.* A **456** 1321
[16] Galloway W J 1954 *J. Acoust. Soc. Am.* **26** 849
[17] Greenspan M and Tschiegg C E 1967 *J. Res. Natl Bur. Stand.* C **71** 299
[18] Zheng Q, Durben D J, Wolf G H and Angell C A 1991 *Science* **254** 829
[19] Caupin F and Balibar S 2001 *Phys. Rev.* B **64** 064507
[20] Caupin F and Fourmond V 2002 *Liquids Under Negative Pressure* (*NATO Science Series: II: Mathematics, Physics and Chemistry* vol 84) ed A R Imre, H J Maris and P R Williams (Dordrecht: Kluwer–Academic)
[21] Appert C, Tenaud C, Chavanne X, Balibar S, Caupin F and d'Humières D 2003 *Eur. Phys.* B **35** 531
[22] Alvarenga A D, Grimsditch M and Bodnar R J 1993 *J. Chem. Phys.* **98** 8392