Escaping the no man’s land: recent experiments on metastable liquid water

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Abstract

The properties of supercooled water have been the subject of intense studies for decades. One of the main goals was to follow the evolution of water anomalies, already present in the stable liquid, as far as possible in the metastable phase. All anomalies were found to become more pronounced, but their origin has hitherto remained hidden because of crystallization into ice. We review the recent experimental developments in the field, with a focus on the techniques used to reach a larger metastability, or to extend the investigations to the negative pressure region of the phase diagram, where the liquid is also metastable with respect to its vapor.

Keywords: water anomalies, supercooled water, negative pressure, Widom line

1. Introduction

When cooled from room temperature, water reaches a well known density maximum near 4°C at ambient pressure. It corresponds to a change in sign of the isobaric expansion coefficient \( \alpha_P \). It is experimentally possible to cool the liquid below the equilibrium melting temperature, and to measure the properties in this metastable state. Density is found to decrease faster and faster upon cooling [1], which corresponds to \( \alpha_P \) becoming more and more negative. No sign of slowing down in the increase in magnitude of \( \alpha_P \) is found down to the lowest

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Figure 1: (Color online) Isobaric heat capacity $C_P$ of water as a function of temperature. The experimental data are from Refs. [3] (blue squares) and [4] (red circles); see Ref. [5] for a review of these and other data. Despite a small discrepancy, they both show an appreciable anomalous increase on cooling. The black solid curve is a power-law fit to Ref. [3] data with a diverging temperature of 228 K. The green dashed curve is a schematic drawing, to illustrate the case in which $C_P$ passes through a maximum at a lower temperature than any that could be studied to date.

In a famous plot (Fig. 4 of Ref [2]), Speedy and Angell noticed that many properties of stable and supercooled water (such as $\alpha_P$, or the isothermal compressibility $\kappa_T$, the heat capacity at constant pressure $C_P$, etc.) could be fitted by power laws which extrapolated to a common temperature of divergence of 228 K at atmospheric pressure, slightly below the lower temperature limit of experiments. The following question therefore arises: if measurements could be performed at lower temperatures, would there be an actual divergence, or would an extremum be reached (Fig. 1)?

This outstanding question has been addressed by many authors, but has remained elusive because of crystallization. In general, only a small degree of
supercooling can be achieved in water, because of heterogeneous nucleation of ice, favored by certain impurities or surfaces. If precautions are taken to avoid these, ice will still nucleate spontaneously from thermal fluctuations in the liquid. This occurs at the homogeneous nucleation temperature \( T_h \), which thus gives a lower bound to the temperature at which measurements can be performed on liquid water cooled from ambient temperature. The exact value of \( T_h \) depends on the experimental volume and cooling rate, and therefore varies between experiments. Nevertheless, a number of studies placed \( T_h \) around 235 K at ambient pressure \[6\]. One might try approaching the problem from the low-temperature end. Indeed, there are ways to prepare water in an amorphous solid state \[7\]. Warming this glassy water might provide a liquid phase at lower temperatures than what can be obtained by directly cooling the room temperature liquid. Unfortunately this approach is also hindered by re-crystallization of the amorphous ice, around 150 K \[7\] (or up to 190 K for films under 150 nm thick submitted to ultrafast heating rates \[8\]) at ambient pressure. The region between the crystallization of amorphous ice and the limit of supercooling (from 150 to 235 K at ambient pressure) is called the “no man’s land”, a name coined by Mishima and Stanley \[9\].

The purpose of this paper is to review the recent experiments which have tried to “escape the no man’s land”, to solve the enduring mystery about water anomalies. Section 2 gives a brief overview of the different theoretical scenarios proposed to explain the increasing anomalies of water when it is supercooled. Section 3 presents two water proxies used to perform measurements below \( T_h \) of pure, bulk water. They provide some evidence in favor of one scenario, which postulates that water can exist in two distinct liquid states (liquid polymorphism). The rest of the discussion comes back to pure bulk water and describes the most recent experimental advances. Section 4 introduces new methods that have allowed to reach unprecedented supercooling (thus in effect lowering \( T_h \)), and gives an updated map of the no man’s land. Finally, Section 5 surveys the progress in a rather untouched region of the phase diagram, at negative pressure, where the key to water anomalies might become accessible.
We should mention that we will not discuss the very interesting possibility to study the ultraviscous liquid(s) that could be obtained by heating the amorphous ices just before crystallization occurs [10]. We also refer the reader to introductions, reviews or books where more details on several topics can be found: metastable liquids and nucleation in general, with large parts about water [11], supercooled and glassy water [12, 13], thermodynamics of supercooled water [5], crystallization in water [14], vitrification of water [15], amorphous ices [7], liquid polymorphism [16], water at negative pressure [17, 18], metastable water with emphasis on negative pressure [19], cavitation in water [20].

2. Theoretical background and controversy

The focus of this review is experimental, but we need to introduce the competing theoretical explanations that have been proposed. We will give a minimal overview; see Refs. [13, 16, 21] for more detailed reviews.

Because of the apparent divergence of many properties extrapolated to 228 K, Speedy looked for a source of instability. Any liquid can be brought below its saturated vapor pressure, but will eventually become unstable with respect to the vapor at the spinodal pressure. Speedy noticed that the equation of state (EoS) of water at positive pressure extrapolated to a spinodal pressure with a non-monotonic temperature dependence [22]. Interestingly, he found a thermodynamic explanation: if the line of density maxima (LDM) intersects the spinodal curve in the pressure-temperature plane (see Fig. 2, top), the latter must reach a minimum pressure. In his stability limit conjecture [22], Speedy further proposed that an instability line of the liquid would also exist at positive pressure. It was later argued by Debenedetti [12] that a liquid-vapor spinodal could not retrace all the way to positive pressure, because it would have to cross the metastable liquid-vapor equilibrium, which can happen only at a liquid-vapor critical point: such a singularity seems unlikely. However, two interesting questions remain: (i) even if the liquid-vapor spinodal does not retrace to positive pressure, does it reach a minimum pressure or not?; (ii) would there exist at
positive pressure a line where the supercooled liquid becomes unstable (towards another phase than the vapor)?

In contrast, molecular dynamics simulations of a water-like potential [23] found a monotonic temperature dependence of the liquid-vapor spinodal pressure. Thermodynamic consistency was preserved, as the LDM reached a maximum temperature at negative pressure, and avoided the spinodal (Fig. 2, bottom). The simulations found another source for water anomalies. In the second critical point scenario [23], a first-order transition separates two liquids with different structures in the supercooled region. This liquid-liquid transition (LLT) terminates at a liquid-liquid critical point (LLCP) (237 ± 4 K and 167 ± 24 MPa for the ST2 potential [24]), responsible for the large increase in many water properties. However, they diverge only at the critical point. Below the critical pressure, they will go through an extremum. Such a LLT was proposed for many other water-like potentials. However, there has been recently an intense debate about the stability of one of the two liquids with respect to crystallization, challenging [25, 26] or reasserting [27, 28, 30, 31, 32, 33] the existence of a LLCP. It is beyond the scope of this review to detail this debate. However, we would like to emphasize the point of view of the experimentalist. Based on a long history of attempts, the LLT, if it exists, would lie in a region accessible to computers but apparently not to experiments. Therefore, even if the LLT or LLCP were virtual, what would matter more is the existence or not of loci of extrema in the response functions of water. They would be associated with the locus of extrema in the order parameter of the LLT, called the Widom line [34, 35]. We also note that, assuming the existence of a LLCP, one can try to locate it without using molecular dynamics simulations, but rather trying to build an EoS consistent with experimental data measured on real water: the LLCP thus predicted lies at much lower pressure than in simulations (227 K, 13 MPa) [36].

We should mention that other scenarios have been proposed. The critical point-free scenario [15, 37, 38] places the LLCP beyond the liquid-vapor spinodal. In that case, upon cooling, there is no extremum in response function,
Figure 2: (Color online) Sketch of the phase diagram of water for two of the scenarios proposed to explain the anomalies of water. The blue curves show the equilibrium curves for the liquid-solid and the liquid-vapor (with critical point C) transitions. The green short-dashed curve is the line of density maxima (LDM), and the red long-dashed curve the liquid-vapor spinodal. In the stability-limit conjecture (top) [22], the LDM intersects the spinodal which reaches a minimum pressure; a line of instability exists in the supercooled liquid on which several response functions of water diverge. In the second critical point scenario (bottom) [23], the LDM avoids the spinodal. Water anomalies are due to a second critical point $C'$ terminating a first-order liquid-liquid transition (purple curve).
but instead a LLT, or if the high density liquid remains metastable with respect to the low density liquid, a divergence on the high density liquid spinodal. The singularity-free interpretation [39] offers a thermodynamically consistent picture, where there is no LLT, but no divergences either. The response functions go through an extremum upon cooling, as a direct consequence of the LDM. It is noteworthy to mention that a cell model involving hydrogen bond cooperativity [21] can realize each of the four above mentioned scenarios by tuning the values of its parameters.

To conclude this section, we give a (non-exhaustive) list of experimental signatures that would help to decide between the available scenarios:

- finding a genuine LLT;
- finding an extremum in one of the responses functions that has a seemingly diverging behavior in the supercooled region;
- measuring the EoS of water at negative pressure to elucidate the shape of its LDM and of its liquid-vapor spinodal curve.

3. Squeeze or hide: tricks to avoid crystallization

A trick of some sort has to be played to be able to perform measurements on water molecules in a liquid phase below the homogeneous nucleation temperature $T_h$ of ice in the bulk. Two leads have been followed: (i) confining water in narrow pores, and (ii) mixing water with a substance that decreases the nucleation rate.

3.1. Confinement

For a detailed review on the effects of confinement on freezing and melting, see Ref. [40]. In a cylindrical pore of diameter $d$ filled with a liquid that perfectly wets the pore walls, the Gibbs-Thomson relation teaches us that the liquid-crystal equilibrium temperature is depressed from its bulk value $T_{eq}$ by an amount:

$$\Delta T_{eq} = \frac{4 \sigma_{LC} T_{eq}}{\rho_c L d}, \quad (1)$$
where $\sigma_{LC}$ is the energy per unit area of the liquid-crystal interface, $\rho_c$ is the mass per unit volume of crystal, and $L$ is the latent heat of melting per unit mass. This direct application of macroscopic thermodynamic laws should be modified to account for microscopic details, but the trend is correctly captured. For water-ice, $\sigma_{LC}$ is in the range $25-44 \text{ mJ m}^{-2}$ [41], so that $\Delta T_{eq} \simeq 100/d$ with $d$ in nm. Remarkably, experiments performed on well defined pores in MCM-41 silica [42] have shown that the Gibbs-Thomson relation is satisfied for nanopores: after a layer of nonfreezing water on the pore wall has been accounted for, it agrees with the observed melting temperatures for pore diameters from 3 to 4.4 nm (from 215.0 to 239.7 K). However, for 2.5 nm pores, differential scanning calorimetry does not detect any first-order transition.

Taking advantage of this effect, Chen, Mallamace and co-workers have used water confined in very narrow nanopores to obtain measurements on a liquid-like phase at very low temperatures. A recent review of all their work is available [43]. Let us simply mention here that, using a variety of techniques (neutron scattering, nuclear magnetic resonance, Fourier transform infrared spectroscopy...), several features compatible with the second critical point scenario were reported, such as: dynamic crossover [44], density minimum [45, 46] and density hysteresis [47]. These works have provoked a passionate debate about the data interpretation [48, 49, 50, 51, 52, 53]. Without taking position about the validity of the results, we would like to emphasize that their relation to bulk water properties is not straightforward. Indeed, to avoid crystallization, pores with a diameter of 1.4 – 1.5 nm have been used [44, 45, 46, 47]. This corresponds to at most 5 layers of water across. Two are in direct contact with the pore walls, and the others are likely affected by its presence. Recently, a careful optical Kerr effect spectroscopy experiment on partially hydrated Vycor glass [54] has shown that the first and second layers from the walls have dynamic properties differing from bulk water.

We would also like to mention that the exact pressure at which experiments in pores are performed is not really known. Helium is used as a pressurizing medium [47], and the applied helium pressure is reported. However, for an hy-
drophilic pore, the liquid-vapor interface has a curvature such that the pressure in the confined liquid is less than the external pressure. If one applies the macroscopic Laplace law, the pressure jump is $2\gamma_{LV}/R \simeq -140/R$ in MPa if $R$ is in nm. In extremely narrow pores the validity of the macroscopic law is questionable. The very notion of pressure as a scalar quantity should be replaced by an anisotropic quantity related to the strong interaction with the pore walls. Still, assuming that confined water might be compared with the bulk phase, one may wonder if it should rather be with a liquid at negative pressure \[55\]. This idea has been recently developed by Soper \[56\]: combining neutron scattering from and simulations of ordered cylindrical pores in silica with 2.5 nm diameter, he concluded that the density of water was not homogeneous, and the density of the core liquid less than that of the bulk, suggesting a pressure around $-100$ MPa.

3.2. Antifreeze

Another way to avoid crystallization is to add a solute to water. At very low solute concentration $c$, this is well known to depress the melting point $T_m$ by an amount proportional to $c$ ($\Delta T_m = -Kc$) but independent of the nature of the solute. This is a colligative property, known as the cryoscopic law. At typical working concentrations, the cryoscopic constant $K$ for water is somewhat different from the infinite dilution limit, but the proportionality still holds with $K = 1.853 \text{ K kg mol}^{-1}$. Interestingly, the homogeneous crystallization temperature of the solution is also depressed by an amount proportional to $c$, which may be written $\Delta T_h = \lambda \Delta T_m = -\lambda Kc$. The parameter $\lambda$ has been measured for many compounds, and the values found to be surprisingly grouped around 2. There are variations, correlated with the self-diffusion coefficient of the solute \[57\].

Murata and Tanaka have chosen glycerol as the solute \[58\]. Using an impressive set of experimental techniques, they concluded that a transition between two different liquids with equal glycerol concentration occurred, without macroscopic phase separation. The fact that the composition remains constant is key to the results, to distinguish the phenomenon from phase separation in
a binary mixture. The simultaneous appearance of cubic ice requires special attention to reach a conclusion [58]. In a subsequent study [59], 14 aqueous solutions of sugar and polyol molecules were studied: only with glycerol and 1,2,4-butanetriol a LLT was reported without concurrent demixing. Experiments at a mole fraction of glycerol less than 0.135 were not possible because of homogeneous crystallization. This means that the no man’s land also extends in the temperature-concentration plane (see Fig. 4 of Ref. [58]), preventing to reach a clear conclusion for pure water.

4. Small and fast: the quest for deeper supercooling

In this Section we discuss experiments on pure, bulk water, that attempt to push the temperature $T_h$ of ice nucleation to lower and lower values.

Nucleation occurring in a metastable liquid is a catastrophic event: once the new phase exceeds a critical size, it will grow very fast and replace a large part or the whole liquid phase. In addition, nucleation is very sensitive to impurities, which can lower the energy barrier for the phase change, leading to heterogeneous nucleation at a lower metastability. For these reasons, it is very advantageous to divide the experimental sample into many independent units.

Nucleation is also a kinetic process. The physics of the transformation determines the nucleation rate per unit volume and time, $\Gamma$, as a function of metastability (e.g. degree of supercooling below the melting point, $T - T_m$). This means that the metastability that can be reached in a given experiment depends on its typical volume $V$ and duration $\tau$: nucleation occurs when $\Gamma V \tau \simeq 1$. Therefore, an experiment performed on a small sample during a short time will reach larger $\Gamma$, and hence larger metastability and lower $T_h$.

To achieve the best conditions for nucleation studies, a technique of choice is therefore to disperse droplets in an emulsified sample. In this way, many determination of the homogeneous crystallization temperature $T_h$ in water have been obtained. For instance, Kanno et al. [60] reported $T_h$ values in the range 0—300 MPa, with a minimum of 181 K at 200 MPa; the data up to 140 MPa is shown
on Fig. 3. Using a calorimetric technique, Taborek [61] was able to measure the nucleation rate at ambient pressure. He investigated the dependence on droplet size, reaching a minimum $T_h = 239$ and $235 \text{ K}$ for $300$ and $6 \mu \text{m}$ diameter droplets, respectively, in line with the exponential temperature dependence of the nucleation rate per unit volume and time (see Fig. 2 of Ref. [61]). He also found an effect of the surfactant used to prepare the emulsion, which shows that heterogeneous nucleation might occur at the droplet surface; he also provides data for heavy water. A recent paper, that presents a microfluidic version of Taborek’s experiment [6], reviews many other nucleation rate measurements, and shows that their scatter is mainly determined by uncertainty in the sample temperature.

To cool down at an even faster rate (and thus reach a shorter experiment duration $\tau$, and a lower $T_h$), droplets suspended in vacuum or in a carrier gas have been used (see Ref. [66] for a review). They can be generated by adiabatic expansion of a gas saturated with water vapor, leading to supersaturation conditions that eventually produce a cloud of liquid droplets, which will freeze upon further cooling. Another geometry involves a supersonic nozzle. A mixture of water vapor and carrier gas flows in a diverging nozzle, leading to fast pressure and temperature drop. The technique was introduced in the field of ice nucleation studies by Huang and Bartell [67]. Recently, Manka et al. [62] combined it with pressure measurements along the nozzle, small angle X-ray scattering to characterize the aerosol distribution, and Fourier transform infrared spectroscopy to detect ice nucleation. With the supersonic nozzle, the droplets are much smaller than in emulsion studies, with diameters between $6.4$ and $11.6 \text{ nm}$. The liquid is therefore subject to a non-negligible Laplace pressure, from $54$ to $29 \text{ MPa}$, respectively. Onset of ice was detected at $202 \text{ K}$ and $215 \text{ K}$, respectively. The small droplet size also makes it possible that surface crystallization plays a non negligible role [62, 68]. The work was recently extended to heavy water [68].

To work with micrometer size droplets, the group of Nilsson uses a gas dynamic virtual nozzle [69]. A liquid water jet is produced, that breaks into
Figure 3: (Color online) Phase diagram of water. The colored areas show the different possible states of liquid water. The delimitating dashed lines were obtained by polynomial extrapolation of the positive pressure data. The pink region is the no man’s land, between the line of crystallization of amorphous ice (left black curve) [9] and the of homogeneous nucleation of ice in the supercooled liquid. The latter was formerly located by an experiment on emulsions [60], but has been pushed to the left by recent experiments: the line connecting purple triangles shows where ice starts to nucleate in the nanodroplets of Ref. [62], and the circle gives the lowest temperature estimated for the microdroplets of Refs. [63, 64]. The red and green thick curves show the path followed in the Brillouin experiment of Ref. [65] (see Section 5), with the pressure estimated from simulations with the TIP4P/2005 potential. These simulations also give the locus of maxima of the isothermal compressibility (brown diamonds), which suggests a divergence at the location of the white plus sign that might be a critical point terminating a liquid-liquid transition. (adapted from Ref. [65]).
micrometer size droplets. The droplets evaporate in vacuum at a high cooling rate. The originality is that each small drop (down to 9\(\mu\)m in diameter) can be probed with a femtosecond long pulse from an ultrabright X-ray laser at Linac Coherent Light Source, and 200 nm ice crystals detected on a single-shot basis. Supercooled water was detected down to a temperature estimated to reach 227 K. Under these extreme conditions, water is liquid only for about a microsecond. Its structure factor, measured down to 229 K, showed that the splitting of its first maximum into two peaks, already known at ambient temperature, increases continuously upon cooling. Although the temperature calibration is a delicate matter (because the evaporation model needs as input some quantities that are presently unknown at this low temperature, such as water heat capacity, see Fig. 1), this is a promising route to probe water at an unprecedented supercooling.

To sum up, Fig. 3 shows an updated map of the phase diagram of water and of its no man’s land. The recent works on evaporating droplets [62, 68, 69] have pushed T_h downward compared to the work on emulsions. Will this be enough to find the origin of water anomalies? For comparison, a prediction of molecular dynamics simulations [65] is included in Fig. 3. Simulations with the potential TIP4P/2005 [70] were chosen, because it is considered to be currently the potential that reproduces the most accurately a series of experimental properties of water [71]. Looking at Fig. 3 thus suggests that a line of isothermal compressibility might exist in the region that has just become accessible. However, as with any water potential, simulations should be taken with caution, and the features they predict might well suffer from a shift in temperature and pressure (or even not exist in real water!). Anyhow, one of the purposes of Fig. 3 is to motivate more measurements of water at extreme supercooling. Note that this will require special techniques, compatible with the very short timescales involved.

I would like to conclude this section with a terminology issue. The most recent works [62, 68, 63] claim that they enter the “no man’s land”. As the boundary of the no man’s land is a matter of experimental definition, this is not
correct. What can be said is that the experimental efforts have been successful in pushing its border to lower temperatures (see Fig. 3), thus reducing the interval spanned by the no man’s land. But the very concept is akin to Tantalus’ punishment: when one tries to enter no man’s land, its location recedes, eluding our grasp.

5. An unexplored territory: water at negative pressure

Instead of heading straight down along the slope of steepest cooling, we may take a detour through a less trodden path, at negative pressures. Water, like any liquid, can be stretched to a metastable state at densities lower than its density at equilibrium with vapor. This is a manifestation of the cohesive forces between the liquid molecules. Their mutual attraction can even counterbalance negative pressure, that is a force literally trying to tear the liquid apart. The existence of negative pressures (mechanical tension) may sound surprising, but this state occurs routinely in nature, in the sap of trees [72].

The knowledge of the properties of water at negative pressure is still in its infancy. The main reason is the difficulty to avoid nucleation of vapor bubbles (cavitation). Section 5.1 discusses the current limiting cavitation pressures that can be reached. Knowing where to stop, liquid properties may be measured before nucleation occurs (Section 5.2), and even in the liquid that is both stretched and supercooled (Section 5.3).

5.1. The cavitation limit

Because water has a strong cohesion, as demonstrated for instance by its high surface tension, one expects it may reach a large degree of metastability. Its maximum value was the topic of our previous review [20], partly updated in [18]. We can give here only a brief summary. First, care must be taken to avoid heterogeneous nucleation, which accounts for a large scatter among experimental values. For the most careful experiments, the agreement is very good in the high temperature region, at positive pressure, commonly denominated
superheated water. However, at lower temperature, where cavitation occurs in
the stretched liquid, there is a surprising splitting of the cavitation pressure $P_{\text{cav}}$
into two sets. A first set of very different methods leads to a consistent value of
$P_{\text{cav}} \simeq -30 \text{ MPa}$ at room temperature. This lies far from the theoretical predic-
tion based on classical nucleation theory (CNT). CNT involves the bulk surface
tension of water and predicts a cavitation pressure $P_{\text{cav}}^{\text{CNT}} \simeq -140 \text{ MPa}$ \[73\].
This value is actually reached by one single method, which was used by differ-
ent groups. This is the microscopic Berthelot tube method, which consists
in cooling a micrometer size water droplet trapped in a quartz crystal, so that
the liquid, which sticks to the hydrophilic walls, follows an isochore (constant
density path). The group of Angell pioneered this technique, observing cav-
itation at a maximum tension of $-140 \text{ MPa}$ at 315 K \[74\], a value confirmed
by subsequent studies \[75, 76, 77\]. The reason for the large gap between the
two sets of cavitation pressures remains unknown, but points towards an ubiqui-
tous impurity that would destabilize the metastable liquid in most experimental
techniques, or more surprisingly stabilize the inclusions of water in quartz \[78\].

Here we would like to update the experimental survey with a few recent
references that were not included in our previous reviews. Nanofabrication
techniques were used to create 120 $\mu$m long channels in silica, with a rectangular
cross section (4 $\mu$m wide and from 20 to 120 nm high) \[79\]. The channels, initially
filled with water, dry by evaporation, creating negative pressure in the liquid
because of the Laplace pressure jump across the liquid-vapor menisci. The
channels empty by cavitation, instead of recession of the menisci. The cavitation
pressure (calculated from the Laplace equation) ranges from $-1 \text{ MPa}$ for the
largest pores, to $-7 \text{ MPa}$ for the narrowest. These values are still far from the
above ones, because nucleation was triggered by an unsthility of the meniscus
that produced a bubble near the pore entrance, which then moved to the center
and expanded.

An usual way to remove pre-existing bubbles (that may be trapped on con-
tainer walls for instance) is to pressurize the sample to large positive pres-
sure, before performing the cavitation experiment \[85\]. Recently, this protocol

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Figure 4: (Color online) Cavitation pressure as a function of temperature for different experiments. Recent acoustic-based experiments are compared to our previous work (filled red circles) [80]: acoustic resonator (empty blue squares) [81], short focused burst (upward green triangle) [82] (from which we have taken the largest negative pressure reached), and reflected shock waves (downward purple triangle) [83]. The result using artificial trees (black crossed square) [84], with the pressure calculated from the controlled vapor activity, is also shown. For a comparison with older data, see Fig. 4 of Ref. [17].
was again tested for acoustic cavitation: negative pressures are generated in a standing wave created by the resonance of the water-filled container [81]. For positive applied pressures $P_{\text{stat}}$ in the range $0 - 30$ MPa, the cavitation pressure was found to exhibit a linear variation: averaging over all temperatures $P_{\text{cav}} = -3.46 - 0.92P_{\text{stat}}$ (with pressures in MPa). This gives a largest negative value $P_{\text{cav}} = -31$ MPa, which perfectly confirms our previous work on acoustic cavitation. A detailed comparison (at each measured temperature) is shown in Fig. 4. In contrast to the technique using a standing wave in a resonator, we used bursts of focused ultrasound. A first, indirect estimate of the pressure [86] led to $P_{\text{cav}}$ from $-26$ MPa at $273.15$ K to $-17$ MPa at $353.15$ K. Using a fiber-optic probe hydrophone, these values were later revised [17]: from $-34$ MPa at $274$ K to $-25$ MPa at $320$ K. We emphasize that no change in $P_{\text{cav}}$ was observed, even after pressurizing the cell to $P_{\text{stat}} = 20$ MPa. This shows the advantage of using a focused wave, which avoids the effect of bubbles trapped at the container wall, because negative pressures occur only in a small region inside the bulk liquid during a short time. This approach was followed in an ultrasound-therapy oriented study [82]. Short pulses of a 1.1 MHz wave were focused in water, tissue-mimicking materials, and real tissues. In water at room temperature, $P_{\text{cav}} = 27.4 \pm 1.3$ MPa, in good agreement with our previous work (Fig. 4).

Ando and colleagues use the reflection at a liquid-vapor interface of a laser-induced shock-wave propagating in water, to generate a pulse of mechanical tension. The pressure is calculated using Euler flow simulations. In a first study [87], the cavitation threshold was reported to be $P_{\text{cav}} = -60 \pm 5$ MPa, exceeding all previously reported dynamic measurements. However, in a subsequent study [83], using two laser beams to create the superposition of two reflected tension pulses, this value was revised to $-20.1 \pm 3.4$ MPa, slightly less negative than other acoustic methods (Fig. 4). The second study included some statistics on cavitation, to report the threshold at a cavitation probability of 0.5. The first study, which only reported an individual threshold at a cavitation probability of 1, thus seems to have overestimated the limit of metastability.
The technique of artificial trees is an interesting alternative to acoustics. The group of Stroock mimicks the mechanism by which trees pump the sap up their trunk. Water exchange through a porous membrane in the leaves allows to reach a metastable equilibrium between an undersaturated vapor in the atmosphere (relative humidity less than 100%), and a liquid at negative pressure. The process is similar to osmotic effects. In the synthetic trees [84], the membrane is a hydrogel, in which are embedded spherical cavities (in the 10 μm range) filled with water. As already noticed [84, 18], $P_{\text{cav}} \simeq -22$ MPa at 293 K, consistent with (although slightly less negative than) $P_{\text{cav}}$ in the acoustic experiments. Here $P_{\text{cav}}$ was calculated based on the relative humidity of the vapor with which the liquid was equilibrated. Interestingly, pressurization up to 54 MPa did not change $P_{\text{cav}}$ [88], demonstrating that trapped pre-existing bubbles do not play a role in the synthetic trees. This method was re-used in the group of Marmottant [89, 90]. Measuring the volume of a cavity just before and just after cavitation, they could estimate the pressure based on the liquid compressibility, although with a large uncertainty: $P_{\text{cav}} = 30 \pm 16$ MPa. The main focus of the work was the bubble dynamics: fast oscillations were observed and accounted for with a model involving the droplet confinement and elasticity. Recent developments in the group of Stroock include the measurement of the equation of state of water down to $-14$ MPa with a microelectromechanical pressure sensor [91], and the interplay between poroelastic mass transport and cavitation in the drying of ink-bottle porous media [92].

From this updated review, it is confirmed that only the microscopic Berthelot tube method (based on water filled inclusions in quartz) is able to reach the theoretical predictions for $P_{\text{cav}}$, around $-140$ MPa. Many other methods, including recent ones, cluster around $-30$ MPa (Fig. 4). The explanation of this discrepancy is still unknown. The most reasonable hypothesis remains that an ubiquitous impurity triggering cavitation at $-30$ MPa is present in all experiments but the one with inclusions[78]. More precisely, for a given quartz sample, the inclusions contain liquid at the same density but exhibit a range of $P_{\text{cav}}$, down to $P_{\text{cav}}^{\text{CNT}}$ [74, 76]. It can be speculated that only a few inclusions are free
from the impurities favoring cavitation. Note that if the cavitation pressure is extremely sensitive to trace impurities, most thermodynamic properties are not expected to be. Therefore any method to generate negative pressure may be used to prepare the liquid and measure its properties. Inclusions in quartz just provide the method that can, at present, access the largest tensions.

5.2. Properties of stretched water

Now that we know down to which negative pressure each experiment can be performed, we may attempt to measure properties of stretched water before if breaks by cavitation. Although the first attempt was published one century ago [93], there have not been many since. The first information of interest is the EoS of the metastable liquid. Indeed, extrapolations of the positive pressure EoS [22] and molecular dynamics simulations (e.g. Refs. [23] and [34] for the ST2 potential) differ qualitatively in their predictions of the liquid-vapor spinodal or the line of density maxima (see Section 2). An experimental test is therefore needed.

The first work is due to Meyer [93] who used a Berthelot-Bourdon tube to measure the relation between pressure and density down to -3.4 MPa at 24°C. In the 1980’s, Henderson and Speedy took over the challenge. Using a modified version of Meyer’s Berthelot-Bourdon gauge, they measured the line of density maxima down to −20.3 MPa where it reaches 8.3°C [94, 95], and the metastable melting curve down to −24 MPa [96]. Davitt et al. [97] used the acoustic method to stretch water, and measured simultaneously two physical quantities of the metastable liquid: the density with a fiber optic probe hydrophone [80], and the sound velocity with a time-resolved Brillouin scattering experiment [97]. They were thus able to obtain the EoS down to -26 MPa at 23.3°C. They found that the EoS is compatible with the standard extrapolation of the positive pressure data [98, 99]. Their finding was recently confirmed down to −14 MPa with a microelectromechanical pressure sensor [91]. However, the qualitative differences between theoretical predictions mentioned above become manifest only at larger negative pressure.
Because of the cavitation pressures measured up to now (see Section 5.1), the only experimental method that makes this region accessible is that using water inclusions in quartz as microscopic Berthelot tubes. Indirect information on the line of density maxima was obtained recently by a statistical analysis of cavitation in one single water inclusion [77]. As the inclusion follows an isochore, the pressure must reach a largest negative value exactly at the crossing point with the LDM. This, combined with the temperature variation of the liquid-vapor surface tension, results in a minimum in the energy barrier for cavitation as a function of temperature. This effect was already noticed by the group of Angell [74], where an inclusion “was observed in repeated runs to nucleate randomly in the range 40 to 47°C and occasionally not at all”, because the energy barrier was just around the value for a finite cavitation probability. In our recent work [77], an inclusion in which cavitation occurred around 325 K was selected, and a total of 154 cavitation experiments were performed at three different cooling rates, to obtain the statistical distribution of cavitation temperatures. This gives the energy barrier as a function of temperature, which was found to exhibit a curvature, from which a minimum was predicted to be reached at $T_{\text{min}} = 321.4 \pm 4.3 \, \text{K}$. From the extrapolation of the positive pressure EoS, $T_{\text{min}} = 317.6 \, \text{K}$ is calculated, in agreement with the experimental value. This means that the LDM cannot depart too far from its extrapolation down to the density studied, $\rho = 922.8 \, \text{kg m}^{-3}$.

The previous result is still indirect. Because of the type of samples, it seems that direct measurements can only be performed by optical methods. Brillouin scattering gives the sound velocity which can, for instance, be compared to the extrapolation of available EoSs. A first measurement was performed [75], but it was not used in a systematic way to compare with an extrapolated EoS. We decided to revisit this experiment [65]. We measured the sound velocity in two samples, along isochores at $\rho_1 = 933.2$ and $\rho_2 = 952.5 \, \text{kg m}^{-3}$. At these densities, the pressure at room temperature is in the $–100 \, \text{MPa}$ range (see Fig. 3). This time, a departure from the extrapolation of the positive pressure EoS was found, with the extrapolated sound velocity being always lower than...
the measured one. But the low temperature behaviour was more surprising, and is described in the next section.

5.3. Doubly metastable water

We are now entering an almost virgin territory: the doubly metastable region where liquid water is simultaneously metastable compared to the vapor and to the ice. Thermodynamically, its borders are the metastable continuations of the liquid-vapor and the liquid-solid equilibrium lines beyond the triple point. Note that these lines have been experimentally located in the pressure-temperature plane, down to 251 K for the former [100] and down to −24 MPa for the latter [96].

Penetration in the doubly metastable region was reported only a couple of times. First by Hayward [101], who reached a modest −0.02 MPa around 268 K with a tension manometer. He humorously compared the water molecules to a “bunch of schizophrenics”, “desperately anxious both to freeze and to boil”.

Using a modified version of Meyer’s Berthelot-Bourdon gauge, Henderson and Speedy navigated along a curve going from −19.5 MPa at 273.15 K to −8 MPa at 255.15 K [95]. The frontier was pushed further with our acoustic method: at 273.25 K we found $P_{\text{cav}} = −26$ MPa [86], which was revised to −34 MPa based on fiber optic probe hydrophone calibration [17]. As before, the only known method to reach larger tensions is to use water inclusions in quartz. It was already noticed by the group of Angell [74] that “no inclusion that survived cooling to 40°C ever nucleated bubbles during cooling to lower temperatures (although ice probably nucleated without being observable)”, but no measurement was performed. The previous Brillouin study on water inclusions [75] did investigate one of these survivors, but unfortunately measurements stopped at 0°C. The two inclusions we selected (at densities $\rho_1$ and $\rho_2$, see Section 5.2 and Fig. 3), had the ability to reach the doubly metastable region, because along these isochores, the minimum energy barrier to cavitation remains high enough. The only limitation to the measurements was the broadening of the Brillouin spectra at low temperature because of viscosity, which made them impossible
to be analyzed properly below 258 K. Still we found interesting anomalies [65]. First, as mentioned in Section 5.2, the sound velocity was found to be higher than the prediction of the extrapolation of the positive pressure EoS. The discrepancy became larger at lower temperatures. This proves that water was not approaching the instability limit of this extrapolated EoS, located at 259 K for the density $\rho_1$, where the sound velocity should have been nearly twice lower than what we measured. Next, the sound velocity along the $\rho_1$ isochore reached a clear minimum near 273 K, which corresponds to a maximum in adiabatic compressibility. Finally, at the lowest temperatures, the sound velocity along an isotherm was found to exhibit a non monotonic behaviour. This led us to propose, based on comparison with molecular dynamics simulations of TIP4P/2005 performed in the group of Valeriani, that the isochores were actually crossing a line of anomalies. This line is the locus of maxima in the isothermal compressibility along isobars (see Fig. 3), one of the proxies used in simulations to detect the Widom line that would be associated with a LLT and its LLCP. Although a line of maxima in isothermal compressibility does not require a LLCP (see the singularity free scenario, Section 2), our results rule out scenarios according to which water properties would diverge on a line of instability (see Section 2).

6. Conclusion

After decades of scrutiny from experimentalists, it may seem surprising that there is still something to measure or progress to be made on supercooled water. Yet this is the case, but scientists have to face a dilemma. They can choose to confine water or mix it with a solute to avoid crystallization. This opens new regions of temperature to measurements, but the relation to pure bulk water is not straightforward. Or they can continue to seek routes to greater supercooling. Recent publications show that they can be successful. However, the very short lifetime of this highly supercooled state makes measurements challenging, but worth working on. An alternative is to dive in the doubly metastable region, which is presumably further away from the putative LLT, but allows for longer
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