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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.

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 α_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 α_P becoming more and more negative. No sign of slowing down in the increase in magnitude of α_P is found down to the lowest measured temperature (239.74 K). In a famous plot (Fig. 4 of Ref [2]), Speedy and Angell noticed that many properties of stable and supercooled water (such as α_P, or the isothermal compressibility κ_T, and the heat capacity at constant pressure C_p) 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.

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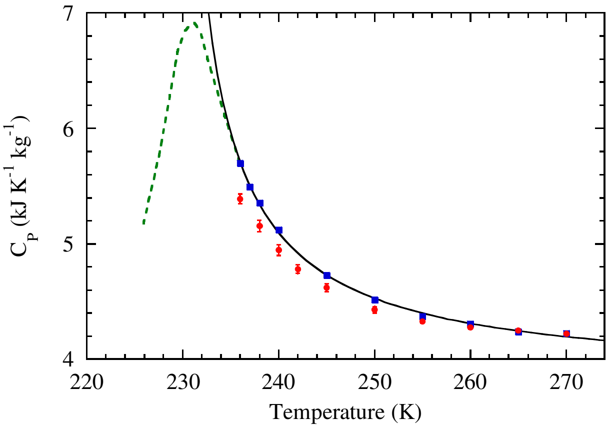

Fig. 1. Isobaric heat capacity C_p of water as a function of temperature. The experimental data are from Refs. [3] (blue squares) and [4] (red circles); see Ref. [5] for a review of these and other data. Despite a small discrepancy, they both show an appreciable anomalous increase on cooling. The black 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.

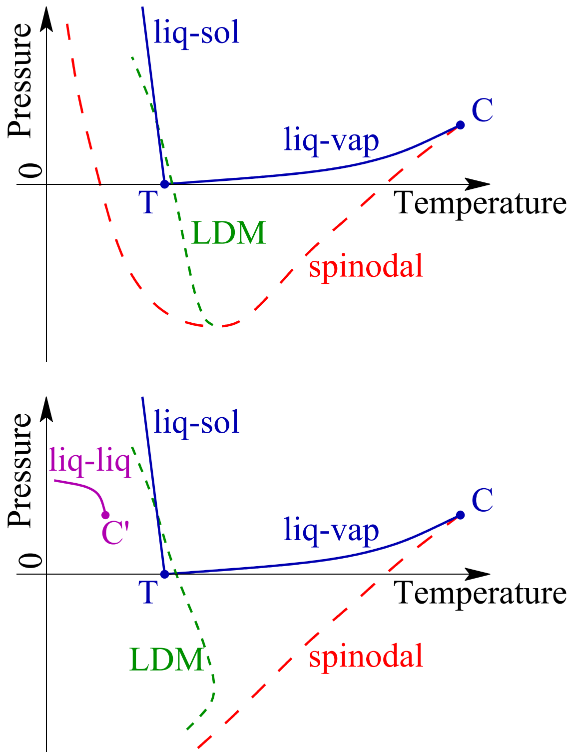

Fig. 2. Sketch of the phase diagram of water for two of the scenarios proposed to explain the anomalies of water. The blue curves show the equilibrium curves for the liquid–solid and the liquid–vapor (with triple point T and critical point C) transitions. The green short-dashed curve is the line of density 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).

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], and 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 [27–33] 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 was 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, but instead a LLT, or if the high density liquid remains metastable with respect to the low density liquid, a divergence