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Unsolved mysteries of water in its liquid and glassy phases

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Abstract. Although H₂O has been the focus of a considerable amount of research since the beginning of the century, its peculiar physical properties are still not well understood. First we discuss some of the anomalies of this ‘complex fluid’. Then we describe a qualitative interpretation in terms of percolation concepts. Finally, we discuss recent experiments and simulations relating to the liquid–liquid phase transition hypothesis that, in addition to the known critical point in water, there exists a ‘second’ critical point at low temperatures. In particular, we discuss very recent measurements at Tsukuba of the compression-induced melting and decompression-induced melting lines of high-pressure forms of ice. We show how knowledge of these lines enables one to obtain an approximation for the Gibbs potential $G(P, T)$ and the equation of state $V(P, T)$ for water, both of which are consistent with the possible continuity of liquid water and the amorphous forms of solid water.

1. Introduction

Liquid water is at first sight not a typical liquid, and hence has no place at the conference to which this Special Issue is devoted. However, recent progress has occurred in understanding its highly anomalous equilibrium and dynamical properties [1–7]. Further, water is a transient gel with structural heterogeneities of very short length scales, so understanding the properties of water is important for understanding phenomena in ‘aqueous solutions’ and the structure of micelles and microemulsions.

Specifically, water is a large macroscopic space-filling hydrogen-bond network, as expected from continuum models of water. However, when we focus on the four-bonded molecules (‘sites’), we find that water can be regarded as having certain clustering features—the clusters being not isolated ‘icebergs’ in a sea of dissociated liquid (as postulated in mixture models dating back to Röntgen) but rather patches of four-bonded molecules embedded in a highly connected network or ‘gel’ [8–10]. Similar physical reasoning applies if we generalize the concept of four-bonded molecules to molecules with a smaller than average energy [11] or to molecules with a larger than average ‘local structure’ [12].

2. The liquid–liquid phase transition hypothesis

A few years ago, a gifted Boston University graduate student, Peter Poole, working with postdocs Francesco Sciortino and Uli Essmann, made computer simulations in this low-temperature region with the goal of exploring in detail with a computer what might happen [13].

What Poole and collaborators discovered in computer water was the apparent existence of a second critical point. That second critical point was in the region of -50°C and 1 kbar. Below this second critical point, the liquid phase separates into two distinct phases—a low-density liquid (LDL) and a high-density liquid (HDL).

3. Plausibility arguments

A non-interacting gas has no critical point, but a gas with arbitrarily weak attractive interactions does since at sufficiently small temperature, the ratio of the interaction to kT will become sufficiently significant to condense the liquid out of the gas. That all interacting gases display a critical point below which a distinct liquid phase appears was not always appreciated. Indeed, in the early years of the twentieth century one spoke of ‘permanent gases’—to describe gases that had never been liquefied. Helium is an example of what was once thought to be a permanent gas [14].

Nowadays, we understand that permanent gases generally do not exist since all molecules exert some attractive interaction, and at sufficiently low temperature this attractive interaction will make a significant contribution. To make the argument more concrete, one can picture droplets of lower specific volume \bar{V} forming in a single-component fluid. Once the interaction between molecules is fixed (and P is fixed at some value above P_C), then the only remaining control parameter is T ; as T decreases the high-density droplets increase in number and size and eventually below T_C they coalesce as a distinct liquid phase.

Water differs from most liquids due to the presence of a line of maximum density (TMD line) in the P – T phase diagram; at 1 atm pressure, $\text{TMD} = 4^\circ\text{C}$. This TMD line is physically very significant, as it divides the entire P – T phase diagram into two regions with remarkably different properties: the coefficient of thermal expansion—which is proportional to the thermal average (‘correlation function’) $\langle\delta\bar{V}\delta\bar{S}\rangle$ —is *negative* on the low-temperature side of the TMD line, while it is *positive* on the high-temperature side. Here \bar{V} is the volume per molecule, \bar{S} the entropy per molecule, and the δX notation indicates the departure of a quantity X from its mean value.

That $\langle\delta\bar{V}\delta\bar{S}\rangle$ is negative is a thermodynamic necessity given the presence of a TMD line. What microscopic phenomenon causes it? One not implausible explanation [8] is related to the presence of local regions of the hydrogen-bond network that are characterized by four ‘good’ hydrogen bonds—and these local regions can be considered as droplets just like the high-density droplets in a gas above C . Stated more formally: the sensitivity of hydrogen bonds to the orientation of the molecules forming it encourages local regions to form that are partially ordered in the sense that if there is a region of the water network where each molecule has four ‘good’ (strong) hydrogen bonds, then the local entropy is lower (so $\delta\bar{S} < 0$) and the local specific volume is larger (so $\delta\bar{V} > 0$), so the contribution to $\langle\delta\bar{V}\delta\bar{S}\rangle$ is negative for such regions.

As the temperature is lowered, there is no *a priori* reason why the ‘droplets’ characterized by negative values of $\delta\bar{V}\delta\bar{S}$ should not increase in number and size, just as the droplets associated with a normal phase transition increase in number, since all water molecules exert mutual interactions on one another, and these interactions—because of their sensitivity to orientation and well as distance—favour the open clusters characterized by $\delta\bar{S}\delta\bar{V} < 0$. It is thus plausible that at sufficiently low temperature these orientation-sensitive interactions will make a larger and larger contribution, and at sufficiently low temperature (and for sufficiently low pressure), a new phase—having roughly the density of the fully hydrogen-bonded network—will ‘condense’ out of the one-fluid region [13, 15–17].

This intuitive picture has received striking support from a recent generalization of the

van der Waals theory. Specifically, Poole *et al* [18] allow each water molecule to be in many bonding states, only one of which corresponds to a ‘good’ quality hydrogen bond (with a larger number of states corresponding to ‘poor’ quality bonds). To build in this feature, Poole *et al* adopt the approach of Sastry and co-workers [19,20] and assume that there are a great number of configurations of a weak bond, all having $\epsilon = 0$, and only a *single configuration* in which the HB is strong with $\epsilon = \epsilon_{\text{HB}}$. Poole *et al* find that for small values of the parameter ϵ_{HB} , there is no critical point (but rather a re-entrant spinodal of the form first conjectured by Speedy [21]). However, for ϵ_{HB} above a threshold (about 16 kJ mol⁻¹), a critical point appears.

The possibility of a second critical point has received recent support from the phenomenological analysis of Ponyatovskii and colleagues [22] and from lattice gas models [20,23]. Also, Roberts and co-workers [24] have shown that simulation results for a microscopic ‘water-like’ Hamiltonian confirms the presence of a second phase transition, previously deduced from approximate calculations [23].

4. Tests of the hypothesis: computer water

We summarize some recent work that might be interpreted as being consistent with (or at least not contradicting) the hypothesis that a HDL–LDL critical point C' exists.

4.1. Does $1/K_T^{\text{max}}$ extrapolate to zero at $(T_{C'}, P_{C'})$?

The compressibility K_T diverges at a second-order critical point. Thus, we expect $1/K_T^{\text{max}}$ to extrapolate to zero at the ‘new’ HDL–LDL critical point C' , exactly as it does for the ‘old’ liquid–gas critical point C . Recent calculations [25] are consistent with a plausible extrapolation to a single point in the phase diagram at which $K_T^{\text{max}} = \infty$ (but see [26]).

4.2. Is there a ‘kink’ in the P – ρ isotherms for sufficiently low temperature?

If there is a critical point, then we expect to find a kink in the P – ρ isotherms when T is below $T_{C'}$. Indeed, such a kink appears to exist for the ST2 potential, at a temperature of 235 K but not at a temperature of 280 K, consistent with $T_{C'}$ somewhere between 235 K and 280 K. This finding, originally made for simulations of 216 particles [13, 16], has very recently been strikingly confirmed for a system eight times larger [17].

4.3. Is there a unique structure of the liquid near the kink point?

If there exists a critical point C' , then we would expect a two-phase coexistence region below C' . Studies just below the estimated value of $T_{C'}$ at two values of ρ on the two sides of $\rho_{C'}$ show that the structure of the liquid state of ST2 at $\rho = 1.05 \text{ g cm}^{-3}$ is similar to the experimental data on high-density amorphous (HDA) solid water, while the structure of the structure at $\rho = 0.92 \text{ g cm}^{-3}$ resembles the data on low-density amorphous (LDA) solid water [25]. The correspondence between the HDA ice phase and ST2 water just above $\rho_{C'}$, and between the LDA phase and ST2 water just below $\rho_{C'}$ suggests that the two phases that become critical at C' in ST2 water are related to the known HDA and LDA phases of amorphous ice [27].

4.4. Does the coordination number approach four as C' is approached?

Sciortino *et al* [25] have studied the coordination number N_{nn} of the ST2 liquid as a function of T and V , where N_{nn} is the average number of nearest neighbours found in the first coordination

shell of an O atom. For the high- T isotherms, their results show that a four-coordinated ‘LDL’-like configuration is approached at negative P . For $T \leq 273$ K, N_{nn} also approaches 4 at positive P . That is, if T is low enough, it appears that a four-coordinated network can form in liquid water even for $P > 0$.

4.5. *Is it possible that two apparent ‘phases’ may coexist below C' ?*

Convincing evidence for a HDL–LDL critical point C' would be the presence of two coexisting phases below C' . This search is the focus of ongoing work, and preliminary work is encouraging [17]. Calculations of the two tentatively identified HDL and LDL phases suggest similarities with experimental results on the two amorphous solid phases HDA and LDA.

4.6. *Do fluctuations appear on all timescales?*

For the ST2 potential, a histogram of hydrogen-bond lifetimes reveals power-law behaviour over as much as two decades, with the region of ‘scale-free behaviour’ extending over a larger time domain as T is decreased [28].

4.7. *Is there ‘critical slowing down’ of a characteristic timescale?*

Slowing down of the dynamics is what one expects near a critical point. For the ST2 potential, the characteristic value of hydrogen-bond lifetime, defined as the value of time at which the power-law distribution of bond lifetimes is cut off by an exponential, depends sensitively on temperature and in fact is consistent with a power-law divergence as T approaches $T_{C'}$ [28]. Appearing to diverge at roughly the same temperature is the inverse of the self-diffusion coefficient D [29]: $1/D$ strongly increases as $N_{nn} \rightarrow 4$. Consistent with this picture, it was found [30] that additional nearest neighbours beyond 4 have a ‘catalytic’ effect on the mobility of the central molecule.

4.8. *Are the characteristic dynamics of each of the ‘phases’ different?*

We can identify molecules as ‘red’/‘blue’ if they are in a region of locally high/low density for a specified amount of time (say 100 ps). Looking at the mean square displacement of the red and blue ‘phases’, we see that the red molecules (corresponding to high densities) move much further than blue molecules (corresponding to low densities) [17]. The nature of transport in each phase is under active investigation, particularly in the light of recent proposals for the nature of the anomalous dynamics taking place in low-temperature water [31].

4.9. *Is there evidence for a HDL–LDL critical point from independent simulations?*

Recently, Tanaka independently found evidence supporting a liquid–liquid critical point by performing simulations for the TIP4P potential [32].

5. Tests of the hypothesis: real water

5.1. *A cautionary remark*

The first statement we must make concerns the presence of an impenetrable ‘Berlin wall’: the line $T_H(P)$ of homogeneous nucleation temperatures [33]. By careful analysis of experimental data above $T_H(P)$, Speedy and Angell [21, 34, 35] pioneered the view that some sort of singular

behaviour is occurring in water at a temperature $T_s(P)$ some five to ten degrees into the ‘no-man’s land’ below $T_H(P)$. Our belief is that, even though the region below T_H is experimentally inaccessible, we want to learn about the liquid equation of state in this region since anything that might occur in this region (such as a line of spinodal singularities [35, 36] or a critical point) will influence the equation of state in a large neighbourhood.

5.2. Previous work

5.2.1. Density fluctuations along the $P = 0.1$ MPa isobar. The correlation length ξ for density fluctuations should increase close to a critical point; this quantity has recently been measured along a $P = 0.1$ MPa isobar [37], down to quite low temperatures (239 K). A gentle increase in correlation length was found, but no indication of a divergence, consistent with the possibility that the HDL–LDL critical point, if it exists, lies at a much higher pressure.

5.2.2. Structure along isobars up to $P = 600$ MPa. Bellissent-Funel and Bosio have recently undertaken a detailed structural study of D_2O using neutron scattering to study the effect of decreasing the temperature on the correlation function [27]. As paths in the P – T phase diagram, they have chosen a family of isobars ranging in pressure up to 600 MPa (well above the HDL–LDL critical point of about 100 MPa). They plot the temperature dependence of the first peak position Q_0 of the structure factor for each isobar. They find that for the 0.1 MPa isobar, Q_0 approaches 1.7 \AA^{-1} —the value for LDA, low-density amorphous ice. In contrast, for the 465 and 600 MPa isobars, Q_0 approaches a 30% larger value, 2.2 \AA^{-1} —the value for HDA, high-density amorphous ice. For the 260 MPa isobar, $Q_0 \rightarrow 2.0 \text{ \AA}^{-1}$, as if the sample were a two-phase mixture of HDA and LDA.

5.2.3. Reversible conversion of LDA to HDA with pressure. Since the HDL–LDL critical point occurs below $T_H(P)$, it is not possible to probe the two phases experimentally. However, two analogous solid amorphous phases of H_2O have been studied extensively by Mishima and co-workers [38]. In particular, Mishima has recently succeeded in converting the LDA phase to the HDA phase on increasing the pressure, and then reversing this conversion by lowering the pressure. The jump in density was measured for a range of temperatures from 77 K to 140 K, and the density jump (when HDA is compressed to LDA) was found to occur at roughly 200 MPa. Moreover, the magnitude of the density jump decreases as the temperature is raised, just as would occur if instead of making measurements on the HDA and LDA amorphous solid phases, one were instead considering the HDL and LDL liquid phases. These results are corroborated by independently performed computer simulations using both the ST2 and TIP4P intermolecular potentials [15].

If we assume that HDA and LDA ice are the glasses formed from the two liquid phases discussed above, then the HDA–LDA transition can be interpreted in terms of an abrupt change from one microstate in the phase space of the high-density liquid to a microstate in the phase space of the low-density liquid. The experimentally detected HDA–LDA transition line would then be the extension into the glassy regime of the line of first-order phase transitions separating the HDL and LDL phases.

5.3. Very recent work

When liquid water is supercooled below the homogeneous nucleation temperature, T_H (-38°C at $P = 1$ atm), crystal phases nucleate homogeneously, and the liquid freezes spontaneously

to the crystalline phase. When amorphous solid ice is heated, it crystallizes above the crystallization temperature, T_X (about -120 °C at $P = 1$ atm). Therefore, amorphous forms of H_2O do not exist in the ‘no-man’s land’ between T_H and T_X .

When we compress the crystalline ice I_h at low temperatures, it transforms to supercooled liquid on its metastable melting line above T_H . Between T_H and T_X , it transforms to a high-pressure crystalline ice at the smoothly extrapolated melting line [39]. Below T_X , ice I_h amorphizes to HDA at a pressure higher than the smoothly extrapolated melting line [1]. To avoid the complication of the usual crystal–crystal transformations interrupting the melting process, we use an ice emulsion (1–10 μm ice particles in oil [40]).

Mishima creates 1 cm^3 emulsified high-pressure ices in a piston–cylinder apparatus, decompresses the sample at a constant rate of 0.2 GPa min^{-1} , and—because melting is endothermic—observes their transitions by detecting a change in the sample temperature using an attached chromel–alumel thermocouple during the decompression. Then, he determines melting pressures at different temperatures. The melting curves he obtains agree with previously reported data [41, 42], which confirms the accuracy of this method. Moreover, he can determine the location of metastable melting lines to much lower temperatures.

Using the measured melting lines of ice phases at low temperatures, we calculate the Gibbs energy and the equation of state [43]). The P – V – T relation is consistent with (but of course does not prove) the existence of a line of first-order liquid–liquid transitions which continues from the line of LDA–HDA transitions and terminates at an apparent critical point C' . The P – V – T relation is also consistent with other known experimental data and also with simulation results [13, 18, 20, 24, 26, 32, 38, 43–47]

In summary, we know the free-energy surface to some level of approximation. Since we know the Gibbs potential as a function of pressure and temperature, by differentiation, we know the volume as a function of pressure and temperature. Having the volume as a function of temperature is just where we want to end this exposition, because volume as a function of pressure and temperature is the equation of state of the liquid. So what ultimately comes out then from these experiments is the complete equation of state. This may look a little bit complicated, so let us take it in stages.

At high temperature, we have a familiar ideal-gas behaviour—the volume is approximately inversely proportional to the pressure. If we look at very low temperatures, we see the two known glassy phases of water: low-density amorphous and high-density amorphous. We have two phases here. The low-density one is grey; the high-density one is pink. They are separated by a first-order transition. ‘First order’ means discontinuity in the first derivative. Volume is the first derivative so there is a discontinuity—we have already mentioned about 25 per cent. So this part is known experimentally without a shadow of a doubt. The other part has been known experimentally for perhaps one hundred years. There is only one little thing missing, which is the connection between them. The connection between them is what is provided by the experiments that traverse the no-man’s land, and some of those experiments are indicated by these little lines that shoot across from one phase, the known part of the phase diagram, to the other part of the phase diagram.

6. Discussion

The most natural response to the concept of a second critical point in a liquid is bafflement—such a thing just does not make sense. To make the concept more plausible, we offer the following remarks. Consider a typical member of the class of intermolecular potentials that go by the name of core-softened potentials [48]. These are potentials with two wells, an outer well that is deeper and an inner well that is more shallow. Recently Sadr-Lahijany and collaborators

have revisited such potentials with a view toward applications to water [49]. These simple potentials might capture the essential physics of water–water interactions because, in the case of water, a hydrogen-bonded interaction leads to a larger intermolecular spacing (say 2.8 Å) compared to a ‘non-hydrogen-bonding’ interaction. Since, at low temperatures, hydrogen bonds predominate—increasing the volume—it follows that the outer well of a core-softened potential must be deeper. Then, as temperature is lowered, the system finds itself more probably in the outer ‘deep’ well than in the inner ‘shallow’ well. Further, pressure has the same effect as raising the temperature, since for a fixed temperature, applying pressure favours the inner shallow well.

An advantage of such double-well potentials is that they can be solved analytically in one dimension and are tractable to study using approximation procedures (and simulations) in higher dimensions [49].

To complete the intuitive picture, let us imagine two (or more) local structures, one favoured at low pressure (the outer deeper well) and the other favoured at high pressure (the inner well). If a system is cooled at a fixed *low* value of pressure, then the system will settle into a phase whose properties are related to the parameters of the outer well. If, on the other hand, the system is cooled at a fixed *high* value of pressure, it will settle into a phase whose properties are related to the parameters of the inner well. Thus it becomes plausible that, depending on the pressure, the liquid could approach different phases as the temperature is lowered. Moreover, if the outer well is deep and narrow, then we anticipate that when $\delta \bar{V} > 0$, $\delta S < 0$ —i.e., volume and entropy fluctuations will be anticorrelated, leading to $\alpha_p < 0$.

A clear physical picture has by no means emerged. However, recent work has addressed the question of whether we can characterize (or at least ‘caricature’) the local structural heterogeneities that appear in liquid water. Specifically, Canpolat and collaborators [50] considered state points of liquid water at different pressures—and especially near its phase boundaries with ice I_h and with ice VI (a high-pressure polymorph of solid H₂O). To this end, in the spirit of the ‘Walrafen pentamer’, they develop a model of interacting water pentamers, and find two distinct local energy minima which they identify with two well-defined configurations of neighbouring pentamers. The ‘Walrafen pentamer’ is defined by four water molecules located at the corners of a tetrahedron that are hydrogen bonded to a central molecule—see, e.g., [51]; the corner molecules are separated from the central molecule by 2.8 Å, corresponding to the first peak in the oxygen–oxygen radial distribution function. They advance the hypothesis that these configurations may be related to the local ‘high-density’ and ‘low-density’ structural heterogeneities occurring in liquid water. These results are consistent with recent experimental data on the effect of high pressure on the radial distribution function, and are further tested by molecular dynamics simulations.

Although such a picture—of two reasonably distinct local structures, differing in local density—may seem to be oversimplified, very recent work of Bellissent-Funel [52] successfully shows that detailed neutron structure data agree with it. Also, the simulation results are in good accord with neutron results (see, e.g., [53]), and very recent work of Sasai also relates these two distinct local structures to dynamic properties [54].

7. Outlook

Before concluding, we ask ‘what is the requirement for a liquid to have such a second critical point?’ In fact, by the arguments above, some other liquids should display second critical points, namely systems which at low temperature and low pressure have anticorrelated entropy and specific volume fluctuations. Thus a natural extension to our work is to consider other tetrahedrally coordinated liquids. Examples of such systems are SiO₂ and GeO₂, known for

their geological and technological importance. Both of these systems display features in their equations of state similar to those found in simulations of water and that can be traced to their tetrahedral configurations. This tetrahedrality of local structure has the implication that locally ordered regions of the liquid will have a *larger* specific volume rather than a *smaller* specific volume than the global specific volume (as in most liquids, for which the local structure, also resembling the global structure of the solid, has a smaller specific volume than the global specific volume). Whenever we are at a state point in the P – T phase diagram to the left of the locus of points where the coefficient of thermal expansion is zero (the ‘TMD line’), then of necessity the volume fluctuations are most unusual in that they are anticorrelated with the entropy fluctuations. These unusual fluctuations grow as one moves further into the ‘anomalous’ region to the left of the TMD line, and ultimately a new phase condenses out of the fluid which has the property that although the entropy of the new phase is low, the specific volume is large—this is what is called the ‘low-density liquid’. Since other tetrahedral liquids have similar features, we might expect similar critical points to occur on the liquid free-energy surface of these liquids. Simulation evidence in favour of this possibility has been reported recently for SiO_2 [55] and a two-level model has been developed for amorphous GaSb [56]. Understanding one such material, water, may help in understanding others—whether they be other materials with tetrahedral local structures (and corresponding TMD lines) such as SiO_2 or whether they be more complex local structures like that of amorphous GaSb, which appears to display strikingly ordered local heterogeneities.

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