

# The puzzling behavior of water at very low temperature

## Invited Lecture

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Although H<sub>2</sub>O has been the topic of considerable research since the beginning of the century, most of its anomalous 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 may exist 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.

### I. Introduction

Liquid water is not a typical liquid (Fig. 1). However, some progress has occurred in understanding its highly anomalous equilibrium and dynamical properties.<sup>1–7</sup> Water is a space-filling hydrogen bond network, as expected from continuum models of water. However, when we focus on the well-bonded molecules (“sites”), we find that water can be regarded as having certain clustering features—the clusters being not iso-

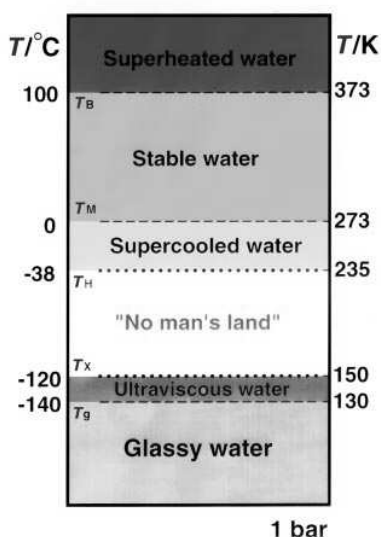
lated “icebergs” in a sea of dissociated liquid (as postulated in mixture models dating back to Röntgen) but rather patches of well-bonded molecules embedded in a highly connected network or “gel”.<sup>8–10</sup> Similar physical reasoning applies if we generalize the concept of well-bonded molecules to molecules with a smaller than average energy<sup>11</sup> or to molecules with a larger than average “local structure”.<sup>12</sup>

### II. Liquid–liquid phase transition hypothesis

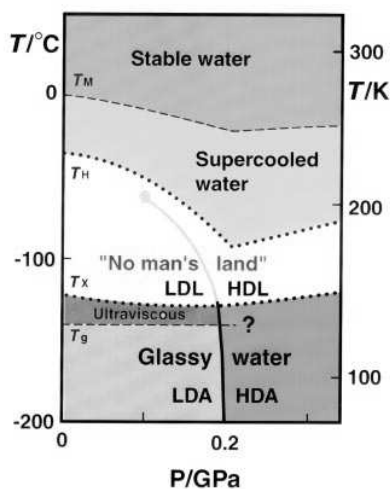
A few years ago, Poole *et al.* made computer simulations in the low-temperature region with the goal of exploring in detail with a computer what might happen.<sup>13</sup> What Poole and collaborators discovered in computer water was the apparent existence of a second critical point. That second critical point was in the range of  $-50\text{ }^\circ\text{C}$  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).

The pressure of the second critical point is around one kilobar. The phase diagram at pressures up to 0.3 GPa (*ca.* 3000 atm) is shown in Fig. 2, which retains the color code of Fig. 1 (Fig. 1 being a slice of the phase diagram at 1 atm). At approximately 1000 atm the grey dot represents where the second critical point might lie. This awkward location is problematic. First, it lies on the side of the line of homogeneous nucleation,  $T_H$ , that we cannot reach experimentally! Here, we describe experimental attempts to characterise the species at the critical point, but we can only get to a point  $5\text{--}15^\circ$  from it.

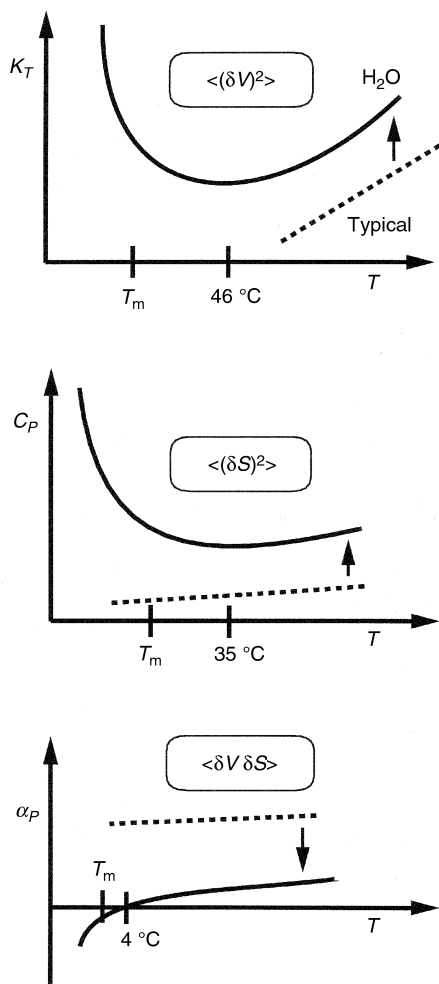
Although we cannot get close to the point itself, it is important. If we have a singularity in our phase diagram at a well-defined critical point, it will have an effect on an entire region around the critical point—a so-called critical region (Fig. 3). The size of this critical region depends on the material, but is usually somewhere between 10% and 100% above the critical



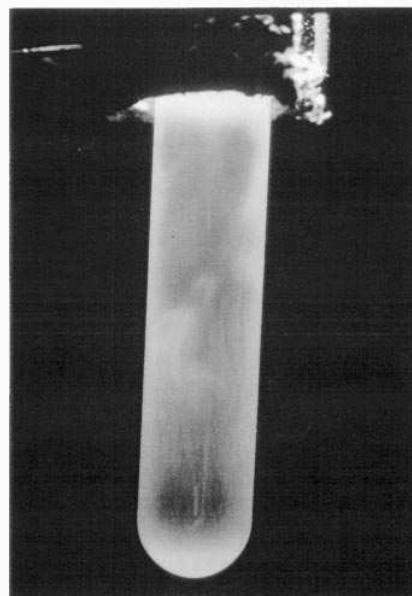
**Fig. 1** Schematic illustration indicating the various phases of liquid water (color-coded) that are found at atmospheric pressure. This figure is courtesy of Dr O. Mishima.



**Fig. 2** Generalization of Fig. 1 to incorporate a second control parameter, the pressure. The colors are the same as used in Fig. 1. This figure is courtesy of Dr O. Mishima.



**Fig. 3** Schematic dependence on temperature of (a) the isothermal compressibility  $K_T$ , (b) the constant-pressure specific heat  $C_p$ , and (c) the thermal expansivity  $\alpha_p$ . The behavior of a typical liquid is indicated by the dashed line, which very roughly is an extrapolation of the high-temperature behavior of liquid water. Note that while the anomalies displayed by liquid water are apparent above the melting temperature  $T_m$ , they become more striking as one supercools below  $T_m$ . This figure is courtesy of F. W. Starr.



**Fig. 4** Critical opalescence of the critical binary mixture cyclohexane–aniline. This figure is courtesy of R. A. Ferrell.

temperature and pressure that response functions are significantly affected (*e.g.*, an ideal gas has an inverse compressibility given by  $T$ , while an interacting gas has an inverse compressibility that deviates significantly from  $T$  a factor of two above the critical point). It is not required that the system is exactly at its critical point in order that the system exhibits remarkable behavior, such as the phenomenon of critical opalescence discovered and correctly explained in 1869 by Andrews<sup>14</sup> in terms of increased fluctuations away from (but close to) the critical point (Fig. 4). It is for this reason that critical phenomena are particularly interesting.

### III. Plausibility arguments

An ideal (or “perfect”) gas with no interactions among its constituent particles has no critical point. However, a gas with arbitrarily weak attractive interactions does—since at sufficiently low 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 this 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.<sup>15</sup>

Nowadays, we understand that permanent gases generally do not exist since all molecules exert some attractive interaction, and at sufficiently low temperature and sufficiently high pressure this attractive interaction will cause a high density liquid phase to condense out of the gas. 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  $PT$  phase diagram; at 1 atm pressure,  $TMD = 4^\circ\text{C}$ . This TMD line is physically very significant, as it divides the entire  $PT$  phase diagram into two regions with remarkably different properties: the coeffi-

cient 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  $\delta X$  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<sup>8</sup> is related to the presence of local regions of the hydrogen bond network that are characterized by four “good” hydrogen bonds—these local regions can be considered as droplets just as 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, favor 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.<sup>13,16–18</sup>

This intuitive picture has received striking support from a recent generalization of the van der Waals theory. Specifically, Poole *et al.*<sup>19</sup> 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<sup>20,21</sup> 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 hydrogen bond (HB) is strong with  $\epsilon = \epsilon_{\text{HB}}$ . Poole *et al.* find that for small values of the parameter  $\epsilon_{\text{HB}}$ , there is no critical point (but rather a re-entrant spinodal of the form first conjectured by Speedy<sup>22</sup>). However, for  $\epsilon_{\text{HB}}$  above a threshold (about 16 kJ mol<sup>-1</sup>), a critical point appears.

The possibility of a second critical point has received recent support by phenomenological analysis of Ponyatovskii and colleagues<sup>23</sup> and by lattice gas models.<sup>21,24</sup> Also, Debenedetti and co-workers<sup>25</sup> have shown that simulation results for a microscopic “water-like” Hamiltonian confirms the presence of a second phase transition, previously deduced from approximate calculations.<sup>24</sup>

#### IV. Tests of the hypothesis: computer water

Simulation studies of liquid water have a rich history and have contributed greatly to our understanding of the subject. In fact, over a quarter century ago, the ST2 (Stillinger-2) potential was introduced. Water is represented by a central point from which emanate four arms—two carrying positive charges to represent the two protons associated with each water molecule, and two carrying negative charges to represent the two lone electron pairs.<sup>26</sup> The central points interact *via* a Lennard-Jones potential, while the point charges and the arms interact *via* a Coulomb potential. Thus every pair of waterlike particles has  $4^2 + 1 = 17$  interaction terms. Corresponding to the rather cumbersome nature of such a potential

is the fact that most studies are limited to extremely small systems, a typical number being  $N = 6^3 = 216$  waterlike particles. Recently some studies have considered larger systems, but the typical size rarely exceeds  $N = 12^3 = 1728$ . It is hoped that by using fast multipole methods one can begin to simulate much larger systems.

One way to obtain less cumbersome simulations is to simplify the intermolecular potential. To this end, the simpler TIP4P potential<sup>27</sup> and the much simpler SPC/E potential<sup>28</sup> have enjoyed considerable popularity. However the opposite direction is also under active investigation: simulating more realistic potentials, such as polarizable potentials.<sup>29</sup> The researcher is left with the perplexing problem of which model potential to adopt!

With these caveats, let us very briefly 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. We emphasize that most of this work has not reached the stage that it can be interpreted as evidence favoring the hypothesis, so we also outline appropriate avenues where future work may strengthen the argumentation.

##### A. Does $1/K_T^{\text{max}}$ extrapolate to zero at $(T_C, P_C)$ ?

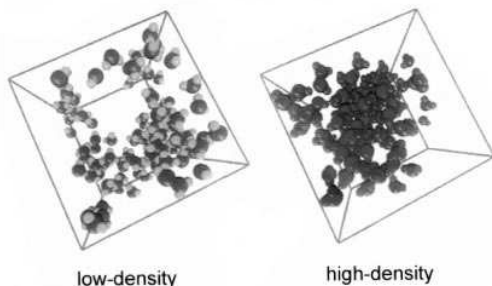
The compressibility  $K_T$  diverges at a second order critical point. Thus, we expect  $1/K_T^{\text{max}}$  to extrapolate to zero at the new HDL–LDL critical point  $C'$ , exactly as it does for the old liquid–gas critical point  $C$ . Recent ST2 calculations<sup>30</sup> are consistent with a plausible extrapolation to a single point in the phase diagram at which  $K_T^{\text{max}} = \infty$ . The caveat is that one can never know that a given quantity is approaching infinity—it could as well just be approaching a very large number. Indeed, the possibility has been raised, and seriously discussed, that there is no genuine singularity.<sup>8,31</sup>

##### B. Is there a “kink” in the $P_\rho$ isotherms?

If there is a critical point, then we expect to find a kink in the  $P_\rho$  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 and 280 K. This finding, originally made for simulations of 216 ST2 particles,<sup>16,17</sup> has very recently been strikingly confirmed for a system eight times larger.<sup>18</sup> An analogous kink has not been found for the TIP4P potential, but a prominent inflection occurs at the lowest temperature studied, suggesting that such a kink may be developing. Work is underway testing for inflections and possible kinks for other water potentials in three, and also in two, dimensions.

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

If there exists a critical  $C'$ , then we would expect a two-phase coexistence region below  $C'$ . To investigate the possible structural difference between these two phases, Sciortino *et al.*<sup>30</sup> have studied the structure of the liquid at a temperature just below the estimated value of  $T_C$  at two values of  $\rho$  on the two sides of  $\rho_{C'}$ . They find 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. 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.<sup>32,33</sup>



**Fig. 5** The results of partitioning the molecules in a computer simulation into two categories, the left picture being the low-density molecules (with coordination number four) and right picture being the high-density molecules (with coordination number above four). This figure is courtesy of S. T. Harrington.

#### D. Does the coordination number approach four as $C'$ is approached?

Sciortino *et al.*<sup>30</sup> have studied the coordination number  $N_{nn}$  of the ST2 liquid as a function of  $T$  and  $V$ , when  $N_{nn}$  is the average number of nearest-neighbors 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  $P$ , in agreement with previous simulations of Geiger and co-workers.<sup>34</sup> For  $T \leq 273$  K,  $N_{nn}$  also approaches four at positive  $P$ . That is, if  $T$  is low enough, it appears that a four-coordinated network can form in liquid water even for  $P > 0$ . This result is consistent with an experimental study of the evolution of the structure function  $S(Q)$  as water is supercooled at atmospheric pressure, in which it was found that the structure tends toward that of the LDA ice.<sup>32</sup>

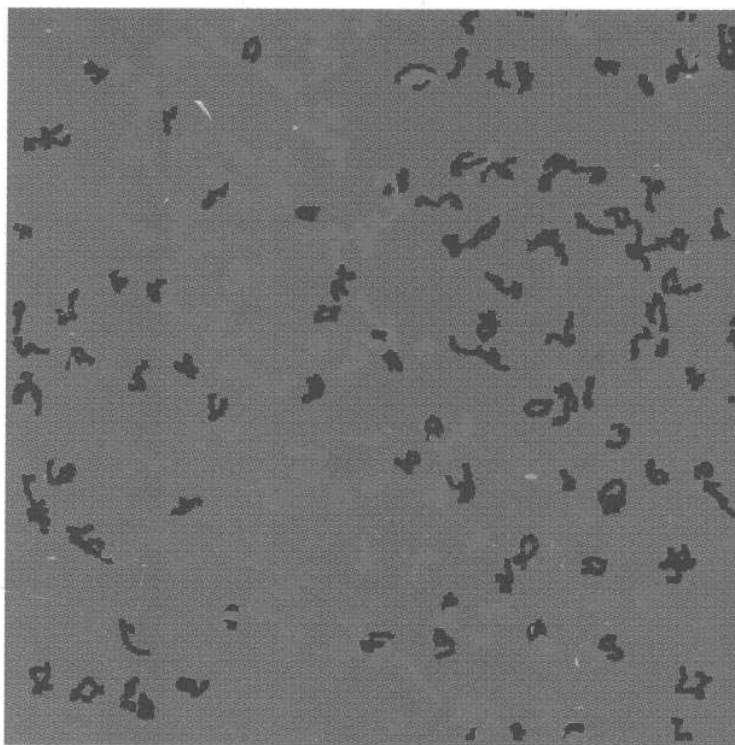
#### E. Is it possible that two apparent phases coexist below $C'$ ?

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. One can, *e.g.*, partition the water molecules into two groups (“red” and “blue” molecules), those with fewer than the average number of nearest neighbors and those with more than the average (Fig. 5). We find that the red molecules and the blue molecules segregate to different regions of the 18 Å box in which they are residing. These preliminary investigations at a temperature somewhat below  $T_C$  do not prove phase coexistence,<sup>18,35</sup> but work is underway to establish this possibility. In particular, one must first rule out the likelihood that the two “phases” are merely large fluctuations due to a large correlation length (because near a critical point there should be fluctuations of all sizes and shapes, while the sample separating into two distinct regions is rather different). Also, one must seek to find the phase separation occurring in much larger systems. To be conclusive, firstly one must demonstrate that phase separation occurs in a much larger system, and secondly one must study systematically the time dependence of  $S(Q)$  as one quenches into the two-phase region from a large value of temperature.

Separate calculations of the weighted correlation function  $h(r)$  for the two tentatively identified HDL and LDL phases suggest similarities with experimental results on the two amorphous solid phases HDA and LDA.<sup>35</sup> Additional work remains to be done to establish this point.

#### F. Do fluctuations appear on all time scales?

For the ST2 potential, a histogram of hydrogen bond lifetimes reveals power law behavior over as much as two decades, with the region of “scale free behavior” extending over a larger time domain as  $T$  is decreased.<sup>36</sup> For the TIP4P potential, no calculations have yet been carried out, but for the SPC/E potential, non-Arrhenius behavior has also been found at high



**Fig. 6** Time-exposure photograph of moving ST2 water-like particles. The red molecules are the molecules with smaller local density, namely with coordination number  $< 4$ . In addition to seeing the phase separation of Fig. 5, we see that the low-density patches move less.

temperatures.<sup>37</sup> At low temperatures, it is possible that power law behavior is found.<sup>18</sup> An important caveat in interpreting these results is that this scale free behavior is exactly what one would expect if the hydrogen bonded network were regarded as possessing defects (corresponding to molecules with fewer than four good bonds), and these defects were allowed to diffuse randomly.<sup>38,39</sup> Possibly some of these ambiguities will be resolved by applying to this problem Sasai's "local structure index" that permits one to study in some detail the local dynamics.<sup>40</sup>

### G. Is there "critical slowing down" of a characteristic time scale?

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  $T_C$ .<sup>36</sup> The temperature dependence of the cutoff has not been studied for other potentials.

Appearing to diverge at roughly the same temperature is a less ambiguous measure of the characteristic time: the inverse of the self-diffusion coefficient  $D$ .<sup>41–44</sup> This slowing down of the dynamics is consistent with what one expects near a critical point. Specifically,  $1/D$  strongly increases as  $N_{nn} \rightarrow 4$ . Consistent with this picture, it was found<sup>41,42</sup> that additional nearest neighbors beyond four have a "catalytic" effect on the mobility of the central molecule, in that they lower the local energy barrier of the molecular exchanges that are the microscopic basis of diffusion, demonstrating the importance for molecular mobility of molecular environments having more than four nearest neighbors.

Because of the relation  $1/D$  and ( $N_{nn} \rightarrow 4$ ), the manner in which  $N_{nn} \rightarrow 4$  is also significant. At high  $T$  the decrease of  $N_{nn}$  with  $P$  is relatively uniform. However, as  $T$  decreases,  $N_{nn}$  is observed to vary more and more abruptly from a high-coordinated structure ( $N_{nn} > 6$ ) to  $N_{nn} \simeq 4$ . It should be possible to collapse this family of curves onto a single "scaling function" if the two axes are divided by appropriate powers of  $T - T_C$ ; these tests are underway.

### H. Is the characteristic dynamics of each "phase" 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" (Fig. 6) we see that the red molecules (corresponding to high densities) move much further than blue molecules (corresponding to low densities).<sup>18,35</sup> The nature of transport in each phase is under active investigation, particularly in light of proposals for the nature of the anomalous dynamics taking place in low-temperature water.<sup>43</sup>

### I. Is there evidence for a HDL-LDL critical point from independent simulations?

Recently, Tanaka independently found supporting evidence of a critical point by simulations for the TIP4P potential.<sup>45</sup> Tanaka's value of the critical temperature  $T_C$  agrees with the earlier estimates, but his critical pressure  $P_C$  occurs at roughly atmospheric pressure, or perhaps at negative pressures.<sup>45</sup> The resolution between the two different values of  $P_C$  is an open question that will hopefully be resolved shortly.

## V. Tests of the hypothesis: real water

### A. A cautionary remark

The first statement we must make concerns the presence of the impenetrable line,  $T_H(P)$ , of homogeneous nucleation tem-

peratures.<sup>46</sup> By careful analysis of experimental data above  $T_H(P)$ , Speedy<sup>22,47</sup> and Angell<sup>48</sup> pioneered the view that some sort of singular behavior is occurring in water at a temperature  $T_i(P)$  some 5–10° 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<sup>48,49</sup> or a critical point) will influence the equation of state in a large neighborhood.

### B. Previous work

**1. Density fluctuations along the  $P = 0.1$  MPa isobar.** The correlation length  $\xi$  for density fluctuations should increase close to a critical point; this quantity has recently been measured along a  $P = 0.1$  MPa isobar,<sup>10,50</sup> 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.

**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.<sup>32</sup> As paths in the  $PT$  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  $1.7 \text{ \AA}^{-1}$ , the value for LDA ice. In contrast, for the 465 and 600 MPa isobars,  $Q_0$  approaches a 30% larger value,  $2.2 \text{ \AA}^{-1}$ , the value for HDA ice.

**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 phase experimentally. However, two analogous solid amorphous phases of  $H_2O$  have been studied extensively by Mishima and co-workers.<sup>51</sup> 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 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.<sup>16</sup>

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 transition separating the HDL and LDL phases.

### C. Very recent work

When liquid water is supercooled below the homogeneous nucleation temperature,  $T_H$  ( $-38^\circ\text{C}$  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  $-120^\circ\text{C}$  at  $P = 1$  atm). Therefore, amorphous forms of  $H_2O$  do not exist in the "no-man's land" between  $T_H$  and  $T_X$ .

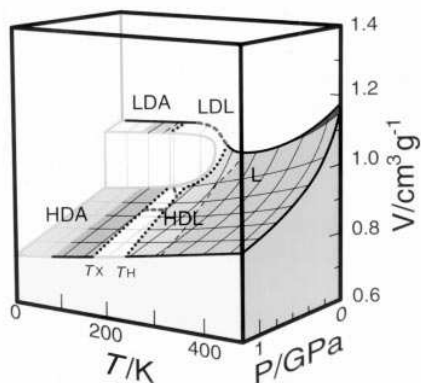
When we compress the crystalline ice  $I_h$  at low temperatures, it transforms to supercooled liquid on its metastable melting line above  $T_H$ . Between  $T_H$  and  $T_X$ , to a high-pressure crystalline ice at the smoothly extrapolated melting line.<sup>52</sup> Below  $T_X$ , ice  $I_h$  amorphizes to HDA at a pressure higher than the smoothly extrapolated melting line.<sup>1</sup> To avoid the complication of the usual crystal–crystal transformations interrupting the melting process we use an ice emulsion (1–10  $\mu\text{m}$  ice particles in oil<sup>53</sup>).

Mishima creates 1  $\text{cm}^3$  emulsified high-pressure ices in a piston-cylinder apparatus, decompresses the sample at a constant rate of 0.2  $\text{GPa min}^{-1}$ , and, because melting is endothermic, observes their transitions by detecting a change in the sample temperature by 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,<sup>54,55</sup> 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.<sup>56</sup> 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.<sup>13,19,21,25,31,40,45,51,56,57–59</sup>

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 (Fig. 7). Having the volume as a function of temperature is an appropriate point to end this paper, 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.

At high temperature, we have a familiar ideal gas behavior—the volume is approximately inversely proportional to the pressure. At very low temperatures, are the two known glassy phases of water: low-density amorphous ice (grey) and high density amorphous ice (pink). The two phases are

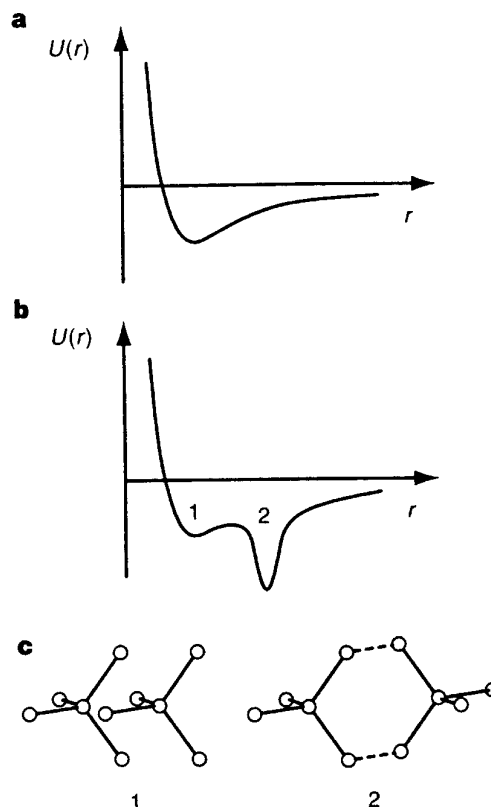


**Fig. 7** Experimentally-derived<sup>56</sup> thermodynamics equation of state  $V = V(P, T)$ , using the same color coding as in Figs. 1 and 2. The specific volumes of the amorphous phases are known for the region below  $T_X$ . Solid lines are the specific volume along the melting lines of ice IV and XIV. The high-temperature liquid appears to separate into two low-temperature liquid phases just below the critical point located at around 0.1 GPa and 220 K. These two liquid phases are continuous with the two amorphous phases that are known to exist below about 150 K. This figure is courtesy of Dr O. Mishima.

separated by a first-order transition. “First order” refers to the discontinuity in the first derivative, (*i.e.* the volume) which is 25%, as has been mentioned previously. So the high temperature part is known experimentally without any doubt. The low temperature part has been known experimentally for perhaps one hundred years. The connection between the two is missing, but this has been provided by the experiments that traverse the no-man’s land, and some of the experiments are indicated by the lines that cross from one phase, the known part of the phase diagram, to the other part of the phase diagram. These experiments are provided by Mishima’s very recent results for  $\text{H}_2\text{O}$ ,<sup>56,57</sup>  $\text{D}_2\text{O}$ ,<sup>60</sup> and dilute solution.<sup>61</sup>

## VI. Discussion

The most natural response to the concept of a second liquid point in a liquid is that it 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 are called core-softened potentials.<sup>62</sup> These are potentials with two wells, an outer well that is deeper and an inner well that is more shallow (Fig. 8). Recently Sadr-Lahijany and collaborators have re-visited such potentials with a view toward applications to water<sup>63</sup> and recent work of Malescio and collaborators using the HNC approximation.<sup>64</sup>



**Fig. 8** Physical arguments relating to the plausibility of the existence of the known liquid–gas critical point  $C$  and the hypothesized LDL–HDL critical point  $C'$ . (a) Idealized system characterized by a pair interaction potential with a single attractive well. At low enough  $T$  ( $T < T_C$ ) and high enough  $P$  ( $P > P_C$ ), the system condenses into the “liquid” well shown. (b) Idealized system characterized by a pair interaction potential whose attractive well has two sub-wells, the outer of which is deeper and narrower. For low enough  $T$  ( $T < T_C$ ) and low enough  $P$  ( $P < P_C$ ), the one-phase liquid can “condense” into the narrow outer “low-density liquid” sub-well, thereby giving rise to a low-density liquid phase, and leaving behind the high-density liquid phase occupying predominantly the inner subwell. (c) Two idealized interaction clusters of water molecules (“Walrafen pentamers”) in configurations that may correspond to the two sub-wells of (b).

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.<sup>63</sup> 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 the temperature is lowered, the system finds itself more likely 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 favors the inner shallow well.

Thus, let us imagine two (or more) local structures, one favored at low pressure (the outer deeper well) and the other favored 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  $\alpha_p < 0$ .

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<sup>65</sup> successfully shows that detailed neutron structure data agree with it. Also, the simulation results are in good accord with neutron results (see, *e.g.*, ref. 33), and very recent work of Sasai also relates these two distinct local structures to dynamic properties.<sup>66</sup> Recent work has addressed the question of whether we can characterize (or at least “caricature”) the local structural heterogeneities that appear in liquid water by simulations. Specifically, Canpolat and collaborators<sup>67</sup> considered state points of liquid water at different pressures, and especially near its phase boundaries with ice I<sub>h</sub> and with ice VI (a high-pressure polymorph of solid H<sub>2</sub>O). 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 neighboring 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.*, ref. 68; 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.

## VII. 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 SiO<sub>2</sub> and GeO<sub>2</sub>, known for their geological and technological importance.<sup>69</sup> 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 anticipate similar critical points occur on the liquid free energy surface of these liquids.

Simulation evidence in favor of this possibility has been reported recently for SiO<sub>2</sub><sup>70</sup> and a two-level model has been developed for amorphous GaSb,<sup>71</sup> and C.<sup>72,73</sup> 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<sub>2</sub> or whether they be more complex local structures like amorphous GaSb which appears to display strikingly ordered local heterogeneities. Recently, clear experimental evidence for a liquid–liquid phase transition has been reported in phosphorus, where the low-density liquid phase is a molecular liquid of tetrahedral P<sub>4</sub> “molecules”.<sup>74</sup> With a change in pressure, the low-pressure low-density molecular liquid transforms to a high-pressure high-density polymeric liquid. The transformation is surprisingly sharp and rapid; it is complete over a pressure range of less than 0.02 GPa and within a few minutes. During the transformation, two forms of liquid coexist, showing that phosphorus has a first-order liquid–liquid phase transition.<sup>74</sup>

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