

# The puzzling statistical physics of liquid water

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## Abstract

Although H<sub>2</sub>O has been the topic of considerable research since the beginning of the century, the peculiar physical properties are still not well understood. We discuss recent experiments and simulations relating to the 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 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. We also comment on some of the evidence that is equally consistent with other scenarios for the behavior of liquid water. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. The puzzle

What is the puzzle of liquid water, and why do we consider water to be anomalous? There are many scholarly works addressing the question (see, e.g., [1–5]), so we begin this talk with a user-friendly survey.

### 1.1. Density

The first anomalous property is extremely familiar to all who cool water below its melting point. In normal liquids, the solid phase has a greater density  $\rho$  than the liquid so the solid phase drops to the bottom of the container. In the case of water, the solid phase, ice, is 10% *less* dense than the liquid and so floats on top.

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At a pressure of 1 atm, the maximum density of water actually is achieved at about 4° above the freezing point. Below that magical temperature the density begins to slightly *decrease*. If we use certain procedures to “supercool” the water, not allowing it to freeze until the temperature reaches  $-30^{\circ}\text{C}$  or even  $-35^{\circ}\text{C}$ , this tiny decrease in density can become as much as a 3% decrease before the water freezes.

### 1.2. Compressibility

A second anomalous property has not just a “10% effect” but a “100% effect”. This is the response function called the *compressibility*. The compressibility measures the *response* of this same quantity, the density  $\rho$ , to an infinitesimal pressure change.

The isothermal compressibility  $K_T$  for a normal liquid gets smaller as temperature decreases and, when water freezes, gets smaller still. The case of water is somewhat different. Although its solid phase has a low compressibility (one would not like to take a dive into a pool of solid water), its liquid phase exhibits something rather remarkable. Below  $46^{\circ}\text{C}$ , the compressibility actually *increases* on cooling.

Because compressibility is a measure of the fluctuations in the specific volume of a fluid, the physicist would expect these fluctuations to get smaller as the temperature of the water decreases. The fact that these fluctuations get *larger* as the temperature decreases is most puzzling.

This effect gets amplified in supercooled water. In fact, the compressibility continues to increase more and more rapidly as one supercools to the lowest attainable temperature until the compressibility value is almost double what it was at its minimum.

### 1.3. Spin-lattice relaxation time

A third anomalous property – one that has a “1000% effect” – is encountered when we look at a characteristic dynamic quantity such as the spin-lattice relaxation time. If we make an Arrhenius plot of that quantity (i.e., plotting the logarithm of that characteristic time on the  $y$ -axis and the inverse of the temperature in Kelvin units on the  $x$ ), water at high temperatures seems to behave like a normal fluid, – i.e., data are approximately linear. At low temperatures, however, there is an upward deviation in the plot, a deviation that becomes more and more pronounced as one lowers the temperature still further such that, at the lowest attainable supercooled temperature (typically about  $-35^{\circ}\text{C}$ ), this deviation from the extrapolation that one would have made from the high-temperature data is as much as a factor of 10, i.e., this is a “1000% effect”.

## 2. The clues

What clues exist that might explain these and other anomalies? The principal clue that has been available to us since the seminal work of Linus Pauling, *The Nature*

of the *Chemical Bond* (a masterpiece of physics insight – written by a chemist), is the fact that, in the case of water, at least 80% of the hydrogen bonds remain intact even when ice is melted. This means that liquid water is a strongly hydrogen-bonded network.

The evidence indicating why so many hydrogen-bonds remain intact is vast. It is now a widely accepted fact that water is an *associated liquid*, which simply means that the individual molecules comprising water are the opposite extreme of argon molecules. In a water molecule, each oxygen is characterized by two strongly -polarized hydrogens. These molecules have a very strong directionality and, unlike argon, are powerfully drawn into strong hydrogen-bonded networks.

All computer simulations support the idea that water is a network. In traditional simulations, we have 216 water molecules in a little box, 18 Å on each edge, and we can visualize the hydrogen bonds that are intact at room temperature. Whatever way we choose to define bonds, we still come back to the fact that it is made up of a strongly hydrogen-bonded network, not isolated molecules.

There is one sense in which water is very much like ice. The distance between nearest-neighbor molecules in liquid water is very similar to what we find in ice, and if we calculate the positions of second-neighbors in liquid water, assuming the orientation of these two molecules and the distance between them to be exactly the same as in ice, we get 4.5 Å. If we measure a histogram experimentally, counting the number of molecules a distance  $R$  from a central molecule, we find peaks of both the nearest- and second-neighbors, and, if we push our luck and the temperature is not too high, we even see a peak at the third neighbors. Thus, the hydrogen-bond network has a remarkable feature: it constrains the positions of the water molecules sufficiently that within “small neighborhoods” (seeing a locale in terms of only a few neighbors) the situation is not that different from what we find in ice.

### 3. A locally structured transient gel

Although there have been many different models used by researchers to describe the structure of liquid water, many would agree that water is a *locally structured transient gel* [6].

#### 3.1. “Locally structured”

We describe liquid water as *locally structured* because its structure – such as it is – extends out only to about 4–8 Å. Within this local structure, the entropy  $S$  is less than the global entropy  $\langle S \rangle$  of the entire network, and the specific volume  $V$  is larger than the specific volume  $\langle V \rangle$  of the entire network. Thus,  $\delta S \equiv S - \langle S \rangle$  is negative, while  $\delta V \equiv V - \langle V \rangle$  is positive.

### 3.2. “Transient gel”

We describe liquid water as a *transient gel* because, although water is a connective network, it does not behave like your average bowl of “Jello”. I can tip a glass of water and it will start to flow. If I tip a container of Jello, it will not. Unlike the bonds in Jello, the bonds in liquid water have a characteristic life that is remarkably short, on the order of a picosecond. Nevertheless, we still call water a gel because its connected network is a random system far above its percolation threshold.

## 4. Microscopic structure: local heterogeneities (“patches”)

To represent this structure dynamically and in three dimensions we need computer simulation resources and a good ability to visualize 3D. To represent it as an instantaneous picture in two dimensions, we can use a square lattice, even a chess board – with the sides of the chess board’s squares representing “bonds”, and the corners of the squares representing “sites” (molecules).

If we take our chessboard and randomly break 20% of its bonds, leaving the other 80% intact, we get a snapshot of the structure of liquid water (Fig. 1). We designate the sites with all four bonds still intact as “black” sites. These have nearest-neighbor distances almost identical to those of solid water. The areas on the grid exhibiting contiguous black sites we call “patches”. The patches have properties that differ from the global properties of the heterogeneous gel: a lower entropy and a larger specific volume. To calculate the number of black molecules – if we neglect the possibility of correlations in this bond-breaking – is fairly simple. The probability that four bonds of a given site are intact is simply the bond probability to the power four ( $f_4 = p_B^4$ ). If the bond probability is  $\approx 0.8$ , as we saw earlier, the probability that four bonds of a given site are intact is  $\approx 0.8^4$  or  $\approx 0.4$ . So about 40% of these black sites are a part of these patches.

This picture of water is sufficient to *qualitatively* rationalize experimental data. For example, this picture can explain the anomalous compressibility behavior of water – water’s compressibility minimum at 46°C (typical liquids have no minimum), and the unusually large size of water’s compressibility (twice that of typical liquids). The patches in water’s hydrogen-bonded network influence the behavior of its compressibility – the fluctuations in its specific volume – these black sites are present with a probability of  $p_B^4$ . As temperature decreases, the bond probability increases. For each 1% rise in bond probability there is a 4% rise in  $f_4$  and thus an amplification in the number of black sites. As we know from percolation theory, when the number of black sites increases, the characteristic size of a cluster or patch increases still more dramatically, providing a second amplification mechanism. The greater increase in compressibility is a result of these two amplification mechanisms. Were there no patches, the increase would not be as great. The amount of this increase goes up as we lower the temperature. If I take a function with constant slope and add this increase I end up with a function that exhibits a minimum.

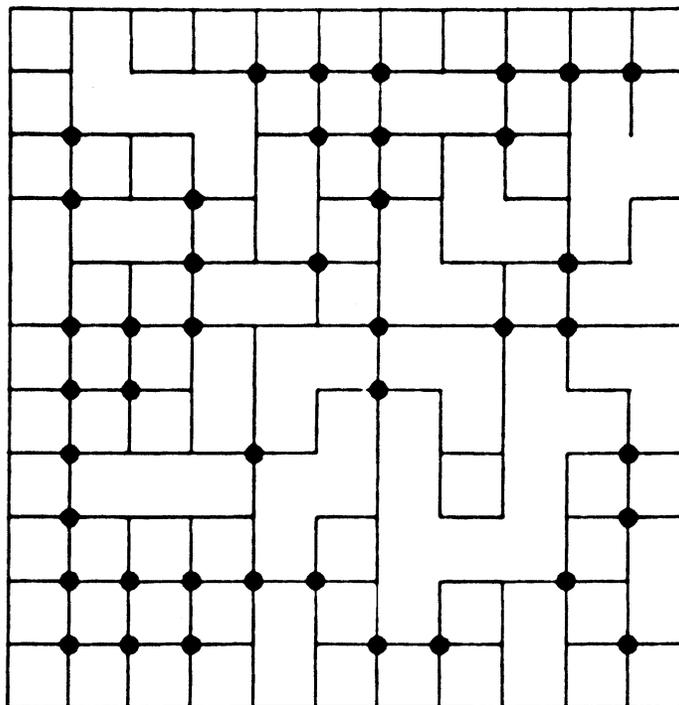


Fig. 1. A subsystem consisting of 100 oxygen atoms, situated (for convenience only) on the vertices of a square lattice. Of course, the detailed connectivity of this square lattice is different from the connectivity in water or ice. Intact hydrogen bonds – randomly present with probability 0.8 – are indicated by solid line segments. Oxygens with four intact bonds are shown as heavy black dots. The “black oxygens” form patches in the hydrogen-bonded network. The site percolation problem defined by the connectivity of these black oxygens is a correlated one; if a given oxygen  $\lambda$  is black, there is a greater probability that the neighbors of  $\lambda$  are also black.

We can use this picture of water to rationalize other anomalies, e.g., an anomaly in water’s specific heat (an anomaly we did not mention earlier). The specific heat is proportional to the fluctuations in entropy. Entropy is often imagined to be a constant quantity, one without fluctuation. But if we treat entropy as a fluctuating quantity, we have a measure of the specific heat at constant pressure – and that also increases dramatically as one lowers the temperature below 35°C, and for approximately the same reasons. As we lower the temperature, the build-up of these little patches is more and more dramatic, causing an additional contribution to the entropy fluctuation due their increasing presence. The anomalous behavior of its specific heat is not just the increase at low temperatures, but also the fact that the average value of its specific heat is larger than one would expect if these patches were not present (water is industrially important because of its high specific heat).

But perhaps the most dramatic of these anomalies – the one students first learn about – is the 4°C anomaly in the coefficient of thermal expansion, the response of the volume to infinitesimal changes in temperature. This coefficient of thermal expansion is anomalous not only because it becomes negative below 4°C, but because it is 2–3 times smaller – even at high temperatures – than it would be in a typical fluid. How can this be understood in terms of these patches?

In Landau and Lifschitz's *Statistical Physics*, a formula is provided (that apparently is not widely appreciated) that tells us that this macroscopic thermodynamic response function is also related to a microscopic correlation function given by the product of the deviation of the specific volume from its average multiplied by the deviation of the specific entropy from its average.

Let us think about this intuitively. What would happen to the entropy of my office if my department chair decided to give me a room twice as big? (I am not expecting this to happen!) It is painfully obvious that the entropy would dramatically increase, because there would be even more ways of arranging all my junk in that bigger office. Similarly, when there is a fluctuation in a little region of a gas that is positive (i.e., when it is given a larger volume), there is a larger entropy associated with it. So the entropy-volume correlation function is positive, and that is how we understand from a microscopic point of view why it is that this coefficient of thermal expansion is a positive quantity for a typical liquid. But how can we possibly understand the behavior of water?

To understand it, we must take into account the fact that, when we lower the temperature, the number and size of the structured patches increase. These structured little regions have as a property that their entropy is smaller than the average (a negative quantity) and their specific volume is larger than the average (a positive quantity). Multiplying the negative quantity by the positive, we get a negative contribution from this macroscopic thermodynamic response function. As we lower the temperature, and the patches become more numerous, the magnitude of this negative response function gets bigger and bigger, and it just happens to pass through zero at a temperature of 4°C.

This is qualitative, but we can test for the existence of these patches in various ways. One way is experimentally. We can not actually see them, but by beaming X-rays into supercooled water (-25°C), Bosio and Teixeira [7] observe a characteristic Ornstein–Zernike Lorentzian, indicating a build-up in correlated regions with a characteristic size proportional to the inverse of the width of that Lorentzian. The characteristic size measured using this experimental technique turns out to be a diameter of  $\approx 8 \text{ \AA}$ , i.e., three atomic spacings; recent data [8] suggests this number may be even smaller (at least at atmospheric pressure).

Another approach to testing this picture is to dilute our water sample with some other liquid. To do that, we go into that wonderfully ordered hydrogen-bonded network with its little patches and replace 10% of the water molecules with something that does *not* form four hydrogen bonds at tetrahedral angles. If that 10% replacement is hydrogen peroxide, the anomalies almost disappear [9]! Evidently the patches are broken up by the impurity.

A particularly simple but striking example is the dependence of the adiabatic sound velocity  $v_s \propto K_S^{-1/2}$  upon the mole fraction  $x$  of ethanol. Although  $v_s$  for pure ethanol ( $x = 1$ ) is much smaller than  $v_s$  for pure water ( $x = 0$ ), one finds a substantial *increase* in  $v_s$  as ethanol is added to pure water. We would interpret this finding as follows: ethanol is “breaking up” the patches, and thereby reducing the compressibility. When

$v_s$  is plotted against  $x$  for a range of temperature from 5°C to 45°C, one finds that all the isotherms intersect at a single “isosbestic point” with  $x = 0.17$  and  $v_s = 1.6$  km/s [10,11]. Thus at 17% ethanol, increasing  $T$  from 5°C to 45°C serves to decrease the fluctuations due to the patches, but this is precisely compensated for by an increase in the fluctuations of the normal regions of the network. It would be desirable to extend these observations to a wider range of temperature and pressure, to other impurities, and to properties other than  $v_s$ . It is my opinion that careful study of judiciously-chosen two-component systems will serve to provide useful clues relevant to the “puzzle of liquid water”.

To summarize thus far, when looking at the bond connectivity problem, water appears as 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”. Similar physical reasoning applies if we generalize the concept of 4-bonded molecules to molecules with a smaller than average energy [12] or to molecules with a larger than average “local structure” [13].

## 5. “Second critical point” hypothesis

An ordinary critical point has a remarkable property: above an ordinary critical point a fluid becomes a “permanent gas”, i.e., liquid is not present, only a homogeneous isotropic fluid that was originally called a permanent gas because no one had succeeded in cooling such gases to a temperature below the critical point [14]. Now we know that if we sufficiently lower the temperature, we discover a critical point in virtually every fluid system. The reason is that at sufficiently low temperatures it becomes possible to condense out of this gas a new phase – called a “liquid phase”.

Water’s critical point is 647 K (374°C); below that temperature we have two phases: the liquid phase at high pressure and the gaseous phase at low pressure. A line of first-order transition separates these phases with a positive slope. Why positive? Because according to the Clapeyron relation the slope of the phase transition line is the ratio of the change in entropy to the change in volume. The liquid that condenses out of the gas has a smaller entropy, so  $\Delta S$  is negative, and a smaller specific volume, so  $\Delta V$  is negative – the ratio of those two negatives is positive, and hence the positive slope.

Already in 1979, it should have occurred to us – but did not – that, if the temperature is sufficiently low, those patches in liquid water “condense out” as a second phase of liquid water. Below this new critical point, a new phase of liquid water called *low-density liquid water* (LDL) is separated out. The liquid left behind is called *high-density liquid water* (HDL). This low-density liquid water, obtained at sufficiently low temperatures, has a lower entropy and a greater specific volume. The slope of this

first-order line separating the two phases, by the Clapeyron relation, is a negative divided by a positive and is thus negative.

Using both experiment and simulation, we have been testing the possibility of whether this second critical point in fact exists. Whether it does exist or not is important because any critical point is not simply a “point.” It is a *singular* point and it affects a huge *critical region*. For the first critical point, this critical region is so huge that it extends as much as a factor of 2 in temperature above the critical point (in which region there are already significant deviations from what would be the case if there were no critical point). In the case of the second critical point, should it actually exist, its influence in its critical region would affect all the well-known anomalies associated with liquid water, e.g., the density with its anomaly at 4°C, the compressibility with its anomaly at 46°C, or the constant-pressure specific heat with its anomaly at 35°C.

To get a critical point, fluctuations are generally correlated. Why are those little patches correlated? Using a simple ball-and-stick model of two water molecules with a probability  $p$  that a bond is occupied, we notice that if we take two four-bonded water molecules, each with a probability of  $p^4$ , and place them next door to each other, the probability of the dimer is not  $(p^4)^2$ . This is because although the probability for occurrence of the first molecule is  $p^4$ , the probability for the second is only  $p^3$ . And, because  $p < 1$ ,  $p^4 \times p^3$  is a number *bigger* than  $p^4 \times p^4$ . The probability of two of these four-bonded water molecules being next to each other is thus enhanced by a factor  $p^{-1}$  ( $p = 0.8$ ). Although this is a relatively weak correlation, it may be significant, because even weak correlations are magnified if the temperature is low enough.

## 6. Experimental tests

### 6.1. 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 [15]. By careful analysis of experimental data above  $T_H(P)$ , Speedy and Angell [16–18] pioneered the view that some sort of singular behavior is occurring in water at a temperature  $T_s(P)$  some 5–10° 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 singularities [5] or a critical point) will influence the equation of state in a large neighborhood.

### 6.2. Previous work

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 pair correlation function and structure factor  $S(Q)$  [19]. For experimental paths, they

choose a family of isobars ranging from 0.1 MPa up to 600 MPa (well above the critical point pressure of about 100 MPa). They plot the temperature dependence of the first peak position  $Q_o$  of  $S(Q)$  for each isobar. They find that for the 0.1 MPa isobar,  $Q_o$  approaches  $1.7 \text{ \AA}^{-1}$  – the value for LDA, low-density amorphous ice. In contrast, for the 465 and 600 MPa isobars,  $Q_o$  approaches a 30% larger value,  $2.2 \text{ \AA}^{-1}$  – the value for HDA, high-density amorphous ice. For the 260 MPa isobar,  $Q_o \rightarrow 2.0 \text{ \AA}^{-1}$ , as if the sample were a two-phase mixture of HDA and LDA.

Since the critical point occurs below  $T_H(P)$ , it is not possible to probe the two phases experimentally. However, two analogous solid amorphous phases of  $\text{H}_2\text{O}$  have been studied extensively by Mishima and co-workers [20]. In particular, Mishima has recently succeeded in converting the LDA phase to the HDA phase by 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. 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 independently corroborated by computer simulations performed using both the ST2 and TIP4P intermolecular potentials [21].

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.

### 6.3. Recent work

We discuss now the very recent measurements 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.

When liquid water is supercooled below the homogeneous nucleation temperature,  $T_H$ , 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,  $T_X$ . Therefore, amorphous forms of  $\text{H}_2\text{O}$  do not exist in the “no-man’s land” between  $T_H$  and  $T_X$  (Fig. 2).

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 [22]. 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  $\mu\text{m}$  ice particles in oil [23]).

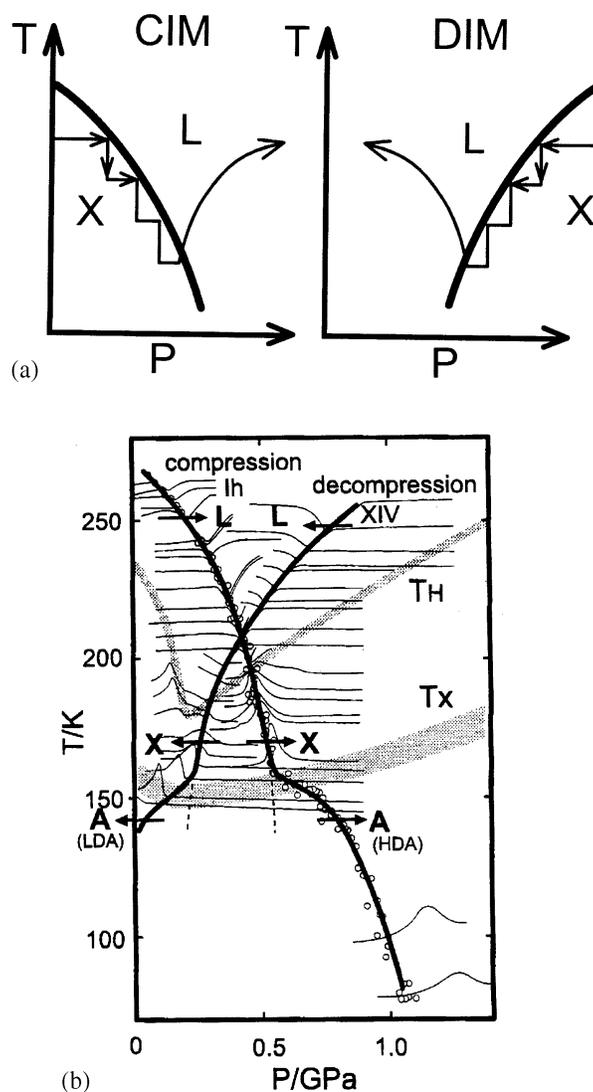


Fig. 2. (a) The endothermic temperature response of the sample during CIM (compression-induced melting) and DIM (decompression-induced melting). During both CIM and DIM, the crystal  $X$  is forced to melt by the pressure, which reduces the sample temperature because the melt absorbs the latent heat quasi-adiabatically. The cooled sample melts by further compression (or decompression). The schematic shows this endothermic temperature response to a sequence of four infinitesimal pressure increments during CIM (and a corresponding temperature response to a sequence of four infinitesimal pressure decrements during DIM). After the entire sample is transformed, the temperature returns to the cylinder temperature. (b) The compression-induced transition of ice  $I_h$  and the decompression-induced transition of ice PNP-XIV.

Mishima creates  $1 \text{ cm}^3$  emulsified high-pressure ices in a piston-cylinder apparatus, decompresses the sample at a constant rate of  $0.2 \text{ GPa/min}$ , 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 (Fig. 2a). The melting curves he obtains agree with previously reported data [24,25], which confirms the accuracy of this method. Moreover, he can determine the location of metastable melting lines to

much lower temperatures. Unexpectedly, he finds what appear to be two possible new phases (PNP) of solid H<sub>2</sub>O, denoted PNP-XIII and PNP-XIV.

Using the measured melting lines of ice phases at low temperatures (Fig. 3), we calculate the Gibbs energy, and the equation of state [26] (Fig. 4). The P–V–T relation (Fig. 5) 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 [20,26–36]

One somewhat speculative argument arises from a recent interpretation of the work of Lang and Lüdemann, who made a series of careful NMR measurements of the spin-lattice relaxation time  $T_1$  [37–40]. Fig. 5 shows the pressure dependence of  $T_1$  for a family of isotherms. Shown as solid lines are the Lang-Lüdemann data and as dashed lines one possible *extrapolation* of their data into the experimentally inaccessible region (below the homogeneous nucleation boundary) which is consistent with, but of course by no means proves, the hypothesized second critical point. This extrapolation is made by eye, not by formula. The extrapolated inflection corresponds to occurrence of a singularity or critical point. This occurs at roughly the same coordinates as found in the experiments reported in Ref. [26] – possibly a coincidence, but the estimated coordinates of  $C'$ , 220 K and 100 MPa, are the same as those obtained by analysis of the metastable melting lines.

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Fig. 3. (a) Schematic Gibbs potential of liquid water relative to that of ice I<sub>h</sub>,  $\Delta G_L \equiv G_L - G_{I_h}$ . The intersection line of  $\Delta G_L$  and the basal plane defines the melting line of ice I<sub>h</sub>. (b) Gibbs potential of a typical high-pressure ice relative to that of ice I<sub>h</sub>,  $\Delta G_{HP} \equiv G_{HP} - G_{I_h}$ . (c) The melting line for the high-pressure ice, defined by the intersection between the Gibbs potential surface of the liquid and that of the high-pressure ice. We obtain numerically the  $\Delta G_{HP}$  along the melting line which must equal  $\Delta G_L$  along the melting line. (d) Schematic construction of the  $\Delta G_L$  surface (the dark region) by smooth graphical interpolation between the  $\Delta G_L$  potentials along the melting lines for different ices (the thick solid lines). Each of the nearly vertical thick solid lines is a melting line. The horizontal line is the melting line of Ice I<sub>h</sub> where the  $\Delta G_L$  is zero (a). These lines define a surface (the  $\Delta G_L$  surface). Once we know the  $\Delta G_L$  surface, we calculate the  $\Delta G_{HP}$  plane for PNP-XIII and PNP-XIV, following the reverse procedure using the melting lines of PNP ice. We also estimate, and show by the thick dashed lines, the  $\Delta G_L$  potentials along the melting lines of PNP ices on these  $\Delta G_{HP}$  planes.

Fig. 4. Application of data obtained in Mishima's experiment to reconstruct the Gibbs potential surface and the thermodynamics equation of state  $V = V(P, T)$ . (a) The  $\Delta G_L(P, T)$  surface in the 80–270 K and 0–0.5 GPa region with constant- $P$  and constant- $T$  lines at 50 MPa and 10 K intervals, as evaluated from experimental data. (b) Plausible qualitative equation of state  $V(P, T)$  of liquid water. The specific volumes of the amorphous phases are known for the region below  $T_X$  [6]. 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; we emphasize that the data cannot locate the coordinates of the critical point with high accuracy due to the possibility that the phase transition line might have a “hook” in it. These two liquid phases are continuous with the two amorphous phases that are known to exist below about 150 K. Note that this phase transition surface differs from that of a typical liquid only in the presence of this critical point – which in turn arises because below the line of density maxima the fluctuations in specific volume and in entropy are anticorrelated by definition.

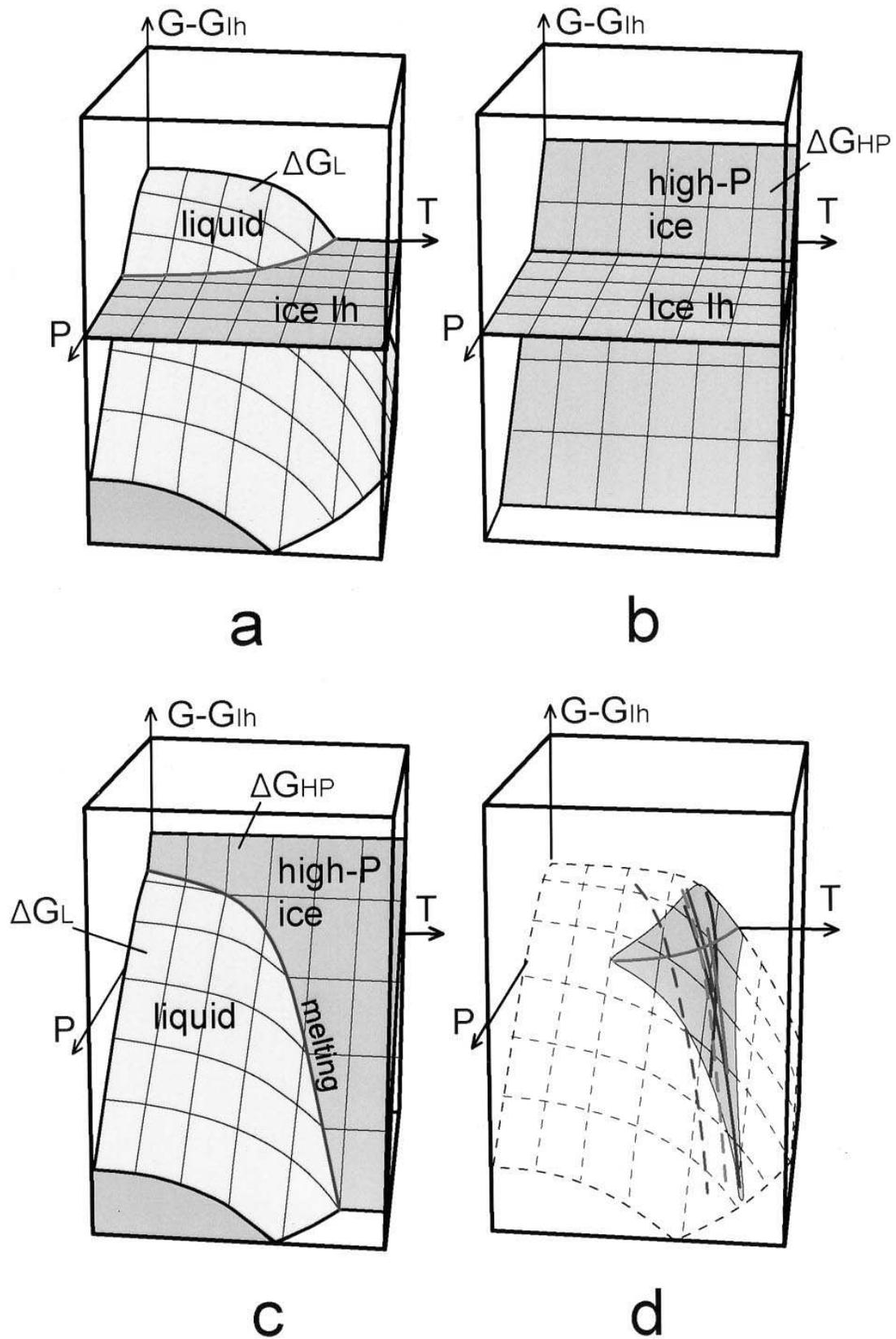


Fig. 3.

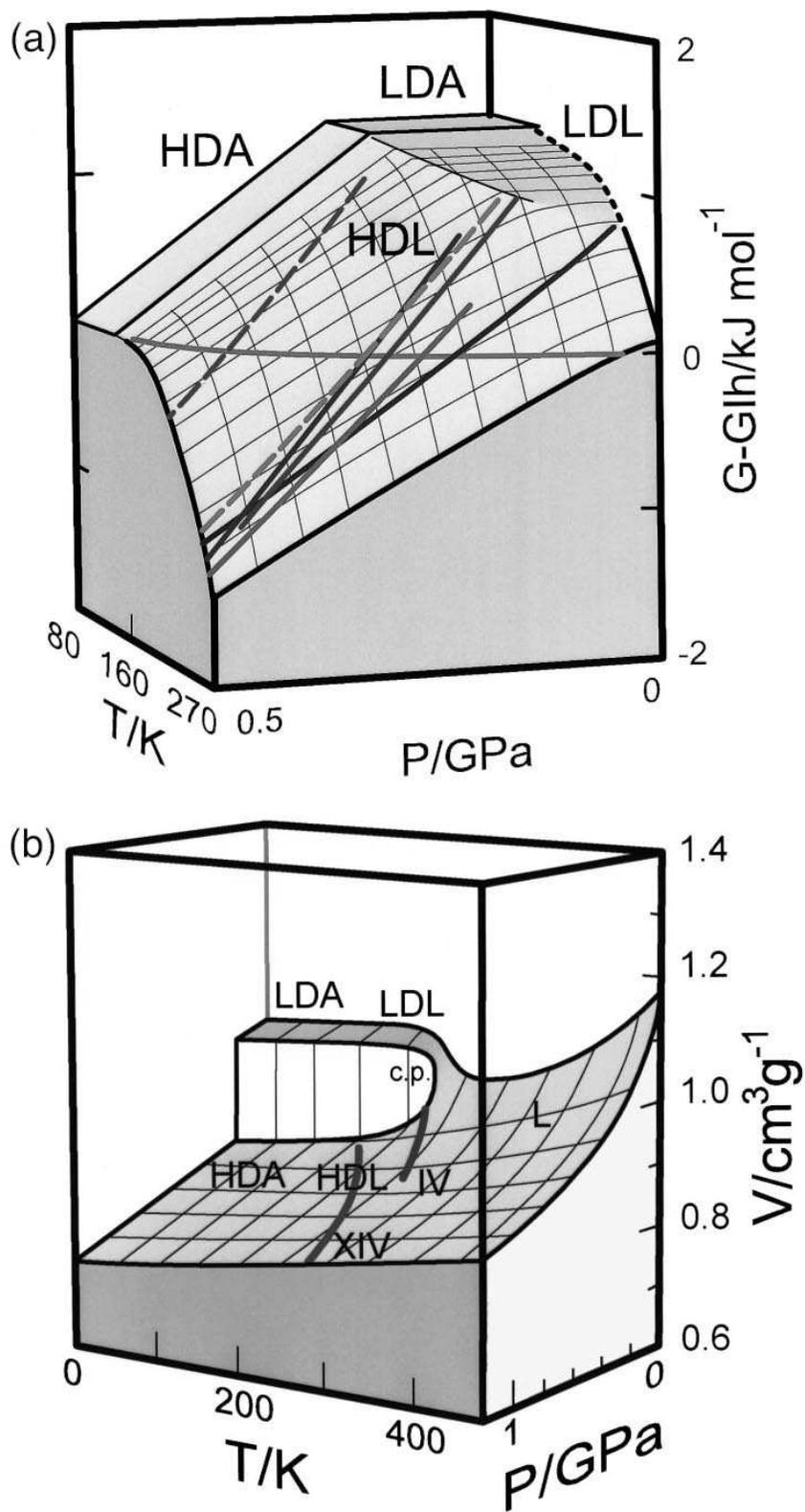


Fig. 4.

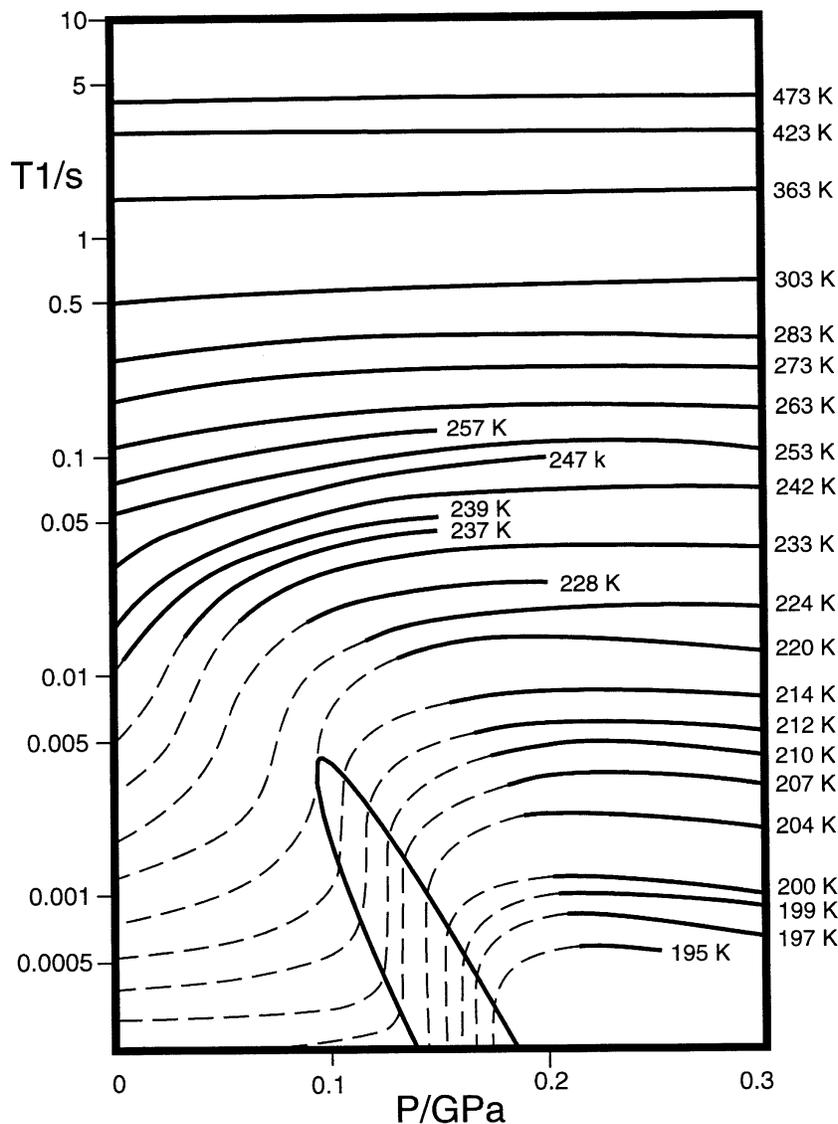


Fig. 5. Pressure dependence of  $T_1$  for a family of isotherms ranging from 473 K down to 195 K, taken from Fig. 1 and Table 1 of Ref. [37]. Lang and Lüdemann noted that for the low-temperature isotherms,  $T_1$  increases with pressure, unlike the behavior in ammonia and hydrogen sulfide. Shown as solid lines are the Lang–Lüdemann data and as dashed lines a possible extrapolation of their data into the experimentally-inaccessible region (below the homogeneous nucleation boundary) which is consistent with, but of course by no means proves, the existence of the hypothesized second critical point.

## 7. Simulation tests

Simulation studies of liquid water have a rich history and have contributed greatly to our understanding of the subject. Corresponding to the rather “cumbersome” nature of most intermolecular potentials in use the fact that most studies are limited to extremely small systems – a typical number being  $N = 6^3 = 216$  water-like particles. Recently studies are beginning to treat larger systems, but the typical size rarely exceeds  $N = 40^3 = 64\,000$  [41].

Despite the rather crude nature of the intermolecular potentials in use, one can still hope to at least in some sense “bound” certain features of the behavior of water by carrying out simulations not for one assumed intermolecular potential but rather for two, and choosing one of the potentials to, say, “overstructure” the liquid and the other potential to “understructure” the liquid. For example, Harrington and collaborators carried out two parallel tests for the existence of a critical point, one using the ST2 potential [42] and the other using the SPC/E potential [43]. Tanaka and Poole et al, have both made extensive use of the TIP4P potential [44,45].

We recently summarized the simulation evidence relevant to the question of whether or not a second critical point exists [46], and concluded that simulations from a number of different research groups, using a number of different potentials, are consistent with (or at least not contradicting) the hypothesis that a HDL–LDL critical point  $C'$  exists. Some very recent simulation results are also consistent with this possible phase transition. For example, Tanaka has studied the fluctuation of local order and connectivity of water molecular and found that the magnitude of the fluctuation differs significantly between two different apparent phases (the low-density and the high-density phase) [47].

In addition to simulations, there has been considerable recent progress in making models of liquid water and then solving them under suitable approximation [48–54]. This work has met with some striking recent successes – such as the possibility of generating more than one scenario of behavior as a suitable parameter in the model is varied [48]. We note that, with some exceptions, some of the work can be criticized for being “mean field” in spirit (i.e., not treating fluctuations fully) [55].

## 8. Discussion

The most natural response to the concept of a second critical point in a liquid is bafflement that 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 [56]. 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 re-visited such potentials with a view toward applications to water [57]. 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 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.

An advantage of such “core-softened” potentials is that they can be solved analytically in one dimension [58] and are tractable to study using approximation procedures (and simulations) in higher dimensions [57].

To complete the intuitive picture, 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 it 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 present, 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 system could approach different phases as the temperature is lowered.

A clear physical picture has by no means emerged. However recent work of Canpolat and collaborators has asked the question if we can characterize the local structural heterogeneities that appear in liquid water. Glaser and Clark have recently investigated a liquid under conditions not far from the freezing line [59]. Using molecular dynamics (MD) simulation of the WCA potential, they find local structural heterogeneities – with a typical diameter of a few atoms – in which the *local* order is not unlike the local order of the solid phase. This idea can be further tested by considering water, which has more than one crystalline phase for which, by tuning a parameter (the pressure), a liquid state point can move from near the freezing line of one phase (ice  $I_h$ ) to near the freezing line of another phase (ice VI). In such a case, the work of Glaser and Clark may lead one to hypothesize that the local structure of the liquid changes drastically from resembling one phase to resembling an altogether different phase.

Specifically, Canpolat and collaborators [60] considered different state points of liquid water near its phase boundaries with ice  $I_h$  and with ice VI (a high-pressure polymorph of solid  $H_2O$ ). To this end, in the spirit of the Walrafen pentamer, they develop a model of interacting water pentamers, and find a local energy minimum which we identify with a well-defined configuration 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., [61]). 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 this configuration may be related to local “high-density” structural heterogeneities occurring in liquid water when subjected to high pressure. Their 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 simplified picture may seem to be oversimplified, recent work of Bellissent-Funel [62] successfully fits detailed neutron structure data to just such a picture. The simulation results are in good accord with neutron results (see, e.g., [41]), so we are optimistic that soon a unified coherent picture will emerge via careful combination of reliable results.

Many open questions remain, and many experimental results are of potential relevance to the task of answering these questions. Among these are the tantalizing

questions concerning the dynamics, where the functional form of the various characteristic times is not clarified either experimentally or theoretically. It was proposed that the apparent singular temperature of liquid water might be identified with the MCT temperature of structural arrest [63,64]. Recent results [63,65] support with this possibility, and complement the scenarios discussed above.

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  $\text{SiO}_2$  and  $\text{GeO}_2$ , 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 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  $\text{SiO}_2$  [66] and a two-level model has been developed for amorphous GaSb [67]. Understanding one such material, water, may help in understanding others – whether they be other materials with tetrahedral structures (and corresponding TMD lines) such as  $\text{SiO}_2$  or whether they be more complex structures like amorphous GaSb which appears to display strikingly ordered local heterogeneities as it is heated toward its crystallization temperature.

We conclude with a final caveat, emphasized by Debenedetti in his recent *News & Views* article [68]. It is not possible to distinguish a sharp phase transition between two well-defined phases (differing in density) from a smeared “apparent” phase transition. In principle, there is no *a priori* way to distinguish a function with a sharp discontinuous “step” from a continuous function with a sharp but still continuous behavior that looks like a step since there exist error bars on experimental data, and since the number of data points is finite, not infinite. Example of such a function is  $y = \tanh 100x$  which appears to jump discontinuously from  $-1$  for negative  $x$  to  $+1$  for positive  $x$ , yet in fact is a continuous function. Hence, we cannot rule out the scenario originally envisioned in the percolation model [6] that the system has no genuine singularity at

all. This “singularity-free scenario” has been examined critically in recent work by Sastry and collaborators [69,70]. Possibly studying the effect on water of salt dilution or confinement will help resolve some of these issues [71,72].

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