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The puzzle of liquid water: a very complex fluid

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Abstract

Although H₂O has been the topic of considerable research since the beginning of the century, its 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 (below which two fluid phases — a lower-density gas and a higher-density liquid — coexist), there exists a “second” critical point at low temperatures (below which two liquid phases — a higher-density liquid and a lower-density liquid — can coexist). ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

First, let me thank the organizers for having invited me here to discuss recent hypotheses concerning a very complex and highly unpredictable system — liquid water. Liquid water is at first sight not a “complex fluid” and hence would seem to have no place at this conference! However, understanding its highly anomalous equilibrium and dynamical properties is generally connected to the view that water, even above its melting temperature, is a transient gel with structural heterogeneities of very short length scales. Moreover, understanding the properties of water is important for understanding phenomena in ‘aqueous solutions’, such as understanding the structure of micelles and microemulsions. For these and other reasons, water is generally included under the rubric of complex fluids.

Although water has been the topic of considerable research since the beginning of the century, its peculiar properties are still not completely understood [1–3]. Standard liquid theories fail to explain its dynamical and thermodynamic properties, which differ from those of most other liquids [4–7]. Although the anomalous properties of water are not understood, many workers believe that a central role is played by the possibility for the water molecule to form hydrogen bonds and to create a tetrahedrally coordinated open network in both the solid and the liquid phases [8–23].

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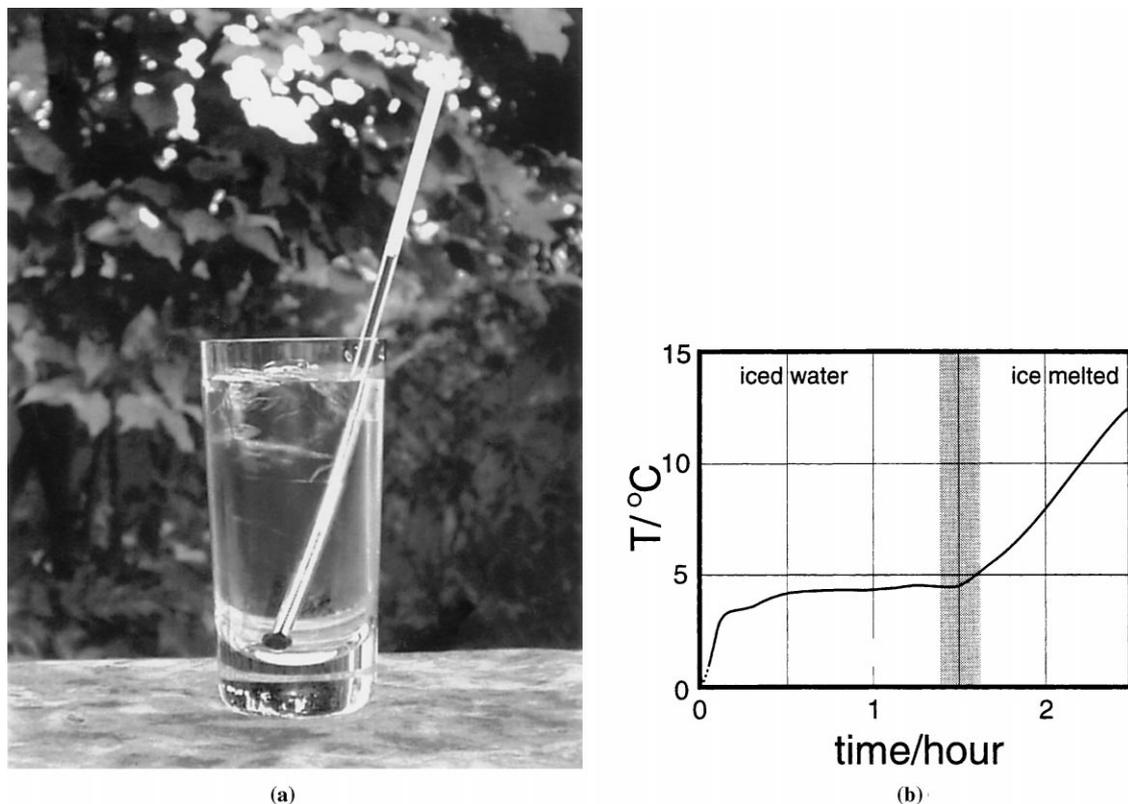


Fig. 1. A glass of iced water with a thermometer reading 4°C at the bottom of the glass. Also shown is the time dependence of the temperature as the ice cubes begin to melt, showing that the temperature remains at 4°C until all the ice cubes are melted. Photograph courtesy of K. Mishima.

2. What is the puzzle of liquid water?

Take a typical solid, and measure its density as you heat it. When the solid melts at the melting temperature there will be a drop in the density because the density is the first derivative of the Gibbs potential, and the melting is a first-order phase transition. This, of course, does not happen if the substance is water. If we take an ordinary ice cube and heat it to its melting temperature, its density ρ jumps up by about 8–9%, not down — and as we continue to heat it, ρ continues to go up. It seems to contradict our fundamental intuitions concerning condensed matter physics. Of course ρ does not go up for long. Above approximately 4°C , ρ starts to drop and water begins to behave more like a “normal” fluid. A kitchen experiment (Fig. 1) demonstrates that the bottom layer of a glass of unstirred iced water remains at 4°C while colder layers “float” on top.

We can study water both in its *stable* regime above the melting temperature and in its *metastable* regime below the melting temperature. If we go down into water’s metastable regime (down to perhaps -37 or -38°C), we see that the density curve continues smoothly down from the density maximum at 4°C . (Roughly speaking, the behavior of ρ in the metastable region is just an extrapolation of polynomial fit to the stable region.) This is no small effect: in the metastable regime the density drops to 97% of its maximum.

Another puzzling feature of liquid water has to do with its compressibility. Compressibility is a response function — the response of the density to an infinitesimal change in pressure. In a typical liquid, as we lower the temperature the compressibility decreases. If the liquid becomes solid, the compressibility is radically decreased. This does not

happen in water. If you lower the temperature of water, the compressibility decreases — but only to 46° C. Below the temperature the compressibility actually increases until it reaches the freezing point, when it drops.

Once again, the phenomena in the supercooled region are an extension of the phenomenon we know in the normal region. On cooling below 46° C, the compressibility increases and, when it reaches the supercooled region, starts to increase very rapidly until, at its lowest temperature, it is approximately double what it was at its 46° C minimum — a 100% effect.

A even stronger effect is seen when we consider the relaxation time using a typical Arrhenius plot. We put the log of the relaxation time on the y -axis and the inverse of the temperature (in Kelvin) on the x -axis. At high temperatures, water acts in a perfectly normal way — roughly a straight line. Below approximately body temperature there is an upward curvature that becomes increasingly pronounced and, the lowest temperatures, the relaxation has increased by approximately a factor of 10, or 1000%.

3. The puzzle of liquid water: clues

There are clues available to us in addressing the puzzle of liquid water. The first was emphasized by Linus Pauling in his book, i.e., “Water is a strongly hydrogen-bonded network”. Suppose we could submerge ourselves in water in a submarine even more remarkable than the Alvin, one that would allow us to observe the water with Angstrom vision and with time slowed so that we could observe the water structure not with the “30 frames per second” capability of the normal eye, but with a time-resolution of 10^{12} frames per second. What would we see? We would see regions of the water in which there are bonds and regions in which there are no bonds, and these would change identification from one frame to the next. We would see that many of the molecules are characterized by having four intact hydrogen bonds, others by having three, others by having two, and perhaps even some that have only one or zero.

If we could add to our Angstrom vision and picosecond time resolution the ability to measure the exact position of these molecules, we would be able to calculate the local specific volume in the regions where we find these bonded “patches”. If we calculate the local specific volume using a computer model of water, we find the local specific volume in these well-bonded regions to be larger than the global specific volume. This is not surprising because we know that in ice the local volume is 10% larger than in liquid water, and if we do not break local bonds in our computer model of water there is no reason to believe the local specific volume in these unbroken regions will be any less than that in ice.

We can also ask about the entropy in these local unbroken regions, and we assume that since they are still structured they will have a lower entropy. Thus these local patches have a specific volume that is larger than the global specific volume and a local entropy that is lower than the global entropy. That means that the fluctuations that occur in every liquid that we see from our remarkable version of submarine Alvin are *anticorrelated*: regions that we encounter that have a larger specific volume than the global will also have an entropy that is smaller than the global.

For someone who works in statistical mechanics, this anticorrelation is extremely nonintuitive. In elementary statistical mechanics of gases, an increase in volume means an increase in entropy. In my personal experience, a larger office invariably means a great increase in entropy. Why does this experience not seem to apply to liquid water in this temperature range? Why does the entropy decrease? Why is the decrease important?

Qualitatively, this picture helps explain the puzzles we mentioned. For example, the compressibility is proportional to a statistical mechanical quantity, the fluctuations in specific volume, $(\Delta V)^2$. If the fluctuations in specific volume of a typical liquid decrease as it is cooled, the compressibility should also decrease. But if we superpose these connected patches on the properties of a normal liquid and increase their number as the liquid is cooled, they give rise to a positive contribution to the density fluctuations. If we lower the temperature further, we increase further

the number of patches. This happens because for each 1% increase in fraction of intact bonds there will be a 4% increase in the number of water molecules that have four intact bonds — contributing significantly to the density fluctuations.

Then there is the part of puzzle associated with the specific heat of constant pressure, c_P , which is important for many reasons — including the utility of water as a coolant. In a normal liquid the value decreases with temperature. In water it is typically double that of a normal liquid (making water useful in engineering), and below 35° C, c_P actually starts to increase — roughly by a factor of two at the lowest temperature range. This is understandable because the specific heat, in addition to being a response function, is also proportional to a statistical mechanical property: the fluctuations in specific entropy. Just the fluctuations in specific volume increase as we lower the temperature, so also the fluctuations in specific entropy increase.

But the most dramatic of properties is the coefficient of thermal expansion, α_P , which is the response of the volume to the temperature. For a typical liquid, α_P is always positive and fairly large, which we can understand because α_P is proportional to the average of the fluctuations $\Delta V \Delta S$ and a larger office has more arrangements so the fluctuations are positively correlated. For water, α_P is smaller than expected for all temperature and decreases as one lowers the temperature, passing below zero at 4° C and below that temperature decreasing very strongly. Inside the patches, the fluctuations in specific volume and specific entropy are anticorrelated and therefore $\Delta V \Delta S$ must always be negative. So we are adding a negative quantity, due to the patches, to an otherwise positive quantity. At low enough temperature, the patches win out and $\alpha_P < 0$.

This is qualitative picture that can be confirmed by simulations and also by small-angle X-ray scattering. But the picture remains qualitative, and the simulations and the scattering experiments also do not tell us why at very low temperatures many quantities, when plotted on the y -axis of a log–log plot versus the log of the temperature minus 228 K on the x -axis, over roughly a decade are very often straight lines, with roughly the same slope. It does not seem to matter which quantity we study. This hints at some kind of critical behavior, with an amazing critical temperature of approximately 228 K or $\approx -45^\circ$ C. This $\approx -45^\circ$ C is lower than the lowest temperature we have been able to achieve in metastable water (about 235 K). This 7 K difference means that one is always 7 parts in 228 or 3% away from the apparent singularity — not impressive by critical phenomena standards, and so this linearity, even though it has been known for some time [5], has been largely ignored by people in the critical phenomena field.

4. The puzzle of liquid water: one hypothesis

Since the time of Andrews in 1869 [24] we have known that a fluid above its critical point is one continuous fluid. There is no difference between liquid and gas; the difference only appears below the critical point, as the cooling fluid crosses the line of first-order transitions, which has a positive slope because the high-pressure phase has a smaller volume *and* a smaller entropy. Lately, there has been some interest in the hypothesis that in addition to the critical point C , there is a second critical point C' [25–32]. Above this hypothesized *second* critical point C' , there is one continuous phase. If we go below C' , there are two distinct phase: (i) a higher-density phase and (ii) a lower-density phase. The lower-density phase corresponds to the condensation of those well-defined little patches or fluctuations, and we know that those fluctuations have a larger specific volume and a smaller specific entropy than the average. If specific volume is positive and specific entropy is negative, then the slope of the first-order transition line must be negative.

This is the picture we get from computer simulations. The problem is that the picture is from computer simulations. It does not necessarily represent real water.

When we begin to work experimentally, we discover a new barrier: the homogeneous nucleation temperature T_H . As the name suggests, when we take a liquid to this line, it nucleates. There is no way to have the liquid cross that

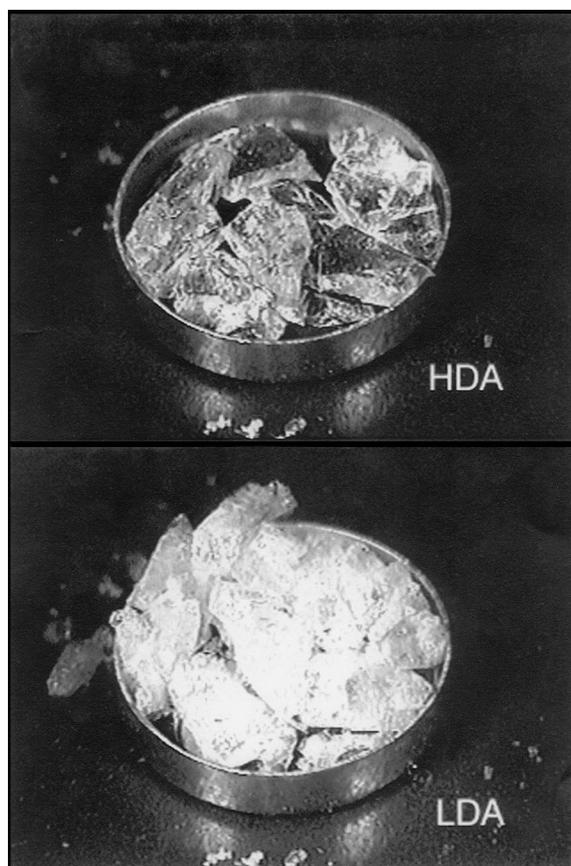


Fig. 2. HDA is readily made at pressures higher than about 200 MPa, and LDA at pressures lower than that amount. The pressure hysteresis becomes larger at lower temperatures. In fact, when the pressure of HDA is decreased at 77 K, HDA does not transform to LDA and can exist at 1 bar, but when subsequently heated to about 120 K at 1 bar, HDA transforms abruptly to LDA. Shown is a photo of this “explosively-quick” transition from HDA to LDA about 125 K during warming-up at 1 bar. Top: just before the HDA→LDA transition. Bottom: just after the transition.

line smoothly. If the second critical point is on the other side of that barrier, why should we care about it? If we cannot have the liquid there, why care at all? The answer is that this second critical point is crucial in understanding the anomalies of liquid water. If that second critical point is there, it influences the equation of state for a huge region in its vicinity — just as the presence of Mount Everest influences the landscape for miles around.

There are four categories of experiment that may be relevant to the liquid–liquid phase transition hypothesis:

1. Mishima et al. [33–35] some years ago discovered that if you take ice cubes from the ice box and subject them to a huge pressure (≈ 10 kbar) they do not simply turn into crushed ice crystals. Instead they form a unique amorphous phase called *high-density amorphous ice*. More recently, Mishima [36] has shown that when the pressure is released and the temperature changed appropriately, high-density amorphous ice changes into low-density amorphous ice, and that there is a line of first-order phase transition separating these two forms of ice (Fig. 2). If amorphous ice is simply “structurally-arrested” water then, corresponding to the amorphous ice high-density and low-density phases, there could be on the liquid water free energy surface a high-density and low-density liquid.
2. There are more precise experiments. If everything is on one smooth potential surface, it should be possible to analytically continue the measurements of high-density amorphous ice until they connect with mea-

measurements of the low-density amorphous ice, and recent unpublished data of Smith and Kay support the possibility.

3. In another approach, neutrons are used to measure the structure of liquid water along horizontal paths, i.e., the pressure is fixed and the temperature decreased [37,38]. Well above the critical point, the structure should approach that of high-density amorphous ice. Well below the critical point, the structure should approach that of low-density amorphous ice.
4. Very recently, Mishima devised an experiment that is simple, elegant, and much less expensive than neutrons [39–41]. A canister is filled with a solid and a gradually increasing pressure is applied until the solid melts. One measurement is taken: temperature as a function of pressure. When melting occurs, there is always a drop in temperature, corresponding to the latent heat. A typical scan will drop and rise each time there is a phase transition. If the melting line drops with pressure then compression-induced melting is taking place. If the melting line rises with pressure then decompression-induced melting is taking place. The melting lines $T_M(P)$ of the various high-pressure amorphous ices are thus mapped (Fig. 3). The goal is to measure these lines in the no-man's land below the homogeneous nucleation temperature. Mishima's experiment does this for the first time.

What is the outcome? The goal is to discover the equation of state, which is volume as a function of pressure, and one gets volume by differentiation if one knows the Gibbs potential as a function of temperature and pressure (Fig. 3). The Gibbs potential of the liquid is not known below that homogeneous nucleation curve (the liquid does not exist in that region). But using the device of melting — for a fraction of a second, using pressure — the high-pressure amorphous ices and recording where that melting line is, we can map the “family” of melting lines on the Gibbs potential of liquid surface, and from that family of melting lines we can obtain by differentiation the equation of state.

5. 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 [42–45]. 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 [46] have re-visited such potentials with a view toward applications to water. 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 “nonhydrogen-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 double-well potentials is that they can be solved analytically in one-dimension [47,48] and are tractable to study using approximation procedures (and simulations) in higher dimensions [46].

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 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 system could approach different phases as the temperature is lowered.

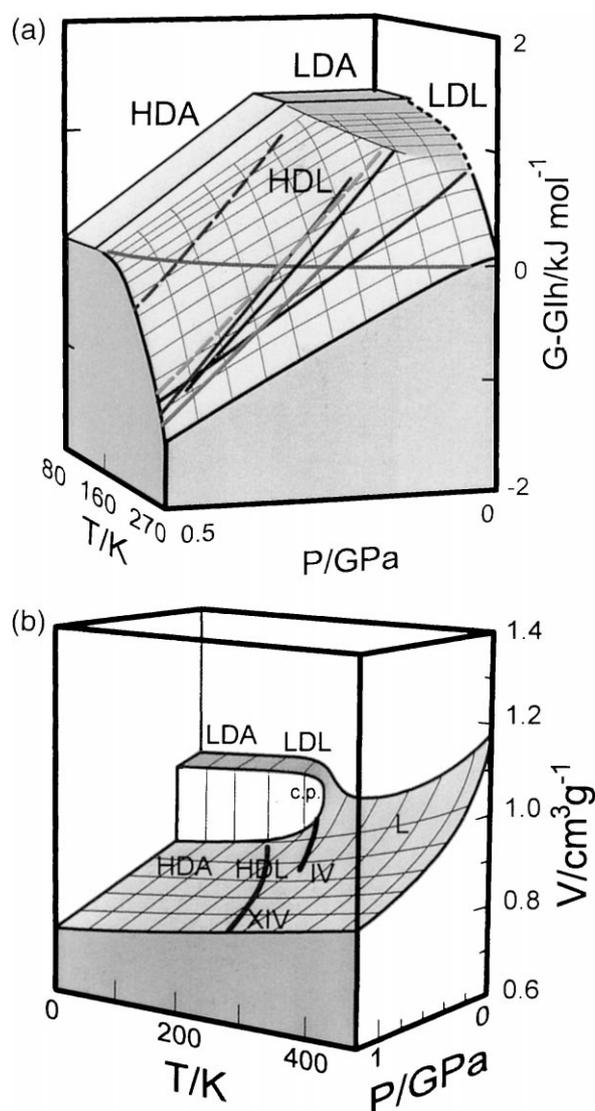


Fig. 3. Application of data obtained in Mishima's experiment to reconstruct the Gibbs potential surface and the thermodynamics equation of state $V = V(P, T)$. (a) The $\Delta G_L(P, T)$ surface in the 80–270 K and 0–0.5 GPa region with constant- P and constant- T lines at 50 MPa and 10 K intervals, 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.

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 [49] have recently investigated a liquid under conditions not far from the freezing line. 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 [50,51] 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 the tetrahedron that are hydrogen-bonded to a central molecule — see, e.g., [52–57]). 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. Our 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 [58] successfully fits detailed neutron structure data to just such a picture. The simulation results are in good accord with neutron results (see, e.g., [59]), so we are optimistic that soon a unified coherent picture will emerge via careful combination of reliable results.

6. Outlook

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 [60,61]. Recent results [60,62] 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 SiO_2 and 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 lines, 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_2 [63] and a two-level model has been developed for amorphous GaSb

[64]. Understanding one such material, water, may help in understanding others — whether they be other materials with tetrahedral structures (and corresponding TMD lines) such as 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 [65]. 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 [8–10] that the system has no genuine singularity at all. This “singularity-free scenario” has been examined critically in recent work by Sastry and collaborators [66,67]. Possibly studying the effect on water of salt dilution or confinement will help resolve some of these issues [68,69].

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