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Liquid water: A very complex fluid

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Abstract. Although H_2O has been the topic of considerable research since the beginning of the century, the peculiar physical properties are still not well understood. First we discuss some of the anomalies of this 'complex fluid'. Then we describe a qualitative interpretation in terms of percolation concepts. Finally, we discuss recent experiments and simulations relating to the 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.

Keywords. Water; second critical point; equation of state.

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1. Introduction

Liquid water is at first sight not a 'complex fluid' and hence has no place at this conference. However, understanding the highly anomalous equilibrium and dynamical properties are 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.

We will organize the lecture around three questions.

Question 1: What is the puzzle of liquid water?
Question 2: Why do we care about this puzzle?
Question 3: What do we actually do?

The 'we' in this case is a rather large number of individuals. I will focus mostly on very recent work that has been published, or at least submitted, this year. This work was done in collaboration with M-C Bellissent-Funel, S V Buldyrev, M Canpolat, M Meyer, O Mishima, R Sadr-Lahijany, A Scala and F W Starr. It is also based on earlier research a few years back with C A Angell, P Debenedetti, A Geiger, P H Poole, S Sastry, F Sciortino, and J Teixeira. Any of these 15 valued collaborators could probably give this lecture as well as, if not better than, I will.

We will organize the answer to this third and principal question in the following way: First, we will attempt to identify, in the spirit of Sherlock Holmes, some interesting clues. Then, we will formulate a working hypothesis, and then we will test the hypothesis, both by experiments on real water, and by simulations of what sometimes is called 'computer water'. These simulations are useful because some of the problems associated with doing experiments on real water can be obviated using computer simulations.

Before beginning, let us note that there are some very good general references on liquid and glassy water. A recent book entitled *Metastable Liquids* [1] is a kind of sequel to Skripov's classic on this subject. There is an even more recent book called *Supercooled Liquids* published by the American Chemical Society [2]. And there are many recent reviews [3–5], including a very recent seven-page mini-review [6]. Finally, and perhaps most interestingly, the accomplished science writer Philip Ball has just prepared a book that surveys the entire story of water, from the earliest times to the present [7]—responding perhaps to the fact that water is one of the most appealing of the open puzzles in all of science.

2. What is the puzzle of liquid water?

We start with the first question, 'What is the puzzle?' There are many puzzles associated with water. Firstly, water exists in many forms. All of us are familiar with one important control parameter that distinguishes these forms, namely temperature (figure 1). Stable water is the water that one is familiar with when one discusses biology (in reality, much of biology takes place when water is in a supercooled regime). Why is that? Because in Boston nothing would survive the winter, were it not for the fact that living systems are able to survive even when the water inside them is metastable, namely supercooled. But below about −38°C, we hit a kind of Berlin Wall, beyond which there is a 'no-man's land' where water exists only in the solid, crystalline phase. That temperature is called the temperature of homogeneous nucleation and denoted T_H. At very low temperature, there is a region in which water exists in the glassy phase. If one heats glassy water gently above its glass transition temperature, $T_g \approx 135\,\mathrm{K}$, one finds a narrow window of 10–15 degrees in which water is liquid, although very, very viscous [8]. If one heats further, one reaches a temperature $T_X \approx 150\,\mathrm{K}$ where the mobility of the ultraviscous water reaches a sufficiently large value that the molecules can readily find out that the crystalline phase indeed has the lowest free energy—and it freezes. Between T_X and T_H, an interval of roughly 80 degrees, there's a kind of no-man's land in the sense that water is stable only in its solid crystalline phases. In short, only ice cubes exist in no-man's land!

2.1 *Volume fluctuations*

So let us begin by asking about the nature of the puzzle of liquid water. What are the features on which we would like to focus? In any short presentation, our choices are necessarily subjective, so we start by considering a simple response function, the isothermal compressibility K_T, which is a thermodynamic response function—the response $\delta\bar{V}$ of the volume per particle to an infinitesimal pressure change δP. As one lowers the temperature of a typical liquid, K_T decreases (figure 2). We understand this feature

Figure 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.

because in statistical mechanics courses we learn that K_T is also related to something statistical, namely the expectation value of the fluctuations in $\bar{V}$. As the temperature is lowered, we expect the fluctuations to decrease. Water is an anomaly in three respects:

(i) First, the compressibility, when normalized by mass and other material parameters, is rather larger than one would expect.

(ii) Second, and very dramatically, although at high temperatures the compressibility decreases on lowering the temperature, below about 46°C, it actually starts to increase, and this is not a small effect. By the time one reaches the Berlin Wall temperature of -38°C, the compressibility is actually increased by a factor of 2. It's a hundred per cent larger than its value at 46°C.

(iii) The third remarkable feature is that if one plots one's data, not linearly as sketched in figure 2, but rather on double-logarithmic paper—where the x-axis is the logarithm of $|T - 228|$ K and the y-axis the logarithm of the compressibility—one finds a region of straight-line behavior, hinting at some sort of critical behavior. In mentioning these experiments, I should emphasize the name of Austen Angell who, together with numerous students, pioneered in the identification of this apparent power-law singularity [9].

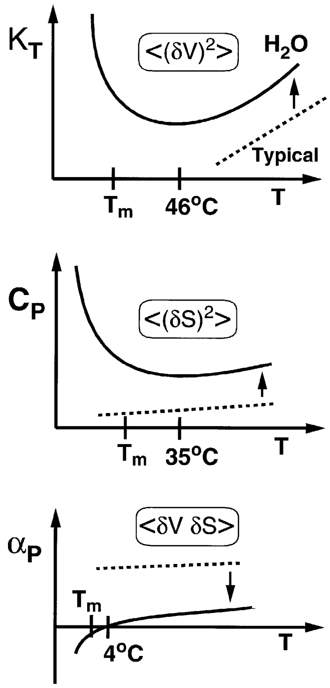

Figure 2. Schematic dependence on temperature of (**a**) the isothermal compressibility K_T, (**b**) the constant-pressure specific heat C_P, and (**c**) the thermal expansivity α_P. The behavior of a typical liquid is indicated by the dashed line, which very roughly is an extrapolation of the high-temperature 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.

2.2 *Entropy fluctuations*

These anomalies associated with the compressibility response function is also shared by other response functions. Consider for example the specific heat at constant pressure C_P, which is the thermodynamic response $\delta\overline{S}$ of the entropy per particle to an infinitesimal temperature change δT (apart from proportionality factors). Once again, for a typical liquid, this quantity is gently decreasing as one lowers the temperature, which we understand because this quantity is also related to a fluctuation—the entropy fluctuations. And one imagines that entropy fluctuations also decrease when one cools. Water is again anomalous in the same three respects. The specific heat for water is, as every engineer knows, rather large. Secondly, below about 35°C the specific heat actually starts to increase. And lastly, that increase can be approximated by a power law (figure 2).

2.3 *Volume–entropy cross-correlations*

The last of the three response functions is the one that is exemplified by the experiment of figure 3 measuring the temperature at the bottom of the glass of ice water. That is

Figure 3. A glass of unstirred ice water with a thermometer. What is the temperature at the bottom of the glass? This photograph is courtesy of K Mishima.

the coefficient of thermal expansion α_P, the response $\delta\bar{V}$ of the volume to an infinitesimal temperature change δT. For a typical liquid α_P is positive. And again, one can understand that positivity, in a statistical mechanics sense, because this coefficient of thermal expansion is proportional to the cross-fluctuations of entropy and specific volume $\langle\delta\bar{V}\delta\bar{S}\rangle$. Normally, if one has a region of the system in which the specific volume is a little larger than the average, then the local entropy in that same region of the system is also larger. (For example, I often complain that the reason my office is so messy is that it is too small, and if I could only get a bigger one it would be less messy. But in reality, I think we all know what would happen if I had a larger office—it would be even messier because there would be even more ways to arrange my huge quantity of material.)

So $\langle \delta\bar{V}\delta\bar{S} \rangle$ is positive because in local regions of the liquid in which the volume is larger than the average ($\delta\bar{V}$ is positive), then the entropy is also larger (so $\delta\bar{S}$ is positive). The product of two positive numbers is positive. Water is unusual in the same three respects. First of all, its coefficient of thermal expansion is about 3 times smaller than that of the typical liquid. Secondly, as one lowers the temperature, the anomaly gets stronger and stronger and at the magic number of 4°C (which has been known for over three centuries [10]), α_P actually becomes negative, and once again this apparent divergence exists in the sense that there appears to be an imminent apparent singularity that's occurring. From a simple kitchen experiment (figure 3), we can understand that the 0°C water in a glass of ice water (or a pond in Boston winter) 'floats' on top of heavier layers of 4°C water—allowing the fish to survive the long winter.

3. Why do we care about liquid water?

Let us turn now to question 2, 'Why care?' There are always lots of reasons to care. Almost all of them are, in some sense, personal. For me, certainly, scientific curiosity is always one reason to care. Why on earth could the behavior of figures 2 and 3 exist? Why could water have such a difference compared to that of a typical liquid no matter what kind of fluctuating quantity we look at? It does not make sense.

A second reason, which I alluded to in the beginning, is that water is a kind of model tetrahedral liquid. It is a model in the sense that it is relatively easy to study. Most of the temperature regions in which one studies water are reasonably accessible. There are other tetrahedral liquids. In fact, the second most common material on our planet is SiO_2, and SiO_2 has many features that are remarkably parallel to those of water. Water and SiO_2 both share that fact that they are tetrahedral liquids; that is to say, they are liquids whose local structure approximates that of a four-coordinated, open, loose-packed lattice.

There are also numerous practical reasons to care about water. I already alluded to the fact that engineering depends very much on the remarkable properties of water, and so also does life itself. Glassy water is relevant to drug preservation: if we make a glass, the dynamics are slowed down by a factor of $\approx 10^{13}$. Hence the time scales of biological processes are similarly slowed down.

4. Clues for understanding water

With this brief introduction behind us, let us consider what we actually do. First we seek for clues. The fundamental clue, perhaps, for the mystery of liquid water dates back more than 50 years to Linus Pauling, who recognized that the distinguishing feature of H_2O, when compared to other materials that otherwise look chemically similar, is the preponderance of hydrogen bonds. A useful cartoon illustrates the implications of a high degree of hydrogen bonding. Each molecule has two arms, corresponding to the two protons, and two attractive spots, corresponding to the lone pairs. The arms reach out to the attractive spots. Since the fraction of intact bonds exceeds the percolation threshold, the basic structure of water is a hydrogen-bonded gel. Because these hydrogen bonds have very, very short lifetimes—typically a picosecond—water does not behave like jello. We can pour water and it flows just like any other liquid.

Computer simulations also 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. For any reasonable definition of 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, locally, 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.

5. Qualitative picture: Locally-structured transient gel

Although there have been many different detailed models used by researchers to describe the structure of liquid water, many would agree that, on a qualitative level, water is a locally-structured transient gel [11].

5.1 *'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.

5.2 *'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.

6. Microscopic structure: Local heterogeneities

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 edges 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. The sites with all four bonds still intact we designate '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 ≈ 0.8, as we saw earlier, the probability that four bonds of a given site are intact is $\approx 0.8^4$ or ≈ 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.

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?

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. Simulations provide unambiguous evidence [12], but in simulations the results always could be wrong if the potential is wrong. Experimentally, we can not actually see them, but by beaming X-rays into supercooled water (-25°C), Bosio and Teixeira [13] observe a characteristic Ornstein–Zernike behavior, indicating a build-up in correlated regions with a characteristic size proportional to the inverse of the width of that Lorenztian. The characteristic size measured using this experimental technique turns out to be a diameter of $\approx 8\,\text{Å}$, i.e., 2–3 atomic spacings; recent data [14] 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 [15]! Evidently the patches are broken up by the impurity.

Another 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 temperatures from 5°C to 45°C, one finds that all the isotherms intersect at a single 'isosbestic point' with $x = 0.17$ and $v_s = 1.6\,\text{km/s}$ [16, 17]. 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. Careful study of judiciously-chosen two-component systems may 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 four-bonded molecules to molecules with a smaller than average energy [18] or to molecules with a larger than average 'local structure' [19].

7. Liquid–liquid phase transition hypothesis

This qualitative picture is sufficient to explain the vertical arrows in figure 2 and the fact that the vertical arrows get longer and hence there is a minimum but they are not sufficient to relate at all to the presence of the apparent power-law singularity. This power-law singularity is reminiscent of critical phenomena. It suggests there might be some sort of critical point—but how could there be a critical point? Water does have a critical point, but water's critical point is a very ordinary critical point. The critical point of water is up around 374°C at a pressure of approximately 227 atmospheres. Above the critical point, water is a homogeneous fluid, while below the critical point, water can exist in either of two distinct phases. That critical point is known and well-studied by individuals such as Anneke Levelt-Sengers at the National Institutes of Standards and Technology in Gaithersburg, Maryland. Water is not unusual in connection with this critical point.

What could this apparent power-law singularity have to do with a critical point? Notice that the temperature here is about −50°C, nowhere near 374°C. So there is a kind of puzzle here. Why would one find critical point phenomena in experimental data?

A possible resolution to this paradox was proposed a couple of years ago. A gifted Boston University graduate student, Peter Poole, working with postdocs Francesco Sciortino and Uli Essmann, made computer simulations in this low-temperature region with the goal of exploring in detail with a computer what might happen [20]. Why a computer? Because 'computer water' does not suffer from this Berlin Wall catastrophe at −38°C. Computer water has a wonderful virtue: in simulations of sufficiently small systems with sufficiently small time scales, the nucleation phenomenon that plagues real experiments simply doesn't occur. One can go as low in temperature as one has computer time to simulate. What Poole and collaborators discovered in computer water was the apparent existence of a second critical point. That second critical point was indeed in the range of −50°C. Exactly where is difficult to say because in computer simulations you get out what you put in to some degree. And it's very difficult to put in an accurate temperature scale, because the actual model that's used to simulate water is itself not terribly accurate. So when I say $\approx -50°\text{C}$, I mean $-50°\text{C} \pm 10°\text{C}$, or even $-50°\text{C} \pm 20°\text{C}$. But what was discovered is that, below this second critical point, the liquid phase separates into two distinct phases—a low-density liquid (LDL) and a high-density liquid (HDL).

8. Plausibility arguments

A non-interacting gas has no critical point, but a gas with arbitrarily weak attractive interactions does since at sufficiently small temperature, the ratio of the interaction to kT will become sufficiently significant to condense the liquid out of the gas. That all interacting gases display a critical point below which a distinct liquid phase appears was not always appreciated. Indeed, in the early years of 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 [21].

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

Water differs from most liquids due to the presence of a line of maximum density (TMD line) in the PT phase diagram. This TMD is physically very significant, as it divides the entire PT phase diagram into two regions with remarkably different properties: the coefficient of thermal expansion—which is proportional to the thermal average ('correlation function') $\langle \delta\bar{V}\delta\bar{S}\rangle$—is *negative* on the low-temperature side of the TMD line, while it is *positive* on the high-temperature side. Here $\bar{V}$ is the volume per molecule, $\bar{S}$ the entropy per molecule, and the δX notation indicates the departure of a quantity X from its mean value.

That $\langle \delta\bar{V}\delta\bar{S}\rangle$ is negative is a thermodynamic necessity given the presence of a TMD line. What microscopic phenomenon causes it? One not implausible explanation [11] is related to the presence of local regions of the hydrogen bond network that are characterized by four 'good' hydrogen bonds—and these local regions can be considered as droplets just 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.

This intuitive picture has received striking support from a recent generalization of the van der Waals theory. Specifically, Poole *et al* [22] 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 [23, 24] and assume that there are $\Omega \gg 1$ configurations of a weak bond, all having $\epsilon = 0$, and only a single configuration in which the HB is strong with $\epsilon = \epsilon_{\mathrm{HB}}$. Thus the thermal behavior of the HBs is represented by independent $(\Omega + 1)$–state systems, each described by a partition function $Z = \Omega + \exp(-\epsilon_{\mathrm{HB}}/kT)$. Poole *et al* found that for small values of the parameter ϵ_{HB}, there is no critical point (but rather a re-entrant spinodal of the form first conjectured by Speedy [25]). However for ϵ_{HB} above a threshold (about $16\,\mathrm{kJ/mol}$), a critical point appears.

The possibility of a second critical point has received recent support by phenomenological analysis of Ponyatovskii and colleagues [26] and by lattice gas models [24, 27]. Also, Roberts and co-workers [28] have shown that simulation results for a microscopic 'water-like' Hamiltonian confirms the presence of a second phase transition, previously deduced from approximate calculations [27].

9. 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 4 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 [29]. 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 [30].

One way to obtain less cumbersome simulations is to simplify the intermolecular potential. To this end, the simpler TIP4P potential [31] and the much simpler SPC/E potential [32] have enjoyed considerable popularity. However the opposite direction is also under active investigation: simulating more realistic potentials, such as polarizable potentials [33]. 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.

9.1 *Does $1/K_T^{max}$ extrapolate to zero at $(T_{C'}, P_{C'})$?*

The compressibility K_T diverges at a second order critical point. Thus, we expect $1/K_T^{\max}$ 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 [34] are consistent with a plausible extrapolation to a single point in the phase diagram at which $K_T^{\max} = \infty$. 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 [35]; this possibility will be discussed briefly at the end of this lecture.

9.2 *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 235K but not at a temperature of 280 K, consistent with $T_{C'}$ somewhere between 235 K and 280 K. This finding, originally made for simulations of 216 ST2 particles [36, 37], has very recently been strikingly confirmed for a system 8 times larger [38]. 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.

9.3 *Is there a unique structure of the liquid near the kink point?*

If there exists a critical point C', then we would expect a two–phase coexistence region below C'. To investigate the possible structural difference between these two phases, Sciortino *et al* [34] have studied the structure of the liquid at a temperature just below the estimated value of $T_{C'}$ at two values of ρ on the two sides of $\rho_{C'}$. They find that the structure of the liquid state of ST2 at $\rho = 1.05\,\mathrm{g/cm^3}$ is similar to the experimental data on high-density amorphous (HDA) solid water, while the structure at $\rho = 0.92\ \mathrm{g/cm^3}$ 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 [39, 40].

9.4 *Does the coordination number approach four as C' is approached?*

Sciortino *et al* [34] have studied the coordination number N_{nn} of the ST2 liquid as a function of T and V, where N_{nn} is the average number of nearest–neighbors found in the first coordination shell of an O atom. For the high-T isotherms, their results show that a 4-coordinated 'LDL'-like configuration is approached at negative P, in agreement with previous simulations of Geiger and co-workers [41]. For $T \leq 273$ K, N_{nn} also approaches 4 at positive P. That is, if T is low enough, it appears that a 4-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 [39].

9.5 *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 (figure 4). 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

Figure 4. The results of partitioning the molecules in a computer simulation into two categories, the left picture being the ‘low-density’ molecules (with coordination number 4) and right picture being the ‘high-density’ molecules (with coordination number above 4). Courtesy of S T Harrington.

temperature somewhat below $T_{C'}$ do not prove phase coexistence [38, 42], 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 [42]. Additional work remains to be done to establish this point.

9.6 *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 [43]. 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 temperatures [44]. At low temperatures, it is possible that power law behavior is found [30, 38]. 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 [45, 46]. 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 [47].

9.7 *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 $T_{C'}$ [43]. 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 [48]. This slowing down of the dynamics is consistent with what one expects near a critical point. Specifically, $1/D$ strongly increases as $N_{\mathrm{nn}} \to 4$. Consistent with this picture, it was found [49, 50] that additional nearest neighbors beyond 4 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 between $1/D$ and $(N_{\mathrm{nn}} - 4)$, the manner in which $N_{\mathrm{nn}} \to 4$ is also significant. At high T the decrease of N_{nn} with P is relatively uniform. However, as T

decreases, $N_{\rm nn}$ is observed to vary more and more abruptly from a high-coordinated structure ($N_{\rm nn} > 6$) to $N_{\rm nn} \simeq 4$. 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.

9.8 *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,' we see that the red molecules (corresponding to high densities) move much further than blue molecules (corresponding to low densities) [38, 42]. The nature of transport in each phase is under active investigation, particularly in light of recent proposals for the nature of the anomalous dynamics taking place in low-temperature water [51].

9.9 *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 [52]. 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 [52]. The resolution between the two different values of $P_{C'}$ is an open question that will hopefully be resolved shortly.

It was actually possible to identify these two phases in the computer (figure 4). I emphasize in the computer because what you find in the computer can be suggestive and frequently can confirm experiments. In this case it actually motivated some experiments—the search in real water for evidence for such a critical point deep in the no-man's land between T_H and T_X.

The pressure of the second critical point is around one kilobar. That is easy to remember because that happens to be the pressure at the bottom of the Marianas Trench! Because it is at a high pressure, I am going to gradually ramp up the complexity of this phase diagram from our first picture (figure 1), keeping the same color codes in the second picture (figure 5). I warned you that this was a slice at one atmosphere and that sooner or later we would have to look at pressures other than one atmosphere, and that is what this diagram does. In fact, it shows pressures all the way up to about 0.3 gigapascals, or approximately 3000 atmospheres.

As you can see, at approximately 1000 atmospheres a little gray dot represents where the second critical point might lie. This awkward location presents us with perplexities. First of all, on which side of the Berlin Wall does this mythical beast lie? It is lying on the side that we can not reach experimentally! I will spend the rest of this talk discussing experiments, but I am talking about experimental attempts to identify a mythical beast that we can not get close to at all, no closer than 5, or 10, or perhaps even 15 degrees from this actual critical point.

If we can not get close to it, why does it matter? It matters for the same reason that Mount Everest matters. Mount Everest, approximately 10,000 meters high, is not a delta function somewhere in Nepal and Tibet. Rather, Mount Everest is a peak that exerts an

Figure 5. Generalization of figure 2 to incorporate a second control parameter, the pressure. The colors are the same as used in figure 2. This figure is courtesy of Dr O Mishima.

influence on its neighboring altitudes, both high above the timberline and well below the timberline (figure 6). In other words, if we have a singularity in our phase diagram at a well-defined critical point, it is going to have an effect on an entire region around the critical point—a so-called critical region. 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 [53] in terms of increased fluctuations away from (but close to) the critical point (figure 7). It is for this reason that critical phenomena are particularly interesting.

10. Tests of the hypothesis: Real water

10.1 *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 [54]. By careful analysis of experimental data above $T_H(P)$, Speedy and Angell [25, 55, 56] pioneered the view that some sort of singular behavior is occurring in water at a temperature $T_s(P)$ some 5–10

Figure 6. Photograph of Mt. Everest and the ‘critical region’ nearby. This photograph is, relevant to understanding why a critical point is important, since the ‘singular’ behavior of the altitude function at Everest itself (the peak being almost 10^4 m) has an effect on the altitude for a huge ‘critical region’ surrounding the peak.

Figure 7. Critical opalescence of the critical binary mixture cyclohexane-aniline. This figure is courtesy of R A Ferrell.

degrees 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 [56, 57] or a critical point) will influence the equation of state in a large neighborhood.

10.2 *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 $S(Q)$ [39, 40]. 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_0 of $S(Q)$ for each isobar. They find that for the 0.1 MPa isobar, Q_0 approaches 1.7 Å^{-1}—the value for LDA, low-density amorphous ice. In contrast, for the 465 MPa and

600 MPa isobars, Q_0 approaches a 30% larger value, 2.2 Å^{-1}—the value for HDA, high-density amorphous ice. For the 260 MPa isobar, $Q_0 \rightarrow 2.0\,\mathrm{A}^{-1}$, 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 H_2O have been studied extensively by Mishima and co-workers [58]. 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 K 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 [36].

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 (figure 8).

10.3 *Recent work*

We discuss now the very recent measurements of the compression-induced melting (CIM) and decompression-induced melting (DIM) 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 H_2O do not exist in the 'no-man's land'' between T_H and T_X (figure 5).

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 [59]. Below T_X, ice I_h amorphizes to HDA at a pressure higher than the smoothly extrapolated melting line [1]. To avoid the complication of the usual crystal–crystal transformations interrupting the melting process, we use an ice emulsion (1–10 μm ice particles in oil [60]).

Mishima creates 1 cm^3 emulsified high-pressure ices in a piston-cylinder apparatus, decompresses the sample at a constant rate of 0.2 GPa/min, and—because melting is endothermic—observes their transitions by detecting a change in the sample temperature by an attached clomel–alumel thermocouple during the decompression. Then, he determines melting pressures at different temperatures (figure 9). The melting curves he

Figure 8. HDA is readily made at pressures higher than about 200 MPa, and LDA at pressures lower than that amount. There is pressure hysteresis, which 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 panel: just before the HDA → LDA transition. Bottom panel: just after the transition. This figure is courtesy of Dr O Mishima.

obtains agree with previously-reported data [61, 62], 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_2O, denoted PNP–XIII and PNP–XIV.

Using the measured melting lines of ice phases at low temperatures (figure 9), we calculate the Gibbs energy (figure 10), and the equation of state [63] (figure 11). 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

Figure 9. The left panel shows the measured DIM temperature response of the ice emulsion during each decompression, while the center panel shows the measured CIM temperature response during each compression. The highlights correspond to the characteristic sudden changes in the sample temperature. Note also that this kink appears well below the homogeneous nucleation line $T_H(P)$, so the possibility that the kink is due to $T_H(P)$ seems unlikely. The right panel shows the melting lines that are extracted from the data shown. Note that the DIM line of ice IV shows a kink at $P \approx 0.1$ GPa and $T \approx 215$ K, and is followed by the line of broad exothermic transitions (the vertical hatched region). The right panel also displays the melting lines of the other ices and the LDA/HDA and I_h/HDA transition lines (the long-dashed lines). The horizontal bar indicates the range of metastability found for the LDA/HDA transition. This figure is courtesy of Dr O Mishima.

Figure 10. (**a**) Schematic Gibbs potential of liquid water relative to that of ice I_h, $\Delta G_{\mathrm{L}} \equiv G_{\mathrm{L}} - G_{I_h}$. The intersection line of ΔG_{L} and the basal plane defines the melting line of ice I_h. (**b**) Gibbs potential of a typical high-pressure ice relative to that of ice I_h, $\Delta G_{\mathrm{HP}} \equiv G_{\mathrm{HP}} - G_{I_h}$. (**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 ΔG_{HP} along the melting line which must equal ΔG_{L} along the melting line. (**d**) Schematic construction of the ΔG_{L} surface (the dark region) by smooth graphical interpolation between the ΔG_{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_h where the ΔG_{L} is zero (figure 3a). These lines locate on a surface (the ΔG_{L} surface). Once we know the ΔG_{L} surface, we calculate the ΔG_{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 ΔG_{L} potentials along the melting lines of PNP ices on these ΔG_{HP} planes. This figure is courtesy of Dr O Mishima.

Figure 11. Experimentally-derived [63] thermodynamics equation of state $V = V(P, T)$, using the same color coding as in figures 1 and 5. 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. 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.

with other known experimental data and also with simulation results [58, 63, 64, 20, 22, 24, 52, 28, 35, 47, 65]

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 [66–69]. Figure 12 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. [63]—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.

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 (figure 11). Having the volume as a function of temperature is just where we want to end this talk, 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

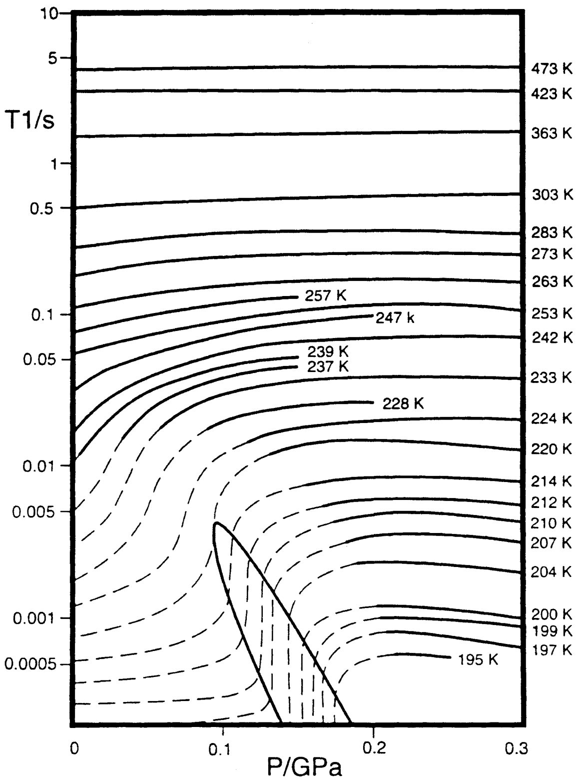

Figure 12. Pressure dependence of T_1 for a family of isotherms ranging from 473 K down to 195 K. These data are read off of figure 1 and Table 1 of ref. [66]. Lang and Lüdemann noted that for the low-temperature isotherms, T_1 increases with pressure, unlike the behavior in ammonia and hydrogen sulfide. 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. This figure is courtesy of Dr O Mishima.

complete equation of state. This may look a little bit complicated, so let us take it in stages.

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

To summarize, we started with a one-dimensional phase diagram (figure 1), went to a two-dimensional one (figure 5), and then to a three-dimensional one (figure 11). Qualitative features of liquid water appear to be connected to the behavior of a locally-structured transient gel. This locally-structured transient gel has the feature that little clusters are formed inside the hydrogen-bonded network. Locally, these clusters have distances and bond angles similar to that of ice and therefore have smaller density, larger specific volume, lower entropy, and contribute to explaining qualitatively the anomalies of water.

11. Discussion

The most natural response to the concept of a second critical point in a liquid is bafflement—such a thing just does not make sense. To make the concept more plausible, we offer the following remarks. Consider a typical member of the class of intermolecular potentials that go by the name of core-softened potentials [70]. 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 [71]. These simple potentials might capture the essential physics of water–water interactions in that 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 (figure 13). 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 and are tractable to study using approximation procedures (and simulations) in higher dimensions [71].

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 liquid could approach different phases as the temperature is lowered. Moreover, if the outer well is deep and narrow, then we anticipate that when $\delta\bar{V} > 0$, $\delta S < 0$—i.e., volume and entropy fluctuations will be anticorrelated, leading to $\alpha_P < 0$.

A clear physical picture has by no means emerged. However recent work has addressed the question if we can characterize (or at least 'caricature') the local structural heterogeneities that appear in liquid water. Specifically, Canpolat and collaborators [72] considered state points of liquid water at different pressures—and especially near its phase

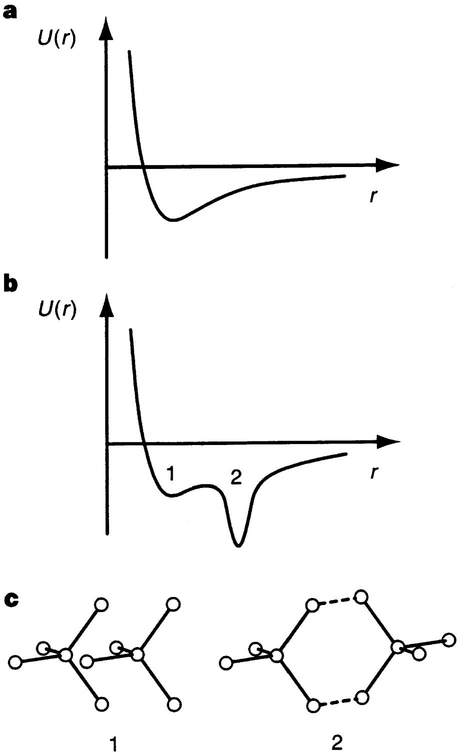

Figure 13. Physical arguments relating to the plausibility of the existence of the known liquid–gas critical point C and the hypothesized LDL–HDL critical point C'. (**a**) Idealized system characterized by a pair interaction potential with a single attractive well. At low enough T ($T < T_c$) and high 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). This figure is courtesy of Dr. O. Mishima.

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 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., [73]; the corner molecules are separated from the central molecule by 2.8 Å, corresponding to the first peak in the oxygen-oxygen radial distribution function. They advance the hypothesis that these configurations may be related to the local 'high-density' and 'low-density' structural heterogeneities occurring in liquid water. These results are consistent with recent experimental data on the effect of high pressure on the radial distribution function, and are further tested by molecular dynamics simulations.

Although such a picture may seem to be oversimplified, very recent work of Bellissent-Funel [74] successfully shows that detailed neutron structure data agree with it. Also, the simulation results are in good accord with neutron results (see, e.g., [40]), so one can be optimistic that some day a unified coherent picture may emerge.

12. Outlook

Many open questions remain, and many experimental results are of potential relevance to the task of answering these questions. For example, the dynamics of water is only beginning to receive some possible clarification—see, e.g., [30, 51, 75] (and references therein). In particular, it is unclear what is the effect on the hypothesized second critical point of modifying water in ways that are interesting. For example, trees survive arctic temperatures because the water in the cell does not freeze, even though the temperature is below the homogeneous nucleation temperature of -38°C. The effect of confinement on the second critical point is just now beginning to be studied [76]. Similarly, the effect on the second critical point of adding a second component is of interest, especially because the interior of the cell is anything but pure water!

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 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_2 [77] and a two-level model has been developed for amorphous GaSb [78]. Understanding one such material, water, may help in understanding others—whether they be other materials with tetrahedral local structures (and corresponding TMD lines) such as SiO_2 or whether they be more complex local structures like amorphous GaSb which appears to display strikingly ordered local heterogeneities.

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References

[1] P G Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton, 1996)
[2] J T Fourkas, D Kivelson, U Mohanty and K A Nelson (eds), *Supercooled Liquids: Advances and Novel Applications* (ACS Books, Washington DC, 1997)
[3] J C Dore and J Teixeira, *Hydrogen-Bonded Liquids* (Kluwer Academic Publishers, Dordrecht, 1991)
[4] S H Chen and J Teixeira, *Adv. Chem. Phys.* **64**, 1 (1985)
[5] M C Bellissent-Funel and J C Dore, *Hydrogen Bond Networks* (Kluwer Academic Publishers, Dordrecht, 1994)
[6] O Mishima and H E Stanley, *Nature*, **396**, 329 (1998)
[7] P Ball, *Water: A Biography* (Farrah Strauss, New York, 1999)
[8] R S Smith and B D Kay, *Nature* **398**, 788 (1999)
K P Stevenson, G A Kimmel, Z Dohnalek, R S Smith, and B D Kay, *Science*, **283**, 1505 (1999)
[9] C A Angell, in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum Press, NY, 1980) Vol. 7, p. 1
[10] R Waller, trans., *Essays of Natural Experiments* [original in Italian by the Secretary of the Academie del Cimento]. Facsimile of 1684 English translation (Johnson Reprint Corporation, New York, 1964)
[11] H E Stanley, *J. Phys.* **A12**, L329 (1979)
H E Stanley and J Teixeira, *J. Chem. Phys.* **73**, 3404 (1980)
H E Stanley, J Teixeira, A Geiger and R L Blumberg, *Physica* **A106**, 260 (1981)
[12] A Geiger and H E Stanley, *Phys. Rev. Lett.* **49**, 1749 (1982)
H E Stanley, R L Blumberg and A Geiger, *Phys. Rev.* **B28**, 1626 (1983)
H E Stanley, R L Blumberg, A Geiger, P Mausbach and J Teixeira, *J. de Physique* **45**, C7[3] (1984)
[13] L Bosio, J Teixeira and H E Stanley, *Phys. Rev. Lett.* **46**, 597 (1981)
[14] Y Xie, K F Ludwig, Jr., G Morales, D E Hare and C M Sorensen, *Phys. Rev. Lett.* **71**, 2050 (1993)
[15] C A Angell, M Oguni, and W J Sichina, *J. Phys. Chem.* **86**, 998 (1982)
[16] A Giacomini, *J. Acoustical Soc. Am.* **19**, 701 (1947)
[17] G W Willard, *J. Acoustical Soc. Am.* **19**, 235 (1947)
[18] R L Blumberg, H E Stanley, A Geiger and P Mausbach, *J. Chem. Phys.* **80**, 5230 (1984)
[19] E Shiratani and M Sasai, *J. Chem. Phys.* **104**, 7671 (1996).
[20] P H Poole, F Sciortino, U Essmann and H E Stanley, *Nature* **360**, 324 (1992)
[21] K Mendelssohn, *The Quest for Absolute Zero: The Meaning of Low-Temperature Physics* (McGraw, New York, 1966), p. 42ff.
[22] P H Poole, F Sciortino, T Grande, H E Stanley and C A Angell, *Phys. Rev. Lett.* **73**, 1632 (1994)
C F Tejero and M Baus, *Phys. Rev.* **E57**, 4821 (1998)
[23] S Sastry, F Sciortino and H E Stanley, *J. Chem. Phys.* **98**, 9863 (1993)
[24] S S Borick, P G Debenedetti and S Sastry, *J. Phys. Chem.* **99**, 3781 (1995)
S S Borick and P G Debenedetti, *J. Phys. Chem.* **97**, 6292 (1993)

[25] R J Speedy, *J. Phys. Chem.* **86**, 3002 (1982)
[26] E G Ponyatovskii, V V Sinitsyn and T A Pozdnyakova, *JETP Lett.* **60**, 360 (1994)
[27] C J Roberts and P G Debenedetti, *J. Chem. Phys.* **105**, 658 (1996)
[28] C J Roberts, A Z Panagiotopoulos and P G Debenedetti, *Phys. Rev. Lett.* **77**, 4386 (1996)
[29] F H Stillinger and A Rahman, *J. Chem. Phys.* **57**, 1281 (1972)
[30] F W Starr, J K Nielsen and H E Stanley, *Phys. Rev. Lett.* **82**, 2294 (1999)
[31] W L Jorgensen, J Chandrasekhar, J Madura, R W Impey and M Klein, *J. Chem. Phys.* **79**, 926 (1983)
[32] H J C Berendsen, J R Grigera and T P Straatsma, *J. Phys. Chem.* **91**, 6269 (1987)
[33] U Niesar, G Corongiu, E Clementi, G R Kneller and D Bhattacharya, *J. Phys. Chem.* **94**, 7949 (1990)
[34] F Sciortino, P H Poole, U Essmann and H E Stanley, *Phys. Rev.* **E55**, 727 (1997)
[35] S Sastry, P G Debenedetti, F Sciortino and H E Stanley, *Phys. Rev.* **E53**, 6144 (1996)
L P N Rebelo, P G Debenedetti and S Sastry, *J. Chem. Phys*. **109**, 626 (1998)
[36] P H Poole, U Essmann, F Sciortino and H E Stanley, *Phys. Rev.* **E48**, 4605 (1993)
[37] P H Poole, F Sciortino, U Essmann and H E Stanley, *Phys. Rev.* **E48**, 3799 (1993)
[38] S T Harrington, R Zhang, P H Poole, F Sciortino and H E Stanley, *Phys. Rev. Lett*. **78**, 2409 (1997)
[39] M C Bellissent-Funel and L Bosio, *J. Chem. Phys.* **102**, 3727 (1995)
[40] F W Starr, M C Bellissent-Funel and H E Stanley, *Phys. Rev.* **E60**, 1084 (1999). Cond-mat 98-11118.
[41] A Geiger, P Mausbach and J Schnitker, in *Water and Aqueous Solutions* edited by G W Neilson and J E Enderby (Adam Hilger, Bristol, 1986) p. 15
[42] S T Harrington, P H Poole, F Sciortino, and H E Stanley, *J. Chem. Phys.* **107**, 7443 (1997)
[43] F Sciortino, P H Poole, H E Stanley and S Havlin, *Phys. Rev. Lett.* **64**, 1686 (1990)
[44] A Luzar and D Chandler, *Phys. Rev. Lett.* **76**, 928 (1996)
A Luzar and D Chandler, *Nature* **379**, 55 (1996)
[45] H Larralde, F Sciortino and H E Stanley, *Restructuring the Hydrogen Bond Network of Water* (preprint)
H Larralde, *Properties of systems with many random walkers,* Ph.D. Thesis (Boston University, 1993)
[46] F Sciortino, A Geiger and H E Stanley, *Phys. Rev. Lett.* **65**, 3452 (1990)
[47] E Shiratani and M Sasai, *J. Chem. Phys.* **108**, 3264 (1998)
[48] F W Starr, C A Angell, R J Speedy, and H E Stanley, *Entropy, Specific Heat, and Relaxation of Water at 1 atm between 136 K and 236 K* (preprint)
[49] F Sciortino, A Geiger and H E Stanley, *Nature* **354**, 218 (1991)
[50] F Sciortino, A Geiger and H E Stanley, *J. Chem. Phys.* **96**, 3857 (1992)
[51] P Gallo, F Sciortino, P Tartaglia, and S H Chen, *Phys. Rev. Lett.* **76**, 2730 (1996)
F Sciortino, P Gallo, P Tartaglia and S H Chen, *Phys. Rev.* **E54**, 6331 (1996)
[52] H Tanaka, *Nature* **380**, 328 (1996)
H Tanaka, *J. Chem. Phys.* **105**, 5099 (1996)
R J Speedy, *Nature* **380**, 289 (1996)
[53] T Andrews, *Phil. Trans.* **159**, 575 (1869)
[54] F Franks (ed.), *Water: A Comprehensive Treatise* (Plenum Press, NY, 1972) Vol. 1–7; F Franks (ed.), *Water Science Reviews* (Cambridge University Press, Cambridge, 1985) Vol. 1–4
[55] R J Speedy, *J. Phys. Chem.* **91**, 3354 (1987)
[56] C A Angell, Supercooled water, in *Water: A Comprehensive Treatise*, edited by F Franks (Plenum Press, New York, 1982)
[57] P H Poole, T Grande, F Sciortino, H E Stanley and C A Angell, *J. Comp. Mat. Sci.* **4**, 373 (1995)
[58] O Mishima, *J. Chem. Phys.* **100**, 5910 (1994)
[59] O Mishima, *Nature* **384**, 546 (1996)
[60] H Kanno, R Speedy, and C A Angell, *Science* **189**, 880 (1975)
[61] P W Bridgman, *Proc. Amer. Acad. Arts Sci.* **47**, 441 (1912)
[62] L F Evans, *J. Appl. Phys.* **38**, 4930 (1967)

[63] O Mishima and H E Stanley, *Nature* **392**, 164 (1998)
[64] O Mishima and H E Stanley, Discontinuity in Decompression-Induced Melting of Ice IV [Proc. Symposium on Water and Ice, Int'l Conf. on High Pressure Science and Technology AIRAPT-16 & HPCJ-38] *Rev. High Press. Sci. Tech.* **6**, 1103 (1998)
[65] H E Stanley, S T Harrington, O Mishima, P H Poole, and F Sciortino, Cooperative Molecular Motions in Water: The Second Critical Point Hypothesis [Proc. 1997 Symposium on Water and Ice, Intl. Conf. on High Pressure Science and Technology AIRAPT-16 & HPCJ-38], *Rev. High Press. Sci. Tech.* **7**, 1090 (1998)
[66] E Lang and H D Lüdemann, *Ber. Bunsenges. Phys. Chem.* **84**, 462 (1980)
[67] E Lang and H D Lüdemann, *Ber. Bunsenges. Phys. Chem.* **85**, 1016 (1981)
[68] E Lang and H D Lüdemann, *J. Chem. Phys.* **67**, 718 (1977)
[69] E Lang and H D Lüdemann, in *NMR Basic Principles and Progress* (Springer-Verlag, Berlin, 1990) vol. 24, pp. 131.
[70] P C Hemmer and G Stell, *Phys. Rev. Lett.* **24**, 1284 (1970)
G Stell and P C Hemmer, *J. Chem. Phys.* **56**, 4274 (1972)
C K Hall and G Stell, *Phys. Rev.* **A7**, 1679 (1973)
[71] M R Sadr-Lahijany, A Scala, S V Buldyrev and H E Stanley, *Phys. Rev. Lett.* **81**, 4895 (1998)
M R Sadr-Lahijany, A Scala, S V Buldyrev and H E Stanley, *Water-Like Anomalies for Core-Softened Models of Fluids: One Dimension* (preprint)
A Scala, M R Sadr-Lahijany, S V Buldyrev and H E Stanley, *Water-Like Anomalies for Core-Softened Models of Fluids: Two Dimensions* (preprint)
[72] M Canpolat, F W Starr, M R Sadr-Lahijany, A Scala, O Mishima, S Havlin and H E Stanley, *Chem. Phys. Lett.* **294**, 9 (1998)
M Canpolat, F W Starr, M R Sadr-Lahijany, A Scala, O Mishima, S Havlin and H E Stanley, *Structural Heterogeneities and Density Maximum of Liquid Water* (preprint)
[73] G E Walrafen, *J. Chem. Phys.* **40**, 3249 (1964); **47**, 114 (1967)
W B Monosmith and G E Walrafen, *J. Chem. Phys.* **81**, 669 (1984)
[74] M C Bellissent-Funel, *Europhys. Lett.* **42**, 161 (1998)
[75] F W Starr, S Harrington, F Sciortino and H E Stanley, *Phys. Rev. Lett.* **82**, 3629 (1999)
F W Starr, F Sciortino and H E Stanley, preprint
[76] M Meyer and H E Stanley, *J. Phys. Chem.* **103** (1999)
[77] P H Poole, M Hemmati and C A Angell, *Phys. Rev. Lett.* **79**, 2281 (1997)
H E Stanley, C A Angell, U Essmann, M Hemmati, P H Poole and F Sciortino, *Physica A* **205**, 122 (1994)
[78] E G Ponyatovskii, *JETP Lett.* **66**, 281 (1997)