Cooperative molecular motions in water: The liquid-liquid critical point hypothesis

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Abstract

We discuss 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). We also discuss briefly some of the evidence relating to this hypothesis. This evidence is rather tentative at the present time, and is largely based on a growing number of computer simulations using the ST2 and TIP4P intermolecular potentials. We also discuss selected experimental results that are consistent with this hypothesis.

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.

Although water has been the topic of considerable research since the beginning of the century, its peculiar properties are still not completely understood [1,2]. Standard liquid theories fail to explain its dynamical and thermodynamic properties, which differ from those of most other liquids [3–6]. 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 [7–13].

In experiments, it is generally observed that the peculiar properties of water become more pronounced when the liquid is supercooled or stretched [5,6]. In particular, thermodynamic response functions such as the specific heat, isothermal compressibility and thermal expansivity, as well as various relaxation times, seem to exhibit a power law type singularity at a certain temperature $T_A \approx 228$ K, similar to the behavior commonly encountered when approaching a second order phase transition [6,14–16]. Accordingly, an analysis that attempts to elucidate the origin of the anomalies in water might wisely focus on the supercooled and superstretched regions in the phase diagram. Unfortunately, detailed experimental studies of deeply supercooled and stretched water remain difficult to perform due to the increasing probability of ice or gas nucleation as deeper metastable states are probed [17]. As a result, theories for the thermodynamic behavior of metastable water, such as the Speedy-Angell "stability limit conjecture" [15,18–20], have yet to be definitively confirmed or refuted by experimental measurements. On the other hand, molecular dynamics (MD) simulations [21,22] of supercooled and stretched liquid water are increasingly feasible due to dramatic increases in computational power.

The applicability of MD simulations as a theoretical tool to investigate the properties of liquid water has been demonstrated by many research studies. The landmark first MD simulations of water were performed in the late 1960's [23,24]. Since then, computer simulation studies on water and aqueous solutions have immensely broadened our knowledge about this ubiquitous and unusual liquid. MD simulations are capable of mimicking a wide range of measurable properties of water, from thermodynamics [25] to structure [26] and microdynamics [27]. Larger systems (on the order of 10^5 molecules) may be simulated using new algorithms, like those found in the fast multipole methods [28].

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 [29,30]. 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.

2. The hypothesis

Science can progress by making hypotheses, and then testing them. Accordingly, in this talk we will examine the hypothesis that the unusual properties of liquid water are related to the existence of a "second" critical point (Fig. 1). First we present the hypothesis, then we explain why this hypothesis is worthy of critical examination, and finally we briefly review some of the facts that are consistent with the hypothesis.

Water has a well-studied critical point C with coordinates (T_C, P_C, ρ_C), where (to one significant figure) $T_C \approx 600$ K is the critical temperature, $P_C \approx 20$ MPa is the critical pressure, and $\rho_C \approx 0.3$ is the critical density characterizing C. We hypothesize that there
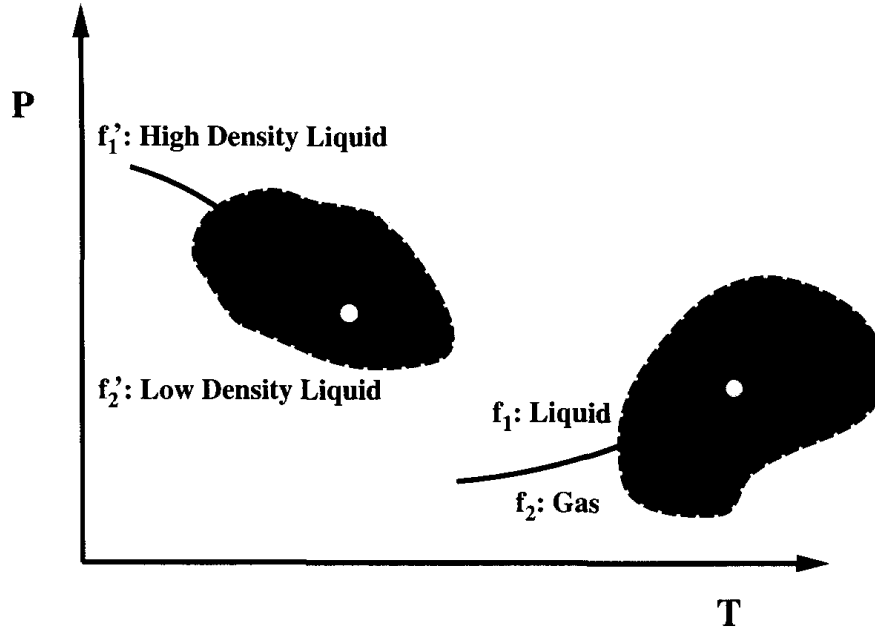
Fig. 1. Schematic projection onto the PT plane of the hypothesized equilibrium phase diagram for water. Shown is the well-known liquid-gas critical point C, which is the terminus of a line of first order phase transitions separating two fluid phases: f_1 (liquid,) and f_2 (gas,), which differ in $\bar{V}$, the first derivative of the Gibbs potential. The shaded area denotes the region of critical behavior. Shown also is the hypothesized HDL-LDL critical point C', which is the terminus of a line of first order phase transitions separating two new fluid phases: f_1' (high-density liquid,) and f_2' (low-density liquid,), which also differ in $\bar{V}$, the first derivative of the Gibbs potential.

may exist a second critical point C' with coordinates $(T_{C'}, P_{C'}, \rho_{C'})$, where (also to one significant figure) $T_{C'} \approx 200$ K, $P_{C'} \approx 100$ MPa, and $\rho_{C'} \approx 1$.

Just as C separates a 1-fluid region (a single phase) above T_C from a 2-fluid region (two phases) below, so also C' separates a 1-liquid region above $T_{C'}$ from a 2-liquid region below $T_{C'}$. The two fluid phases that can co-exist below C – called liquid and gas – differ in volume per molecule $\bar{V}$. The specific volume difference between liquid and gas phases is a suitable "order parameter," which continuously approaches zero as one approaches C displaying a power law singularity characterized by the critical exponent β. Similarly, the two liquid phases that can co-exist below C' differ in specific volume; we shall call these two liquid phases high-density liquid (HDL) and low-density liquid (LDL). Again, this density difference, because it approaches zero as one approaches C', is an order parameter characterizing the liquid-liquid critical point.

The phases differ not only in their volume per molecule $\bar{V}$; they also differ in the entropy per molecule $\bar{S}$. Below T_C, the gas has the larger entropy, while below $T_{C'}$ the HDL phase has the larger entropy. Hence, using the Clausius-Clapeyron relation, the coexistence line in the PT phase diagram has positive slope for C but negative slope for C' (Fig. 1).
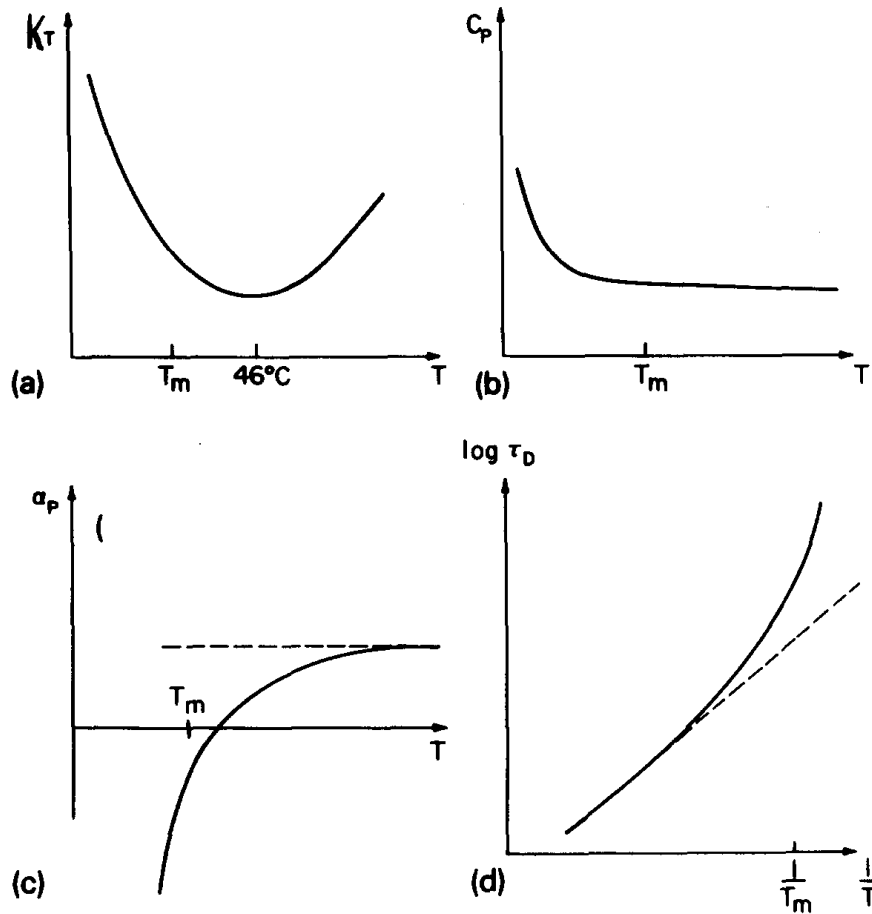
Fig. 2. Schematic dependence on temperature of (a) the isothermal compressibility K_T, (b) the constant-pressure specific heat C_P, (c) the thermal expansivity α_P, and (d) a characteristic time, such as the dielectric relaxation time τ_D. The behavior of a typical liquid is indicated by the dashed line, which very roughly is an extrapolation of the high-temperature behavior of liquid water. Note that the anomalies displayed by liquid water become more striking as one supercools below the melting temperature T_m.

3. Why care?

One might think it senseless to invest much energy studying the critical point, as it is only a single point in an entire phase diagram. However we know that this "one little point" exerts an immense influence on properties at points in the phase diagram that are far away. For example, there are significant deviations in response functions from their corresponding values for a non-interacting fluid at temperatures more than twice the value of the critical temperature T_C.

For water, response functions are also anomalous at temperatures roughly twice the temperature $T_{C'}$ (Fig. 2). For example, the isothermal compressibility K_T is anomalously *large* at temperatures as high as 400 K (100°C); K_T actually passes through a minimum at 319 K (46°C), below which it increases by almost a factor of two as temperature is further decreased. Similarly, the coefficient of thermal expansion α_P is anomalously *small* for temperatures as high as 400 K, and actually decreases to zero at 277 K (4°C), below which it continues decreases at a continually faster rate. Finally, the constant-pressure specific heat

C_P is anomalously large for temperatures as high as 400 K, a fact of tremendous practical importance for using water as a coolant in, e.g., a car engine. The dynamic properties of water are also anomalous, with pronounced non-Arrhenius (often power law) behavior typically occurring at low temperature. Thus if there were a critical point at, say, 200 K, then the influence of this critical point could be of relevance to the anomalies observed in water at much higher temperatures.

4. Why believe?

In the remainder of this talk, we shall discuss some tentative results that are not inconsistent with the critical point hypothesis. First we present an intuitive plausibility argument, then we discuss evidence from simulations and experiments.

4.1. 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 [31].

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 (Fig. 3). 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 [7] 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
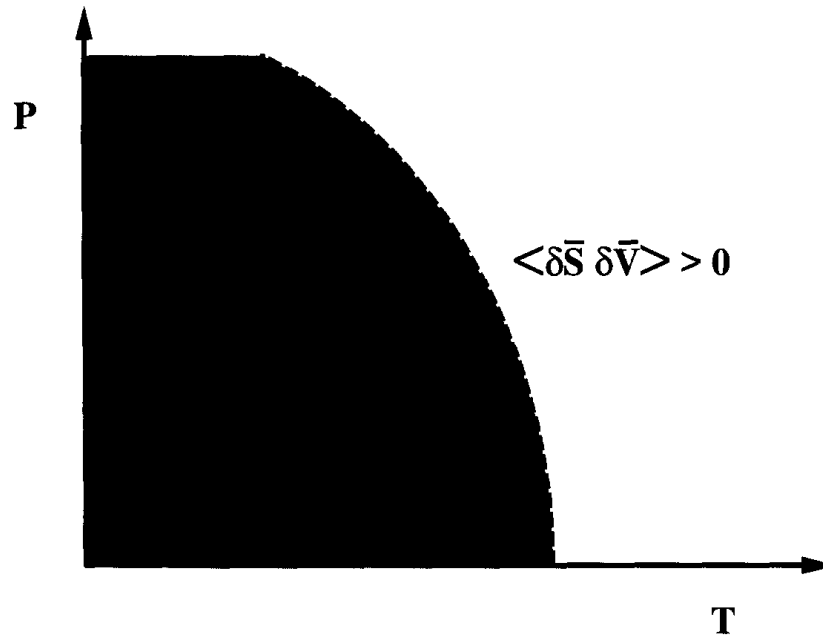
Fig. 3. Schematic illustration of the line of density maxima in the PT plane for water. At all points to the left of this line, the fluctuations in specific entropy $\bar{S}$ and $\bar{V}$ are anti-correlated: if one is positive, the other is more likely to be negative. This fact corresponds to the formation of droplets with lower specific entropy and larger specific volume, and this novel phase is hypothesized to condense out, as a distinct phase, the low-density liquid (LDL), for temperatures below $T_{C'}$.

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. [32] allow each water molecule to be in many bonding states, only one of which corresponds to a "good" quality hydrogen bond (HB) 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 [33,34] 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 $\epsilon = \epsilon_{HB}$. Thus the thermal behavior of the HBs is represented by independent $(\Omega + 1)$-state systems, each described by a partition

function $Z = \Omega + \exp(-\epsilon_{HB}/kT)$. Poole et al. find that for small values of the parameter ϵ_{HB}, there is no critical point (but rather a re-entrant spinodal of the form first conjectured by Speedy [19]). However for ϵ_{HB} above a threshold (about 16 kJ/mol), a critical point appears.

The possibility of a second critical point has received recent support by phenomenological analysis of Ponyatovskii and colleagues [35] and by lattice gas models [34,36]. Also, Roberts and co-workers [37] have shown that simulation results for a microscopic "water-like" Hamiltonian confirms the presence of a second phase transition, previously deduced from approximate calculations [36].

4.2. Evidence from simulations

Simulation studies of liquid water have a rich history and have contributed greatly to our understanding of the subject. In fact, this year is the 25th anniversary of the introduction of the ST2 ("Stillinger-2") potential, in which 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 [24]. 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 (Fig. 4). 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 [38].

One way to obtain less cumbersome simulations is to simplify the intermolecular potential. To this end, the simpler TIP4P potential [39] and the much simpler SPC/E potential [40] have enjoyed considerable popularity. However the opposite direction is also under active investigation: simulating more realistic potentials, such as polarizable potentials [41]. The the researcher is left with the perplexing problem of which model potential to adopt!

Is it more important to steadily improve the reliability of the potential (and therefore approach, however slowly, a genuinely realistic water potential)? Or is it more important to find an extremely simple potential that encompasses the essential physics of liquid water and use this potential to study large-scale properties of the liquid? With some notable exceptions, chemists sometimes favor the former approach, and physicists the latter. Indeed, a physicist would like to discover a potential so simple that the actual connection between the various features of the potential and the resulting predictions can be understood. To this end, recent work of Buldyrev and collaborators [42] using a tunable "soft-core" potential is promising.

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
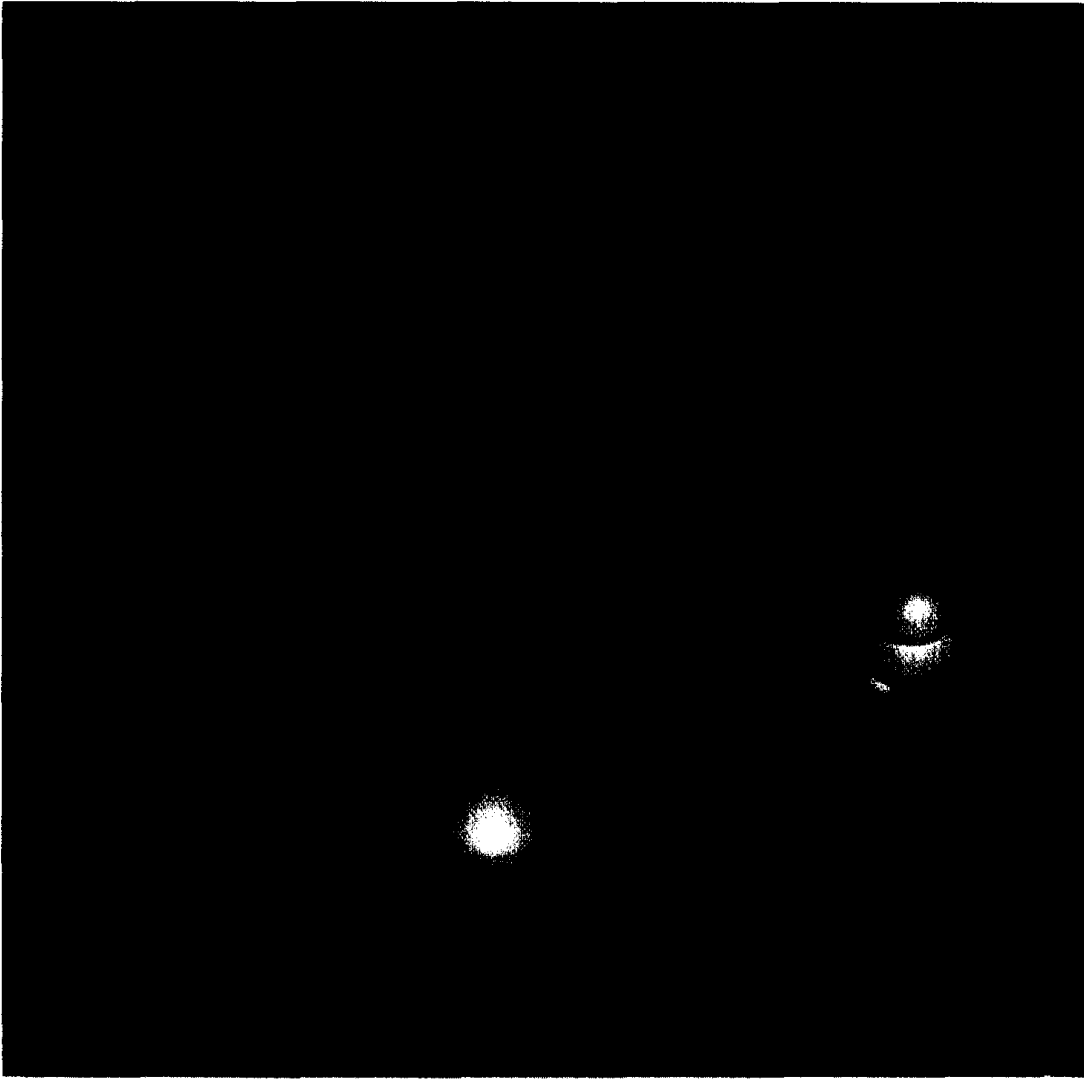
Fig. 4. Screen shot showing the system most commonly studied in molecular dynamics computer simulations, $6^3 = 216$ water molecules confined to a fixed volume and at a fixed energy (the [NVE] ensemble). The colors shown are proportional to the energy of each molecule, with the red end of the spectrum denoting the most strongly bond molecules.

appropriate avenues where future work may strengthen the argumentation.

4.2.1. 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 [43] 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 [44]; this possibility will be discussed briefly at the end of this lecture.

4.2.2. Is there a "kink" in the $P\rho$ isotherms for sufficiently low temperature?

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 [25,45], has very recently been strikingly confirmed for a system 8 times larger [46]. 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 [42,47].

4.2.3. 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. [43] 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 $\rho = 1.05$ g/cm^3 is similar to the experimental data on high-density amorphous (HDA) solid water, while the structure of the structure at $\rho = 0.92$ 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 [48].

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

Sciortino et al. [43] 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 [49]. 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 [48].

4.2.5. Is it possible that two apparent "phases" may coexist below C'?

Convincing evidence for a HDL-LDL critical point C' would be the presence of two coexisting phases below C'. This search is the focus of ongoing work. 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 and find (Fig. 5) that the red molecules and the blue molecules segregate to opposite sites of the 18 A box in which they are residing. These preliminary investigations at a

temperature somewhat below $T_{C'}$ do not prove phase coexistence [46,50], 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 [50]. Additional work remains to be done to establish this point.

4.2.6. 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 [51]. 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 [52]. At low temperatures, it is possible that power law behavior is found [46,38]. 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 [53,54]. 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 [55].

4.2.7. 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 $T_{C'}$ [51]. 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 [56]. This slowing down of the dynamics is consistent with what one expects near a critical point. Specifically, $1/D$ strongly increases as $N_{nn} \to 4$. Consistent with this picture, it was found [57,58] 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 $(N_{nn} - 4)$, the manner in which $N_{nn} \to 4$
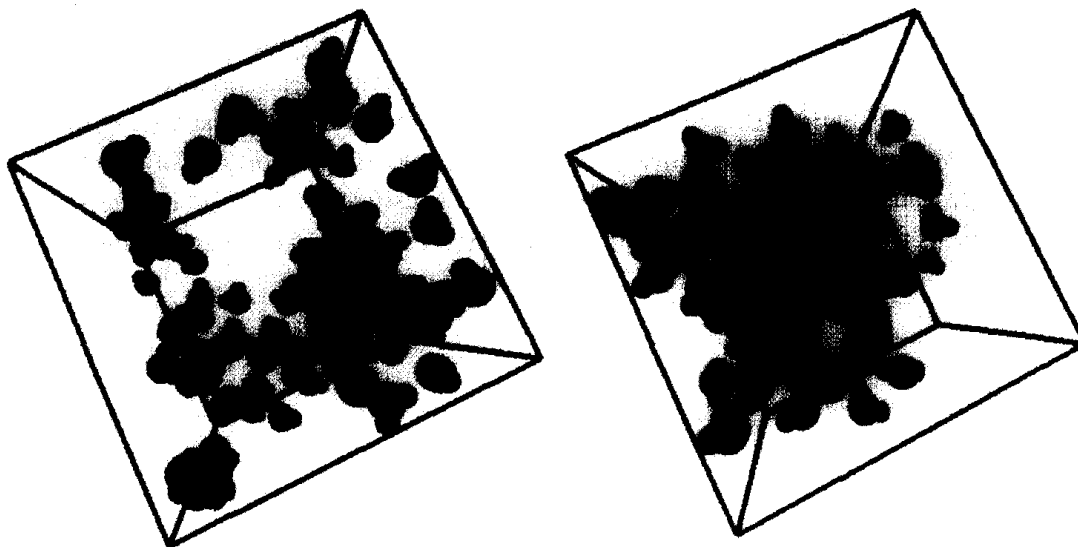
Fig. 5. Preliminary work showing the results of partitioning the molecules in Fig. 4 into two categories, the left picture being the low-density molecules (with coordination number 4) and right picture being the high-density molecules (with coordination number above 4).
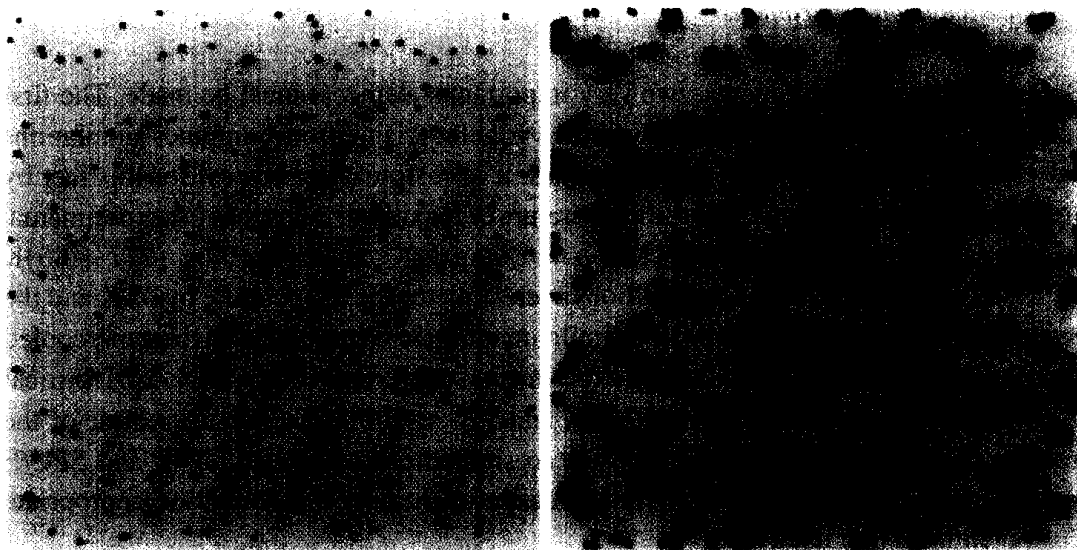

Fig. 6. Preliminary work showing the different time dependence of the two sorts of molecules projected onto 2 dimensions. The left figure is at small time, while the right one is at larger time. One can see that the low-density molecules trace out far less space than the high-density molecules in the same time interval.

is also significant. At high T the decrease of N_{nn} with P is relatively uniform. However, as T decreases, N_{nn} is observed to vary more and more abruptly from a high-coordinated structure ($N_{nn} > 6$) to $N_{nn} \simeq 4$. It should be possible to collapse this family of curves onto a single "scaling function" if the two axes are divided by appropriate powers of $T - T_{C'}$; these tests are underway.

4.2.8. 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" (Fig. 6), we see that the red molecules (corresponding to high densities) move much further than blue molecules (corresponding to low densities) [46,50]. 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 [59].

4.2.9. 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 [60]. 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 [60]. The resolution between the two different values of $P_{C'}$ is an open question that will hopefully be resolved shortly.

4.3. Evidence from experiments

Before discussing experiments, two very important statements must be made. The first is that the numerical values of thermodynamic variables arising from computer simulations are always rather different from the true values. It is customary to correct for this fact by comparing the values of T and P at the temperature of maximum density to the experimental values. In the case of ST2, e.g., the TMD $\rho = 1.00$ g cm^{-3} appears at $T = (277 + 35)$K and $P = 82$ MPa, so ST2 at these conditions overestimates the temperature by 35 K and the pressure by 82 MPa. If a correction of a similar magnitude were to hold in the supercooled region, then we would anticipate that the experimental coordinates of the HDL-LDL critical point would be approximately $T_{C'} \approx 200$ K and $P_{C'} \approx 100$ MPa. The magnitude of the correction depends upon the potential used, so simulations using the TIP4P and SPC/E potentials can be compared with ST2 or with experiment only if a correction appropriate to that potential is first made.

The second statement concerns the presence of an impenetrable "Berlin wall": the line $T_H(P)$ of homogeneous nucleation temperatures [1,4]. By careful analysis of experimental data above $T_H(P)$, Speedy and Angell pioneered the view that some sort of singular behavior is occurring in water at a temperature $T_s(P)$ some 5–10 degrees below $T_H(P)$. Regardless of the pressure, they found that the identical value of $T_s(P)$ could be used to fit the behavior of quite distinct equilibrium and dynamic quantities.

With these two caveats, one can begin to discuss relevant experimental work. Three general types of experiments have been performed, the first corresponding to a single isobar at 0.1 MPa, the second to a family of isobars up to 600 MPa, and the third to a family of isotherms below $T_{C'}$.

4.3.1. Density fluctuations along the P = 0.1 MPa isobar

The correlation length ξ for density fluctuations should increase close to a critical point; this quantity has recently been measured along a $P = 0.1$ MPa isobar [61], down to quite low temperatures (239 K). A gentle increase in correlation length was found, but no indication of a divergence, consistent with the possibility that the HDL-LDL critical point, if it exists, lies at a much higher pressure.

4.3.2. Structure along isobars up to P = 600 MPa

Bellissent-Funel and Bosio have recently undertaken a detailed structural study of D_2O using neutron scattering to study the effect of decreasing the temperature on the correlation function [48]. As paths in the PT phase diagram, they have chosen a family of isobars ranging in pressure up to 600 MPa (well above the HDL-LDL critical point of about 100 MPa). They plot the temperature dependence of the first peak position Q_o of the structure factor for each isobar. They find that for the 0.1 MPa isobar, Q_o approaches 1.7 A^{-1} – the value for LDA, low-density amorphous ice. In contrast, for the 465 and 600 MPa isobars, Q_o approaches a 30% larger value, 2.2 A^{-1} – the value for HDA, high-density amorphous ice. For the 260 MPa isobar, $Q_o \rightarrow 2.0\ A^{-1}$, as if the sample were a two-phase mixture of HDA and LDA.

4.3.3. Reversible conversion of LDA to HDA with pressure

Since the HDL-LDL critical point occurs below $T_H(P)$, it is not possible to probe the two phases experimentally. However two analogous solid amorphous phases of H_2O have been studied extensively by Mishima and co-workers [62–64]. In particular, Mishima has recently succeeded in converting the LDA phase to the HDA phase on increasing the pressure, and then reversing this conversion by lowering the pressure. The jump in density was measured for a range of temperatures from 77 K to 140 K, and the density jump (when HDA is compressed to LDA) was found to occur at roughly 200 MPa. Moreover, the magnitude of the density jump decreases as the temperature is raised, just as would occur if instead of making measurements on the HDA and LDA amorphous solid phases, one were instead considering the HDL and LDL liquid phases. These results are corroborated by independently performed computer simulations using both the ST2 and TIP4P intermolecular potentials [65].

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

5. Discussion

Thus far in this talk, we have presented some tentative evidence that is consistent with the hypothesis that there exists a second HDL-LDL critical point C', in addition to the well-known liquid-gas critical point C. There are also some facts, which we next present, that do not favor the existence of C'.

First, the vast experimental work of Angell and co-workers [4,6] is equally consistent with a line of spinodal singularities or with a HLD-LDL critical point, and the generalized van der Waals theory is equally consistent with both possibilities [32].

Moreover, the observed polymorphism of amorphous *solid* water which was invoked to support the possibility of a line of liquid-liquid phase transitions terminating in a critical point supports, but certainly does not prove, the existence of a phase transition in the behavior of the supercooled *liquid*. Merely a large but finite value of K_T might be sufficient to account for abrupt density changes in the amorphous ices in the glass regime [66,67].

Very recently, the dynamics of SPC/E water have been found to be well described by mode coupling theory, with no need to invoke the presence of a critical point [59]. For ST2 water, on the other hand, the situation may be somewhat different [68,46,50].

Perhaps the most compelling argument against the hypothesized existence of a HDL-LDL critical point C' is parsimony: "the correct physics is often the physics with the minimum of assumptions". Of necessity, it is not possible to experimentally verify for metastable water divergences of response functions as convincingly as one can for the liquid-gas critical point. Thus, it remains conceivable that response functions that would diverge at a critical point in fact remain finite in metastable water. In particular, Sastry and co-workers [44] have demonstrated that the low temperature increase of compressibility upon lowering temperature arises strictly as a thermodynamic consequence of the presence and negative slope of the TMD line. Without further assumptions, such increase in the compressibility results simply (and at most) in a compressibility maximum at low temperatures. Actually, the thermodynamic analysis of Sastry et al., however, lends indirect support to the HDL-LDL critical point hypothesis, for it shows that the expectation of *extrema* in the compressibility is reasonable given the type of "density anomaly" observed at higher temperatures in simulations. A thermodynamic analysis alone suffices to predict that a locus of compressibility extrema exists at low temperatures, given the locus of density maxima (TMD) as seen in simulations. What remains to be shown is that these extrema at low enough (but *finite*) temperatures are *singular* extrema, i.e., that the compressibility either diverges (as at the critical point) or becomes discontinuous (along the associated first order line) along the locus of compressibility extrema predicted by the thermodynamic analysis.

It is possible that there are other amorphous materials for which fluctuations in their local structure are enhanced due to tetrahedrality or other considerations [69]. 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 [70] or whether they be more complex structures like amorphous carbon which appears to display strikingly ordered local heterogeneities as it is heated toward its crystallization temperature (Fig. 7).

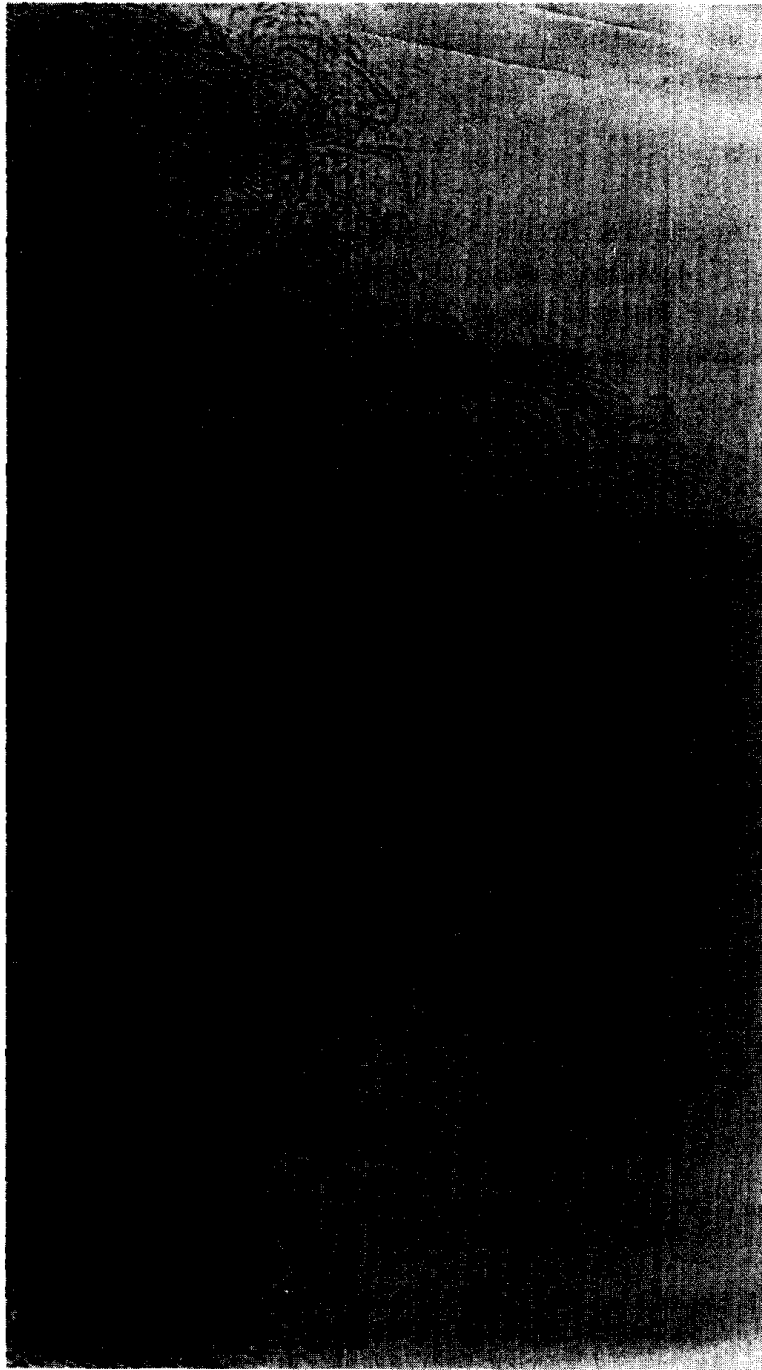Many open questions remain, and many experimental results are of potential relevance

Fig. 7. Photograph of amorphous carbon, being heated to just below the point where it crystallizes into coal. This very heterogeneous system is characterized by visually-apparent clusters, of partially ordered carbon rings. Courtesy of Robert L. Hurt.

to the task of answering these questions. For example, the collective excitations that occur at low frequency and large wave vector [71] have been the object of much recent work [72,73]. Also, the full implications of a re-entrant spinodal possibility [74–77] may not have been fully incorporated into our understanding of water. The minimum exhibited by the *adiabatic* compressibility in atmospheric pressure experiments [78] is of potential

relevance since a maximum in any quantity that would be singular at a spinodal may be relevant to placing the critical point at a larger pressure than atmospheric.

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