Cooperative Molecular Motions in Water

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We discuss evidence relating to the hypothesis that, in addition to the known critical point in water (below which two fluid phases—a lower-density gas and a higher-density liquid—coexist), there exists a "second" critical point at low temperatures (below which two liquid phases—a higher-density liquid and a lower-density liquid—can coexist).

§1. The hypothesis

Water has a well-studied critical point C with coordinates (T_C, P_C, ρ_C), where (to one significant figure) $T_C \approx 600\text{K}$ is the critical temperature, $P_C \approx 20\text{MPa}$ is the critical pressure, and $\rho_C \approx 0.3$ is the critical density characterizing C. It has been hypothesized [1] that there may exist a second critical point C' with coordinates $(T_{C'}, P_{C'}, \rho_{C'})$, where (also to one significant figure) $T_{C'} \approx 200\text{K}$, $P_{C'} \approx 100\text{MPa}$ 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 $T_{C'}$.

§2. Motivation

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. Thus if in water there were a critical point at, say, 200K, then the influence of this critical point could be of relevance to the anomalies observed in water at much higher temperatures.

§3. Tentative evidence

3.1. *Plausibility arguments and calculations based on models*

Water differs from most liquids due to the presence of a line of maximum density (TMD line) in the PT phase diagram. This TMD line 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 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.[2] 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 support from a recent generalization of the van der Waals theory,[3] from phenomenological analysis[4] and from lattice gas models.[5],[6]

3.2. *Evidence from simulations*

We 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.

3.2.1. 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[7] are

consistent with a plausible extrapolation to a single point in the phase diagram at which $K_T^{\max} = \infty$ (but see Ref. 8)).

3.2.2. 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,[1],[9] has very recently been strikingly confirmed for a system 8 times larger.[10] 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.

3.2.3. 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'. Studies just below the estimated value of $T_{C'}$ at two values of ρ on the two sides of $\rho_{C'}$ show 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.[7] 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.[11]

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

Sciortino et al.[7] 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. For $T \le 273$ 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.[11]

3.2.5. 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, and preliminary work is encouraging.[10] Calculations of the two tentatively identified HDL and LDL phases suggest similarities with experimental results on the two amorphous solid phases HDA and LDA.

3.2.6. 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.[12]

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

Slowing down of the dynamics is what one expects near a critical point. 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 $T_{C'}$.[12]

Appearing to diverge at roughly the same temperature is the inverse of the self-diffusion coefficient D:[13] $1/D$ strongly increases as $N_{nn} \to 4$. Consistent with this picture, it was found [14] that additional nearest neighbors beyond 4 have a "catalytic" effect on the mobility of the central molecule.

3.2.8. 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", we see that the red molecules (corresponding to high densities) move much further than blue molecules (corresponding to low densities).[10] 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.[15]

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

Recently, Tanaka independently found evidence supporting a liquid-liquid critical point by performing simulations for the TIP4P potential .[16]

3.3. *Evidence from experiments*

3.3.1. 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,[17] down to quite low temperatures (239K). 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.

3.3.2. 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.[11] 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, $Q_o \to 2.0A^{-1}$, as if the sample were a two-phase mixture of HDA and LDA.

3.3.3. 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.[18] 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.[19]

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.

§4. Discussion

Many open questions remain, and many experimental results are of potential relevance to the task of answering these questions. For example, we are undertaking a complete analysis of the newly-available experimental equation of state data on water to test if the data exhibit the data-collapse characteristic of a critical point when a critical point is assumed to exist.

Before concluding, we note that possibly there are other amorphous materials for which fluctuations in their local structure are enhanced—whether they be other materials with tetrahedral structures (and corresponding TMD lines) such as SiO_2 or whether they be more complex structures like amorphous carbon which appears to display strikingly ordered local heterogeneities as it is heated toward its crystallization temperature.

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