Pronounced structural crossover in supercritical water

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There have been ample studies of H$_2$O states and transitions between those states. We address the hitherto unexplored deep supercritical state, where no transitions are thought to take place and where all properties are expected to vary smoothly. We find that supercritical water undergoes a structural crossover at deep supercritical pressure up to 45 times the critical pressure, giving a new insight into water phase diagram and opening up a new avenue into water research. Specifically, the crossover is sharp and pronounced at low pressure and is seen in the dramatic changes of pair distribution functions at the Frenkel line. We relate this crossover to the transformation from tetrahedral-like structure at low temperature to more closely packed arrangement at high temperature. At higher pressure, the crossover takes place in the closely-packed structure of deeply supercritical water.

H$_2$O is the most abundant and studied compound. Its properties in crystalline, amorphous, liquid and supercooled states are well documented, yet not well understood due to a variety of interesting anomalies that continue to inspire [1, 2]. Critically, little is known about the properties of supercritical water despite its increasing deployment in important industrial processes and environmental applications [3–6].

Here, we extend pressure and temperature deep into the supercritical state and find that supercritical water undergoes a sharp and pronounced structural crossover which we attribute to the dynamical crossover at the Frenkel line (FL) proposed previously. At low pressure, the crossover is from tetrahedral-like to a more closely-packed structure. At high pressure, the crossover takes place within the closed-packed arrangement. Our results give a new insight into the phase diagram of water, serve as a guide for future high-pressure and high-temperature experiments, and have practical applications because dissolving and extracting properties are optimised at the FL [7].

We note that high-pressure and high-temperature experiments in water are challenging and scarce as a result. The structure of high-pressure water was studied along the melting curve [8], however very few studies used pressure and temperature conditions above the melting curve and close to the FL [9]. The experimental challenges resulted in a widely-spaced grid of temperature and pressure on the phase diagram as shown in Fig. 1. Coupled with no guide from theory, this precluded the identification of the FL crossover in supercritical water.

Traditionally, deeply supercritical state was thought to undergo only smooth changes in response to pressure and temperature but with no qualitative changes [6]. Recent discussion challenged this understanding. A proposal based on the qualitative change of particle dynamics in the supercritical state introduced the Frenkel line (FL) separating two supercritical states [10,12]. Below the line, particle dynamics combine solid-like oscillations around quasi-equilibrium positions and diffusive jumps between different positions. Above the line, particle dynamics lose the oscillatory component and become purely diffusive [10,12]. This gives a practical criterion to calculate the FL based on the disappearance of minima of the velocity autocorrelation function (VAF). The FL corresponds to the loss of solid-like transverse quasiharmonic modes from the system spectrum, corresponding to the specific heat $c_v$ equalling 2$k_B$ in the harmonic case for simple systems [12]. Since structure and dynamics are related, the dynamical crossover results in a change in how the structure evolves with temperature, which in simple Lennard-Jones liquids is seen as a change in behaviour of the pair distribution function peak heights above and below the FL [13]. Here, we find that unlike in simple liquids, the structural crossover in water is unusually sharp and pronounced and takes place at the FL.

Interesting and anomalous effects in water are related to its tetrahedral structure and transitions to higher-coordinates states, as discussed below in detail. At and above GPa pressures, water becomes high-coordinated

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{(Colour online) Phase diagram of H$_2$O showing the Frenkel line, together with earlier experimental ($P,T$) points [8,9] and currently used state points. We show the Widom line using the data of Ref. [18].}
\end{figure}
and its tetrahedral network is lost [8]. Close to FL conditions and below 1 kbar, water is a tetrahedral network at low temperature, but its properties are affected by persisting near-critical anomalies, obscuring structure-related effects. This gives an interesting and unexplored window around 1-10 kbar where water is tetrahedral at low temperature and is unaffected by the vicinity of the critical point.

The FL for H\textsubscript{2}O was previously calculated using the VAF criterion \[7\]. This gives the following state points at the FL in 1–10 kbar pressure range: (1 kbar, 525 K), (2.5 kbar, 550 K), (5 kbar, 580 K), and (10 kbar, 680 K). We recall that the FL extends to arbitrarily high pressure and temperature above the critical point, but at low temperature it touches the boiling line at around 0.8\(T_c\), where \(T_c\) is the critical temperature \[12\] (note that the system does not have cohesive liquid-like states at temperatures above approximately 0.87\(T_c\) \[21\], hence crossing the boiling line at those conditions can be viewed as a gas-gas transition \[12\].) The critical point of water is \(P_c = 0.22\) kbar, \(T_c = 647\) K, hence the first three state points are above \(P_c\) and below \(T_c\), whereas the last point is above both \(P_c\) and \(T_c\). We note that the supercritical state is often defined as the state at \(P > P_c\) and \(T > T_c\). This definition is loose, not least because an isotherm drawn on \((P,T)\) diagram above the critical point crosses the melting line (see Fig. 1), implying that the supercritical state can be found in the solid phase. As a result, one can meaningfully speak about near-critical part of the phase diagram only (see Ref. \[22\] for details). As far as our state points are concerned, they correspond to temperatures much higher than the melting temperature and pressures far in excess of \(P_c\), where near-critical anomalies are non-existent \[22\].

We perform extensive molecular dynamics (MD) simulations using the DL_POLY package \[14\] using the TIP4P/2005 potential for water optimised for high pressure and temperature conditions \[15\]. A careful analysis \[10, 17\] has assigned this potential the highest score in terms of the extent to which the results agree with different experimental properties, including the equation of state, high-pressure and temperature behavior and structure. The potential was used in a high-pressure and high-temperature study of the Widom line in supercritical water \[18\]. The Widom line (WL) is the line of persisting critical anomalies above the critical point, defined as the line of maxima of heat capacity \[19\]. Differently from the WL, the FL is (a) unrelated to the critical point and exists in systems with no boiling line and critical point, (b) extends to arbitrarily high pressure and temperature as long as the chemical bonding is unaltered (the WL disappears above the critical point fairly quickly as is seen in Fig. 1) and (c) independent on the path taken on the phase diagram \[11, 12, 20\].

We equilibrated the system of 32768 water molecules in the constant temperature and pressure ensemble at 1, 2.5, 5, 10 kbar and 30 kbar for 30 ps. The data were collected from subsequent production runs at the constant energy and volume ensemble for 70 ps. We have simulated 19-21 temperature points at each pressure in the range enveloping the temperature at the FL (see below). Electrostatic interactions were handled by the smooth particle mesh Ewald method. The FL for water was calculated with same potential using the VAF criterion \[7\] and is shown in Fig. 1.

We show the calculated pair distribution functions (PDFs) in Fig. 2 (the interatomic potential treats H\textsubscript{2}O molecules as rigid units, and we show O-O correlations).

We observe a sharp and pronounced crossover in the low-pressure range. At 1 kbar we see the disappearance of the second and third peaks at temperature corresponding to the FL, \(T_F\) (see Figs. 2 and 3). Concomitantly, a new second peak sharply emerges at a new radial position at \(T_F\). This is clearly seen in the temperature behavior of peak heights in Fig. 3. The crossover seen in the peak heights is accompanied by equally pronounced crossovers of the peak positions at \(T_F\) in Fig. 4 second and third peaks sharply terminate at the FL and are followed by the newly emerged peak. A similar behavior is seen in Figs. 3,4 at 2.5 kbar.

As discussed above, experimental PDFs at conditions close to the FL are scarce. We have selected the state points in the experimental work \[9\] that are close to the simulated ones at the FL and show the corresponding PDF, together with the PDF simulated at the same state points, in Fig. 2. We observe a good agreement between experimental and simulated PDFs at ambient conditions (a slight overestimation of the first peak height in simulations is a known feature of the potential \[17\]). At high pressure and temperature, we observe a similar behavior in the experimental data to that seen in Fig. 2-a: the second and third peaks disappear at high temperature, and the new second broader peak emerges around 6 Å.

At 5 kbar, the lowest temperature PDF displays the second and third peaks which soon disappear. At 10 kbar, the PDFs continuously evolve with no new peaks appearing but still demonstrate the expected \[14\] change in structural evolution over the FL, as can be seen by the change of gradient of the peak heights in Fig. 3 (d).

We attribute the observed pronounced crossovers of PDF features at low pressure to the crossover at the FL, coupled with a water-specific structural transformation. As discussed above, the FL corresponds to the dynamical crossover of molecular motion from combined diffusion and oscillation to pure diffusion. The solid-like oscillatory component implies that average molecular positions do not change during time \(\tau\), the liquid relaxation time \[23\]. On the other hand, a purely diffusive character of motion implies continuous molecular rearrangements. As a result, structural correlations are also expected to undergo a crossover at the FL.

In water, this crossover results in the sharp and pro-
FIG. 2: (Colour online) (a)-(d): O-O PDFs of simulated supercritical water at different pressure and temperature. (e) Simulated and experimental PDF at low and high temperature, offset by 1 for convenience.

FIG. 3: O-O PDF peak heights of supercritical water (note that the “second peak” in (c) corresponds to the third peak at lower temperatures). The dashed vertical line corresponds to temperature at the Frenkel line. The straight lines are drawn as guides.
nounced crossover of the second and third peaks of PDFs for the following reason. Water is known to undergo a structural transformation from tetrahedral-like structure governed by hydrogen bonding at low temperature to a more closely-packed structure at high temperatures and at high pressures \cite{24,26}. The second peak in the low-temperature tetrahedral-like structure, corresponding to next-nearest neighbours, disappears during this transformation. In the higher-coordinated structure at high temperature, the second peak corresponds to a new distance which is between the second and the third peaks in the low-temperature structure (see Fig. 4). This behavior was seen in subcritical water in both quantum-mechanical calculations and experiments \cite{8,9}.

In this picture, the FL acts as a facilitator to water’s structural crossover between the tetrahedral-like and more closely-packed structures. Indeed, once the solid-like oscillatory component of molecular motion is lost in the tetrahedral structure at the FL, water molecules acquire purely diffusive motion and hence flexibility to arrange into a denser structure in response to high pressure.

We support this interpretation by two direct calculations of the structural data: the coordination numbers calculated as the area below the first PDF peak and distributions of angles from a given molecule to its neighbours, shown in Fig. 5. At 1 kbar and 2.5 kbar, the coordination number \( n_c \) are close to 4 as expected in the tetrahedral-like structure and notably increases with temperature. Such an increase is anomalous (in a sense that \( n_c \) and density usually decrease with temperature) and is characteristic for water where higher temperature breaks tetrahedral hydrogen-bonded structure, enabling extra water molecules to move closer to a given molecule. We further observe that \( n_c \) at low pressure increases up to about \( T_F \), at which point the transformation to the closely-packed structure is complete, in line with our earlier interpretation that the disappearance of solid-like oscillatory component of molecular motion at the FL promotes the disappearance of the tetrahedral-like structure and enables densification to the closely-packed arrangement. The increase of \( n_c \) up to \( T_F \) is followed by its decrease and the formation of maxima of \( n_c \). The decrease of \( n_c \) takes place in a closely-packed structure and is a generic effect of density decrease with temperature. Unlike at low pressure, no maxima are seen at higher pressure where the closely packed structure forms at the low temperature already and where \( n_c \) follow a generic decrease with temperature.

The transformation from low-density tetrahedral-like to more closely-packed structure is also seen in the angular distribution in Fig. 5. The distribution has a peak at the tetrahedral angle of around 110° at low temperature. As temperature increases, a new peak at around 60° emerges and increases, representing close packing. The new peak reaches its maximum close to \( T_F \), corresponding to the largest number of closely-packed molecules. The angular distribution starts to flatten at yet higher temperature, corresponding to the progressive loss of order in the structure. Representative structure snapshots with 4-fold and 6-fold coordinated water molecules are shown in Fig. 5. We also observe the regions of high density (of about 15-30 Å above the FL). This agrees with small-angle neutron scattering results in supercritical \( \text{CO}_2 \), which reported the appearance of droplets above the FL \cite{24}.

We now return to the PDF features at higher pressure. As mentioned earlier, water’s structure at high pressure is no longer tetrahedral even at low temperatures, implying that the crossover at the FL takes place in the closely-packed structure between states with the same coordi-
FIG. 5: (a): Average coordination number $n_c$ of water molecules at supercritical pressures as temperatures across the Frenkel line. $n_c$ is not shown at low temperature at 5 kbar because the minimum between the first and second peaks in Fig. 2 disappears at those temperatures, removing the integration limit of the area below the first peak. (b): Inter-molecular angular distribution function of supercritical water at 1 kbar. The dashed line shows the distribution at temperature corresponding to the Frenkel line. (c): Snapshots of simulated water structure at ($P = 1$ kbar, $T = 300$ K) (top) and ($P = 1$ kbar, $T = 930$ K) (bottom) showing 4- and 6-fold coordinated water molecules.

In summary, we have identified a structural crossover in supercritical water at the FL. Sharp and pronounced at low pressure, the transition takes place at the FL which facilitates the transition from tetrahedral-like to more close-packed structure. At high pressure, the crossover similarly takes place at the FL but in the closely-packed arrangement, similar to that seen in simple liquids [13].

The structural transition of supercritical water importantly adds to the previous experimental work revealing the structural crossover in liquid Ne [27] and CH$_4$ [28] at the FL. It is also important for two further reasons. First, our results serve as a stimulus and a guide for future high-pressure and high-temperature experiments aimed at elucidating the supercritical water phase diagram. Second, experimental data suggest that dissolving and extracting properties of supercritical fluids are optimised at the FL [11]. Supercritical water is increasingly used in dissolving and environmental applications [6], hence our results are industrially relevant.

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