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Communication: Diffusion constant in supercooled water as the Widom line is crossed in no man's land

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According to the liquid-liquid critical point (LLCP) hypothesis, there are two distinct phases of supercooled liquid water, namely, high-density liquid and low-density liquid, separated by a coexistence line that terminates in an LLCP. If the LLCP is real, it is located within No Man's Land (NML), the region of the metastable phase diagram that is difficult to access using conventional experimental techniques due to rapid homogeneous nucleation to the crystal. However, a recent ingenious experiment has enabled measurement of the diffusion constant deep inside NML. In the current communication, these recent measurements are compared, with good agreement, to the diffusion constant of E3B3 water, a classical water model that explicitly includes three-body interactions. The behavior of the diffusion constant as the system crosses the Widom line (the extension of the liquid-liquid coexistence line into the one-phase region) is analyzed to derive information about the presence and location of the LLCP. Calculations over a wide range of temperatures and pressures show that the new experimental measurements are consistent with an LLCP having a critical pressure of over 0.6 kbar. *Published by AIP Publishing.* https://doi.org/10.1063/1.5029822

The anomalous properties of supercooled water continue to fascinate researchers in the field.[1–8] One example is the increasing compressibility as the temperature is lowered[8–10] (for normal substances, the compressibility is expected to decrease with decreasing temperature). A possible scenario explaining this behavior is the presence of a liquid-liquid critical point[11,12] (LLCP) located in the high-pressure region of the metastable phase diagram. The putative LLCP terminates a coexistence line separating high-density liquid (HDL) and low-density liquid (LDL) phases. Extension of the coexistence line into the one-phase region gives rise to the Widom line[13,14] which denotes the line of maximum correlation length. Within the LLCP scenario, the Widom line extends from the critical point at high pressures, all the way to (and past) 1 bar. Notably, the Widom line is closely approximated by the line of maximum compressibility,[14–17] and hence, within this scenario, at 1 bar the compressibility grows because the Widom line is being approached.

This LLCP, if it exists, is thought to be located in No Man's Land (NML),[11,12] the region of the metastable phase diagram that cannot be easily accessed by conventional experimental techniques, either by lowering the temperature for supercooled water or raising the temperature for amorphous ices, because of homogeneous nucleation to crystalline ice.[18,19] Still, some have inferred the presence and location of the LLCP by extrapolating the properties of supercooled water to lower temperatures[20–23] or by analyzing the melting curves of various ice phases.[24,25]

Others have performed ingenious experiments where the system actually manages to enter into NML. In 2012, Wyslouzil and co-workers measured infrared (IR) spectra of 5.8 nm radius water droplets at temperatures ranging from 217 to 229 K and at internal Laplace pressures near 290 bars.[26] In 2014, Nilsson and co-workers measured the x-ray scattering from somewhat larger droplets (such that the internal pressure is approximately 1 bar) and from that deduced the height of the second peak of the oxygen radial distribution function, g_2, from 323 K down to 227 K.[27] The metrics of the IR line shape changed linearly from 217 K to 229 K, as did the value of g_2 over the range 227 K to 245 K. In late 2017, Nilsson and co-workers published additional data for these larger droplets, determining the compressibility from the $q \to 0$ limit of the x-ray scattering structure factor.[28] These data showed that the compressibility (at 1 bar) has a maximum at 229 K (as does the correlation length), which provides evidence for the LLCP scenario[28,29] (and in which case the Widom line at 1 bar would be at 229 K). By comparing the value of the observed compressibility at the maximum to the results from MD simulations, these authors conclude that the critical pressure is about 800 bars.

Both Nilsson experiments were performed only at atmospheric pressure, and so the best estimate of the Widom line in the p-T plane comes from the venerable Kanno-Angell compressibility experiments, performed from 1 bar to 2 kbar.[10] For each pressure, the compressibility data were extrapolated to lower temperatures and fit with a power law to obtain a series of "singularity temperatures." Even though the compressibility is not actually expected to diverge at the Widom line according to the high-pressure LLCP scenario (it should simply be a maximum), the line of extrapolated singularity temperatures may nonetheless be a reasonable approximation to the Widom line. Indeed, at 1 bar, the singularity temperature from the Kanno-Angell experiments is 228 K, while the temperature of the maximum compressibility from the Nilsson experiments is 229 K.

In Fig. 1, we show the homogeneous nucleation line (the high-temperature border of NML),[18] the Kanno-Angell (putative Widom) line,[10] the temperature of the maximum compressibility at 1 bar,[28] one possible location of the experimental LLCP (at 1.95 kbar and 168 K),[30,31] and the extrapolated HDL/LDL coexistence line. We also show the range of temperatures for the Wyslouzil experiments (at 290 bars)[26] and the range of temperatures for the two Nilsson experiments (at 1 bar).[27,28] Notably, one sees that the state points for these experiments cross the Kanno-Angell line (which is at 228 K for 1 bar). What would one expect for g_2 or IR line shapes as the Widom line is crossed? If one crosses the Widom line close to the critical point, the system should change rapidly from being HDL-like to LDL-like, and observables like g_2 and IR line shapes, which depend on density and structure, should exhibit a sigmoidal temperature dependence.[30,31] On the other hand, when one is far from the critical point and the distinction between HDL-like and LDL-like regions becomes much less clear, g_2 and IR line shapes should change more slowly and linearly.[30–32] The fact that the experimental g_2 and IR line shapes change linearly suggests that either: (1) there is no LLCP; (2) the estimate of the Widom line is not correct; or (3) the LLCP is at much higher pressure (than 1 bar or 0.29 kbar).

From the theory side, there has been much controversy concerning the presence and location of the possible LLCP from different simulation models.[33–51] However, there is a growing consensus that many reasonable simulation models do show an LLCP.[11,30,51–54] For example, simulations with the TIP4P/2005 model are consistent with an LLCP at about 1.7 kbar and 182 K.[54] We have been working with a related model that includes explicit three-body interactions called the E3B3 model[55] which uses TIP4P/2005 as the two-body reference. The LLCP in this model is located at about 2.1 kbar and 180 K.[30] We have calculated g_2[30] and IR line shapes[31] for this model at various state points in the metastable region of the p-T plane: at pressures (1 bar to 1 kbar) much lower than the (theoretical) critical pressure, we find that these properties change smoothly as one crosses the theoretical Widom line, but at higher pressures (1.5 to 2 kbar), these properties show dramatic changes, consistent with the expectation described above. Moreover, the E3B3 model provides good agreement with both experimental observables over the relevant temperature ranges.[30,31] We thus conclude that the E3B3 model is a reasonable one for supercooled water and that the existing experimental observables change smoothly because the experimental pressures (1 bar and 0.29 kbar, respectively) are much lower than the experimental critical pressure (possibly near 2 kbar[30]).

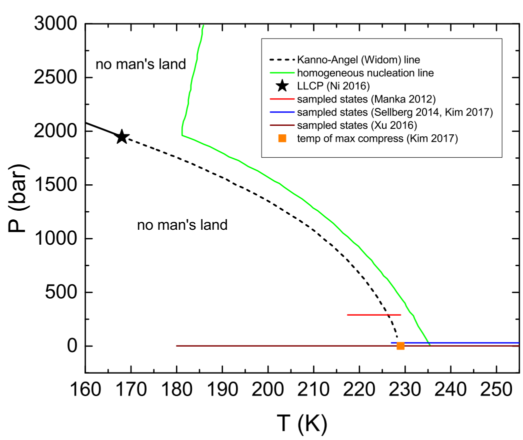

FIG. 1. Proposed metastable phase diagram for supercooled water. The black star at 168 K and 1.95 kbar represents a proposed location of the LLCP.[30] The LLCP terminates the coexistence line (solid black) separating HDL and LDL phases. The Kanno-Angel (Widom) line (dashed black)[10] emanates from the LLCP and extends into the one-phase region. Also shown are the homogeneous nucleation line (green),[18] the temperature of maximum compressibility at 1 bar[28] (orange square), and the states sampled by Wyslouzil and co-workers (solid red),[26] Nilsson and co-workers (solid blue),[27,28] and Xu *et al.* (solid dark red).[56]

In late 2016, a new set of experiments appeared,[56] using another ingenious technique, which measured the motion of the phase boundary between crystalline ice and supercooled water deep inside NML at 1 bar. From these data, the authors inferred the diffusion constant, which changed by 11 orders of magnitude from 126 to 262 K. Notably, the diffusion constant changed smoothly over the entire temperature range (although there is a gap in the data between 151 and 180 K where experiments could not be performed), including as the putative Widom line is crossed at 229 K. The range of temperatures for the higher-temperature set of experiments is shown in Fig. 1. The authors concluded that the data rule out the possibility of a "singularity at or near 228 K at ambient pressures," provide "no evidence of a liquid-liquid transition line extending to negative pressures," are "consistent with a previous prediction... that assumed no thermodynamic transitions in NML," and are "consistent with a liquid-liquid critical point at positive pressures."[56] So the following questions arise: are the data consistent with an LLCP at about 2 kbar, as is our best guess from simulation and other experiments, and can our simulation model reproduce the experimental diffusion data? In this communication, we provide answers to these two questions.

To this end, we need to understand how the diffusion constant changes as the Widom line is crossed over a range of pressures at different distances from the theoretical critical pressure. To explore this, we calculate the diffusion constant for a number of isobars from 1 bar to 2.25 kbar, for the E3B3 model, using the trajectories from simulations reported previously.[30] We note that the calculated diffusion constants do not include the finite-size correction,[57–59] since we did not calculate the viscosity. The results are shown on a logarithmic scale in Fig. 2. For each pressure, the temperature of the theoretical Widom line is shown as a vertical dotted line, except for at 2.25 kbar, which is above the theoretical critical pressure of 2.1 kbar, where the temperature of the coexistence line is shown by the vertical solid line. One sees that at 2.25 kbar the data show a jump of over 1 order of magnitude as the system crosses the theoretical coexistence line, consistent with a discontinuous change. At 2 kbar, just 0.1 kbar below the critical pressure, the diffusion constant shows a strongly sigmoidal behavior (on this log plot), while at 1.5 kbar, the diffusion constant shows only a weakly sigmoidal behavior. For pressures of 1 kbar and below, the diffusion constant appears to change smoothly (the slope with temperature changes monotonically) as the Widom line is crossed.

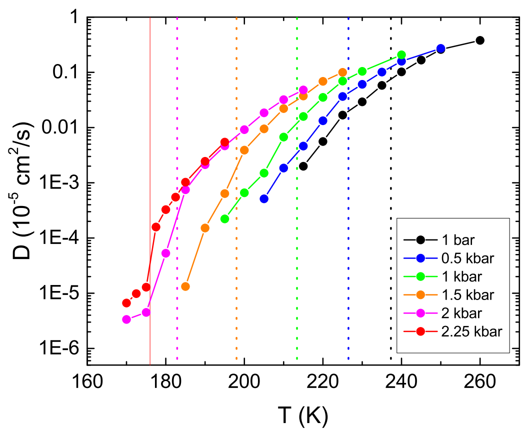

FIG. 2. The temperature dependence of the diffusion constant of E3B3 water for several isobars. For each pressure, a vertical dotted line of the same color indicates the temperature at which the theoretical Widom line is crossed. For the 2.25 kbar isobar, which is at a higher pressure than the theoretical LLCP, the vertical solid red line indicates the temperature at which the theoretical coexistence line is crossed.

Thus, we observe that the diffusion constant exhibits behavior similar to g_2 and the IR line shapes: when one is far from the critical point (1 kbar and below), the data change smoothly and do not show any signature of crossing the Widom line and when one is close to the critical point (1.5 to 2 kbar), the data show a sigmoidal change as the Widom line is crossed. As mentioned before, this is because the structure and density, and hence the dynamics, are changing rapidly from an LDL-like to an HDL-like fluid (as T increases). When one crosses the coexistence line (above the critical point), the diffusion constant appears to change discontinuously as the structure and density, and hence the dynamics, change discontinuously from LDL to HDL. These theoretical data suggest that the experimental diffusion constant at 1 bar would show a signature of the critical point if the critical pressure was 0.6 kbar or lower but would not show a signature if the critical pressure were higher than 0.6–1.0 kbar. Therefore, we conclude that the experiments are consistent with an LLCP at about 2 kbar.

Finally, we compare our results from the E3B3 model with experimental data from the higher-temperature set of experiments (from 180 to 262 K)[56] in Fig. 3. The (putative experimental[28]) position of the Widom line at 1 bar, 229 K, is shown by the dotted vertical line in the figure. Notably, there appears to be no signature in the experimental data of crossing the Widom line. One also sees that theory and experiment agree quite well over nearly 6 orders of magnitude. So, our simulation model can reproduce the experimental data. Figure 3 also shows a comparison of our E3B3 results to more conventional measurements of the diffusion constant at higher temperatures,[60] again with good agreement.

In conclusion, these new experimental data for the diffusion constant, at 1 bar and deep inside NML, are consistent (according to our model and simulations) with an LLCP at a pressure of 1.95 kbar (or any pressure greater than 0.6 kbar). Moreover, theoretical calculations of the diffusion constant within the E3B3 model are in semi-quantitative agreement with the experimental data, over nearly 6 orders of magnitude in the diffusion constant, and from 195 to 260 K. Similar

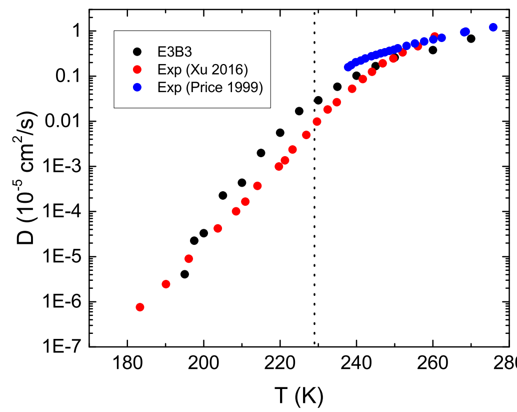

FIG. 3. The experimentally measured diffusion constant (red[56] and blue[60] circles) compared to the diffusion constant for E3B3 water (black circles) at 1 bar.

experiments at higher pressures, if they could be performed, might lead to more direct evidence for a high-pressure LLCP in NML.

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