Percolation in supercritical water: Do the Widom and percolation lines coincide?

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Hydrogen bonding distinguishes water from simpler fluids. Here, we use classical molecular dynamics to study the percolation transition in the hydrogen bond network of supercritical water. We find that, contrary to some previous work, the percolation line in both the pressure-temperature and density-temperature planes does not coincide with the Widom line. This difference stems from a fundamental distinction between the Widom line, which is thermodynamic in nature, and the percolation transition, which depends only on connectivity. For example, we show that percolation-related quantities collapse onto master curves when plotted with respect to a measure of connectivity rather than thermodynamic variables. We then use the Galam-Mauger formula to understand the properties of the hydrogen bonding network. We find that the percolation transition in supercritical water can shed light on the hydrogen bonding network in room temperature liquid water. *Published by AIP Publishing.*
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I. INTRODUCTION

Supercritical fluids have numerous industrial applications, from decaffeination[1] to "green" biomass gasification[2] and hazardous waste cleanup.[3] Most of these applications stem from a single property of supercritical fluids: their tunable density. Normal (subcritical) fluids exist only in very narrow ranges of density because the density is discontinuous across the liquid-vapor phase transition. Since many useful physical properties of fluids are strong functions of the density, the tunable density of supercritical fluids translates into tunable properties. By tuning the density of a supercritical fluid, one can find a fluid that has both good mass flow properties like a gas as well as good solvent properties like a liquid.

Despite these practical industrial advantages, supercritical fluids remain poorly understood from a theoretical perspective, especially in non-trivial fluids like water. One feature of the supercritical fluid is the Widom line: the continuation of the liquid-vapor coexistence line into the supercritical phase.[4,5] The liquid-vapor coexistence line ends in a critical point, where thermodynamic susceptibilities like compressibility β_T and heat capacity C_P, as well as the correlation length, diverge. Above the critical point, these quantities remain finite but reach maxima along various isobars or isotherms. The Widom line is defined by the locations of these maxima. The position of the Widom line depends both on the susceptibility used to define it and on the path taken through the phase diagram (e.g., isobar or isotherm).[6–10] The Widom line was first studied in terms of maxima in C_P along isobars[4] and was later defined by the maxima in the correlation length.[5] Sufficiently close to the critical point, these definitions

coincide because all of the susceptibilities become functions of the correlation length. In principle, this removes ambiguity from the choice in susceptibility, but the ambiguity in the choice of path through the phase diagram remains.[9,10] These ambiguities call into question any ideas that lend meaning to the Widom line beyond a simple continuation of the coexistence line.

Despite these ambiguities, the concept of the Widom line has been used in a variety of contexts. It was first used as evidence of a nearby critical point in the context of the postulated liquid-liquid critical point in supercooled water.[5,11] This concept was later applied to the liquid-vapor critical point, where there is evidence that the Widom line demarcates a crossover between a "liquid-like" supercritical fluid and a "gas-like" one.[12–14] This crossover is marked by changes in the dynamics, including sound dispersion,[13] diffusion,[5,15] and viscosity.[7,15] Others believe that these dynamical crossovers are, however, better described by the so-called "Frenkel line," which is itself defined in terms of the system's dynamics, rather than thermodynamics, as in the case of the Widom line.[16–18] Still others have looked beyond the dynamics for structural differences between the two "states."[19]

One hypothetical structural difference pertains to the hydrogen bonding network in supercritical water. It is well known that room temperature liquid water is dominated by percolating hydrogen bond networks and that the gas is not.[20] Therefore, as one passes continuously from the gas to the liquid, through the supercritical region, there must be some point where this hydrogen bond network forms. This transition can be understood in the context of percolation theory. Percolation theory was originally developed to study the formation of percolating, or system spanning, networks in regular lattices.[21,22] The central question in "bond" percolation is as follows: if each bond between nearest-neighbor lattice sites is occupied

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randomly with probability p, at what critical probability p_c does an infinite, system spanning cluster form? In an infinite system, this transition is sharp and has the features of a second-order thermodynamic phase transition including universality and a divergent correlation length.[22]

Percolation theory can be extended to continuum, off-lattice systems, like supercritical fluids.[23] This requires a suitable way to decide whether two particles are "connected" or not. Simple distance cutoffs can be used,[24,25] but in the case of water, the hydrogen bonding network presents a natural way to define connectivity. In this manner, both computer simulations[26] and experiments coupled with simulations[27] have found that the percolation transition of the hydrogen bonding network in supercritical water coincides with the Widom line.

If the Widom line is viewed as the dividing line between gas-like and liquid-like fluids, this conclusion seems natural. On the other hand, one might not expect the two phenomena to be related at all. A simple hard sphere fluid, for example, does not have a critical point and therefore no Widom line.[28] One can, however, still find a percolation transition by defining connectivity in terms of hard sphere contacts, among other possible definitions.[29] On the other hand, a Lennard-Jones fluid has a Widom line,[6] but it is not so obvious how to define percolation.[24,30] In agreement with this intuition, both Raman spectroscopy[31] and a simple comparison of hydrogen bond counts[32] suggest that the Widom line is distinct from the percolation transition. Initially, simulations found that the percolation and Widom lines coincide as discussed above,[26] but later work suggested that they do not,[33] highlighting the need for clarity in this literature.

Here, we use classical molecular dynamics simulations to locate both the Widom line (Sec. II B) and the percolation transition (Sec. II C) in the supercritical region of the phase diagram. We find that the Widom line does not coincide with the percolation transition (Sec. III A). We use finite size scaling and dense sampling in the phase diagram to locate the percolation transition accurately, and in this way, we are able to distinguish the percolation transition from the Widom line, where previous work could not.[26,27] Our results do not eliminate the possibility that the Widom line separates a liquid-like supercritical fluid from a gas-like one, with qualitative observable differences, but they do demonstrate that hydrogen bond percolation is not one of these differences.

To understand the difference between percolation and the Widom line (Sec. III B), we note that the Widom line is a thermodynamic phenomenon. It is described by thermodynamic susceptibilities, which are derivatives of the free energy. Percolation, on the other hand, is a geometric phenomenon. It depends *only* on the connectivity of the system. While the number of hydrogen bonds depends on the thermodynamic state of the system, the structure and connectivity of the underlying network depends very weakly on the thermodynamics. Thermodynamics is the knob that tunes the system through the percolation transition, analogous to the bond probability p in random-bond percolation theory. This is fundamentally different from the role thermodynamics plays in phase coexistence, the critical point, and the Widom line, where

discontinuities in various derivatives of the free energy dictate the behavior.

II. METHODS

A. Simulation details

We perform classical molecular dynamics simulations with the E3B3[34] rigid water model. Section III C contains a discussion of the choice of water model. Intermolecular geometries are constrained with the LINCS algorithm.[35] The dynamics are integrated using the leap-frog algorithm[36] with a 1 fs time step and a Nosé-Hoover thermostat with a 0.1 ps damping time.[37,38] The NPT simulations use a Parrinello-Rahman barostat with a 1 ps damping time.[39] We use periodic boundary conditions with the particle mesh Ewald method for long range electrostatic interactions.[40] Simulations are performed with the GROMACS package[41] modified to use the E3B3 force field. The modified code can be downloaded at https://ime.uchicago.edu/skinner_group/research.

B. Widom line

We locate the Widom line in the pressure-temperature (P, T) plane by performing NPT simulations along isobars.[7] We compute the compressibility β_T using the fluctuations in the box volume (Fig. 1).[42] The temperature that maximizes the compressibility for each isobar describes a point (P, T) on the Widom line in the pressure-temperature plane. For a given isobar, the temperature that maximizes the compressibility is only known to be between the two temperatures that bound the maximum on either side. The error in the temperature at the compressibility maxima is therefore given by this resolution in temperature. We sample with a resolution of 5 K near the compressibility maximum. The error in the pressure position of the Widom line is given by the standard deviation of the mean of the pressure time series, sampled every 1 ps.
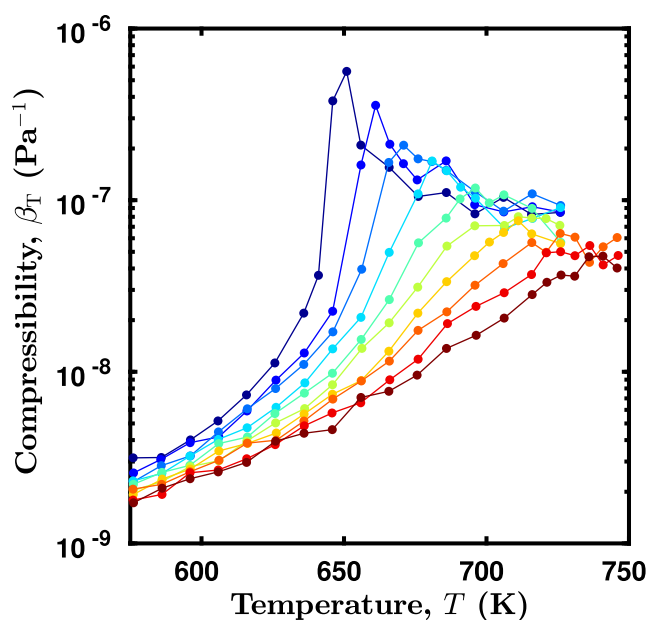

FIG. 1. The compressibility β_T along equally spaced isobars from 163 bar (blue) to 393 bar (red). These simulations use the E3B3 water model, which has a critical point at 143 bar and 626 K.[34]

We convert the Widom line in the (P, T) plane to the (ρ, T) plane by computing the average density of the simulation at each compressibility maximum. The confidence interval in density is given by the average densities of the simulations at the two temperatures that bound the maximum. This confidence interval can be quite large near the critical point because there the density is a very strong function of the temperature. Much higher resolution in temperature could reduce this error and pin down the location of the Widom line more precisely.

C. Percolation threshold

In an infinite system with a critical point, the correlation length ξ diverges to infinity at the critical point. In a finite system, the correlation length cannot diverge, but the ratio of the correlation length to the system size ξ/L goes to a constant value, independent of system size L.[43,44] We use this finite-size scaling property to locate the critical point. The relevant correlation length is the root mean squared distance between water molecules that are on the same hydrogen bonded cluster[22,44]

$$\xi^2 = \left\langle \sum_{i,j} \Delta_{ij} r_{ij}^2 \right\rangle \Big/ \left\langle \sum_{i,j} \Delta_{ij} \right\rangle, \quad (1)$$

where Δ_{ij} is unity if molecule i and j are on the same hydrogen bonded cluster and zero otherwise, and the averages $\langle \cdot \rangle$ are over configurations sampled at constant density.

In order to discuss hydrogen bonded clusters, we must define a hydrogen bond. We implement three geometric hydrogen bond definitions for comparison. The definitions are described in terms of the coordinates introduced by Kumar et al.[45] and illustrated in Fig. 2. We use the (R, β) definition of Luzar and Chandler,[46] which defines a hydrogen bonded pair as one with $R < 3.5$ Å and $\beta < 30°$. We contrast this intuitive definition with the one based on charge transfer between the oxygen lone pair and the OH antibonding orbital. Kumar et al.[45] used electronic structure theory to define hydrogen bonding based on the occupancy of the OH antibonding orbital. They mapped this occupancy to the nuclear coordinates (r, ψ) (Fig. 2) and identified a pair of molecules as hydrogen bonded if

$$\exp(-r/0.343 \text{ Å})(7.1 - 0.050\psi + 0.000\,21\psi^2) > 0.0085, \quad (2)$$

with $\psi \in [0°, 90°]$.[45] Finally, we use an (r, R) definition to allow comparison with the work of Pártay and Jedlovszky.[26]
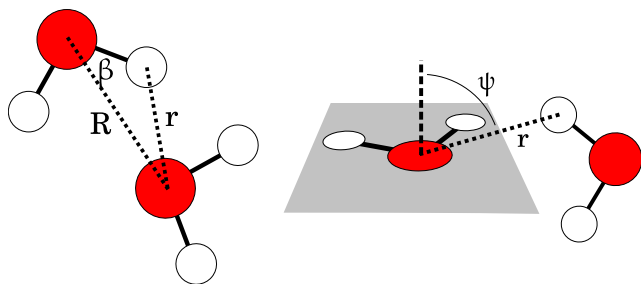

FIG. 2. The intermolecular coordinates used to describe different hydrogen bonding definitions. R is the OO distance, r is the OH distance, β is the OOH angle, and ψ is the angle between the intermolecular OH vector and the acceptor molecule normal.
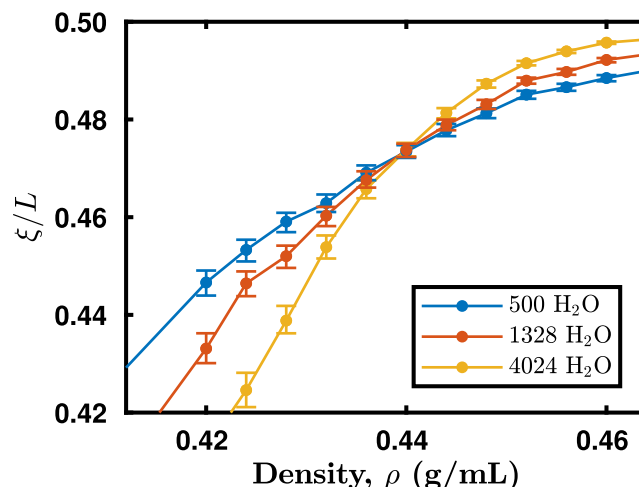

FIG. 3. The ratio of the cluster correlation length ξ to the linear system size L as a function of the density ρ at 1.05 T_c using the (R, β) hydrogen bond definition (see the text). The intersection of the curves for different system sizes (colors) gives the critical percolation density.

They define a pair of molecules as hydrogen bonded if $r < 2.5$ Å and $R < 3.5$ Å.

We find the percolation threshold in the (ρ, T) plane by performing NVT simulations along isotherms. For each temperature, the critical density is where ξ/L is independent of system size (Fig. 3). We compute the critical density by a linear extrapolation between simulated points. Figure 3 shows three different system sizes with 500 water molecules, 1328 water molecules, and 4024 water molecules. For two system sizes L, L', the estimate of the critical density becomes exact as the two system sizes $L, L' \to \infty$. With several different pairs of sizes L, L', one can extrapolate to the infinite-size limit using the Nightingale formula.[44] We find that a Nightingale extrapolation is unnecessary, however, because the critical density varies by less than 0.01 g/ml for all three pairs of sizes. Indeed, the intersection of all three curves ξ/L appears to occur at the same point in Fig. 3. The extra simulation time required to perform a Nightingale extrapolation would be significant, and the change in the critical density would be small. Furthermore, we are interested in qualitative comparisons between the critical percolation density and the Widom line, which does not require extremely accurate critical densities. For all other percolation calculations, we therefore simulate only the two smallest sizes ($N = 500$ and $N = 1328$).

The error on the correlation length ξ is given by the 95% confidence interval of a 1000-sample bootstrap distribution.[47] The intersection of the upper error bars for the smaller system ($N = 500$) with the lower error bars for the larger system ($N = 1328$) defines the upper error of the critical density. The opposite combination defines the lower error of the critical density. These intersections are found by linear extrapolation, as for the critical density itself.

III. RESULTS

A. Phase diagram of supercritical water

The phase diagram of supercritical water, in both the (P, T) and (ρ, T) planes, is shown in Fig. 4. In line with previous
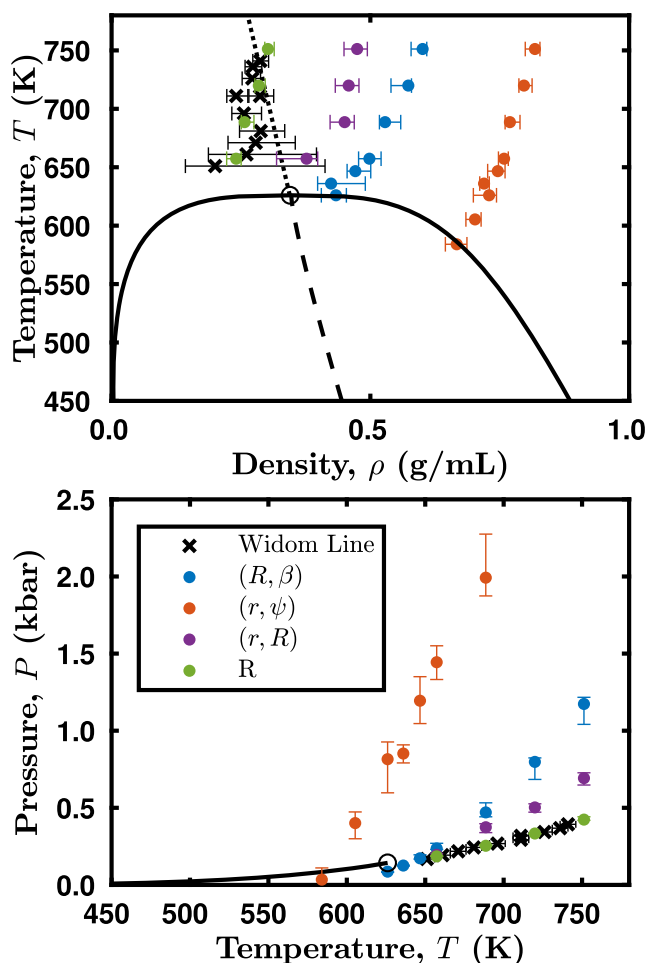
FIG. 4. The phase diagram for supercritical E3B3 water in the temperature-density plane (top panel) and pressure-temperature plane (bottom panel).[34] In both diagrams, the critical point is indicated by an open circle. The critical point for E3B3 water is at 0.34 g/ml, 143 bars, and 626 K.[34] The Widom line ($\times$) is an extrapolation of the coexistence line in the (P, T) plane; in the (ρ, T) plane, it is an extrapolation (dotted line) of the binodal diameter line (dashed line, see the text). The coexistence line in the (ρ, T) plane is that of the E3B3 model.[34] The coexistence line in the (P, T) plane is a schematic based on experimental results meant for illustration only.[48] The location of the percolation transition depends on the hydrogen bonding definition used (colored points). The hydrogen bonding definitions are described in Sec. II C. For any reasonable hydrogen bonding definition, the percolation transition is distinct from the Widom line.

work, we find that the isobaric Widom line ($\times$) extrapolates the liquid-vapor coexistence curve in the (P, T) plane.[5,7] It is interesting to note that in the (ρ, T) plane, this Widom line appears to extrapolate the binodal diameter line (dashed/dotted black line, Fig. 4). The binodal diameter is the average density of the coexisting liquid and gas phase at a given temperature.

We now turn to the percolation transition. For the three hydrogen bonding definitions described in Sec. II C, the percolation line is clearly distinct from the Widom line. The location of the percolation line depends sensitively, however, on the choice of hydrogen bonding definition. The three definitions considered lead to different amounts of hydrogen bonding for a given density and temperature, ranging from the most lenient definition (r, R) with the most hydrogen bonds to the most strict definition (r, ψ). It follows, then, that at a given

temperature, the critical percolation density would be smallest for the former and largest for the latter, as indicated in Fig. 4.

An extreme example further demonstrates the ambiguity in the choice of hydrogen bond definition. Consider a naive hydrogen bonding definition based only on the intermolecular OO distance R. A pair of molecules can be defined as "hydrogen bonded" if R is less than some cutoff value R_{cut}. By tuning the value of R_{cut}, one can continuously tune the critical percolation density and choose a value of R_{cut} so that the Widom line and the percolation line coincide. In the E3B3 water model, $R_{cut} = 3.5$ Å yields a percolation line that is indistinguishable from the Widom line (green circle, Fig. 4). This is a very lenient hydrogen bond definition, however, which counts many structures as hydrogen bonded that do not satisfy other definitions or our intuition. For example, two water molecules with their hydrogen atoms pointed away from each other will be "hydrogen bonded" according to this R definition if they are within 3.5 Å.

On top of this ambiguity in the percolation line for different hydrogen bond definitions, the location of the Widom line also depends on the choice of the susceptibility used to define it and the path through the phase diagram.[6–10] Here we define the Widom line using the compressibility along isobars (Sec. II B). Corradini *et al.*[7] showed that Widom lines in supercritical water based on the heat capacity or thermal expansion coefficient are at slightly higher densities and pressures. This moves the Widom line closer to the percolation transition, but the change is very small and does not impact our conclusions. Defining the Widom line using isotherms instead of isobars yields a Widom line that is at lower densities and pressures (data not shown) in agreement with the results of Schienbein and Marx.[10] This moves the Widom line further from the percolation lines, so it does not affect our conclusions.

Even though the quantitative location of the percolation line depends on the choice of hydrogen bond definition, Fig. 4 still clearly demonstrates that for any *reasonable* hydrogen bond definition, the percolation transition is at higher density and pressure than the Widom line. This conclusion contradicts the results of Pártay and Jedlovszky[26] and Bernabei *et al.*[27] The discrepancy can probably be attributed to three factors: First, due to computational limitations, both groups studied a combined total of only 12 points in (P, T, ρ) space, compared to 336 in this study. This sparsity in (P, T, ρ) space made it difficult to pin down the location of the percolation transition relative to the Widom line precisely. Second, Pártay and Jedlovszky[26] used the (r, R) hydrogen bond definition, which is the most lenient of the "real" hydrogen bond definitions we consider, yielding a percolation line that is quite close to the Widom line (purple circle, Fig. 4). In our simulations, we are able to distinguish this percolation line from the Widom line, but this distinction is outside the resolution of Pártay and Jedlovszky. Finally, Refs. 26 and 27 used spanning cluster and cluster size distribution methods to find the critical percolation density. These methods do not account for finite-size effects, making it more difficult to precisely locate the percolation transition.

As discussed in the Introduction, if one regards the Widom line as the separatrix between a gas-like and liquid-like state

in the supercritical phase, then one should expect the liquid-like hydrogen bond network to break down as one crosses the Widom line. This is not what we observe (Fig. 4). To understand this discrepancy, in Sec. III B, we study the connectivity of the hydrogen bond network.

B. Connectivity and cluster statistics

The simplest descriptor of connectivity is the average number of hydrogen bonds per water molecule n_{HB}. We use a molecule-centric definition of n_{HB}, which is double-counted from the bond-centric perspective,

$$n_{HB} = \frac{1}{N} \sum_{i,j} b_{ij}, \tag{3}$$

where N is the number of water molecules and b_{ij} is unity if molecules i and j are directly connected by a hydrogen bond and zero otherwise. The value of n_{HB} depends on the temperature, density, and the hydrogen bond definition (Fig. 5). Strikingly, the percolation transition (colored points, Fig. 5) happens at a fixed value of n_{HB}, independent of the values of these parameters or hydrogen bond definition. For E3B3 water, the percolation transition happens at the critical value of n_{HB}^{*} = 1.63. Blumberg *et al.*[49] found that for ST2 water, the percolation transition is at n_{HB}^{*} = 1.53. Blumberg *et al.* relate this off-lattice percolation problem to the simpler random-bond percolation theory on a regular lattice by equating the critical probability p_c in percolation theory to n_{HB}^{*} using the number of nearest neighbors z: $n_{HB}^{*} = zp_c$. On the regular ice I$_h$ lattice, $z = 4$, and $p_c = 0.388$,[50] yielding $n_{HB}^{*} = 1.55$.[49,51] The ST2 water model has been criticized for being too ice-like,[49,52,53] so it is perhaps not surprising that the difference between n_{HB}^{*} in ST2
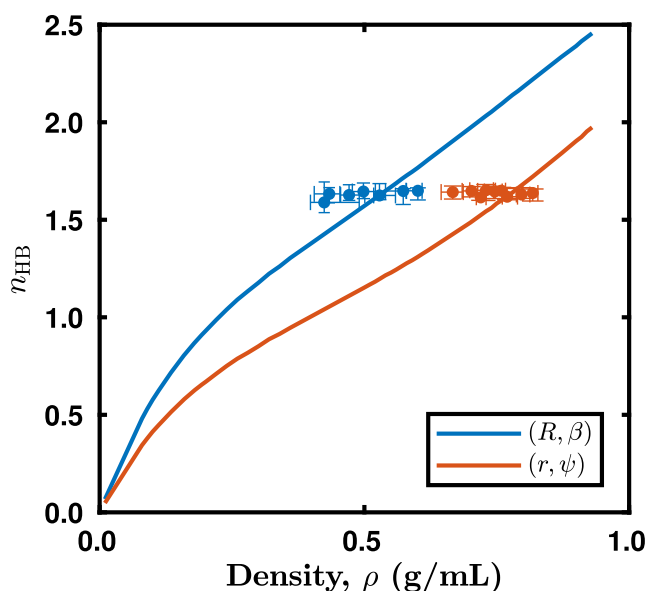

FIG. 5. The average number of hydrogen bonds per water molecule n_{HB} in simulations of E3B3 water, over a range of densities at $T = 1.1 T_c$. The hydrogen bond definition, density, and temperature (not shown) control the average number of hydrogen bonds (solid lines). For each definition, and a range of temperatures, the percolation densities are indicated by the colored points. The percolation transition happens at a fixed value of n_{HB}, regardless of the temperature and hydrogen bonding definition.

versus an ice lattice is smaller than the difference between n_{HB}^{*} in E3B3 water versus an ice lattice.

The universality of n_{HB}^{*} with respect to both thermodynamic state point and hydrogen bond definition indicates that n_{HB} is playing the role of the bond probability p in percolation theory. In percolation theory, the critical probability p_c is a fundamental property of the lattice structure and connectivity, and there is no concept of temperature or thermodynamics. Likewise, here, we find that n_{HB}^{*} is independent of temperature, density, and hydrogen bond definition, so the network that describes the water structure must also be independent of these parameters. In other words, the percolation transition is a geometric one, defined by connectivity, not thermodynamics. The Widom line, on the other hand, is a thermodynamic concept: it is defined in terms of thermodynamic susceptibilities, which are derivatives of the free energy. Thermodynamic variables like the temperature and pressure tune the system through transitions described by the free energy, like the liquid-vapor phase transition, the critical point, and the Widom line. The same thermodynamic variables tune the value of n_{HB} (Fig. 5) which controls percolation in the system, but the critical value n_{HB}^{*} is *not* controlled by the free energy. It is controlled by the geometry of the underlying network on which hydrogen bonds are broken and formed. This distinction between the geometric percolation transition and the thermodynamic Widom line is more stark in terms of the clustering statistics.

The cluster probability $P_M(\rho) = Mn_M(\rho)/N$ is the probability that a molecule chosen at random is part of a cluster of size M, where $n_M(\rho)$ is the average number of clusters of size M at a given density ρ.[49] Like n_{HB}, $P_M(\rho)$ depends on the temperature, density, and hydrogen bond definition. When plotted as a function of n_{HB} instead of ρ, however, the curves P_M collapse onto a single master curve regardless of temperature and hydrogen bond definition (Fig. 6). Following the work of Blumberg *et al.*,[49] we demonstrate that these master curves are well described by the predictions of random-bond percolation theory on an ice I$_h$ lattice (black lines, Fig. 6).

While the regular ice lattice does a decent job describing both n_{HB}^{*} and the form of P_M, the comparison can only go so far. In the ice lattice, each site has exactly 4 nearest neighbors ($z = 4$). This is not true in fluid water, where the number of "nearest neighbors," or possible hydrogen bond partners, of a given molecule fluctuates in time. Furthermore, the long range order in ice is absent in fluid water. Fluid water is better imagined as a random network with short range tetrahedral order. In the context of percolation theory, a random network is simply a collection of points that are connected in an irregular, "random" way. For regular lattices, with a well-defined number of nearest neighbors z, the Galam-Mauger formula approximates the percolation threshold p_c from z and the dimensionality d by

$$p_c = p_0 \left(\frac{d}{(d-1)(z-1)} \right)^a, \tag{4}$$

with $p_0 = 0.7541$ and $a = 0.9346$ for random-bond percolation theory.[54] In a random network, the number of nearest neighbors is the number of connections that a given site makes. Depending on the procedure used to define connectivity, each
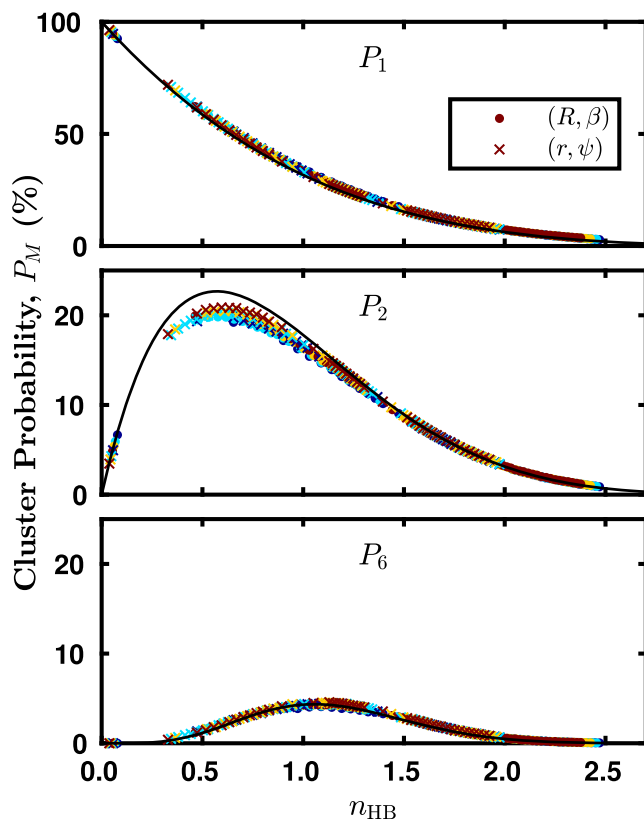
FIG. 6. The probability P_M that a randomly chosen molecule belongs to a cluster of exactly M molecules, for $M = 1$, 2, and 6 (see the text). The points and crosses correspond to the (R, β) and (r, ψ) hydrogen bond definitions, respectively (see Sec. II C). The colors correspond to a range of temperatures linearly spaced from $1.05T_c$ (dark blue) to $1.2T_c$ (dark red). The probability P_M depends only on n_{HB}, not on temperature, density, or the hydrogen bond definition. The dependence on n_{HB} is well described by random-bond percolation theory on an ice lattice (black lines).[49]
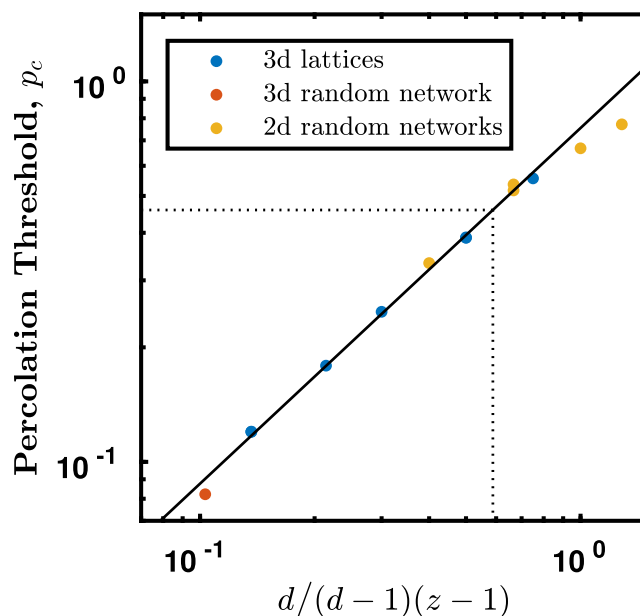

FIG. 7. The percolation transitions p_c for various regular 3d lattices (blue), as well as a 3d (orange) random network and 2d (yellow) random networks (see text). Both the random networks and regular lattices follow the Galam-Mauger formula [black line, Eq. (4)] that relates the critical percolation threshold to the average number of nearest neighbors z and the system dimension d. In our system, the Galam-Mauger formula predicts that the average number of nearest neighbors is $z = 3.55$ (dotted lines).

point may have a fixed number of nearest neighbors, as in the case of various Voronoi schemes,[55] or there may be a distribution of nearest neighbor numbers, like in water, in which case z is the average number of nearest neighbors of each site.

The Galam-Mauger formula [Eq. (4)] has been criticized for its failure to meet several intuitive criteria (e.g., $0 < p_c < 1$),[56] as well as its failure for lattices in different universality classes.[57,58] Alternatives have been suggested which fix these flaws, but these do not provide intuitive measures of the structure of a lattice, like z in the Galam-Mauger formula.[59] To demonstrate that the Galam-Mauger formula is adequate for our purposes, we compare its predictions to percolation thresholds on various random networks (Fig. 7). As a baseline, we first compare to regular 3d regular lattices since our system has $d = 3$. The 3d lattices in Fig. 7 are (8,3),[60] simple cubic,[61] ice I$_h$,[50] diamond,[62] face-centered cubic,[61,62] and body-centered cubic.[61,62] The (m, n) notation used to describe the (8,3) lattice indicates a lattice with n nearest neighbors and m members in the smallest closed loop.[60] We then compare Eq. (4) to percolation thresholds in random networks. Since there are very limited results available for 3d random networks, we also compare to 2d random networks. The 3d random network is a Voronoi network,[63] and

the 2d random networks are a relative-neighborhood graph,[64] a Voronoi tessellation,[65] a Voronoi covering,[65] a Delauney triangulation,[65] and a Gabriel graph.[66] Having established that Eq. (4) holds for random networks, we apply it to the hydrogen bonding network in water. Here, $p_c = n^*_{HB}/z$, $n^*_{HB} = 1.63$, and $d = 3$, so the solution of Eq. (4) is $z = 3.55$. This implies that fluid water can be thought of as a random network with an average of 3.55 nearest neighbors or potential hydrogen bonding partners. The number of hydrogen bonds that are actually occupied (n_{HB}) is determined by the density, temperature, and hydrogen bond definition.

Assuming that the structure of the underlying network in ambient liquid water is similar to that in supercritical water, one could argue that at room temperature *all* of these 3.55 hydrogen bonds are occupied. In dense liquid water, almost every molecule is part of the percolating cluster. In the context of percolation theory, this corresponds to a bond probability $p \sim 1$. In this limit, the value of n_{HB} at room temperature corresponds to the average number of nearest neighbors in the network (so $n_{HB} \sim z$), and, to the extent that the above assumption holds, this is the *same* network that describes the percolation transition in the supercritical state. So, by measuring $z = 3.55$ via Eq. (4), one could conclude that $n_{HB} \sim 3.55$ in room temperature water. This is consistent with various estimates (3.4–3.7) of n_{HB} in simulations of liquid water.[45] The assumption that the network structure of the room temperature liquid is similar to the supercritical fluid may seem unreasonable, but there is some evidence to support it: First, as discussed and shown above, percolation theory is independent of thermodynamics. Since there are no discontinuous phase transitions separating the percolation transition in the supercritical fluid from the ambient liquid, one might expect the network

structure to remain relatively unchanged. Second, Blumberg *et al.*[49] showed that the same percolation transition, which we study in supercritical water, can alternatively be studied using liquid water at ambient conditions and simply varying the hydrogen bond definition parameters (e.g., R_{cut}) continuously to tune n_{HB} through the percolation transition.

Note that the concept of water as a random network is only relevant at relatively high densities near and above the percolation transition. At low densities, clearly, there is no network that describes water's structure because the hydrogen bonds that uphold this structure are short ranged. Percolation theory is blind to such considerations because the connections between points on a network need not have a physical meaning.

C. Water models

All the results above use the E3B3 water model.[34] Here, we compare with TIP4P/2005[67] and E3B2[68] water models to explore the sensitivity of our results to different simulation models. The E3B2 and E3B3 models include explicit three-body terms in the potential. The TIP4P/2005 model is a pairwise potential and is the two-body reference on which the E3B3 model is based. We use these models to understand the importance of three-body interactions near the critical point, where the lower density and the long length scale fluctuations might permit exotic structures that are not present in the liquid. For example, one might imagine chains of hydrogen bonded molecules, each accepting one hydrogen bond and donating another.[69,70] These would be energetically favorable due to the cooperativity of hydrogen bonding but entropically suppressed.[71] These structures are impossible in liquid water because each water molecule forms more than 3 hydrogen bonds on average,[45] meaning that any cooperative hydrogen bonds are accompanied by anticooperative ones as well.
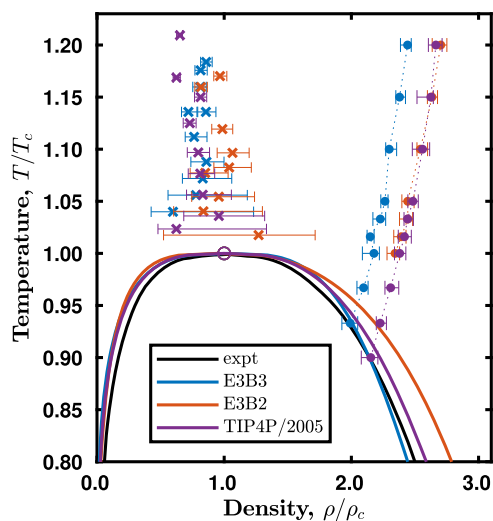

FIG. 8. The temperature-density phase diagram showing the Widom line ($\times$) and the (r, ψ) percolation transition (colored points, Sec. II C) for several different water models. In terms of the reduced temperature T/T_c and reduced density ρ/ρ_c, the location of the percolation transition depends quantitatively, but not qualitatively, on the choice of water model. The boundaries of the liquid-vapor coexistence regions for the various water models are solid lines, and the critical point is indicated by unfilled circles. The experimental liquid-vapor coexistence region (black) is shown for comparison.[72,73]

Actually, we find little evidence of these structures in our simulations presumably due to the high temperature near the critical point and the weakness of the three-body interactions in E3B3.[34]

Furthermore, although the location of the percolation line depends on the hydrogen bond definition used (Fig. 4), it is relatively insensitive to the water model chosen (Fig. 8). The other results presented above also hold with the E3B2 and TIP4P/2005 water models, except that the critical value of n_{HB} changes slightly. For E3B2, $n_{HB}^* = 1.61$, and for TIP4P/2005, $n_{HB}^* = 1.65$.

IV. CONCLUSION

We find that the percolation transition of the hydrogen bonding network in supercritical water depends on the hydrogen bond definition used. For any reasonable choice of hydrogen bond definition, however, the percolation transition is distinct from the Widom line. This means that the Widom line does not separate a "gas-like" supercritical fluid from a "liquid-like" one, at least from the perspective of the hydrogen bonding network. This result was anticipated[32] by a simple comparison of the value of n_{HB} at the Widom line with n_{HB}^* estimated by Blumberg *et al.*[49] But perhaps, we should not even expect the Widom and percolation lines to coincide. The Widom line is a thermodynamic phenomenon. It is described in terms of derivatives of the free energy that diverge at the nearby critical point and phase coexistence line. Percolation, on the other hand, is a purely geometrical phenomenon that depends only on the connectivity of the system. While the average number of hydrogen bonds n_{HB} does depend on the thermodynamic state, the percolation transition happens at the same critical value n_{HB}^*, regardless of temperature, density, or hydrogen bond definition. The critical value n_{HB}^* is analogous to the critical probability p_c in percolation theory and is a fundamental property of the lattice or network. This percolation threshold in supercritical water therefore contains useful information, surprisingly, about the hydrogen bonding network of room temperature liquid water.

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