Relation Between the Widom line and the Strong-Fragile Dynamic Crossover in Systems with a Liquid-Liquid Phase Transition

L. Xu*, P. Kumar*, S. V. Buldyrev*, S.-H. Chen†, P. H. Poole§, F. Sciortino¶, H. E. Stanley*

*Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215 USA
†Department of Physics, Yeshiva University, 500 West 185th Street, New York, NY 10033 USA
‡Nuclear Science and Engineering Department, Massachusetts Institute of Technology, Cambridge, MA 02139 USA
§Department of Physics, St. Francis Xavier University, Antigonish, Nova Scotia B2G 2W5, Canada
¶Dipartimento di Fisica and Istituto Nazionale Fisica della Materia
Unita’ di Ricerca: Complex Dynamics in Structured Systems,
Universita’ di Roma “La Sapienza” – Piazzale Aldo Moro 2, I-00185, Roma, Italy

We investigate, for two water models displaying a liquid-liquid critical point, the relation between changes in dynamic and thermodynamic anomalies arising from the presence of the liquid-liquid critical point. We find a correlation between the dynamic fragility transition and the locus of specific heat maxima $C_P^{\text{max}}$ (“Widom line”) emanating from the critical point. Our findings are consistent with a possible relation between the previously hypothesized liquid-liquid phase transition and the transition in the dynamics recently observed in neutron scattering experiments on confined water. More generally, we argue that this connection between $C_P^{\text{max}}$ and dynamic crossover is not limited to the case of water, a hydrogen bond network forming liquid, but is a more general feature of crossing the Widom line. Specifically, we also study the Jagla potential, a spherically-symmetric two-scale potential known to possess a liquid-liquid critical point, in which the competition between two liquid structures is generated by repulsive and attractive ramp interactions.

I. INTRODUCTION

By definition, in a first order phase transition, thermodynamic state functions such as density $\rho$ and enthalpy $H$ change discontinuously as we cool the system along a path crossing the equilibrium coexistence line [Fig. 1(a), path $\beta$]. However in a real experiment, this discontinuous change may not occur at the coexistence line since a substance can remain in a supercooled metastable phase until a limit of stability (a spinodal) is reached [Fig. 1(b), path $\beta$].

If the system is cooled isobarically along a path above the critical pressure $P_c$ [Fig. 1(b), path $\alpha$], the state functions continuously change from the values characteristic of a high temperature phase (gas) to those characteristic of a low temperature phase (liquid). The thermodynamic response functions which are the derivatives of the state functions with respect to temperature [e.g., isobaric heat capacity $C_P = (\partial H / \partial T)_P$] have maxima at temperatures denoted $T_{\text{max}}(P)$. Remarkably these maxima are still prominent far above the critical pressure [2, 3, 4, 5], and the values of the response functions at $T_{\text{max}}(P)$ (e.g., $C_P^{\text{max}}$) diverge as the critical point is approached. The lines of the maxima for different response functions asymptotically approach one another as the critical point is approached, since all response functions become expressible in terms of the correlation length. This asymptotic line is sometimes called the Widom line, and is often regarded as an extension of the coexistence line into the “one-phase region.”

If the system is cooled at constant pressure $P_0$ and $P_0$ is not too far from the critical pressure $P_c$, then there are two classes of behavior possible. (i) If $P_0 > P_c$ (path $\alpha$), then experimentally-measured quantities will change dramatically but continuously in the vicinity of the Widom line (with huge fluctuations as measured by, e.g., $C_P$). (ii) If $P_0 < P_c$ (path $\beta$), experimentally-measured quantities will change discontinuously if the coexistence line is actually seen. However the coexistence line can be difficult to detect in a pure system due to metastability, and changes will occur only when the spinodal is approached where the gas phase is no longer stable. The changes in behavior may include not only static quantities like response functions [2] but also dynamic quantities like diffusivity.

In the case of water—the most important solvent for biological function [6, 7]—a significant change in dynamical properties has been suggested to take place in deeply supercooled states [8, 9, 10, 11]. Unlike other network forming materials [12], water behaves as a fragile liquid in the experimentally accessible window [3, 13, 14]. Based on analogies with other network forming liquids and with the thermodynamic properties of the amorphous forms of water, it has been suggested that, at ambient pressure, liquid water should show a crossover between fragile behavior at high $T$ to strong behavior at low $T$ [8, 12, 15, 16, 17, 18, 19] in the deep supercooled region of the phase diagram below the homogeneous nucleation line. This region may contain the hypothesized liquid-liquid critical point [20], the terminal point of a line of first order liquid-liquid phase transitions. According to one current hypothesis, the liquid-liquid critical point is the thermodynamic source of all water’s anomalies [20, 21, 22, 23]. This region has been called the “no-man’s land” because to date no experiments have been able to make direct measurements on the bulk liquid phase [21]. Recently the fragility transition in confined water was studied experimentally [24, 25, 26] since nucleation can be avoided in confined geometries. Also, a dynamic crossover has been associated with the liquid-liquid phase
transitional behavior along the path β.

We provide evidence that, for all three potentials, a dynamic crossover occurs when the Widom line is crossed. Our results for the TIP5P potential are based on MD simulations of a system of $N = 512$ molecules, carried out both in the NPT and NVT ensembles using the techniques described in [33]. For ST2 simulations $N = 1728$ molecules are used and all the simulations are carried out in NVT ensemble. For the Jagla potential, discrete molecular dynamics simulations [32] implemented for $N = 1728$ particles interacting with step potentials [34] is used in both NVT and NVE ensembles.

### III. RESULTS

Fig. 2(a) shows for TIP5P the relevant portion of the $P - T$ phase diagram. A liquid-liquid critical point is observed [33, 35], from which the Widom line develops. The coexistence curve is negatively sloped, so the Clapeyron equation implies that the high-temperature phase transition in silicon and silica [23, 25]. In this work, we offer an interpretation of the dynamic crossover (called a fragility transition or fragile-strong transition by many authors) in water as arising from crossing the Widom line emanating from the hypothesized liquid-liquid critical point [23] [Fig. 1(c), path α]. Our thermodynamic and structural interpretation of the dynamic crossover may not hold for liquids for which the fragile-strong dynamic crossover can be caused by other mechanisms, as discussed in [29].

### II. METHODS

Using molecular dynamic (MD) simulations, we study three models, each of which has a liquid-liquid critical point. Two of the models, (the TIP5P [30] and the ST2 [31]) treat the water molecule as a multiple-site rigid body, interacting via electrostatic site-site interactions complemented by a Lennard-Jones potential. The third model is the spherical “two-scale” Jagla potential with attractive and repulsive ramps [Fig. 2] which has been studied in the context of liquid-liquid phase transitions and liquid anomalies [16, 32]. For all three models, we evaluate the loci of maxima of the relevant response functions, compressibility and specific heat, which coincide close to the critical point and give rise to the Widom line. We provide evidence that, for all three potentials, a dynamic crossover occurs when the Widom line is crossed.
is a high-density liquid (HDL) and the low-temperature phase is a low-density liquid (LDL). Fig. 3(b) shows the $T$ dependence of the diffusion coefficient $D$, evaluated from the long time limit of the mean square displacement along isobars. The isobars crossing the Widom line [Fig. 3(c), path $\alpha$] show a clear crossover from a non-Arrhenius behavior at high $T$ [which can be well fit by a power law function $D \sim (T - T_{MCT})^{-\gamma}$, consistent with the mode coupling theory predictions [38]], to an Arrhenius behavior at low $T$ [which can be described by $D \sim \exp(-E_d/T)$]. The crossover between these two functional forms takes place when crossing the Widom line.

For paths $\beta$ [Fig. 3(d)], crystallization occurs in TIP5P [33], so the hypothesis that there is no fragility transition cannot be checked at low temperature. Hence we consider a related potential, ST2, for which crystallization is absent within the time scale of the simulation. Simulation details are described in [37]. This potential also displays a liquid-liquid critical point [20, 57], as seen in the phase diagram of Fig. 4(a). The analog of Fig. 3(b) is shown in Fig. 4(b). We confirm that along paths $\alpha$ a fragility transition takes place [Fig. 4(c)]. Moreover, along paths $\beta$ the $T$ dependence of $D$ does not show any sign of crossover to Arrhenius behavior and the fragile behavior is retained down to the lowest studied temperature (note that $10^3 T$ extends to 4.8K$^{-1}$). Indeed, for paths $\beta$, the entire $T$ dependence can be fit by a power law $(T - T_{MCT})^{-\gamma}$ [Fig. 4(c)]

Thus we see that the simulations for both TIP5P and
ST2 water models support the connection between the Widom line and the dynamic fragility transition. It is natural to ask which features of the water molecular potential are responsible for the properties of water discussed here, especially because water’s unusual properties are shared by several other liquids whose inter-molecular potential has two energy (length) scales [27, 28]. We next investigate the two-scale spherically symmetric Jagla potential. The Jagla model displays—without the need to supercool—a liquid-liquid coexistence line which, unlike water, has a positive slope, implying that the Widom line is now crossed along $\alpha$ paths with $P > P_c$ [Figs. 1(d) and 5(a)]. There is a crossover in the behavior of $D(T)$ when the $C_P^\text{max}$ line is crossed [Figs. 5(b) and 5(c)]. At high temperature, $D$ exhibits an Arrhenius behavior [Figs. 5(b) and 5(c)], while at low temperature it follows a non-Arrhenius behavior, consistent with a power law. Along a $\beta$ path ($P < P_c$), $D(T)$ follows the Arrhenius behavior over the entire studied temperature range [Figs. 5(b) and 5(d)]. Thus, the dynamic crossover coincides with the location of the $C_P^\text{max}$ line, extending the conclusion of the TIP5P and ST2 potentials to a general two-scale spherically symmetric potential.

IV. DISCUSSION AND SUMMARY

Before concluding, we note that our findings are consistent with the possibility that the observed dynamic crossover along path $\alpha$ is related to the behavior of $C_P$, suggesting that enthalpy or entropy fluctuations may
FIG. 5: Analog of Figs. 3 and 4 for the two-scale Jagla potential. (a) Phase diagram in the vicinity of the liquid-liquid critical point located at $P_c \approx 0.24$ and $T_c \approx 0.37$, the line of isobaric specific heat maxima $C^\text{max}_P$, the line of isothermal compressibility maxima $K^\text{max}_T$, and the spinodal lines. (b) The $T$-dependence of diffusivity along constant pressure paths. Several paths $\alpha$ and paths $\beta$ are shown: (i) $P = 0.175, 0.200, 0.225 < P_c$ (paths $\beta$ in Fig. 4(d), along which the system remains in the LDL phase). (ii) $P = 0.250, 0.275, 0.30 > P_c$ (paths $\alpha$ in Fig. 4(d), along which the system does not remain in the LDL-like state, but the dynamic behavior changes from Arrhenius to non-Arrhenius). (c) $D$ as a function of $1/T$ for $P = 0.250$ (path $\alpha$). At high temperatures, the fit is Arrhenius $D \sim \exp(-1.59/T)$ (solid line), while at low temperatures the results are consistent with $D \sim (T - T_{\text{MCT}})^\gamma$ with $T_{\text{MCT}} \approx 0.27$ and $\gamma \approx 2.7$ (dashed line, also shown in the inset). (d) For $P = 0.225$ (path $\beta$), $D$ is Arrhenius for the entire temperature range and can be fit by $D \sim \exp(-1.62/T)$. The unit of $D$ is $a\sqrt{U_0/m}$ and the unit of $P$ is $U_0/a^3$.

have a strong influence on the dynamic properties. The role of $C_P$ is consistent with expectations based on the Adam-Gibbs [38] interpretation of the water dynamics [39, 40] and of the fragility transition [10, 27].

For both water and the Jagla model, crossing the Widom line is associated with a change in the $T$-dependence of the dynamics. In the case of water, $D(T)$ changes from non-Arrhenius (“fragile”) to Arrhenius (“strong”) behavior, while the structural and thermodynamic properties change from those of HDL to those of LDL. For the Jagla potential, due to the positive slope of the Widom line, $D(T)$ changes from Arrhenius to non-Arrhenius while the structural and thermodynamic properties change from those of LDL to those of HDL.

In summary, our results for water are consistent with the experimental observation in confined water of (i) a fragility transition for $P < P_c$ [25, 26], and (ii) a peak in $C_P$ upon cooling water at atmospheric pressure [41]. Thus our work offers a plausible interpretation of the results of Ref. [26] consistent with the existence of a liquid-liquid critical point located in the no-man’s land.

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