

Molecular Dynamics Simulations of a Fluid near Its Critical Point

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We present computer simulations for the static and dynamic behavior of a fluid near its consolute critical point. We study the Widom-Rowlinson mixture, which is a two component fluid where like species do not interact and unlike species interact via a hard core repulsion. At high enough densities this fluid exhibits a second order demixing transition that is in the Ising universality class. We find that the mutual diffusion coefficient D_{AB} vanishes as $D_{AB} \sim \xi^{-1.26 \pm 0.08}$, where ξ is the correlation length. This is different from renormalization-group and mode coupling theory predictions for model H , which are $D_{AB} \sim \xi^{-1.065}$ and $D_{AB} \sim \xi^{-1}$, respectively.

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The behavior of fluids near their critical point is a topic of long-standing and continuing interest. Critical phenomena are interesting because there are divergences in many static and dynamic properties and because fluids display universal features that are independent of the nature of the short-ranged interactions. A quantitative explanation of the scaling behavior of static properties is one of the enduring successes of modern statistical mechanics.

Although the static critical properties of a simple fluid are considered fairly well understood, considerably less is known about critical dynamics, especially the behavior of the transport properties near a critical point. One reason for this is that direct measurements of transport properties are difficult near the critical point. For example, recent measurements of the viscosity [1] were performed on the space shuttle in order to avoid the detrimental effects of gravity. Computer simulation studies, so important to our understanding of static critical properties, are notoriously difficult for critical dynamics because of the phenomenon of critical slowing down, where the dynamics become slower and slower as the critical point is approached. In this Letter, we report computer simulation studies for the dynamics of a fluid near its consolute critical point. To our knowledge, this is the first comprehensive study of the critical dynamics of an off-lattice fluid model using molecular dynamics.

Our study is made feasible by our choice of model, namely, the Widom-Rowlinson (WR) model [2]. This is a symmetric two component (A and B) mixture where the interaction potentials $u_{AA} = u_{BB} = 0$, and $u_{AB}(r) = \infty$ for $r < \sigma$ and $u_{AB}(r) = 0$ for $r > \sigma$. When the density is increased for a fixed mole fraction of $\phi = 0.5$, the WR model exhibits a second order phase transition, which has been shown to belong to the Ising universality class [3,4]. The critical point occurs for a density $\rho_c \sigma^3 = 0.762 \pm 0.016$, where ρ_c is the total number density of spheres at the critical point.

The WR model offers several advantages over models with continuous potentials. First of all, the inherent A - B symmetry allows us to locate the critical point very

accurately for any system size. Second, the impulsive nature of the forces allows us to evolve the system collision by collision using discontinuous molecular dynamics (DMD) [5], which has been shown to be considerably faster than conventional molecular dynamics [6]. Finally, the transport properties can be conveniently calculated using Einstein relations, thus avoiding the integration of Green-Kubo relations.

In this work, we study the dynamics of the WR mixture near the critical point and obtain results for the concentration fluctuation susceptibility χ and several dynamic properties including the shear viscosity η , the thermal conductivity λ , and the mutual diffusion coefficient D_{AB} . We verify that $\chi \sim \xi^{\gamma/\nu}$, where ξ is the correlation length and γ and ν are the usual critical exponents. We find that at the critical point, $D_{AB} \sim \xi^{-1.26 \pm 0.08}$. This exponent is different from existing theories, but consistent with some experiments.

In the neighborhood of a critical point, a fluid experiences large fluctuations. Pure fluids exhibit a gas-liquid critical point (plait point) with large density fluctuations, and binary mixtures can also exhibit a liquid-liquid critical point (consolute point) with large concentration fluctuations. An analogy can be drawn between these two types of critical point [7,8] and they are believed to belong to the same universality class. Relaxation rates are generally determined by the ratio of a kinetic coefficient to a static susceptibility for the order parameter. For example, for the thermal diffusivity near a plait point, the kinetic coefficient is the thermal conductivity (λ) and the static susceptibility is the specific heat (C_p). The analogous quantity near a consolute point is the mutual diffusion coefficient, for which kinetic coefficient is the Onsager kinetic coefficient (L) and the static susceptibility is obtained from concentration fluctuations (χ). In general, both the kinetic coefficient and the static susceptibility can diverge at a critical point, with different exponents.

There have been many theoretical studies of dynamical critical phenomena. The mode coupling theory (MCT) of Kadanoff and Swift [8,9] and Kawasaki [10] originated

from the ideas of Fixman [11], who proposed that the critical anomalies of transport coefficients can be understood as a result of nonlinear coupling between hydrodynamic modes of the system. The dynamic renormalization-group (RG) theory, first formulated by Halperin *et al.* [12], is an extension of the ideas of the static RG theory of Wilson and Fisher [13] to dynamic critical phenomena. A phenomenological theory known as dynamic scaling theory has been developed by Ferrell and Bhattacharjee [14].

There have been several experiments for the dynamical critical exponents against which theoretical predictions can be tested. Experiments suggest $\eta \sim \xi^a$ with $a = 0.065$ to 0.069 at a plait point as well as a consolute point [1,15]. This is probably consistent with the RG theory of Halperin *et al.* [12] and the theory of Ferrell and Bhattacharjee [14], which predict $\eta \sim \xi^{0.065}$ and $\eta \sim \xi^{0.067}$, respectively. Note, however, that the most recent results on xenon [1] show that $\eta \sim \xi^{0.0690 \pm 0.0006}$, and the small uncertainties place this value outside the realm of the theoretical predictions. λ has no divergent part at a consolute point, although there is a small critical enhancement [16]. L is believed to diverge at the critical point, although not as strongly as χ . Early MCT predictions of Kadanoff and Swift [8] yield $L \sim \xi$ (and $D_{AB} \sim \xi^{-1}$), while RG theories [12] predict $L \sim \xi^{0.895}$ (and $D_{AB} \sim \xi^{-1.065}$). Although experiments for D_{AB} have not been performed close enough to the critical point to unambiguously determine the scaling exponent, it is possible to fit the data using the RG value for the exponent provided the critical temperature is floated as an adjustable parameter [17–19].

In this work, we use semigrand ensemble Monte Carlo (MC) simulations and DMD simulations, respectively, to study the static concentration fluctuations and transport properties of the WR model. In the semigrand ensemble MC simulations [3] the total number of particles N , the total volume V , and the temperature T are fixed. Initial configurations are generated by randomly inserting spheres into a cubic simulation cell, and the system is evolved using either a particle move or a particle identity interchange, which are chosen randomly with equal probability, and accepted according to the Metropolis criterion. The simulations are carried out for $N = 128, 256, 512, 1024, \text{ and } 2048$ and for several densities, with V adjusted to achieve the desired density. (Results for $N = 16384$ are available from previous work [3].) Properties are averaged over 10^8 – 10^9 attempted moves, and error bars are obtained from block averaging. The concentration fluctuations and the distribution of the order parameter are directly monitored and the critical point for each system size is obtained from the latter. The static susceptibility χ of the order parameter is given by

$$\rho k_B T \chi = 4(\langle N_A N_B \rangle - \langle N_A \rangle \langle N_B \rangle) / N, \quad (1)$$

where ρ is the total number density, k_B is the Boltzmann's constant, N_j is the number of atoms of species j , $N = N_A + N_B$, and $\langle A \rangle$ denotes the ensemble average of A .

In DMD simulations [5] the system evolves via successive collisions between particles. First, the time to the next collision is calculated, and then all the particles are advanced forward until the collision occurs. Postcollision velocities of the colliding pair are determined from the conservation of total linear momentum and energy, and the process is repeated. Dynamical properties are calculated using the method of running averages. For the DMD simulations we fix the mole fraction at $\phi = 0.5$ and study several densities for a number of system sizes. The simulations are carried out for $N = 128, 256, 512, 1024, 2048, \text{ and } 16384$. Initial conditions are obtained by randomly inserting spheres into a box and equilibrating these using MC simulations. The number of collisions in a single run vary from 10^7 to 5×10^7 , depending on the system size. We estimate the longest relaxation time from the decay of the intermediate scattering function at the smallest wave vector accessible. Properties are averaged over time durations roughly an order of magnitude larger than this longest relaxation time. Statistical uncertainties are obtained by averaging over the results of completely independent runs (with uncorrelated initial configurations).

The dynamic properties η , λ , and L are obtained from the Einstein relations [6]. For example, L is given by

$$L = \frac{M^2}{6V k_B T t} \left\langle \left| \sum_{i=1}^{N_A} \mathbf{r}_{A_i}(t_0 + t) - \sum_{i=1}^{N_A} \mathbf{r}_{A_i}(t_0) \right|^2 \right\rangle, \quad (2)$$

where M is the mass of a particle, t is time, and \mathbf{r}_{A_i} is the position of particle i of species A . We define our length, mass, and energy scales by setting $\sigma = 1$, $M = 1$, and $k_B T = 1$.

Critical exponents are obtained in simulations using finite size scaling. The key idea is that the correlation length ξ scales as the finite system's linear dimension l when the correlation length grows beyond l : $\xi \sim l$. Ratios of the critical exponents can be obtained by computing the specific quantity at the critical point as a function of l . For example, $\chi \sim \epsilon^{-\gamma} \sim (\xi^{-1/\nu})^{-\gamma} \sim \xi^{\gamma/\nu} \sim l^{\gamma/\nu}$, where $\epsilon = |(\rho - \rho_c)/\rho_c|$, $\xi \sim \epsilon^{-\nu}$, and $\nu = 0.63$ is the usual finite size scaling exponent. Figure 1 shows χ plotted as a function of l , on a log-log scale. The symbols correspond to the critical points from simulations with $N = 128, 256, 512, 1024, \text{ and } 2048$ (with corresponding critical densities of $\rho_c = 0.65, 0.68, 0.70, 0.71, \text{ and } 0.72$). The line is a fit to equation $\chi = A l^{\gamma/\nu}$ and the slope is $\gamma/\nu = 1.96 \pm 0.03$, consistent with the literature value of $\gamma/\nu = 1.96$. With $\nu = 0.63$, this gives $\gamma = 1.23 \pm 0.02$.

We cannot determine conclusively, from our simulations, if there is a divergence in the shear viscosity or thermal conductivity. A plot of η and λ (not shown) at the critical point of a finite sized system as a function of $l^{-1/\nu}$ is roughly linear, and an extrapolation to $l \rightarrow \infty$ is

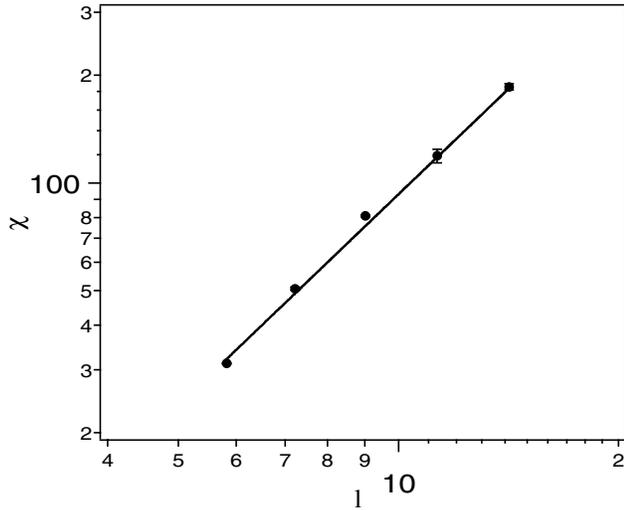


FIG. 1. The static susceptibility χ , plotted as a function of the simulation box length l , on a log-log scale. The symbols are simulation results for systems with $N = 128, 256, 512, 1024,$ and 2048 , at the critical density in each case. The line is a linear fit and has a slope of $\gamma/\nu = 1.96 \pm 0.03$.

possible. On the other hand, a log-log plot of η (or λ) as a function of l does not plateau for the range of system sizes studied. By fitting the last two data points on this plot, we place an upper bound on the value of the exponent. We conclude that η (λ) must diverge *slower* than $\xi^{0.09}$ ($\xi^{0.08}$). λ is expected to be finite at the consolute point, and η is believed to diverge as $\eta \sim \xi^{0.069}$. This exponent is too small to be observed in computer simulations, where the box sizes cannot be made large enough. Although our simulations are not inconsistent with the experiments, we cannot be definitive regarding the behavior of η and λ at the critical point except to say that there is a critical enhancement.

Our simulations show that the Onsager kinetic coefficient diverges at the critical point and, since this divergence is slower than that of χ , the mutual diffusion coefficient goes to zero at the consolute point. Figure 2 depicts L as a function of l on a log-log scale for N ranging from 128 to 16384. The symbols correspond to the values of L at the respective critical densities and clearly support a power-law behavior. The solid line is a linear fit to the simulation results, and the slope of the line is $y/\nu = 0.70 \pm 0.05$, where y is defined as the critical exponent for the divergence of L ($L \sim \epsilon^{-y}$ and $L \sim \xi^{y/\nu}$). Since $D_{AB} = L/\chi$, $D_{AB} \sim \xi^{-1.26 \pm 0.08}$ ($D_{AB} \sim \epsilon^{0.79 \pm 0.05}$). Our estimate for these critical exponents is different from theoretical estimates. Early MCT predictions [8] yield $L \sim \xi$ and the RG theories [12] yield $L \sim \xi^{0.895}$, which correspond to $D_{AB} \sim \xi^{-1}$ and $D_{AB} \sim \xi^{-1.065}$, respectively, which may be compared to our result, i.e., $D_{AB} \sim \xi^{-1.26 \pm 0.08}$. A dotted line with a slope of 0.895, i.e., the RG prediction, is shown in Fig. 2 for comparison.

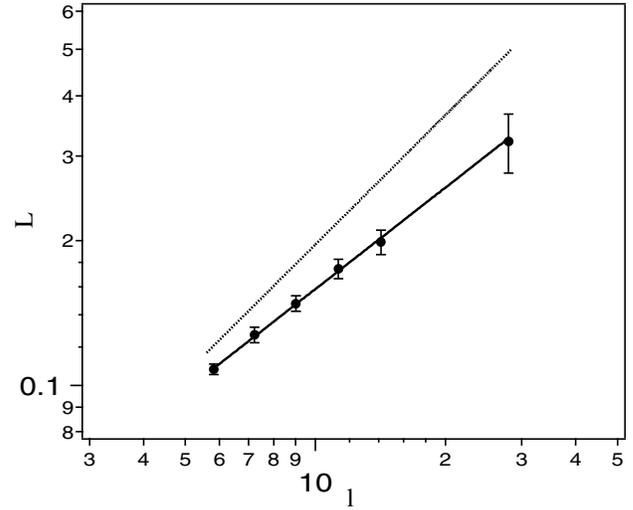


FIG. 2. The Onsager kinetic coefficient L , plotted as a function of the simulation box length l , on a log-log scale. The symbols correspond to critical points from simulations with $N = 128, 256, 512, 1024, 2048,$ and 16384 . The solid line is a least-squares fit to the data with slope, $y/\nu = 0.70 \pm 0.05$. The dotted line has a slope of 0.895, which is the RG prediction.

The value of the exponent for D_{AB} is not well established in the literature. D_{AB} is normally obtained from the width of the Rayleigh line in a light-scattering experiment. The slope of the linewidth (Γ) as a function of q^2 (q is the momentum transfer variable) gives D_{AB} . Sufficiently close to the critical temperature, the condition $q\xi \ll 1$ is often violated, and Γ/q^2 becomes independent of temperature, making the determination of the critical exponent difficult. Early experiments [17] on isobutyric acid-water and phenol-water mixtures obtained a value for the exponent $p = 0.68 \pm 0.04$ [p is the exponent in $D_{AB} \sim \epsilon^p$, where $\epsilon = |(T - T_c)/T_c|$ and T_c is the critical temperature], consistent with the RG prediction. But more recent experiments present a more complicated picture. For example, when we fit the data from recent experiments on hexane-nitrobenzene [18], we obtain an exponent of $p = 0.74 \pm 0.02$ if we use the critical temperature ($T_c = 292.56$ K) reported in the paper. When we fit light-scattering measurements on methanol-cyclohexane mixtures [19], we obtain an exponent of $p = 1.23 \pm 0.05$ if we use the literature value for the critical temperature ($T_c = 319.05$ K). It has been suggested [19] that the critical temperature should also be fit, even though independent measures of T_c are available. If we treat p and T_c as adjustable parameters, we find $p = 0.85 \pm 0.07$ and $T_c = 291.7 \pm 0.6$ K for the hexane-nitrobenzene experiments [18] and $p = 0.6 \pm 0.1$ and $T_c = 319.6 \pm 0.1$ K for the methanol-cyclohexane experiments [19]. These large uncertainties suggest that the data are not sufficient for a precise determination of both T_c and p . An experimental study for the thermal diffusivity α of

argon [20] (similar to D_{AB} for a binary mixture) obtained $p = 0.739 \pm 0.005$. Clearly, the values for this exponent vary widely in the different experiments and may be compared with our estimate of $p = 0.79 \pm 0.05$.

The reason for the discrepancy between the exponent obtained in this work and those obtained in experiments and theory is unclear. For the reasons given above, it is difficult to estimate this exponent from experiments. On the other hand, the simulations are performed for finite systems. Although we do a careful finite size analysis, we miss dynamic correlations that occur on length scales larger than our system sizes. The RG exponent is obtained from calculations on model H . In the context of static critical phenomena, there is a clear correspondence between these field theoretic models, Ising lattice models, and real fluids. For dynamical critical phenomena, however, the correspondence is much weaker.

In summary, we present results of the first molecular dynamics simulations for the transport properties of fluids near the critical point. The simulations are made feasible by a choice of model where the particles interact via discontinuous potentials. Our main result is that the Onsager kinetic coefficient diverges at the critical point with the exponent $L \sim \xi^{0.70 \pm 0.05}$. Consequently, the mutual diffusion coefficient vanishes as $D_{AB} \sim \xi^{-1.26 \pm 0.08}$. These results are different from the RG estimates of $D_{AB} \sim \xi^{-1.065}$ for model H and the MCT estimate of $D_{AB} \sim \xi^{-1}$. Interestingly, no *definitive* estimates of this exponent have been reported in the literature. In fact, the available data are for state points sufficiently far from the critical point that both the RG exponent and that obtained from our simulations are able to fit the data, with different values for the critical temperature. We hope that our simulations will stimulate further experimental and theoretical work on this interesting and fundamental aspect of critical phenomena.

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