Critical Dynamics in a Binary Fluid: Simulations and Finite-Size Scaling

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We report comprehensive simulations of the critical dynamics of a symmetric binary Lennard-Jones mixture near its consolute point. The self-diffusion coefficient exhibits no detectable anomaly. The data for the shear viscosity and the mutual-diffusion coefficient are fully consistent with the asymptotic power laws and amplitudes predicted by renormalization-group and mode-coupling theories *provided* finite-size effects and the background contribution to the relevant Onsager coefficient are suitably accounted for. This resolves a controversy raised by recent molecular simulations.

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Introduction.—Thermodynamic and transport properties exhibit critical-point singularities with exponent values and amplitude ratios that are the same for systems belonging to the same universality class. As regards static critical behavior, it has been well established that fluids of molecules with short-range interactions belong to the universality class of three-dimensional Ising-type systems [1]. It is expected that the dynamic critical behavior of fluids conforms to that of model H in the nomenclature of Hohenberg and Halperin [2]. Recently, there has been a revival of interest in critical phenomena, one reason being that computer-simulation techniques have matured sufficiently that they can provide interesting detailed information concerning the static critical behavior [3–5]. For instance, recent Monte Carlo simulations have provided new insights concerning the nature of the scaling fields in asymmetric fluids [5].

The status of computer simulations of the dynamic critical behavior of fluids is much less satisfactory. Specifically, on the basis of a recent molecular dynamics simulation of a binary fluid Jagannathan and Yethiraj (JY) [6] concluded that the dynamic exponent x_D that governs the slowing down of critical fluctuations differs substantially from the value predicted by renormalization-group or mode-coupling theory [2,7]. It has also been noted that this conclusion disagrees with reliable experimental evidence [8].

To address the general issue we have undertaken a comprehensive study of the dynamic critical behavior of a symmetric Lennard-Jones mixture ($A + B$) near its consolute point. We find that the data for the transport property that determines the nature of critical slowing down are significantly affected by finite-size effects and by a ''background'' contribution arising from fluctuations at small length scales. After properly accounting for both these effects our extensive simulations of the critical dynamics prove to be fully consistent, both with current theoretical predictions and with the best available experimental evidence.

The model.—Starting from the standard (12, 6) Lennard-Jones potential with parameters $\varepsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ (α, $\beta = A$, B) we construct a truncated potential which is strictly zero for $r > r_c$ and makes both the potential and the force continuous at $r = r_c$ [9]. For the parameters, we take $\sigma_{AA} = \sigma_{BB} = \sigma_{AB} = \sigma$, $\varepsilon_{AA} = \varepsilon_{BB} = 2\varepsilon_{AB} = \varepsilon$, $r_c = 2.5\sigma$, and define the reduced temperature as $T^* = k_B T/\varepsilon$. The total particle number $N = N_A + N_B$ and the volume $V = L^3$ are chosen so that the reduced density $\rho^* = \rho\sigma^3 = N/V$ is unity and the simulation box edge is $L/\sigma \equiv L^* = N^{1/3}$. For these parameters the system is far from solid-liquid and liquid-gas transitions in the temperature regime of interest here.

In order to evaluate the results of computer simulations of dynamic critical behavior, accurate information regarding the static critical behavior is a prerequisite. We have obtained this by using a semi-grand-canonical Monte Carlo (SGMC) approach [9–11]. In the SGMC method, in addition to displacement moves, the particles may switch identity ($A \rightarrow B \rightarrow A$) with both the energy change ΔE and the chemical potential difference $\Delta\mu = \mu_A - \mu_B$ entering the Boltzmann factor. For the case $\Delta\mu = 0$, of interest here, one has $\langle x_A \rangle = \langle x_B \rangle = 1/2$ (with $x_\alpha = N_\alpha/N$) for $T > T_c$.

Static properties.—Since our focus is on the dynamic critical behavior, we simply state the results found for the static behavior [9]. An accurate, unbiased estimate for the reduced critical temperature was obtained by plotting the fourth-order cummulant $U_L = \langle (x_A - 1/2)^4 \rangle_L / \langle (x_A - 1/2)^2 \rangle_L^2$ as a function of T for various box sizes L and identifying T_c from the asymptotically common intersection point [5,9,12]: this yields $T_c^* = 1.4230 \pm 0.0005$ [9]. The concentration susceptibility $\chi(T)$ was calculated from $k_B T \chi = \chi^* T^* = N(\langle x_A^2 \rangle - \langle x_A \rangle^2)$ ($T > T_c$). The correlation length $\xi(T)$ was determined from Ornstein-Zernike plots of the Fourier transform of the concentration-concentration correlation function, $S_{cc}(q) = T^* \chi^* / [1 + q^2 \xi^2 + \ldots]$. In the thermodynamic limit (i.e., in the absence of finite-size effects) these properties diverge as $\chi^* \approx \Gamma_0 \epsilon^{-\gamma}$ and $\xi \approx \xi_0 \epsilon^{-\nu}$, where $\epsilon = (T - T_c)/T_c$

and we may adopt $\gamma = 1.239$ and $\nu = 0.629$ as the universal critical exponents for the three-dimensional Ising universality class [13]. Our SGMC simulations [9] then yield $\Gamma_0 = 0.076 \pm 0.006$ and $\xi_0/\sigma = 0.395 \pm 0.025$.

Dynamics.—We investigated the dynamic behavior by implementing a microcanonical molecular dynamics (MD) simulation [14]. For this study, multiple independent initial configurations were prepared from SGMC runs with 5×10^5 Monte Carlo steps (MCS) per particle. This was followed by a microcanonical thermalization for 2×10^5 MD steps in the NVT ensemble using the Andersen thermostat [14] before the production runs commenced. For the MD simulations, the particle masses were taken equal: $m_A = m_B = m$. The standard Verlet velocity algorithm [14] was employed with a time step $\delta t^* = 0.01/\sqrt{48}$ [in units $t_0 = (m\sigma^2/\epsilon)^{1/2}$].

Self-diffusion.—Restricting attention to temperatures $T \geq T_c$ and to the critical concentration $x_c = x_A = x_B = 1/2$, the symmetry of our model dictates that the self-diffusion constant is the same for A and B particles: $D_A = D_B = D$. We have calculated the reduced self-diffusion coefficient D^* from mean square displacements via $(\sigma^2/t_0)D^* \equiv D = \lim_{t\to\infty}\langle[\vec{r}_i(0) - \vec{r}_i(t)]^2\rangle/6t$, where the average $\langle\bullet\rangle$ includes all A and B particles. The results are shown in Fig. 1(a) as a function of ϵ. No anomalous critical behavior is detected and the linear behavior is consistent with previous simulation studies [6,15]. MD calculations [16] have suggested a weak singularity in the self-diffusion near vapor-liquid criticality but no corresponding anomaly has yet been detected experimentally [17].

Shear viscosity.—The shear viscosity is expected to diverge as ξ^{x_η} with $x_\eta \simeq 0.0679$ according to recent theoretical calculations [18]; this value is in good agreement with the best available experimental information [8,19]. We have calculated the reduced shear viscosity η^* from the appropriate Green-Kubo formula [20]

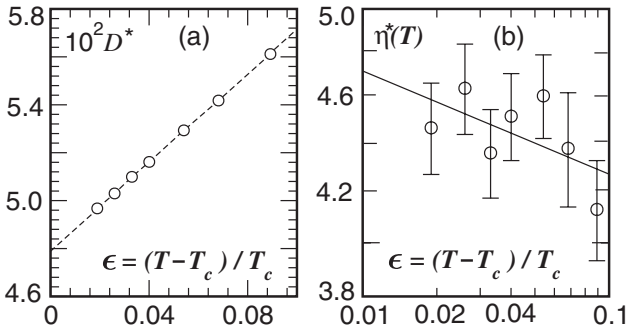

FIG. 1. (a) Reduced self-diffusion constant D^* for a system of $N = 6400$ particles as a function of T. The dashed line guides the eye and shows that $D(T_c)$ is nonzero. (b) Log-log plot of the reduced shear viscosity for the same system: the fitted line embodies the theoretical values for ν and x_η.

$$\eta^* = (t_0^3/\sigma V m^2 T^*)\int_0^\infty dt\langle\sigma_{xy}(0)\sigma_{xy}(t)\rangle, \qquad (1)$$

where the pressure tensor is $\sigma_{xy}(t) = \sum_{i=1}^{N}[m_i v_{ix} v_{iy} + \frac{1}{2}\sum_{j(\neq i)}|x_i - x_j|F_y(|\vec{r}_i - \vec{r}_j|)]$ with $\vec{F}$ and $\vec{v}_i$ the force between particles i and j and the velocity of particle i, respectively. The numerical data for η^* obtained from simulations with $N = 6400$ particles are shown in Fig. 1(b). As always in MD simulations, accurate estimation of the shear viscosity is difficult and the $\pm 5\%$ error bars prevent us making any strong statements about the singular behavior of η^*. But the slight increase of η as $T \to T_c$ is consistent with the predicted divergence $\eta^* \approx \eta_0 \epsilon^{-\nu x_\eta}$ with $x_\eta = 0.068$ (and $\nu \simeq 0.63$, as above); see Fig. 1(b). Furthermore, on imposing the exponent values, a least-squares fit yields the amplitude estimate $\eta_0 = 3.8_7 \pm 0.3$.

Mutual diffusion.—Dynamic renormalization-group and mode-coupling theories predict that mutual-diffusion coefficients $D_{AB}(T)$ vanish as ξ^{-x_D} where

$$x_D = 1 + x_\eta \simeq 1.068, \qquad (2)$$

so that there is only one independent exponent characterizing the dynamic critical behavior of fluids [2]. This relation has been verified experimentally [21].

The mutual-diffusion coefficient $D_{AB} = (\sigma^2/t_0)D^*_{AB}$ is related to a corresponding Onsager coefficient $\mathcal{L}$ via $D^*_{AB} = \mathcal{L}/\chi^*$ [22]. We have calculated D^*_{AB} by adopting the result $\chi^*(T) \approx \Gamma_0 \epsilon^{-\gamma}$ previously obtained, and using MD simulations to determine $\mathcal{L}(T)$ from the appropriate Green-Kubo formula [20]

$$\mathcal{L}(T) = (t_0/NT^*\sigma^2)\int_0^\infty dt\langle J_x^{AB}(0)J_x^{AB}(t)\rangle, \qquad (3)$$

where $\vec{J}^{AB}(t) = x_B\sum_{i=1}^{N_A}\vec{v}_{i,A}(t) - x_A\sum_{i=1}^{N_B}\vec{v}_{i,B}(t)$, in which $\vec{v}_{i,\alpha}$ is the velocity of particle i of species α.

If, somewhat naively, one fits the numerical values for D_{AB} obtained for $N = 6400$ particles and $\epsilon > 0.01$ to a power law of the form $D^*_{AB} \propto \xi^{-x_{\text{eff}}}$ one finds a value of about 1.6 for the effective critical exponent; this is even larger than the corresponding value $x_{\text{eff}} = 1.26 \pm 0.08$ derived by Jagannathan and Yethiraj [6] from their MD simulations. Both values differ substantially from the theoretical prediction recorded in (2).

To resolve this issue we must focus on the Onsager coefficient $\mathcal{L}$ since the simulation data for χ^* in our model are consistent with Ising criticality [9]. While the divergence of χ^* near T_c is strongly dominated by long-range fluctuations, it is known that the Onsager coefficient of fluid mixtures near a consolute point (or, its equivalent, the thermal conductivity of a fluid near a vapor-liquid critical point) contains a critical enhancement $\Delta\mathcal{L}(T)$ due to long-range fluctuations *together* with a significant background which arises from fluctuations at small length scales [22,23] and has weak temperature dependence [24]: thus we write

$$\mathcal{L}(T) = \Delta\mathcal{L}(T) + \mathcal{L}_b(T). \quad (4)$$

Such a separation has proved essential in reconciling experimental data for $D_{AB}(T)$ with theory [24].

In Fig. 2 we show a plot vs ϵ of the numerical data obtained for $\mathcal{L}$ from the simulations with $N = 6400$ particles. The data do indeed suggest the presence of a significant background. Theory predicts that $\Delta\mathcal{L}$ satisfies a Stokes-Einstein relation of the form $\Delta\mathcal{L} = R_D T^* \chi^* \sigma / 6\pi\eta^*\xi$, where R_D is a universal dynamic amplitude ratio that is of order unity [2,23]. On accepting the exponent (2) we thus obtain

$$\Delta\mathcal{L} \approx Q T^* \epsilon^{-\nu_\lambda} \quad \text{with} \quad \nu_\lambda = x_\lambda \nu \simeq 0.567 \quad (5)$$

and $x_\lambda = (\gamma/\nu) - x_D \simeq 0.902$. Adopting the value $R_D \simeq 1.05$ [23] we find, using the values for Γ_0, ξ_0, and η_0 reported above, that a sound theoretical estimate of the amplitude Q for our model is

$$Q = (2.8 \pm 0.4) \times 10^{-3}. \quad (6)$$

Finite-size scaling.—Since the background $\mathcal{L}_b(T)$ derives from atomic length scales, it should vary little with L. However, the possibility of significant finite-size effects on the critical part, $\Delta\mathcal{L}(T)$, must be recognized and allowed for. Note, in particular, that although static properties may (as in [9]) exhibit negligible finite-size deviations for the range of $(T - T_c)$ and L simulated (see Fig. 3), the same need not be true for transport coefficients. To tackle this problem we write the finite-size scaling ansatz [5,25,26] as

$$\Delta\mathcal{L}/T^* \approx Q W(y) \epsilon^{-\nu_\lambda}, \quad (7)$$

where $y = L/\xi$ while $W(y)$ is a finite-size scaling function that must vary as $W_0 y^{x_\lambda}[1 + O(y^{1/\nu})]$ for small y, since $\Delta\mathcal{L}(T_c; L)$ is finite for $L < \infty$ [5,25,26]. For large y one may quite generally write

$$W(y) = 1 + W_\infty e^{-ny}/y^\psi + \ldots, \quad (8)$$

where $W(\infty) = 1$ is needed to reproduce (5) when $L \to \infty$ while, for static properties in short-range systems, n is a small integer [5,25,26]. However, for dynamic coefficients, where long-time tails, etc., may enter, one must be prepared for $n = 0$ implying only an $L^{-\psi}$ decay of finite-size deviations; the exponent ψ demands more detailed, currently unavailable theory.

To analyze the $\mathcal{L}(T; L)$ data a scaling plot of $\mathcal{W}_L(T) \equiv (\Delta\mathcal{L}/T^*)\epsilon^{\nu_\lambda}$ vs y is desirable: by (7) and (8) this should approach Q for large y. But the background $\mathcal{L}_b(T)$, albeit slowly varying, is unknown. To meet this challenge, we introduce an effective background parameter $\mathcal{L}_b^{\text{eff}}$, and adjust it to optimize data collapse: see Fig. 3 which presents $\mathcal{W}_L(T)$ for three illustrative values of $\mathcal{L}_b^{\text{eff}}$ vs the bounded variable $[y/(y_0 + y)]^{x_\lambda}$ in which x_λ is taken from (5) while, purely for convenience of display, we have set $y_0 = 7$. The optimal value, which serves as a rough estimate of $\mathcal{L}_b(T_c)$, proves to be $\mathcal{L}_b^{\text{eff}} = (3.3 \pm 0.8) \times 10^{-3}$ [9]. For this assignment we find that a good fit (see the dashed line in Fig. 3) is provided by $\mathcal{W}_L \simeq Q/[1 + p_0/y(1 + y^2/p_1^2)]^{x_\lambda}$ with $p_0 = 5.8 \pm 0.5$ and $p_1 \simeq 13.8$ while $Q = (2.7 \pm 0.4) \times 10^{-3}$. This estimate for Q is in

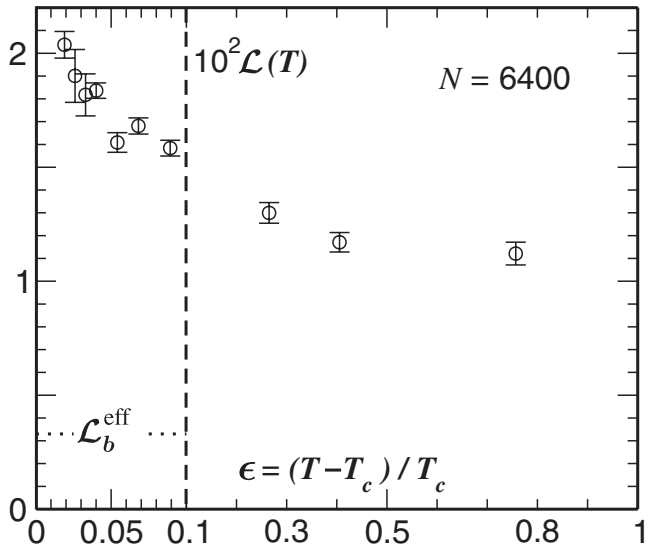

FIG. 2. Variation with temperature of the Onsager coeffecient $\mathcal{L}(T)$ for a system of $N = 6400$ particles. Note the expansion of the scale for $\epsilon \leq 0.1$. The dotted line represents an effective background contribution: see text.

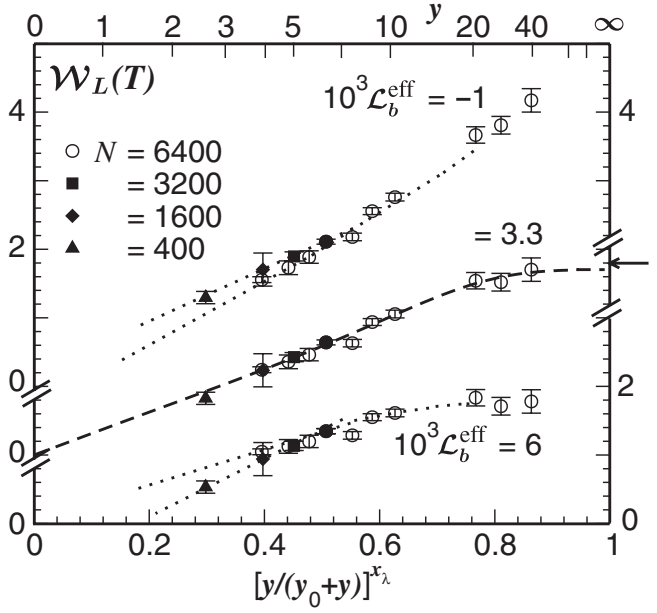

FIG. 3. Finite-size scaling plots of the critical part of the Onsager coefficient for trial values of the effective background $\mathcal{L}_b^{\text{eff}}$ with $y = L/\xi$. We have accepted the theoretical value $x_\lambda \simeq 0.90$ and, for convenience, set $y_0 = 7$. The filled symbols represent data for different system sizes at $T^* = 1.48$. The arrow on the right marks the theoretical value (6) for the critical amplitude Q. The dotted lines guide the eye; the dashed line is a scaling-function fit embodying the optimal value of $\mathcal{L}_b^{\text{eff}}$: see text.

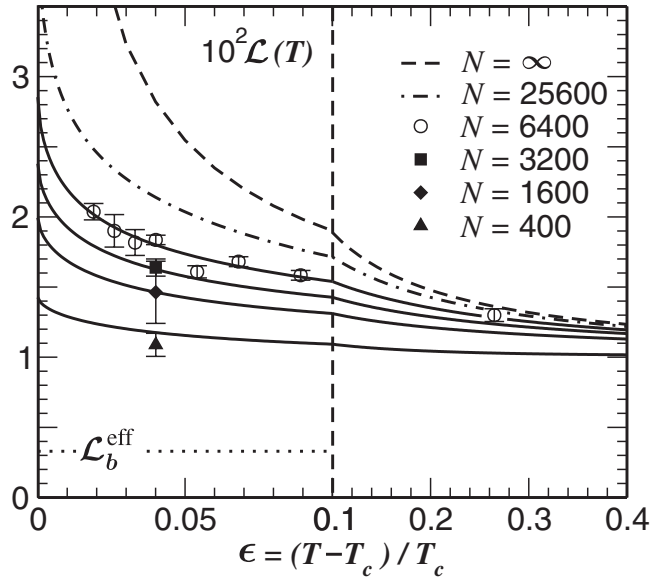

FIG. 4. Variation of the Onsager coefficient with T for systems of increasing size based on the fitted scaling function and the optimal value of $\mathcal{L}_b^{\rm eff}$ [$\simeq \mathcal{L}_b(T_c)$]: see the dotted line. For T within 1% of T_c, reliable estimates of $\mathcal{L}(T)$ would require $N > 3 \times 10^4$ and system sizes exceeding 30σ.

gratifying agreement with the theoretical value reported in (6).

The quantitative significance of the finite-size effects can be appreciated from Fig. 4 where the scaling-function fit has been used to estimate $\mathcal{L}(T)$ for $N = 2.56 \times 10^4$ and $N \to \infty$. Note also that the fit for $\mathcal{W}_L(y)$ corresponds to $n = 0$ and $\psi = 3$ in (8). Further exploration suggests that if an ultimate exponential decay does arise [e.g. if $n = 1$ in (8)] it sets in only for $y = L/\xi \gg 30$.

In summary.—The extensive simulations we have performed for the transport properties near the demixing point of our symmetric but otherwise not unrealistic binary fluid model are, when appropriately analyzed with due attention to strong finite-size effects and a background contribution, completely consistent with current theoretical predictions and the best available experimental data. Not only are the theoretical exponent values and the dynamic exponent relation (2) in accord with the data, but the amplitude value (6) is directly confirmed. While increased computer power and more refined analysis might eventually provide more stringent tests of theory, such as the value of R_D, the necessary resources appear rather demanding.

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