Simulating critical dynamics in liquid mixtures: Short-range and long-range contributions

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Recently, Das *et al.* [J. Chem. Phys. **125**, 024506 (2006)] established that computer simulations of critical dynamics in a binary Lennard-Jones mixture are consistent with the predicted Stokes-Einstein behavior of the asymptotic decay rate of the order-parameter fluctuations near criticality. Here, we show that the noncritical or "background" contributions to the computed diffusion coefficient are also in agreement with both theory and experiment, thus further validating the feasibility of molecular dynamics simulations for studying dynamic critical behavior. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2770736]

I. INTRODUCTION

During the past decade, computer-simulation techniques for investigating the nature of the critical behavior of fluids and fluid mixtures have improved considerably. Specifically, it has become possible to obtain accurate information from Monte Carlo simulations regarding properties such as the equation of state and the correlation length near critical points.[1–7] However, molecular dynamics (MD) simulations of the dynamic critical behavior of fluids or fluid mixtures have turned out to be more challenging. There are two physical reasons why simulating dynamic critical behavior is more complicated. The first is that the critical slowing down of the fluctuations has its origin in the so-called long-time tails of the dynamic correlation functions.[8,9] As a consequence, finite-size effects in simulations of dynamic critical behavior are even more pronounced than those encountered in simulating static critical behavior.

The second reason is that the commonly known predictions of dynamic renormalization group theory[10] and mode coupling theory[11] apply only to the most singular critical part of the transport properties and not to the subleading contributions that are related to short-range fluctuations; clearly, however, short-range contributions are likely to be significant in computer simulations of the transport properties.

Because of these complications, some early MD simulations appeared to yield a value for the dynamic critical exponent for fluids that differed significantly from the value previously established both theoretically and experimentally.[12,13] In a subsequent computer simulation, Chen *et al.*[14] were able to determine a dynamic critical exponent consistent with theory; but their work did not yield any information concerning the amplitudes of the asymptotic dynamic behavior close to criticality.

In two previous publications in collaboration with Horbach and Binder,[15] we have demonstrated that MD simulations of liquid-liquid criticality in a Lennard-Jones mixture are fully consistent with theory and experiment, provided that the two complicating features mentioned above are properly accounted for in the analysis of the simulation data. For this purpose, a value for the noncritical "background" of the relevant Onsager coefficient was estimated by requiring that the observed data obeyed universal finite-size scaling. It was then found that a finite-size scaling plot led, in the thermodynamic limit, to values for the dynamic amplitude consistent with the Stokes-Einstein behavior of the diffusion coefficient that had been predicted by the mode coupling theory of critical dynamics.[11]

It turns out that it is also possible to derive an estimate for the "noncritical" or subleading part of the diffusion coefficient from mode coupling theory.[16] This estimate has been used in the interpretation of experimental diffusion coefficient data for liquid mixtures near criticality. In the present paper we show that not only is the most singular critical contribution, deduced from our MD simulation data, consistent with theory and experiment, but so also is the noncritical background for the diffusion coefficient. This further confirms that it has now become possible to obtain rather reliable information from computer simulations of critical dynamics.

This paper is organized as follows. In Sec. II we summarize the predictions of mode coupling theory for the asymptotic behavior of the diffusion coefficient and the viscosity near the critical point of liquid mixtures. The experimental evidence in support of these theoretical predictions is reviewed briefly in Sec. III. Finally, in Sec. IV we then show that our MD simulations are fully consistent with both the theoretical predictions and the experimental evidence. A concluding remark is presented in Sec. V.

II. MODE COUPLING THEORY OF CRITICAL DYNAMICS

The decay rate of the order-parameter fluctuations in the critical region is determined by a diffusivity D, which in turn can be written as the ratio of an Onsager coefficient $\mathcal{L}$ and a susceptibility χ. In the case of a one-component fluid near the vapor-liquid critical point, D is to be identified with the thermal diffusivity, $\mathcal{L}$ with the thermal conductivity, while χ is associated with the isobaric heat-capacity density; in a nearly incompressible liquid mixture near the critical point of mixing, D is the binary mutual or interdiffusion coefficient, $\mathcal{L}$ is a concentration conductivity, while χ represents the osmotic compressibility.[10,17] The Onsager coefficient or conductivity $\mathcal{L}$ can be decomposed into a critical contribution $\Delta\mathcal{L}$ arising from long-range critical fluctuations and a noncritical background contribution or "bare coefficient" $\mathcal{L}_b$ associated with short-range fluctuations.[11,17,18] This decomposition of the conductivity $\mathcal{L}$ induces a decomposition of the diffusion coefficient D into a critical contribution ΔD and a background diffusion coefficient D_b, that is,

$$D = \Delta D + D_b \tag{1}$$

with

$$\Delta D = \Delta\mathcal{L}/\chi \quad \text{and} \quad D_b = \mathcal{L}_b/\chi. \tag{2}$$

Both the mode coupling theory of critical dynamics and dynamic renormalization group theory predict that in the long-wavelength or hydrodynamic limit, ΔD should, asymptotically close to the critical point, satisfy a relation of the form[10,11]

$$\Delta D \approx R_D k_B T/6\pi\eta\xi, \tag{3}$$

where k_B is Boltzmann's constant, T is the temperature, η is the shear viscosity, ξ is the diverging correlation length, while $R_D = 1.05 \pm 0.03$ is a universal dynamic amplitude ratio.[16,19,20] With $R_D \simeq 1$, Eq. (3) is commonly referred to as the Stokes-Einstein relation; it has been pointed out, however, that it is more appropriate to call it the Stokes-Einstein-Sutherland relation.[21] The shear viscosity is predicted to behave as[16,22,23]

$$\eta \approx \eta_b (q_0 \xi)^{x_\eta}, \quad \text{with } x_\eta \simeq 0.068, \tag{4}$$

where q_0 is a system-dependent wave number[24] that will play a role in the subsequent discussion. Unlike the conductivity, the viscosity η should evidently exhibit a multiplicative anomaly,[25] that is, the amplitude of its critical power-law divergence is proportional to the noncritical background viscosity η_b. It follows from Eqs. (3) and (4) that ΔD vanishes as

$$\Delta D \sim \xi^{-(1+x_\eta)}, \quad \text{with } 1 + x_\eta \simeq 1.068. \tag{5}$$

In terms of the reduced variable $t = (T - T_c)/T_c$, where T_c is the critical temperature, the susceptibility χ and the correlation length ξ diverge as

$$\chi \approx \Gamma_0 t^{-\gamma} \quad \text{and} \quad \xi \approx \xi_0 t^{-\nu}, \tag{6}$$

with $\gamma \simeq 1.239$ and $\nu \simeq 0.629$, while Γ_0 and ξ_0 are system-dependent amplitudes.[26] As a consequence, the viscosity diverges as

$$\eta \approx \eta_0 t^{-\nu x_\eta}, \quad \text{with } \eta_0 = \eta_b (q_0 \xi_0)^{x_\eta}, \tag{7}$$

while the singular part $\Delta\mathcal{L}$ of the Onsager coefficient diverges as

$$\Delta\mathcal{L} \approx Q k_B T t^{-\nu_\lambda}, \quad \text{with } Q = R_D \Gamma_0/6\pi\eta_0\xi_0, \tag{8}$$

where $\nu_\lambda = \gamma - \nu - \nu x_\eta \simeq 0.567$.

The background contribution D_b for liquid mixtures, in the hydrodynamic limit of zero wave number, can be written as[16]

$$D_b = k_B T/16\eta_b \xi^2 q_C = k_B T \Lambda_C/16\eta_b \xi^2, \tag{9}$$

where $\Lambda_C \equiv 1/q_C$ is a system-dependent wavelength. As discussed by Bhattacharjee and co-workers,[16,22] this parameter has been related to the wave number q_0 in the power law (4) for the viscosity via

$$q_0^{-1} = (\Lambda_C + \Lambda_D) e^{4/3}/2, \tag{10}$$

where $\Lambda_D \equiv q_D^{-1}$ is a cutoff wavelength in the mode coupling integrals for the critical contributions to the transport coefficients. This relation, however, will not play an explicit role in our subsequent analysis of the computer-simulation data.

III. COMPARISON WITH EXPERIMENTS

We briefly review here the experimental information bearing on the theoretical predictions, since experience in analyzing experimental data will provide us with additional guidelines for the analysis of simulation data. Experiments for transport properties of fluids near the vapor-liquid critical point are affected by the presence of density gradients induced by gravity.[27] In the case of liquid mixtures near a critical mixing point, gravity may induce a concentration gradient. However, it is often possible to perform experiments before such a concentration gradient is actually established, since in many liquid mixtures the difference between the densities of the two phases is rather small and the overall mass diffusion is slow. Consequently, there are considerable quantities of experimental data available for liquid mixtures near criticality, which is the focus of our current attention.

A. Shear viscosity

Experimental data for the shear viscosity of fluids near the critical point need to be corrected for the presence of shear gradients and frequency effects. An analysis of early experiments for the critical viscosity exponent x_η yielded values of about[28] 0.066. Subsequently, Berg and Moldover[29] measured the viscosity of four binary liquid mixtures near their critical mixing points and found values for x_η that varied from 0.064 up to 0.070. A recent experiment of Berg *et al.*,[30] performed in xenon in a low-gravity environment to suppress gravitational stratification, yielded $x_\eta = 0.0690 \pm 0.0006$ in good agreement with the most recent theoretical estimate 0.0679 ± 0.0007 of Hao *et al.*[23] New experimental viscosity data reported by Souto-Caride *et al.*[31] for two binary liquid mixtures are also consistent with this critical exponent value.

A survey of the values reported for the factor $q_0\xi_0$ in the amplitude for the viscosity power law (7) of many liquid mixtures has been presented by Wagner *et al.*[32] For liquid mixtures, this factor ranges from 0.05 to 0.25 so that the ratio $\eta_b/\eta_0 = (q_0\xi_0)^{-x_\eta}$ varies between 1.1 and 1.2. Hence, the estimate

$$\eta_b/\eta_0 = 1.15 \pm 0.05 \tag{11}$$

covers the range of values observed for the relationship between the background viscosity η_b and the amplitude η_0 in liquid mixtures. The subsequent viscosity measurements of Souto-Caride *et al.*[31] are also consistent with this estimate.

Attempts have also been made to determine Λ_C and Λ_D in Eq. (10) from experimental viscosity data.[32] However, while the data do yield a value for q_0, it is difficult to obtain reliable estimates for Λ_C and Λ_D separately in the absence of independent information about the diffusion coefficient owing to the high correlation between these two lengths in the expression for the viscosity.

B. Diffusion coefficient

Light scattering is a suitable method for investigating critical fluctuations. Burstyn *et al.*[19,33,34] have made a detailed experimental study of the dynamics of critical fluctuations in a liquid mixture of nitroethane and 3-methylpentane using light scattering. This mixture has the special property that the difference between the refractive indices of the two liquid components is sufficiently small that multiple-scattering corrections are minor, while, nevertheless, it is large enough that the light scattering can still be attributed to the fluctuations in concentration.[35]

Light scattering yields the decay rate of the fluctuations at finite wave number q. To account for the wave-number dependence of the diffusion coefficient, Eq. (3) can be extended to

$$\Delta D = \frac{R_D k_B T}{6\pi\eta\xi}\Omega(q\xi), \tag{12}$$

where $\Omega(z)$ is a universal dynamic scaling function, normalized by $\Omega(0)=1$, while one must have

$$\Omega(x) \propto z^{1+x_\eta}, \quad \text{for } z \gg 1. \tag{13}$$

In terms of the so-called Kawasaki function[11]

$$\Omega_K(z) = (3/4z^2)[1 + z^2 + (z^3 - z^{-1})\arctan z], \tag{14}$$

Burstyn *et al.*[16] have proposed the explicit expression

$$\Omega(z) = \Omega_K(z)[1 + (z/2)^2]^{x_\eta}, \tag{15}$$

for this universal scaling function: this is normalized and satisfies the asymptotic condition (13).

In the experiments,[33] the diffusion coefficient was investigated for $q\xi$ both small and large. It follows from Eq. (13) that at temperatures asymptotically close to T_c, the critical contribution ΔD should vary with the wave number as q^{1+x_η}, thereby yielding the experimental estimate[33] $1+x_\eta = 1.06\pm0.02$. This agrees with the predicted value of 1.068. It may be noted that this determination is independent of the value assumed for the correlation length exponent ν.

By combining independent measurements of the diffusion coefficient, the correlation length, and the viscosity, Burstyn *et al.*[16,34] also verified that ΔD satisfies a Stokes-Einstein-Sutherland relation for small $q\xi$ in accordance with Eq. (3); they found $R_D=1.02\pm0.04$ or 1.01 ± 0.04, depending on some details of the analysis, both estimates being consistent with the theoretical value 1.05 ± 0.03. Experimental values reported for R_D by Beysens *et al.*,[36] Hamano *et al.*,[37] Agosta *et al.*,[38] and Güttinger and Cannell,[39] as reviewed by Privman *et al.*,[40] are also consistent with the theoretical estimate. Finally, for the cutoff wavelength $\Lambda_C \equiv q_C^{-1}$ in the expression (10) for the background diffusion coefficient D_b, Burstyn *et al.*[16] derived the estimate $\Lambda_C=0.18\pm0.04$ nm which, when compared with $\xi_0 \simeq 0.216$ nm for nitroethane+3-methylpentane, leads to

$$\Lambda_C/\xi_0 = 0.8_3 \pm 0.2. \tag{16}$$

This value will be compared in the subsequent section with a corresponding estimate derived from the computer MD simulations.[15]

IV. COMPARISON WITH COMPUTER SIMULATIONS

Das *et al.*[15] have made a numerical study of the static and dynamic critical behavior of a binary mixture of molecules A and B interacting with truncated Lennard-Jones (LJ) potentials by a combination of semigrandcanonical Monte Carlo and molecular dynamics methods. The length and energy parameters of the LJ potentials were taken to be $\sigma_{AA} = \sigma_{BB} = \sigma_{AB} = \sigma$ and $\varepsilon_{AA}=\varepsilon_{BB}=2\varepsilon_{AB}=\varepsilon$. For this section all physical quantities have been made dimensionless by expressing temperature in terms of ε/k_B and lengths in terms of σ.

From the Monte Carlo calculations, adopting the theoretical values for the critical exponents $\gamma\simeq1.239$ and $\nu \simeq 0.629$, Das *et al.*[15] obtained the following critical amplitudes for the susceptibility χ and the correlation length ξ in the power laws (6), namely,

$$\Gamma_0 = 0.076 \pm 0.006 \quad \text{and} \quad \xi_0 = 0.395 \pm 0.025. \tag{17}$$

From their MD simulations, by adopting the theoretical values $x_\eta \simeq 0.068$ and $\nu_\lambda \simeq 0.567$ for the dynamic critical exponents, they deduced amplitudes for the viscosity η and for the critical part $\Delta\mathcal{L}$ of the conductivity in the power laws (7) and (8). Specifically they found

$$\eta_0 = 3.87 \pm 0.30 \quad \text{and} \quad Q = (2.7 \pm 0.4) \times 10^{-3}. \tag{18}$$

On the other hand, using the estimates above for Γ_0, ξ_0, and η_0 and accepting $R_D=1.05$ in the theoretical expression (8) for the amplitude Q, they found the alternative estimate

$$Q = (2.8 \pm 0.4) \times 10^{-3}. \tag{19}$$

The good agreement between this value for Q and the value recorded in Eq. (18) enables one to conclude that the critical slowing down of the fluctuations implied by the MD simulations is completely consistent with the theoretically predicted Stokes-Einstein-Sutherland behavior.

In the analysis of the MD data for the Onsager conductivity coefficient $\mathcal{L}$, large finite-size effects are observed. To accommodate these and gain reliable estimates in the thermodynamic limit for critical amplitudes such as Q in Eq. (8), a finite-size scaling analysis proves imperative. In such an analysis, because the divergence of the Onsager coefficient, namely, $\mathcal{L}(T) \sim t^{-\nu_\lambda}$ with $\nu_\lambda \simeq 0.57$ is much weaker than that of the susceptibility $\chi \simeq t^{-\gamma}$ with $\gamma\simeq1.239$, it is essential to recognize the presence of the background term $\mathcal{L}_b(T)$: see Sec. II, Eqs. (1) and (2). Then the MD data were well described by a universal finite-size scaling function[15] which led to the estimate for Q quoted in Eq. (18). In the fitted range

$T/T_c = 1.01-1.28$, the corresponding background was satisfactorily accounted for by an effective constant value, namely,

$$\mathcal{L}_b^{\text{eff}} = (3.3 \pm 0.8) \times 10^{-3}. \tag{20}$$

At $T/T_c = 1.07$ this background contribution amounts to 20% of the numerical value of $\mathcal{L}(T)$ and it increases up to 26% at $T/T_c = 1.30$.

We now ask whether this effective background value has some physical significance. To this end, we note that the background contribution D_b to the diffusion coefficient, introduced in Eqs. (1) and (2), embodies the basic critical slowing down of the fluctuations predicted by the classical Van-Hove-type theories.[10,11] Thereby, D_b is related to the cutoff wavelength $\Lambda_C \equiv q_C^{-1}$ invoked in Eq. (9). We may rewrite and combine these relations to obtain

$$\Lambda_C = 16\xi_0^2 \eta_b \mathcal{L}_b / T\Gamma_0 t^{2\nu-\gamma}, \tag{21}$$

where $2\nu - \gamma \simeq 0.019$ is a very small exponent.[41] Note that Boltzmann's constant k_B no longer appears explicitly, because we have adopted dimensionless quantities.

To evaluate this expression for the MD simulations, we may use Eq. (17) for ξ_0 and Γ_0 and replace $\mathcal{L}_b$ by $\mathcal{L}_b^{\text{eff}}$ as given by Eq. (20). Indeed, in experiments[42] it has been found that over the temperature range T/T_c from 1.015 to 1.28, with a log-mean $T/T_c \simeq 1.06$, the values of $\mathcal{L}_b^{\text{expt}}$ vary by no more than 4%–5%. We also note that in the fitted temperature range $(T/T_c)t^{2\nu-\gamma}$ can be taken as 1.01 ± 0.03 in Eq. (21), while from the simulations we have[15]

$$T_c \equiv k_B T_c/\varepsilon \simeq 1.4230. \tag{22}$$

Although the numerical data for the viscosity yield the estimate (18) for the critical amplitude η_0, they are insufficient to provide a separate value for the background viscosity η_b that enters Eq. (21) via the mode coupling analysis: see Eqs. (4) and (7). In addition, there is no direct information for the cutoff wavelength Λ_D appropriate to the LJ-type model studied by Das *et al.*,[15] so we are unable to utilize the relation (10). Instead, we note that the product $(q_0\xi_0)^{x_\eta}$ in the relation (7) between η_0 and η_b is close to unity for real fluid mixtures, as is evident from Eq. (11) in Sec. III A. Insofar, as the model mixture is fairly realistic, we may reasonably expect a similar result to hold. Accordingly, on accepting the experimental value (11) for η_b/η_0 and using Eq. (21), the simulation data lead to $\Lambda_C \simeq 0.3_4 \pm 0.1$, which when compared with Eq. (17) for ξ_0 yields our computationally based estimate

$$\Lambda_C/\xi_0 = 0.85 \pm 0.26. \tag{23}$$

The relatively large uncertainty here arises mainly from the difficulty of estimating $\mathcal{L}_b^{\text{eff}}$ numerically. Nevertheless, the result is in remarkably good agreement with the independent, experimentally derived value (16)—a perhaps surprising but gratifying result!

V. CONCLUSION

In summary, we have shown that both the long-range and the short-range or "background" contributions to the decay of the order-parameter fluctuations observed in the MD simulations of Das *et al.*[15] are fully consistent with the detailed expectations from established theory and extensive experimental information. Thus, when due allowance is made for significant finite-size effects, we may conclude that the art of molecular simulations has now progressed sufficiently to provide reliable and useful information regarding critical dynamics. Indeed, with the benefit of hindsight, one can see that the results of Das *et al.*[15] could have been significantly improved with the expenditure of relatively modest additional computer time. In particular, it is worth stressing that time spent in *precise* computations for numbers of *smaller* systems enhances confidence in the essential finite-size scaling analysis and its accuracy and may, hence, be significantly more rewarding than the same time expended simulating larger system sizes. It remains true, nevertheless, that to explore dynamic critical behavior much closer to criticality than so far achieved will surely demand greater computational power.

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