Universal Dynamic Exponent at the Liquid-Gas Transition from Molecular Dynamics

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The liquid-gas system is expected to exhibit distinct dynamic behavior in the fluid's critical region (model H). We present molecular dynamics simulations of a Lennard-Jones fluid model starting from specially designed, near-equilibrium, initial conditions. By following the fluid's relaxation towards equilibrium, we calculate the requisite transport coefficients in the critical region. The results yield the scaling behavior of the thermal diffusion coefficient $D_T \sim \xi^{-1.023 \pm 0.018}$ (ξ is the correlation length) and a nonconventional divergent heat conductivity, all of which are in accord with mode-coupling and renormalization group predictions, as well as some experimental data.

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The liquid-gas (LG) critical point is the archetypical continuous phase transition and has been extensively studied for more than a century [1–3]. Its universal critical properties at equilibrium are well understood, based upon scaling and renormalization group (RG) theories [2]. Numerical values for its universal equilibrium critical exponents are also known to a high degree of accuracy from both sophisticated analytic approximations and precise numerical simulations of simple models belonging to the same universality class [2] (namely, the class of models with a scalar order parameter and short-range attractive interactions). Most importantly, these values are in excellent agreement with a vast collection of experimental data [1–3].

Given the significant amount of effort that has been devoted to establishing equilibrium LG critical exponents, it is surprising how relatively little is known about their dynamic counterparts [4]. In this regard, the simple lattice gas system falls into either model A or B, in the Hohenberg-Halperin classification [5] (where the order parameter is nonconserved or conserved, respectively). Model H of the LG system, however, is more complex since the gradient of the conserved scalar order parameter is now coupled to the transverse components of the fluid's momentum [6,7]. This, taken together with the phenomenon of critical slowing down, has made the task of computing the critical dynamic exponents of the simple LG system a formidable one to the present time. However, by crafting appropriate initial conditions and thereafter following the system relaxation to equilibrium, we are able to circumvent these difficulties and use MD simulations to directly compute the LG dynamic exponents, for the first time.

To review dynamic scaling in the context of model H, we recall that the order parameter field $q(\mathbf{r}, t)$ is the heat due to entropy fluctuations ($dq = Tds$) [3,4]. In the presence of a temperature gradient the heat flux $\mathbf{Q}$ obeys the linear response relation $\mathbf{Q} = -\kappa \nabla T$, where κ is the thermal conductivity. Combined with energy conservation this leads to the equation $\partial q / \partial t = \kappa \nabla^2 T$.

Expressing ∇T in terms of the density gradient $\nabla \rho$ and of ∇q leads to the *heat equation*

$$\partial q / \partial t = D_T \nabla^2 q, \tag{1}$$

where the thermal diffusion coefficient D_T is given by

$$D_T = \kappa / c_p. \tag{2}$$

We emphasize that c_p, and not c_v, appears in the denominator of D_T (c_p and c_v are the specific heats at constant pressure and volume, respectively). This comes about from density fluctuations and from the fact that, in the diffusive regime, the local fluctuation of the density $\delta\rho(\mathbf{r}, t)$ is directly proportional to that of the thermal field $q(\mathbf{r}, t)$ [3]. For this reason the mass (Fickian) diffusion coefficient D is, in fact, identical to D_T.

Hence, the behavior of D_T may be obtained from analyzing density fluctuations. This has been well known since the work of Landau and Placzek who, in 1934, showed [8] that the light-scattering structure factor $S(\mathbf{k}, \omega)$ (Fourier transform of density-density correlations) has, at $\omega = 0$, a diffusive (Rayleigh) peak of width $D_T k^2$. In addition, $S(\mathbf{k}, \omega)$ has two symmetric (Brillouin) peaks at $\omega = \pm c_0 k$ (c_0 is the sound velocity), of width Γk^2 (Γ is the sound attenuation coefficient).

Accordingly, given a density fluctuation $\rho_{\mathbf{k}}(0)$ of wave number $\mathbf{k}$ at $t = 0$, its subsequent behavior at $t > 0$ is given by [9]

$$\frac{\rho_{\mathbf{k}}(t)}{\rho_{\mathbf{k}}(0)} = \frac{c_p - c_v}{c_p} e^{-D_T k^2 t} + \frac{c_v}{c_p} e^{-\Gamma k^2 t} \cos(c_0 kt). \tag{3}$$

The first term on the right-hand side is purely diffusive, while the second describes oscillating (and attenuating) sound waves. The ratio of their coefficients, $\frac{c_p}{c_v} - 1$ diverges as a function of the temperature difference from the critical point ($\tau = T/T_c - 1$) since $c_v \sim |\tau|^{-\alpha}$, while $c_p \sim |\tau|^{-\gamma}$ (γ, the scaling exponent of the isothermal compressibility, is always larger than α). Moreover, while

D_T vanishes at criticality, Γ does not and the second term decays much more quickly than the first [10]. Thus, the nondiffusive term is negligible, compared with the diffusive one, near the LG critical point. This is true, in particular, if one is interested in the diffusive behavior since the time period for sound oscillations $2\pi/c_0 k$ is much shorter than the diffusion time decay $1/D_T k^2$ at the same small wave number. For this reason longitudinal density and pressure fluctuations are neglected at the outset in postulating model H [5].

Our starting point for this work is thus the relationship:

$$\rho_{\mathbf{k}}(t) = e^{-D_T k^2 t}\rho_{\mathbf{k}}(0). \tag{4}$$

Close to the critical transition the correlation length ξ diverges as $|t|^{-\nu}$. As long as it is smaller than the system size L, the longest relaxation time, τ_ξ, is obtained by the substitution of k with ξ^{-1}, so that $\tau_\xi = \xi^2/D_T$. The dynamic critical exponent z is then defined through the relation $\tau_\xi \sim \xi^z$, with the scaling form of the thermal diffusion constant given by $D_T \sim \xi^w$, so that

$$w = 2 - z. \tag{5}$$

Using Eq. (2) the scaling dimension y of the heat conductivity (defined by $\kappa \sim \xi^y$), may be related to w and $2 - \eta = \gamma/\nu$:

$$y = 2 - \eta + w, \tag{6}$$

where $2 - \eta$ is the exponent of the static correlations at T_c: $S(k, \omega = 0) \sim 1/k^{2-\eta}$. The exponent y is linked to the shear viscosity scaling exponent x_η by the relationship $y = 1 - \eta - x_\eta$, since we have [11] that $-w = 1 + x_\eta$.

Approximate values for some of these exponents have been calculated from analytical approaches. Mode-coupling theory [12] predicts $y = 0.946$ while the RG ϵ-expansion [5] estimate is $y = 0.916$. Using $\eta = 0.032$ [2], these approximations yield $w = -1.022$ and -1.052, respectively. Two-loop RG calculations [13] with a straightforward substitution of $\epsilon = 1$ yield to order ϵ^2 $w = -1.0712$.

Obtaining accurate estimates for universal critical exponents like those shown above from model potentials has been a long-standing challenge in the computer simulation field. Given that there is a single independent dynamic exponent in the long-time regime, dynamical critical properties may be expressed in terms of the dynamic exponent z characterizing the longest time scale. These results have been obtained for models A and B usually with Monte Carlo (MC) simulations [14]. Simulations of model H, on the other hand, cannot utilize these MC methods since, in this case, algorithms are required that account for the fluid's translational degrees of freedom. Therefore, MD is more appropriate to this situation and most existing molecular dynamics (MD) simulations [15] for the LG at its *critical point* have focused almost exclusively on equilibrium properties, or employed to study dynamical properties in this system, however, usually be-

low the critical point transition, i.e., for investigating domain-coarsening dynamics [16], spinodal decomposition [17], etc.

To the best of our knowledge, there are no extant direct numerical calculations of the critical dynamic scaling exponents in a 3D LG system, a situation that provided the impetus for the work presented here. Our simulation approach for doing this is based on relaxation dynamics whereby we chose to follow the slowest decay mode of a density fluctuation initially introduced into the system. The method has recently been successfully used [18] in the context of MC simulations of model B and here, for the first time, we generalize its application to MD as well.

The approach consists of initially preequilibrating two independent chambers, both of them at the critical temperature T_c, with densities $\rho_{1,2} = \rho_c \pm \Delta\rho(t = 0)/2$, where ρ_c and T_c are the equilibrium critical density and temperature of the system. Both chambers are then brought into contact with each other and the partition between them removed. Following the relaxation of $\Delta\rho(t)$ in each chamber, the relaxational decay properties are computed. To extract the diffusion constant D_T, we look at the decay of the slowest mode with $k = 2\pi/L$.

When the initial square-wave density profile $\rho(\mathbf{r}, 0)$ is expanded in a Fourier series, this slowest mode has the largest coefficient. More importantly, the higher harmonics decay relatively quickly and the error due to the omission of higher order terms decreases exponentially with time. This error can be very precisely calculated and controlled [18]. Another subtle advantage of the simulation approach employed here is the unambiguous way in which the initial conditions are established. The square-wave initial profile allows for the preequilibration of the system so that the introduced fluctuation can be made to fall within an arbitrarily small density region about the equilibrium one; i.e., one may be confident of reaching the linear response regime, in which the Onsager theory applies, after some initial time t_0. Other relaxation dynamics methods have not easily accommodated this situation.

A precondition to doing these particular simulations was the availability of published equilibrium critical properties for the pure LJ system found with MD simulations. To our surprise, a literature review showed that these are rare, the majority of such simulations having been carried out with MC methods, usually using truncated potentials with tail corrections added to include long-range effects. This cannot be done with MD methods, however, since truncated potentials lead to infinite forces at the cutoff point. As a result, MD methods use truncated and shifted potentials, which provide different critical property values to those given by truncated potentials. In the literature, we found MD critical values for only one set of truncated and shifted LJ potentials, and these were used in this study. The potential function used was taken from Litniewski [19] with continuous (and zero) potential at the cutoff distance, and is given by

$$u(r) = \begin{cases} 4[(\frac{1}{r})^{12} - (\frac{1}{r})^6] & \text{for } r \leq R_s = 3.0 \\ 4(r - R_c)^2[A_1 + A_2(r - R_c)] & \text{for } R_s \leq r \leq R_c = 3.75 \,. \\ 0 & \text{for } r \geq R_c \end{cases} \qquad (7)$$

In Eq. (7) r is the distance between two particles and the constants $A_1 = -3.657\,978\,97 \times 10^{-3}$ and $A_2 = -1.630\,228\,7 \times 10^{-3}$ are chosen so that the force of this modified potential is continuous at R_c and R_s. The cutoff distance R_c is chosen to be 3.75 and the force at this distance is continuous, therefore ensuring that this potential is suitable for MD simulations. The corresponding critical properties of the infinite system for this potential were found to be $T_c = 1.2600$, $P_c = 0.1193$, and $\rho_c = 0.3170$ [19]. The reduced units in this work were also normalized with respect to the LJ diameter σ and potential parameter ε. The length $L^* \equiv L/\sigma$, energy $U^* \equiv U/\varepsilon$, density $\rho^* \equiv \rho/\sigma^3$, time $t^* \equiv t/(m\sigma^2/\varepsilon)^{1/2}$, and similarly for the thermodynamic and transport variables.

The simulation algorithm we used, as described earlier, employed MD procedures to guide the relaxation dynamics process. The preequilibration of each of the two chambers was performed in an *NVT* ensemble using MD simulations, in which the thermostats were implemented by a reversible Nose-Hoover chain algorithm [20]. The ensemble averages $\Delta\rho(t)$ for each time scale were found from 50 simulation data blocks over 200 different initial nonequilibrium states in each block. The momenta in the two chambers were initially set to zero so that there would be no momentum difference between the two chambers before and after the relaxation dynamics. As a consequence, convective motion and shear forces in the cubic system can be avoided.

The behavior of the density relaxation in the denser chamber is shown in Fig. 1. We note that the relaxation time for the density to approach equilibrium is more than 25.0 (in the above reduced units). Initially, there is a pressure difference across the interface that also experiences dynamical relaxation after the interface is removed. In Fig. 2, we show the "pressure" relaxation in the system. The out-of-equilibrium pressure is calculated from the interparticle distances and forces using the virial theorem

[21] and thus coincides with the thermodynamic (hydrodynamic) pressure at (close to) equilibrium. The time taken to approach the equilibrium value for the pressure, however, is much shorter than that of the density relaxation process, especially in the critical region. For example, for the system shown in Fig. 2 there is a transient behavior in region 1 for times smaller than $t \sim t_0 = 4.46$ before the clear exponential decay sets in. At this time, the pressure in both chambers has practically reached its thermodynamic equilibrium value. Given the much faster relaxation of the pressure difference, it does not affect the mass diffusion on the time scale it takes the density to exponentially relax (region 2). This feature is also consistent with the underlying assumption of model H as discussed above [5,7].

From the slope in region 2 of Fig. 1 the relaxation time is obtained, which then yields D_T from Eq. (4) with $k = 2\pi/L$. To extract the critical behavior of D_T, we used finite-size scaling. In Fig. 3 we draw the dependence of $\ln D_T$ at the critical point (of the infinite system) as a function of $\ln L$, the logarithm of the system size. The slope yields the exponent $w = -1.023 \pm 0.018$, thus, from Eq. (5), $z = 3.023 \pm 0.018$. Using Eq. (6) with the known value [2] of $\eta = 0.032 \pm 0.003$, we find $y = 0.945 \pm 0.021$ (for comparison, the corresponding values [14,18] for model B are $w = -1.971$ and $z = 3.971$). We note that the approximate values of the exponents of both the mode-coupling approximation and the ϵ expansion with $\epsilon = 1$, as quoted previously, are in good agreement with the simulation results presented here.

In comparing with experiments we adopted an approach that did not rely upon the use of thermal conductivity scaling data, which are not considered sufficiently accurate for this purpose [22]. Thus we compared our simulation results with light-scattering data that measure directly the relaxation rate of the order parameter fluctuations. Our results are in excellent agreement (to within 1%) with the
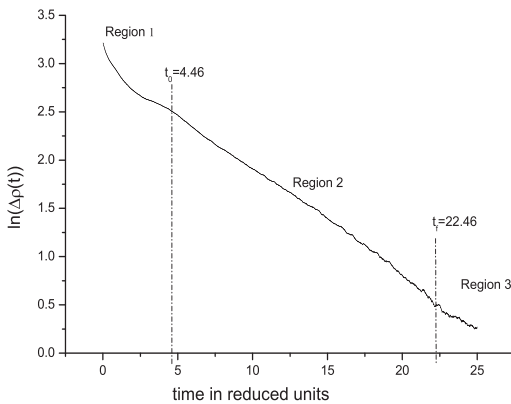

FIG. 1.　Density relaxation in a system with size $L = 10$ at the critical point.
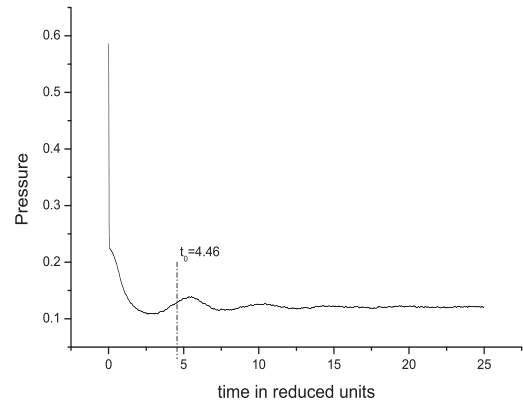

FIG. 2.　"Pressure" relaxation in a system with size $L = 10$ at the critical point.
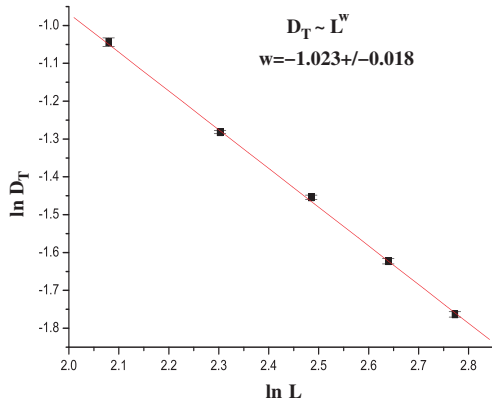
FIG. 3 (color online).   The heat diffusion coefficient D_T at T_c versus system size L (log- log plot).

very recent results of one group [23] and overlap within the error bars with those of another one [24]. In addition, the values of w derived from the measurements of xenon viscosity on the space shuttle ($w \cong -1.07$) [25] and of the mutual diffusion coefficient of a binary liquid-liquid system ($w \cong -1.09$) [26] are within 5% of our largest bound.

In conclusion, we have presented simulation results for critical dynamic exponents in a model H fluid, based upon a relaxation dynamics simulation method. The exponents found are in good agreement with some experimental data and in good agreement with theoretical predictions of mode-coupling and RG theories.

After this work was finished, a Letter appeared [27] in which the authors use MD to compute the critical dynamic properties of the Widom-Rowlinson (WR) model of a binary mixture at the consulate (separation) point. They find $w = -1.26$ for the mutual diffusion coefficient. The authors correctly point out that, while there is a clear correspondence between the WR model (where there is no temperature *per se* and the phase separation is driven by increased density) and other model H systems in equilibrium, the correspondence between their dynamic critical properties is much weaker (see also [11,28]. We hope that in the future more investigations will help clarify this question.

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