Transport phenomena in fluids: Finite-size scaling for critical behavior

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Abstract – Results for transport properties, in conjunction with phase behavior and thermodynamics, are presented to understand the critical behavior of a binary Lennard-Jones fluid, on the basis of Monte Carlo and molecular dynamics simulations. Evidence for much stronger finite-size effects in dynamics compared to statics has been demonstrated. Results for bulk viscosity are the first in the literature where the critical divergence is quantified via a novel application of finite-size scaling. Our results are in accordance with the theoretical predictions of mode-coupling and dynamic renormalization group calculations.

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Introduction. – Understanding the properties of fluids is important from both the basic research and the technological point of view. Particularly, fluid behavior in the vicinity of a critical point poses many interesting questions of fundamental importance [1–18]. Fluids with short-range interactions, exhibiting gas-liquid and liquid-liquid transitions, are expected to have the static critical exponents $\beta = 0.325$, $\gamma = 1.239$, $\nu = 0.63$, $\alpha = 0.11$, respectively, for order-parameter, susceptibility ($\chi$), correlation length ($\xi$) and specific heat, thus belonging to the three-dimensional Ising universality class [17]. On the other hand, it is expected that model H [18] should define the dynamic universality class for both gas-liquid and liquid-liquid transitions. In dynamics the quantities of interest are shear ($\eta$) and bulk ($\zeta$) viscosities, thermal diffusivity and its analog, the mutual diffusivity ($D_{AB}$) in a binary fluid, the critical singularities for which are given by [2–9]

$$D_{AB} \sim \xi^{-x_D}, \quad \eta \sim \xi^x, \quad \zeta \sim \xi^z; \quad \xi \sim \epsilon^{-\nu}, \quad \tau \sim \xi^z \sim L^z,$$

where $z$ characterizes the divergence of the relaxation time $\tau$, at $T_c$, with system size $L$ as

$$\tau \sim \zeta^z \sim L^z. \quad (3)$$

In addition to other static and dynamic properties, a particular focus of this work is to understand the critical behavior of bulk viscosity that describes the response of a fluid to a compression or expansion. Even though the study of bulk viscosity is thought to be important for compressible fluids, the theoretical prediction, as our simulation results will also reveal, for similar critical enhancement for both gas-liquid (with strong divergence of compressibility) and liquid-liquid (where compressibility at best can have a weak divergence) transitions is certainly interesting. While there are experiments [19,20] probing the critical behavior of $\zeta$, simulations are rare [21–24], even for non-critical fluids, despite this being very important in the description of the damping of longitudinal sound waves. Dyer et al. [24] in fact pointed out the difficulty of studying bulk viscosity and suggested the need for a significant effort to understand the dynamics of continuous model fluids. The only noteworthy study of bulk viscosity in the context of criticality, so far, is due to Meier et al. [22] for the gas-liquid transition of a single-component Lennard-Jones (LJ) fluid; however, they did not quantify the critical divergence. While their data suffered from large errors close to $T_c$, their observation, confirmed by us, of detectable enhancements of $\zeta$ far above $T_c$ ($\simeq 4.5T_c$) due to an extremely slow decay of
pressure fluctuations, is very interesting. In fact, to the
best of our knowledge, ours is the first simulation study of
bulk viscosity that quantifies its critical divergence.
In addition to confirming the theoretical predictions for
critical exponents, this work also provides direct evidence
for stronger size effects in dynamics compared to statics.

Apart from understanding the universality, computer
simulations have been instrumental in providing many
other details [12–16] as far as static properties are
concerned. In contrast, simulations of critical dynamics
are very rare [22,25–30], the primary reason for that being
the critical slowing-down, as embodied in eq. (3), that
brings in additional complexity for the computation of
dynamics over statics where finite-size effects are the only
difficulty. Also, for molecular dynamics (MD) simulations
in microcanonical ensemble, which is used for perfect
preservation of hydrodynamics, it is extremely difficult
to control the temperature to the desired value for a
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The phase diagram of such a system can be obtained
from a semi-grandcanonical Monte Carlo (SGMC) simu-
lation [35,36], where in addition to standard displace-
ment trials, one introduces identity-switch (A → B → A)
moves, thus allowing for fluctuations in concentration
\( x_\alpha (N_\alpha / \sum_\beta N_\beta) \) of species \( \alpha \). The distribution \( P(x_\alpha) \)
of concentration fluctuation has double- and single-peak
structures, respectively, at temperatures below and above
\( T_c \). While from the location of the peaks below \( T_c \) one can
obtain the phase diagram in the \( x_A-T \) plane, the static
concentration susceptibility (\( \chi \)) above \( T_c \) can be calculated via

\[ k_B T \chi = \chi^\ast T^\ast = N(\langle x_\alpha^2 \rangle - 1/4), \]  

where the term 1/4 corresponds to a critical concentration
\( \chi^\ast = 1/2 \) dictated by the symmetry of the model.

The critical temperature for this model has been esti-
mated in various independent ways. An unbiased method
noting down the intersections of temperature-dependent
Binder parameter [37] for different system sizes gave [26]
\( T_c = k_B T_c / J \sim 1.423 \). However, finite-size effects were not
appropriately taken care of in the above estimation. On
the other hand, two other estimates, one by a fitting exer-
cise to the order parameter including data only in the
range unaffected by the finite size of the systems while
fixing \( \beta \) to its Ising value and another via a finite-size
scaling analysis of the accurately computed susceptibility
data [26], where results from different system sizes were
made to collapse by fixing \( \gamma \) to 1.239 and adjusting
\( T_c \); gave results approximately 0.1% lower than 1.423.
In this paper we adopt the value \( T_c = 1.421 \) which gave best
finite-size data collapse for concentration susceptibility.

Transport properties were studied via MD simulations
in the microcanonical ensemble with viscosities and the
Onsager coefficient \( \mathcal{L} = \chi D_{AB} \) being calculated from
Green-Kubo (GK) relations [34,38], namely,

\[ Y = \left( \frac{t_0^3}{dV T^4 \mu^2} \right) \int_0^t dt' \langle \sigma'_{\mu}(0) \sigma'_{\nu}(t') \rangle; \quad \mu, \nu \in [x, y, z], \]

\[ \mathcal{L} = \left( \frac{t_0}{N T} \right) \int_0^1 dt' \langle I_x^{AB}(0) I_x^{AB}(t') \rangle. \]

For diagonal elements of the stress tensor \( \sigma_{xx} = \sigma_{xx} - P \),
\( Y \) corresponds to \( \zeta + \frac{1}{3} \eta \), with

\[ \sigma_{xx} = \sum_{i=1}^N \left[ m_i v_{ix} v_{ix} + \frac{1}{2} \sum_j (x_i - x_j) F_{ij} \right]; \quad P = \langle \sigma_{xx} \rangle \]

and for off-diagonal elements, \( Y = \eta \) (then, of course, one
should replace \( P \) by 0). In eq. (10),

\[ I_x^{AB}(t) = T_B \sum_{i=1}^{N_A} \tilde{v}_{i,A}(t) - x_A \sum_{i=1}^{N_A} \tilde{v}_{i,B}(t) \]

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Fig. 1: Plot of time-dependent transport properties at temperature $T^* = 4$. The bulk viscosity reaching a flat value much later than the others is indicative of the difficulty one faces to estimate it in the closer vicinity of the critical point.

Fig. 2: Log-log plot of concentration susceptibility $\chi$ vs. $\epsilon$, for $L^* = 10$, and 18.6, as indicated on the figure. The solid line represents the critical divergence of $\chi$ with exponent $\gamma = 1.239$.

Fig. 3: Plot of the critical part of the Onsager coefficient $\Delta L / T^*$ vs. $\epsilon$ for $L^* = 10$, and 18.6, on a log scale. The solid line here has critical exponent $\nu_3 = 0.567$ and amplitude $Q = 0.0028$. For details about the background contribution that has been subtracted, see text.

is the concentration current with $\vec{v}_{i,\alpha}(t)$ being the velocity of particle $i$ of species $\alpha$ at time $t$. In eqs. (9) and (10), $V$ is the volume of the simulation box, $m$ is the mass of a particle and $t_0 = (mv^2/J)^{1/2}$ is the LJ time unit, which we set to unity. All results for dynamics are obtained from MD runs, with integration time step $\Delta t = 0.005$ for $T^* < 3$ and 0.0025 for $T^* \geq 3$, in a periodic cubic box of length $L$, in units of $d$, after averaging over more than 100 independent initial configurations which were prepared via SGMC simulation followed by MD runs in the NVT ensemble with the application of an Andersen thermostat [34,36].

**Results.** – In fig. 1 we show representative plots of the transport properties, calculated from eqs. (9) and (10), as a function of time at a high temperature, viz., $T = 4$. This figure demonstrates the difficulty, that one may face, to obtain these quantities at temperatures closer to the critical value. It nicely shows the effects of long-time tails because of which a quantity having stronger divergence takes longer to settle down to a flat plateau. Thus, it may turn out to be meaningless, with the computational resources available to us, to aim to calculate $\zeta$ close to $T_c$. To avoid that in the following we revisit the static and dynamic quantities of which we already have reasonable understanding about the critical behavior. This may help using a finite-size scaling strategy where one needs to deal with smaller systems at higher temperatures.

In fig. 2 we show the results for $\chi$ as a function of $\epsilon$ for $L^* = L/d = 10$ and 18.6 containing, respectively, 1000 and 6400 particles. The continuous line there has a power-law form with the exponent $\gamma$ being fixed to its Ising value 1.239. While this confirms the Ising-like behavior, the consistency of the data for $L^* = 18.6$ with the solid line over the whole region is suggestive that finite-size effects did not appear yet. One reasonable way to study the singularity of $\zeta$ would have been to calculate it for appropriate system size in a region of temperature where static quantities are unaffected by finite size. However, in view of the fact that finite-size effects were pointed out to be stronger in dynamics and a very strong background contribution was found in the study of mutual diffusion [25–27], below we take a closer look.

In fig. 3 we study the critical enhancement

$$\Delta \mathcal{L}(T) = \mathcal{L} - \mathcal{L}_b$$

(13)
of the Onsager coefficient, with $\mathcal{L}_b$ being the contribution coming from short-range fluctuations \cite{9,27} that needs to be taken care of far above $T_c$, where the critical enhancement is expected to be small. In the following we treat $\mathcal{L}_b$ as a constant neglecting, albeit, the weak temperature dependence that it might have. Here we plot $\Delta \mathcal{L}(T)$ which has the expected critical divergence \cite{9}

$$\Delta \mathcal{L} = Q T \epsilon^{-\nu_\lambda}, \quad \nu_\lambda = 0.567,$$  \hspace{1cm} (14)

as a function of $\epsilon$, by adopting the constant value of $\mathcal{L}_b = 0.0033$ as obtained in an earlier study \cite{25}. Upon imposing \cite{25} $Q = 0.0028$ and $\nu_\lambda = 0.567$, good consistency with the solid line is obtained with the simulation data for large $\epsilon$. This, in addition to directly confirming the theoretical predictions as well as the conclusion drawn from the previous finite-size scaling study \cite{25} (with very limited data), regarding both the exponent and amplitude, is also indicative of a rather wide critical range which will be further confirmed by our presentation of appropriate finite-size scaling analysis. On the other hand, it is interesting to note from the comparison between fig. 2 and fig. 3 that size effects are appearing much earlier in $\mathcal{L}$ than in $\chi$; which requires appropriate attention to be taken care of far above $T_c$, where the critical enhancement is expected to be small. This will, of course, be tested by using the better understood transport property $\mathcal{L}$ first, before applying it to $\chi$.

As a first step, in fig. 4 we show the phase behavior of the present model for different values of $L$ that exhibit strong size effects close to the critical point. We define a finite-size critical point \cite{40}, $T_c^L$, as the temperature where $P(x_A)$ in the SGMC simulation yields a single-peak structure from a double-peak one with the increase of temperature. This is represented by the filled symbol for $L^* = 8$. Note that the true meaning of a critical temperature can be assigned only when $L \to \infty$, which for the present case is marked by a cross. In fig. 5 we demonstrate the variation of $T_c^L$ with $L$. The solid line there is a fit to the expected scaling form,

$$(T_c^L - T_c) \sim L^{-1/\nu}; \quad \nu = 0.63,$$ \hspace{1cm} (15)

which is consistent with the simulation results. This fitting was used to obtain $T_c^L$ for intermediate values of $L$ for which we did not calculate $T_c^L$ directly. Note that the scatter of the simulation results around the solid line is negligible compared to the temperature fluctuation in the microcanonical MD simulation which is used to calculate the transport properties.

At this stage, we define an effective finite-size critical point \cite{16} from $T_c^L$ as

$$T_c^L(f) = T_c + f(T_c^L - T_c),$$  \hspace{1cm} (16)

which has the same power-law convergence to $T_c$ as (15). Note that according to this definition $T_c^L(1) = T_c^L$ and $T_c^L(0) = T_c$. One can study the critical behavior along different $f$-loci as a function of $L$, when, for an observable $O (\sim \epsilon^{\zeta\nu})$, one obtains the scaling law

$$_0O \sim L^{-z_0\nu/\nu}.$$ \hspace{1cm} (17)

Of course, the amplitude in (17) will depend upon the value of $f$. Figure 6 demonstrates this for $\Delta \mathcal{L}$ for three values of $f$ including $f = 1$. A linear look, on a log-scale, of all the data sets which are parallel to the theoretical prediction (marked by the solid lines nicely
passing through the data points for each value of $f$) validates this strategy. Note that the largest value of $f$ considered here is 65 which gives $T_c^L(65) = 3.875$ for $L^* = 8$. The nice consistency of the data, even for $f = 65$, confirms the wide critical range for dynamics, in addition to convincingly verifying the theory.

Having demonstrated the usefulness of this method, encapsulated in eqs. (16) and (17), we adopt it to quantify the critical divergence of $\zeta$. Due to the technical difficulties in calculating $\zeta$ at lower temperatures for larger systems, in fig. 7(a) we present results only for $f = 24, 40$ and 65 for a smaller range of $L$ than was used for the Onsager coefficient. The linear behavior of all the data sets on a log-log plot is suggestive of only a small background contribution. The significant increase of $\zeta$ over the range of $L^* \in [8, 14]$, signals a strong divergence. The continuous lines in the figure correspond to a power-law form $\sim L^{x_\zeta}$ with $x_\zeta \approx 2.89$. Note that more recently [6] it has been pointed out that $x_\zeta$ should be closer to $z$; indeed, the exponent obtained from a free fitting to all the three data sets is more consistent with this. However, for data sets containing points as few as here, obtaining the critical exponent from such fitting is not a reasonable exercise. Indeed, in the study of critical phenomena via computer simulation a primary objective has always been to show only consistency. While this confirms the expected theoretical behavior, we estimate the non-universal critical amplitude from the following exercise which will also provide a more direct confirmation of the exponent. In fig. 7(b), we plot $\zeta$ as a function of $\epsilon$, Here, from our experience with $L'$, we choose a range with $\epsilon > 1$ (that includes the last four points) for a fitting to the form $\zeta \sim \epsilon^{-\nu x_\zeta}$ by fixing $x_\zeta$ to 2.89, which gives a critical amplitude $A_\zeta = 6.6 \pm 1.0$. Here the point of deviation of the simulation data from the solid line is consistent with the appearance of a finite-size effect in $L'$. While the solid line provides an excellent fit to the selected region, an effective, though much smaller and misleading, exponent could also have been obtained from a fitting to the whole data set which has an average linear look on a log-scale.

**Summary.** — Dynamic critical phenomena is studied in a symmetric binary fluid. Consistency with predictions of dynamic renormalization group and mode-coupling theories has been established. The quantitative understanding of the bulk viscosity via computer simulations is the first in the literature. The critical region for the transport properties appears to be rather wide so that with appropriate application of a finite-size scaling method it has been possible to obtain useful results using only small systems at high temperatures. A possible reason for stronger finite-size effects in dynamics compared to statics could be a back-flow arising from periodic boundary conditions — however, significant attention is required to settle this important issue. In a future study, we will
discuss details of the calculation of the transport properties of the long-time tail, etc. The usefulness of appropriate hydrodynamics preserving thermostat in the study of critical dynamics will also be addressed.

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