Study of Critical Dynamics in Fluid via Molecular Dynamics in Canonical Ensemble

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With the objective of demonstrating usefulness of thermostats in the study of dynamic critical phenomena in fluids, we present results for transport properties in a binary Lennard-Jones fluid that exhibits liquid-liquid phase transition. Results from the molecular dynamics simulations in canonical ensemble, with various thermostats, are compared with those from microcanonical ensemble. It is observed that the Nosé-Hoover and dissipative particle dynamics thermostats are useful for the calculations of mutual diffusivity and shear viscosity. The Nosé-Hoover thermostat, however, appears inadequate for the study of bulk viscosity.

I. INTRODUCTION

In the vicinity of a critical point [1], various static [1–3] and dynamic [3–11] quantities exhibit power-law singularities. Computer simulations played crucial role in the understanding of static critical phenomena [12]. In dynamics, on the other hand, simulations are recent, particularly for fluid criticality. There, in addition to the finite-size effects, critical slowing down poses enormous difficulty. Note that the slowest relaxation time, \( \tau_{\text{max}} \), diverges at criticality as \( \tau_{\text{max}} \sim L^z \), (1)

where \( L \) is the linear dimension of the system and \( z \) is a dynamic critical exponent.

For the computational study of critical dynamics using microscopic models, one carries out molecular dynamics (MD) [13–15] simulations. Typically one considers microcanonical ensemble (constant N, V, E, which are respectively the number of particles, confining volume and energy) where requirements of hydrodynamics are satisfied. However, as seen in Eq. (1), close to the critical point, overwhelmingly long simulation runs are required to avoid finite-size effects even at a moderate level. In such a situation, control of temperature (thermostat) is required to avoid finite-size effects even at a moderate level. In such a situation, control of temperature (thermostat) is required to avoid finite-size effects even at a moderate level. In such a situation, control of temperature (thermostat) is required to avoid finite-size effects even at a moderate level. In such a situation, control of temperature (thermostat) is required to avoid finite-size effects even at a moderate level. In such a situation, control of temperature (thermostat) is required to avoid finite-size effects even at a moderate level.

Various thermostats [13, 14] are used to maintain temperature in MD simulations in NVT ensemble, e.g., Andersen thermostat (AT), Langevin thermostat (LT), Nosé-Hoover thermostat (NHT), dissipative particle dynamics thermostat (DPDT), etc. Even though all the above mentioned thermostats control the temperature of the system well, only few are useful for calculation of transport properties. Crucial tests of such usefulness of a thermostat lie in nontrivial phenomena like phase transition dynamics which is the objective of this paper.

In AT [15], the temperature is controlled via random assignments of velocities to a fraction of particles according to Maxwell distribution, mimicking collisions of the particles with a heat bath. Due to this stochastic nature like Monte Carlo, AT is not useful for the calculation of transport properties. With increasing collision frequency, the transport coefficients deviate further and further from the desired value. This stochastic character is also true for LT. Note that for MD in NVE ensemble, one solves the Newton’s equations of motion involving the inter-particle force. In NVT ensemble, based on the thermostat, additional rules are imposed. In case of LT, an additional drag force proportional to the velocity is introduced, in addition to a random force, both coming from the background solvent particles. There, for i\textsuperscript{th} particle one solves the equation [16]

\[
\frac{d^2 \vec{r}_i}{dt^2} = -\nabla U_i - \gamma \frac{d\vec{r}_i}{dt} + \vec{W}_i,
\]

(2)

where \( \vec{r}_i \) is the position, \( U_i \) is the interparticle potential, \( t \) is the time, \( \gamma \) the drag coefficient and \( \vec{W}_i \) is a Gaussian noise with mean zero at a temperature \( T \). The noise correlation between two times \( t \) and \( t_0 \) follows the fluctuation-dissipation relation

\[
\langle W_{i\mu} W_{j\nu} \rangle = 2k_B T \delta_{ij} \delta(t - t_0) \delta_{\mu\nu}.
\]

(3)

In Eq. (3), \( \mu \) and \( \nu \) correspond to the Cartesian axes of space coordinates. Due to their momentum conservation inability by construction, AT and LT are used for equilibration purpose. Nevertheless, for the sake of completeness, we will present some results using these thermostats as well. But there exist number of thermostats that preserve hydrodynamics reasonably well, e.g., NHT, DPDT, etc., though, to the best of our knowledge, they were never tested before against critical dynamics. Also, the understanding is primarily restricted to single particle motion.

In DPDT [17–19], the dissipative force in Eq. (2) is given by \( \gamma \omega^D(r_{ij}) \hat{e}_{ij} \) or \( \gamma \omega^R \hat{r}_{ij} \hat{e}_{ij} \) where \( r_{ij} \) and \( \hat{e}_{ij} \) are respectively the relative position and velocity between \( i \) and \( j \) particles with \( \hat{r}_{ij} = \vec{r}_{ij}/r_{ij} \) and \( \hat{e}_{ij} = \vec{e}_{ij}/ \vec{e}_{ij} \). Here \( \omega^D \) or \( \omega^R \) is a weight function equaling \( \omega(r_{ij})^2 \), the latter being connected to the random force as \( \sqrt{2k_B T \omega^R(r_{ij})} \xi_{ij} \hat{e}_{ij} \), where \( \xi_{ij} \) are Gaussian random numbers with \( \xi_{ij} = \xi_{ji} \). For the choice of \( \omega^D \) or \( \omega^R \), there is no fixed prescribed rule. In this work we use them to be unity for distance \( r_{ij} < 1 \) and 0 otherwise. This choice keeps the temperature at desired value better than other standard choices. From the property of random force and the expression of the dissipative force, it is appreciable...
that DPDT will preserve local momentum, thus hydro-dynamics. However, this thermostat has issues related to keeping the temperature constant. For the choice of the weight function mentioned above and $\gamma = 10^{-6}$, we obtained very reasonable temperature control in this work. Note that for LT we used $\gamma = 1$.

In NHT \cite{13}, an additional degree of freedom $\Xi$ is introduced and one solves the equations \cite{13}

$$m_i \ddot{r}_i = p_i, \quad (4)$$

$$\dot{p}_i = -\frac{\delta U}{\delta r_i} - \Xi p_i, \quad (5)$$

$$\dot{\Xi}_i = \sum_{i=1}^{N} p_i^2/m_i - 3N/\beta)/\Xi; \quad (6)$$

where $\beta = 1/k_B T$, $\Xi$ is a time dependent drag, $p_i$ is the momentum and $\Xi$ is the coupling strength of the system with the thermostat. Essentially, in this case, the simulation is done in microcanonical ensemble \cite{13,17} with modified Hamiltonian that provides averages equivalent to those of canonical ensemble with original Hamiltonian.

In this paper, we provide results for the utility of NHT and DPDT with respect to the study of dynamic critical phenomena. Despite its problems, which are corrected to varying degrees in more recent versions \cite{14}, NHT still remained popular for the study of transport in NVT ensemble. Of course, every hydrodynamic preserving thermostat has some disadvantage, e.g., DPDT suffer from temperature control problem.

The rest of the paper is organized as follows. In Section II, we introduce the model. The results are presented in Section III. Finally, the paper is concluded in Section IV with a summary and discussion.

II. MODEL AND PHASE BEHAVIOR

In our binary ($A + B$) mixture model \cite{20,22}, particles interact via Lennard-Jones pair potential

$$u(r) = 4\epsilon_{\alpha\beta} \left( \frac{d}{r} \right)^{12} - \left( \frac{d}{r} \right)^{6}, \quad (7)$$

where $r$ is the inter-particle separation, $d$ is the particle diameter and $\epsilon_{\alpha\beta}$ [$\alpha, \beta = A, B$] is the interaction strength. For the sake of computational convenience, we have introduced a cut-off and shifting of the potential to zero at $r_c = 2.5d$. Further, the discontinuity of force at $r_c$ was removed by adding a term $\left(r - r_c\right)\left(du/dr\right)_{r=r_c}$. We work with a symmetric model by setting $\epsilon_{AA} = \epsilon_{BB} = 2\epsilon_{AB} = \epsilon$.

Phase diagram for this model was studied \cite{20,22} via a semi-grandcanonical Monte Carlo \cite{12,13} method. In this scheme, in addition to the standard particle displacement moves, one tries identity switches $A \rightarrow B \rightarrow A$ which are accepted or rejected according to standard Metropolis criterion. For the identity moves it is necessary to include in the Boltzmann factor \cite{13} the chemical potential difference between the two species. This difference, however, in our case, due to the symmetry of the model, is zero along coexistence and for $50:50$ composition above the critical temperature $T_c$.

Below the critical temperature, the structure of distribution crosses over from double peak to a single peak one. But this critical temperature is system-size dependent that we will denote as $T_c^L$, which, in the limit $L \rightarrow \infty$, will converge to the thermodynamic critical temperature, $T_c$. In Table I we list the values of $T_c^L$ for a few system sizes.

The transport properties are studied via MD simulation in NVE as well as NVT ensembles, for the latter various temperature controlling methods, discussed in the previous section, were used. Details of the calculation of transport properties will be provided in the next section.

III. RESULTS

Using MD, we present results for the Onsager coefficient ($\mathcal{L}$), shear viscosity ($\eta$) and bulk viscosity ($\zeta$) which are calculated from the Green-Kubo (GK) relations \cite{22} as

$$\mathcal{L}(t) = \left( \frac{t_0 \epsilon}{k_B NT d^2} \right) \int_0^t dt' \langle J_{AB}^r(t') J_{AB}^r(0) \rangle, \quad (8)$$

$$\eta(t) = \left( \frac{t_0^3 \epsilon}{dVT m^2} \right) \int_0^t dt' \langle \sigma_{\mu\nu}(t') \sigma_{\mu\nu}(0) \rangle, \quad (9)$$

and

$$Y(t) = \left( \frac{t_0^3 \epsilon}{dVT m^2} \right) \int_0^t dt' \langle \sigma_{\mu\nu}'(t') \sigma_{\mu\nu}'(0) \rangle, \quad (10)$$

where $t_0$ is the LJ time unit ($= \sqrt{md^2/\epsilon}$) and $m$ is the mass which is same for all particles in our model. In Eq.

| $L$ | 8   | 10  | 12  | 14  | 16  |
|-----|-----|-----|-----|-----|-----|
| $T_c^L$ | 1.461 | 1.447 | 1.440 | 1.436 | 1.433 |
\[ J_{AB}(t) = x_B \sum_{i=1}^{N_A} \vec{v}_{i,A}(t) - x_A \sum_{i=1}^{N_B} \vec{v}_{i,B}(t), \quad (11) \]

\[ \vec{F}_{\alpha} \] being the force between particles \( i \) and \( j \); \( \mu_i \) is a Cartesian coordinate for the position of particle \( i \). In Eq. (10), \( Y = \zeta + \frac{4}{9} \eta \) and \( \sigma'_{\mu\nu} = \sigma_{\mu\nu} - P, P \) being the pressure. These quantities can also be calculated from the corresponding mean squared displacements (MSD) in the Einstein relations, e.g., \[ L(t) = \left( \frac{t_0 N^2 \varepsilon}{2k_B T d^2} \right) \langle |R_x^\alpha(t) - R_x^\alpha(0)|^2 \rangle, \quad (13) \]

where \( R_x^\alpha \) is the \( x \)-component of the centre of mass (CM) of species \( \alpha \). In the rest of the paper, we set \( m, \varepsilon, d, t_0 \) and the Boltzmann constant \( (k_B) \) to unity. In this paper, we present results obtained from the GK relations only.

\[ \frac{L}{T} \sim \xi^{x_\lambda}, \quad (14) \]

with \( x_\lambda \approx 0.9 \). To verify the consistency of our simulation results with this number, we take the route of finite-size scaling analysis \[ \text{FIG. 2.} \] A finite-size scaling plot of Onsager coefficient, after subtracting the background contribution, using data at \( T_L \). Results from both NVE and NVT ensembles are shown. For NVT ensemble, we have included data from NHT and DPDT. The continuous line corresponds to the theoretical prediction for critical divergence.

\[ \text{FIG. 3.} \] Plot of shear viscosity as a function of time. We have shown results from NVE, NHT and DPDT calculations. All results correspond to \( L = 10 \) and \( T = 2.5 \).

\[ \text{FIG. 1.} \] Plot of Onsager coefficient as a function of time from MD calculations in NVE and NVT ensembles. For NVT ensemble, as indicated, four different thermostats were used. In all the cases values of \( T \) and \( L \) were set to 2.5 and 10, respectively.

We start by showing a comparison of the time dependent Onsager coefficient in Fig. 1 for calculations from NVE ensemble as well as from NVT. For NVT ensemble we have included results from AT, LT, NHT and DPDT as temperature controller. As expected, AT and LT do not provide results consistent with the NVE one. However, the results from NHT and DPDT are very much in agreement with the latter. For NHT, even though we have presented the result using only \( Q = 1 \), we have done the calculations with values of \( Q \) upto 100 and observed that the results are not very sensitive to the choice of the variable. The final values of the transport quantities are obtained from the flat portions of these time-dependent plots. The temperature in Fig. 1 is rather far above \( T_c \). In the following we focus in the critical region.

Note that \( \mathcal{L} \) is expected to diverge at criticality as \[ \text{FIG. 2.} \] A finite-size scaling plot of Onsager coefficient, after subtracting the background contribution, using data at \( T_L \). Results from both NVE and NVT ensembles are shown. For NVT ensemble, we have included data from NHT and DPDT. The continuous line corresponds to the theoretical prediction for critical divergence.
\( \xi \) scales with \( L \), for results obtained at \( T_c^L \),
\[
\frac{\mathcal{L}}{T} \sim L^{x_\lambda}.
\tag{15}
\]

It was observed in previous computer simulation of this model \cite{20, 21} that \( \mathcal{L} \) has reasonably strong background contribution \( \mathcal{L}_b \). The value of \( \mathcal{L}_b \) was estimated to be \( \simeq 0.0033 \pm 0.0008 \). In Fig. 2 we will thus deal with the critical part \( \Delta \mathcal{L}(= \mathcal{L} - \mathcal{L}_b) \) only. So, when calculated at \( T_c^L \)'s, a plot of \( \Delta \mathcal{L}/T \) vs \( L \) will be consistent with a power-law with exponent 0.9. This is demonstrated in Fig. 2. Note that we have shown results from NHT, DPDT as well as from NVE ensemble calculations. All of them are in very good agreement. This essentially demonstrates that NHT and DPDT are good devices for the calculation of mutual diffusivity \( (D_{AB}) \) even for quantitative understanding of critical dynamics. Here note that \( D_{AB} = \mathcal{L}/\chi \) where \( \chi \) is the concentration susceptibility that can be calculated from concentration fluctuation in Monte Carlo simulations.

Having demonstrated the usefulness of NHT and DPDT in calculation of diffusion constants (note here that in many previous works it was shown that these thermostats are good for the calculation of self diffusivity), we turn our attention to viscosities. In Fig. 3 we show the time dependent integration of shear viscosity, using Eq. 9 for NVE, NHT and DPDT. Here we do not show the results obtained using AT and LT which, we have already understood, are not appropriate for the study of transport properties. Satisfactory agreement is achieved with the NVE calculation for results from both the thermostats. Considering the fact that \( \eta \) has very weak critical divergence, one needs huge statistics to verify that. Therefore we do not take up that task in this work.

Even though, so far it appears that the NHT is a good tool to study dynamic critical phenomena, we have encountered difficulty in the calculation of bulk viscosity, for this value of the coupling constant. This is clear from Fig. 4 which is similar to Fig. 3 but for bulk viscosity. Here, even though a very good agreement is obtained involving NVE and DPDT, result for NHT is in clear disagreement. For the latter probably one needs to choose the coupling constant \( \mathcal{L} \) very judicially. In this connection, a discussion on the improvement of NHT is provided in the next section. We mention here that for the same system size, conclusion similar to Fig. 3 and Fig. 4 are drawn when calculations are performed at \( T_c^L \).

\section{IV. CONCLUSION}

In this paper we presented comparative results for transport properties in a binary fluid mixture obtained from molecular dynamics \cite{13} calculations in microcanonical as well as canonical ensembles. It appears that even at criticality the Nosé-Hoover thermostat \cite{13} and dissipative particle dynamics provide results for diffusivities and shear viscosity that are in excellent agreement with the microcanonical ensemble. However, while the dissipative particle dynamics appears to work well for bulk viscosity as well, the Nosé-Hoover thermostat fails for this purpose.

The importance of the paper lies in the following fact. Very close to the critical point, for big enough systems, one needs extended simulation runs. In that case, for runs in microcanonical ensemble, it becomes difficult to avoid drift in temperature. Thus, calculation of transports in canonical ensemble may be of help. Nosé-Hoover thermostat still being a very commonly used one for hydrodynamic purpose, despite criticisms, one needs to check its validity in situations as nontrivial as critical dynamics.

A criticism about Nosé-Hoover thermostat is that it is not Galilean invariant \cite{17, 22, 26}. If there is external force, e.g., drag, there is problem with momentum conservation. Recently, such problem is being taken care of \cite{17, 22, 26} by introducing additional soft pair potential and relative velocities.

Despite some deficiencies, even the basic Nosé-Hoover thermostat appears to provide reasonable description of dynamics for a number of quantities as seen here. Even for nonequilibrium dynamics we have observed \cite{27} recently that this thermostat produces expected results.

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