Critical anomaly and finite size scaling of the self-diffusion coefficient for Lennard–Jones fluids by non-equilibrium molecular dynamic simulation*

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We use non-equilibrium molecular dynamics simulations to calculate the self-diffusion coefficient, D, of a Lennard–Jones fluid over a wide density and temperature range. The change in self-diffusion coefficient with temperature decreases by increasing density. For density $\rho^* = \rho\sigma^3 = 0.84$ we observe a peak at the value of the self-diffusion coefficient and the critical temperature $T^* = kT/\varepsilon = 1.25$. The value of the self-diffusion coefficient strongly depends on system size. The data of the self-diffusion coefficient are fitted to a simple analytic relation based on hydrodynamic arguments. This correction scales as $N^{-\alpha}$, where α is an adjustable parameter and N is the number of particles. It is observed that the values of $\alpha < 1$ provide quite a good correction to the simulation data. The system size dependence is very strong for lower densities, but it is not as strong for higher densities. The self-diffusion coefficient calculated with non-equilibrium molecular dynamic simulations at different temperatures and densities is in good agreement with other calculations from the literature.

Keywords: self-diffusion coefficient, non-equilibrium molecular dynamic simulation, Lennard–Jones fluid, critical dynamics

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1. Introduction

Long-range interactions can lead to significant dependences on the system size in computer simulations of condensed matter under periodic boundary conditions.[1] Hydrodynamics can also lead to effective long-range interactions, which can cause significant finite-size effects, as shown by Dünweg and Kremer[2,3] for the diffusion coefficients of polymers. For the diffusion of small single-stranded ribonucleic acid (RNA) molecules in water, it has been recently observed that the calculated diffusion coefficients deviate from the extrapolated infinite system limit by a factor of $2 \sim 3$ for a typical system size.[4] For a system of about 2000 water molecules in a periodically replicated cubic simulation cell, it was observed that the diffusion coefficient is underestimated by approximately 10%. Correcting such systematic errors is particularly important in the comparison of simulations with experiments,[5,6] and if transport properties are used to assess and fit interaction potentials.

The diffusion coefficient of a solute molecule is an important quantity for chemical processes in solution. The diffusion coefficient has been intensively studied in theories based on non-equilibrium statistical physics.[7,8] Molecular dynamic (MD) simulation is another powerful tool for the study of dynamic processes in the liquid phase and the self-diffusion processes in neat liquids have also been simulated.[9,10] To calculate the transport properties of simple and molecular fluids, non-equilibrium molecular dynamics (NEMD) simulations have also emerged as a powerful tool. Non-equilibrium molecular dynamic simulation has been successfully used to calculate the thermphysical properties of a triple point Lennard–Jones (LJ) fluid and water.[11,12] Linear response theory derivations are considered to be closely related to the measurement of the diffusion coefficient with non-equilibrium methods.[13,14]

Spatially extended fluctuation in fluid density is a feature of the compressible region of a phase diagram.[15] The divergence of the fluctuation at the

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critical point leads to singularities in the thermodynamic and transport properties of the fluids. To the best of our knowledge, the effect of local density nonuniformity on the molecular diffusion coefficient is little known, which is an important transport property for the prediction of the chemical reaction rate and the design of supercritical fluid reactors. The divergence of the compressibility near the critical point complicates real experiments and MD simulations in the critical region. Drozdov and Tucker[16] presented a method of calculating an average self-diffusion coefficient that avoids this difficulty.

Existing experimental and simulation results in the critical region are controversial, and are unable to clarify the situation of critical anomaly.[16−18] Recently, a highly accurate self-diffusion coefficient was calculated by Qin and Eu[19] by using the modified free volume (MFV) theory of diffusion. They have also concluded that the self-diffusion coefficient of LJ fluids can be improved significantly compared with the results obtained by using previous methods. The self-diffusion coefficient is usually calculated from the equilibrium molecular dynamics (EMD), which are usually considered to be more accurate. In recent studies EMD simulations have been used to calculate thermophysical properties.[20−22] The controversial results of the self-diffusion coefficient in the critical region by EMD simulations motivated us to study the self-diffusion coefficient by NEMD simulations. As diffusion coefficient involves a long process, the long duration behaviour of correlation functions may create problems in the calculation of the self-diffusion coefficient through EMD. This kind of problem can be avoided by using the technique of applying perturbation theory and then measuring the steady state response to such a perturbation.

The LJ potential serves as an important reference model in many applications of statistical mechanics. Furthermore, it is often used to predict the thermophysical properties of simple fluid or as a building block for intermolecular potential models of complex molecules. The knowledge of its macroscopic thermophysical properties forms an essential basis of these applications. Thermodynamic property surfaces are now well characterized and can be readily calculated from the latest and most accurate fundamental equation of state for the LJ fluid developed by Mecke and Trappeniers.[23] However, transport properties, the self-diffusion coefficient, viscosity, thermal conductivity and bulk viscosity are less well understood. In previous studies, e.g. Refs. [24]–[29], the uncertainties of simulation data were still up to two orders of magnitude higher than those commonly achieved in experiment.

This paper focuses on the self-diffusion coefficient of LJ fluid. We use non-equilibrium molecular dynamics simulation to calculate the diffusion coefficient in the critical region. The objectives of this study are to explore the behavior of the self-diffusion coefficient near the critical temperature and the finite size scaling for different densities. The self-diffusion coefficient D, one of the fundamental transport coefficients in a simple liquid, has been studied by experiment and molecular level simulation for many years.[30,31] It should be noted, however, that D as obtained by simulations is always affected by the finiteness of the simulation box, and the correction to it is not negligible (about 10% in the case of a 500-particle dense hard-sphere fluid).[29] Although this correction has been argued in connection with the long-time behaviour of the velocity autocorrelation function, the argument is not applicable for D of a heavy particle moving in a fluid of lighter particles.[30] System size corrections will be useful when results from different simulations are compared.[32]

In order to explain the behaviour of the self-diffusion coefficient through NEMD the paper is divided into the following sections. In Section 2 the simulation details are explained. Results along with the discussion are given in Section 3. Finally, conclusions are drawn in Section 4.

2. Simulation method

The NEMD simulation technique consists of solving a set of differential equations obtained by applying Newton's laws to all particles of the system. Thus, given an interaction potential between two particles (assuming pair-wise additivity) and an initial configuration (positions and velocities) at a given time t, it is possible to determine the new positions, velocities and accelerations of all particles at time $t + \Delta t$, to a convenient degree of accuracy.[28] We develop a computer program in C to run non-equilibrium MD simulations in the canonical (NVT) ensemble, starting from which we calculate the self-diffusion coefficient of LJ fluids of different system sizes for a wide range of densities and temperatures. Each LJ molecule is modeled as

freely interacting by the potential

$$\phi(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \quad (1)$$

where ε and σ are the LJ potential parameters. In order to obtain the continuous particle trajectories, we have used the velocity Verlet algorithm. The Nosé-Hoover algorithm is used to keep the temperature at the specified set point. The variables of the simulated data are made dimensionless with LJ parameters ε, σ, and the molecular mass, m,

$$T^* = kT/\varepsilon, \quad \rho^* = \rho\sigma^3, \quad D^* = D\sqrt{\frac{m}{\varepsilon\sigma^2}}. \quad (2)$$

In the simulation, a full LJ potential with cut-off radius of $r_c^* = r_c/\sigma = 5.5$ has been used. The self-diffusion coefficient is calculated from the following expression:

$$D = \lim_{t\to\infty}\frac{1}{6t}\left\langle [r(t) - r(0)]^2\right\rangle, \quad (3)$$

where r is the position of the particle and $\left\langle [r(t) - r(0)]^2\right\rangle$ is the mean square displacement.

In order to calculate the self-diffusion near a critical point we use the approach of instantaneous local density by defining a local solvent around a tagged particle.[16] The simulations are carried out in a cubic box with periodic boundary conditions imposed in all directions and the minimum image convention is adopted. A perturbation is applied by using the Ashurst–Hoover[33] homogenous shear algorithm to start the NEMD simulation. The total numbers of molecules (N) into the box are fixed to be 108, 256, 500, 864, and 1372. Some simulations with $N = 5000$ are also performed to verify the optimum value of the fitting parameter. The equations of motion are integrated using $\Delta t^* = (\varepsilon/m\sigma^2)^{1/2} = 0.005$ up to $N = 1372$, whereas for $N = 5000$ the time step of 0.01 is used. The simulation is performed over 5000 time steps and the self-diffusion coefficient is calculated using Eq. (3). Its value is taken as an average over 50 subsequent and independent origins to improve the results.

Near the critical point. the extended regions of high and low densities are generated by critical fluctuation, hence the distribution of local densities experienced by the diffusing particles becomes broad and the diffusing particles will sample many local densities over time.[34] It is also known that the time spent by a particle surrounded by a given local density $\tau_{\rho l}$ will become longer.[35] However, for very a long time $t \gg \tau_{\rho l}$ the diffusing particle will sample many different local densities and many different values of diffusion coefficients D_l (ρ_l, T). Hence the mean value of the diffusion coefficient is calculated by the following relation:

$$\langle D_l(\rho_l)\rangle_{\rho,T} = \int_{\rho_{\min}}^{\infty} \mathrm{d}\rho_l D_l(\rho_l, T) P(\rho_l; \rho, T), \quad (4)$$

where the time average over the particle's local environment ρ_l(t) has been replaced with an ensamble average over these environments. The distribution function $P(\rho_l; \rho, T)$ is the probability that a solvent particle will have a surrounding local density of ρ_l at any given instant t and is given by

$$P(\rho_l; \rho, T) = \left\langle N^{-1}\sum_{j=1}^{N}\delta\left[\rho_l - \rho_l^{(j)}(t; \rho, T)\right]\right\rangle, \quad (5)$$

where δ is the Dirac delta function and the right-hand side is self-averaging in a sufficiently large system. The detailed procedure to calculate Eq. (5) is given in Refs. [16] and [34].

3. Results and discussion

The average self-diffusion coefficient is calculated by using Eq. (4). As shown in Fig. 1, the calculation of the self-diffusion coefficient with taking into account the mean local density enhancement exhibits an anomalous behaviour near the critical point. The observed behaviour of the self-diffusion coefficient near the critical point is attributed to a shift of the distribution of local density just below the critical density to one of higher mean local densities.

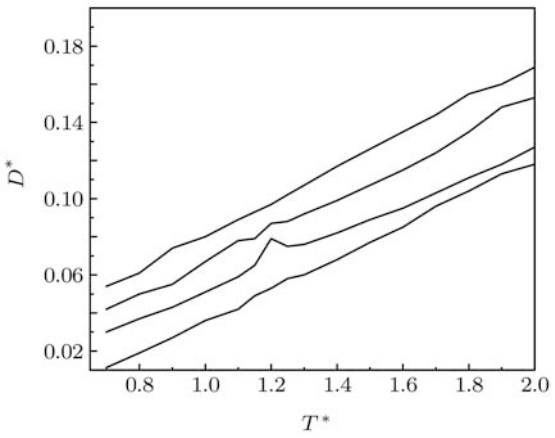


Fig. 1. Temperature dependences of the self-diffusion coefficient for different densities. The values of ρ^* from top to bottom are 0.75, 0.80, 0.84, and 0.9. The anomalous behaviour is visible at $\rho^* = 0.84$ and $T^* = 1.25$.

We also test the system-size correction for the average self-diffusion coefficient of an LJ fluid at a reduced temperature of $T^* = 0.7$ and the values of reduced density ρ^* ranging from 0.4 to 0.8. For thermodynamic quantities, all finite-size corrections to the leading order vary as $O(N^{-1})$.[36] In this work, the data of the MD self-diffusion coefficient computed for different values of N and a given ρ^* are fitted to the analytic form

$$D(\rho, N) = D_\infty(\rho) - A(\rho)N^{-\alpha}, \tag{6}$$

where $D_\infty(\rho)$ is the diffusion coefficient in the thermodynamic limit, $A(\rho)$ is the magnitude of the finite size correction and its dependence on N and α is treated as a free parameter. Equation (6) is also used to show the system size dependence of hard sphere fluids[37] and to extrapolate to the case of infinite N the self-diffusion coefficient of liquid para-hydrogen computed by ring-polymer molecular dynamics.[38]

Figure 2 shows the plots of D^* against $N^{-1/3}$ for different density values. The apparent errors in the non-linear curve fitting are very small for all the density values. The limited sampling space might be the cause of one of the possible errors, particularly at higher densities, which is quantified by performing longer simulations. It is important to note that the value of $\alpha = 1$ is one possible source of the N dependence of the self-diffusion coefficient. In order to generalize the value of α, we investigate the data fitting quality for different values of α.

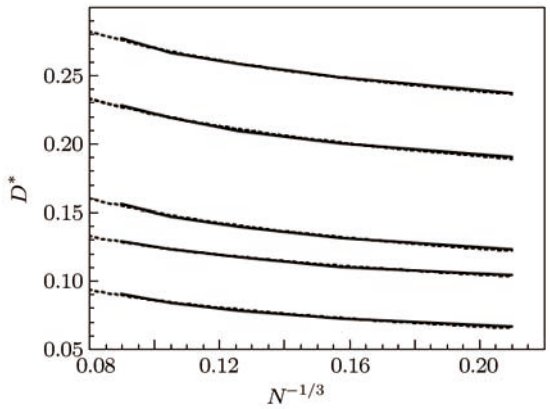


Fig. 2. Plots of D^* against $N^{-1/3}$ for a set of MD diffusion coefficient values. The values of density ρ^*, from top to bottom are 0.4, 0.5, 0.6, 0.7, and 0.8. The solid lines represent the simulation data and the dotted lines refer to linear regression least-squares fits to the simulation data using Eq. (6) with $\alpha = 1/3$.

Figures 2–5 show the plots of these data with $\alpha = 1/3$, $1/2$, $2/3$, and 1, respectively, for different values of densities. The curve fittings with $\alpha = 1/2$ and $2/3$ are as good as with $1/3$, but with $\alpha = 1$ the plot exhibits a noticeable deviation from the simulation data especially with higher values of N. The values of the parameters obtained by fitting Eq. (6) to the simulation data are shown in Table 1. It is interesting to note that for all the values of α, both $D_\infty(\rho)$ and $A(\rho)$ increase with density decreasing. The same kind of behaviour was also observed for a hard sphere model by Heyes.[37] In order to make the value of α more accurate, we performed some simulations with $N = 5000$ for $\rho^* = 0.7$ and $T^* = 0.7$. The values of $D_\infty(\rho)$ and $A(\rho)$ are fixed at 0.0710 and 0.045, respectively. We observe that the value of $\alpha = 1/3$ can give the value of the self-diffusion coefficient that is closer to the data already obtained in Refs. [19] and [39]. The comparison of the values of the self-diffusion coefficient in the thermodynamic limit and the simulation data is given in Table 2. It is important to note that the simulation data obtained in our simulation is in good agreement with that obtained in the thermodynamic limit.

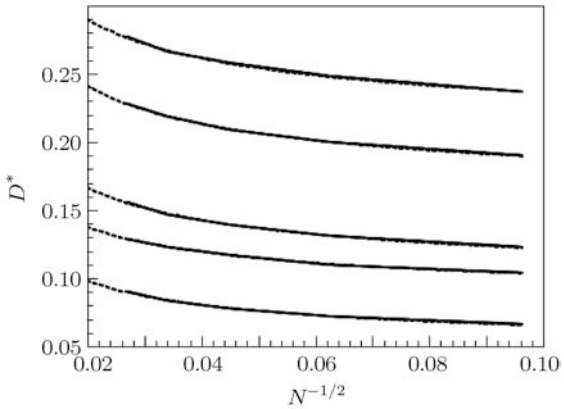


Fig. 3. The same as for Fig. 2, except that the diffusion data are plotted against $N^{-1/2}$ and $\alpha = 1/2$ in Eq. (6).

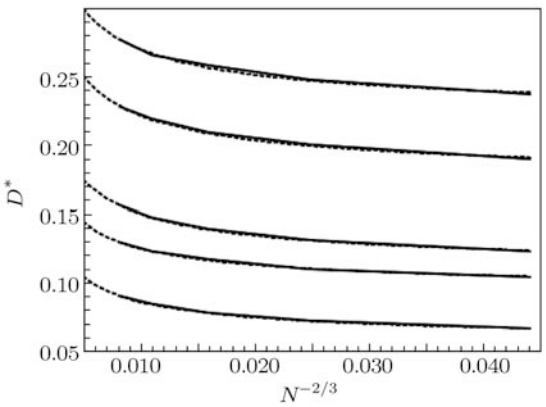


Fig. 4. The same as for Fig. 2, except that the diffusion data are plotted against $N^{2/3}$.

Furthermore, as shown in Figs. 2–5, the system size dependence is very obvious for low densities. For $\rho^* = 0.4$, the change in the diffusion coefficient is 4% up to $N = 1372$ and this change is only 2.4% for $\rho^* = 0.8$. A similar behaviour of the diffusion coefficient in water molecules, hard spheres and LJ fluids has also been observed in Refs. [40] and [37]. It is concluded that the origin of this system size dependence at low density lies in the divergence in the mean path between collisions as compared with the dimensions of the simulation cell.

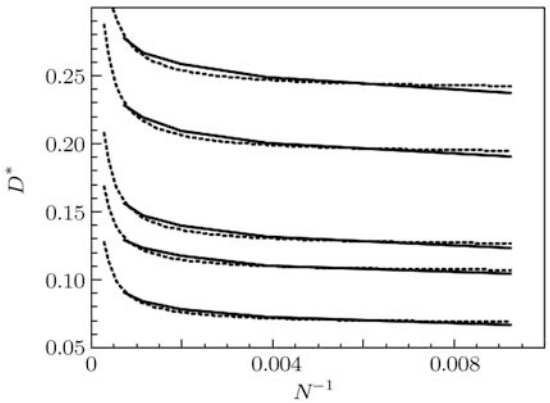


Fig. 5. The same as for Fig. 2, except that the diffusion data are plotted against N^{-1}.

Table 1. The self-diffusion coefficient of LJ fluid in the thermodynamic limit, D_∞ obtained from non-linear square fit to the $D(N)$ simulation data using Eq. (6), where $\alpha = 1/3$. δ_D is a standard error.

ρ^*	D_∞	δ_D	$A(\rho)$
0.4	0.28	0.002	0.0713
0.5	0.23	0.004	0.0691
0.6	0.16	0.001	0.0595
0.7	0.13	0.004	0.045
0.8	0.09	0.0005	0.04

Recently, Nie *et al.*[40] used the memory function formalism and the frequency moments of the velocity autocorrelation function method to calculate the self-diffusion coefficient of metastable LJ vapour. The self-diffusion coefficient is reported to show a plateau and anomalous behaviour.

Table 2. Self-diffusion coefficient of LJ fluid for finite system D and in the thermodynamic limit D_∞ obtained using Eq. (6), where $\alpha = 1/3$.

ρ^*	D	D_∞
0.4	0.275	0.28
0.5	0.226	0.23
0.6	0.156	0.16
0.7	0.127	0.13
0.8	0.0876	0.09

4. Conclusion

A non-equilibrium molecular dynamics simulation of LJ fluid for the self-diffusion coefficient is performed by defining the instantaneous local density around a particle. A weak anomalous behaviour of the average self-diffusion coefficient in the vicinity of the critical region is observed. This anomalous behaviour in the critical region is attributed to a shift of the distribution of local densities just below the critical density to one of higher mean local densities. It is observed that density change affects the long-time diffusion process near the critical point. Furthermore, finite size scaling is found in the self-diffusion coefficient of LJ fluid. The data are fitted to a simple analytic form shown in Eq. (6), a generalization of one derived from Refs. [41]–[43]. The value of α is chosen as an adjustable parameter and for the cases studied in this work, a very accurate curve fitting is obtained for $\alpha = 1/3$.

Furthermore, we conclude that our calculations of self-diffusion coefficient with non-equilibrium molecular dynamics simulations are consistent with the experimental and simulation results available.

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