Diffusion and viscosity in a supercooled polydisperse system

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We have carried out extensive molecular dynamics simulations of a supercooled polydisperse Lennard-Jones liquid with large variations in temperature at a fixed pressure. The particles in the system are considered to be polydisperse both in size and mass. The temperature dependence of the dynamical properties such as the viscosity ($\eta$) and the self-diffusion coefficients ($D_i$) of different size particles is studied. Both viscosity and diffusion coefficients show super-Arrhenius temperature dependence and fit well to the well-known Vogel-Fulcher-Tammann (VFT) equation. Within the temperature range investigated, the value of the Angell’s fragility parameter ($D \approx 1.4$) classifies the present system into a strongly fragile liquid. The critical temperature for diffusion ($T^{cD}_o$) increases with the size of the particles. The critical temperature for viscosity ($T^{c\eta}_o$) is larger than that for the diffusion and a sizeable deviations appear for the smaller size particles implying a decoupling of translational diffusion from viscosity in deeply supercooled liquid. Indeed, the diffusion shows markedly non-Stokesian behavior at low temperatures where a highly nonlinear dependence on size is observed. An inspection of the trajectories of the particles shows that at low temperatures the motions of both the smallest and largest size particles are discontinuous (jump-type). However, the crossover from continuous Brownian to large length hopping motion takes place at shorter time scales for the smaller size particles.

I. INTRODUCTION

The rapid cooling of a liquid below its freezing temperature transforms it into a long-lived metastable amorphous solid or glass [1]. Understanding the dynamics of the system near the glass transition is an intense field of research since the last few decades. There have been many experimental [2,3,4,5,6,7] as well as simulation studies [8,9,10,11,12,13] which focus on the dynamics of dense supercooled liquids well above the glass transition and also near the glass transition temperature ($T_g$). The basic aim of all these studies was to characterise quantitatively the observed very complex dynamics of the system near the glass transition from the above. Close to the glass transition, the shear viscosity ($\eta$) and the microscopic structural relaxation time ($\tau$) of the so-called fragile glass-forming liquids show divergence with a strongly non-Arrhenius temperature dependence [1]. This divergence is often well represented by the Vogel-Fulcher-Tammann (VFT) equation

$$\eta(T) = A_\eta \exp\left[\frac{E_\eta}{(T - T^{c_\eta})}\right]$$  \hspace{1cm} (1)

where $A_\eta$ and $E_\eta$ are temperature-independent constants and $T^{c_\eta}$ ($< T_g$) is the temperature at which $\eta$ diverges. Note that at low temperatures the increasingly slow dynamics of the so-called fragile liquids is simultaneously manifested in the stretched exponential decay of the stress correlation function (with a strongly temperature dependent stretching parameter) [3,4]. The VFT dependence (Eq. 1) is thus accompanied by the strong non-exponential relaxation observed near the glass transition temperature.

The dramatic slow down of the dynamics near the glass transition is not well understood and still remains the most challenging problem in the physics of glasses. Several theories have been proposed to understand the anomalous relaxation dynamics of deeply supercooled liquids. Although the ideal version of the non-linear mode coupling theory (MCT) [4] gives a microscopic picture of this slowing down, it predicts a structural arrest, i.e., a transition from ergodic to nonergodic behavior, at a critical temperature $T_c$ well above the laboratory glass transition temperature $T_g$. Near $T_c$, the importance of the influence of potential energy landscape on the relaxation processes has now widely been accepted [15,19] and the strongly correlated jump motion is observed to be the dominant mode for mass transport [13,21,22], which is not included in ideal MCT.

Another important characteristic feature in the dynamics of deeply supercooled liquids is the decoupling between translation diffusion and the shear viscosity of the medium [23,24,25]. At high temperature, over a wide range of liquid states, the translational diffusion is inversely proportional to viscosity, in accordance to the Stokes-Einstein (SE) relation given by

$$D_T = \frac{k_BT}{C\pi \eta R}$$  \hspace{1cm} (2)

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where $R$ is the spherical radius of the diffusing particle and $C$ is a numerical constant that depends on the hydrodynamic boundary condition. However, several recent experimental [26,27,28] and simulation studies [29,30,31,32,33] on strongly supercooled 'fragile' glass forming liquids have shown significant deviations from the SE relation. As the temperature is lowered toward $T_g$, it is found that the translational diffusion is larger than the value predicted by the SE relation and in some cases even two to three orders of magnitude larger [28]. The enhanced diffusion at low temperatures is sometimes explained in terms of a power law behavior $D_T \propto \eta^{-\alpha}$ with $\alpha < 1$ [28,29]. Both the experiments and simulation studies have recently evidenced the enhancement of the translational diffusion coefficient is due to the spatially heterogeneous dynamics in deeply supercooled liquids [27,28,31,32].

Computer simulations have played a key role in augmenting our understanding of various aspects of the dynamics of the supercooled liquids from a microscopic viewpoint. Unfortunately, the simple one-component systems such as soft or hard spheres or Lennard-Jones systems crystallize rapidly on lowering the temperature below the melting point ($T_m$) and, therefore, cannot be utilized as a model for studying the complex dynamical behavior near the glass transition temperature. A natural way to avoid crystallization is to use binary mixtures of atoms with different diameters. A large number of molecular dynamics (MD) simulations have recently been carried out in supercooled model binary mixtures near the glass transition as well as below the glass transition temperature [2,27,28,31,32].

However, one is often interested in the consequences of the disorder introduced by the dissimilarity of the particles. Synthetic colloids, by their very nature, frequently exhibit considerable size polydispersity [37,38]. Polydispersity is also common in industrially produced polymers which always contain macromolecules with a range of chain length. Colloidal particles are an excellent model of hard spheres and perhaps the simplest possible experimental system of interacting particles to study the glass transition. Several experiments [37] and simulations [33,34] have shown that the crystal phase of the colloidal systems can exist as a thermodynamically stable phase only for polydispersities (standard deviation of the size distribution divided by the mean) less than a 'terminal' value, in the range of 0.05-0.15.

Interestingly, recent experiments on colloidal supercooled fluids and colloidal glasses allowed one to obtain the information on the microscopic details of the dynamics of the individual particles [4]. These experiments have shown the presence of dynamic heterogeneity in deeply supercooled colloidal systems. The motion of the relatively fast moving particles is found to be highly correlated and form connected clusters, whose size increases as one approach the glass transition. More recently, Sear [11] has carried out MD simulation of a dense polydisperse hard sphere fluid to study the effect of polydispersity on the slow dynamics. The simulation results also show the clustering of the fast-moving particles in agreement with the experiments, though the dynamics appears to be less heterogeneous. The heterogeneous nature of the dynamics has also been observed in the Monte Carlo simulation study of polydisperse hard spheres close to the glass transition [12].

It is worth mentioning that besides the short-range hard-core interaction, addition of a nonadsorbing soluble polymer in the stable colloidal suspension gives rise to a weak, long-range attraction between the colloidal particles by means of the depletion interaction [38]. Recently, the consequences of this attractive interaction on the glass transition are nicely explained in a combined experimental, theoretical, and simulation study by Pham et.al. [43]. Interestingly, with increase in the strength of the short-range attractive interaction, two qualitatively different glassy states are found with a reentrant glass transition line.

The size distribution in real colloids generally leads to a distribution in mass of the particles. The importance of the mass polydispersity on the dynamics of a realistic system having size polydispersity has recently been analyzed in molecular dynamics simulation study of a Lennard-Jones (LJ) polydisperse fluid near the triple point of the corresponding monodisperse LJ system [44]. Polydispersity is commonly found in many systems of industrial applications and to mimic the interparticle interactions, the Lennard-Jones potential generally serve as a good starting model. Thus, it will be a general interest to study the impact of polydispersity on the dynamics of a deeply supercooled polydisperse fluid, where particles interacting via the LJ potential. More importantly, this will enable us to compare the properties of the system with model binary LJ mixtures whose dynamics near the glass transition has been studied extensively in simulations.

In this study, we have performed extensive molecular dynamics simulations of a system of polydisperse LJ spheres with continuous range of diameters and mass. The temperature dependence of the dynamic properties such as viscosity ($\eta$) and the self-diffusion coefficients ($D_i$) for the different size particles is studied by varying the temperature ($T$) over a large range at a constant high pressure ($P$). Both the viscosity and diffusion show super-Arrhenius temperature dependence and the calculated value of the fragility parameter (D) show that the present system is more fragile than the well-known Kob-Andersen binary mixture. The critical temperature obtained from the VFT fit to the diffusions ($T^p_{c}$) show strong dependency on the radius ($R$) of the particles. In addition, the critical temperature obtained from the VFT fit to the viscosity ($T^\eta_{c}$) is much higher when compared to those of diffusion coefficients, where the deviation is largest for the smaller size particles. This clearly reflects the deviation from the Stokesian diffusion in the proximity of the glass transition temperature. Most interest-
ing, at lower temperatures the diffusion shows a highly nonlinear size dependence when plotted against the inverse of the radius ($R$) of the particles. The reason for the breakdown of the Stokes-Einstein (SE) relation can be analyzed from the trajectories of the particles. We find that at low temperature the hopping processes being the primary mode of particle diffusion for both the smaller and bigger size particles.

The organization of the rest of the paper is as follows. In the next section, we describe in detail the system studied here and the details of the simulations. The simulation results are analyzed and discussed in section III. Finally, we end with some concluding remarks in section IV.

II. SYSTEM AND SIMULATION DETAILS

We have performed a series of equilibrium isothermal-isobaric ensemble (N P T) molecular dynamics simulations in three dimensions of a system of $N = 256$ particles of mean radius $\bar{\sigma}$ and mass $\bar{m}$ with polydispersity in both size and mass. The interaction between any two particles is modeled by means of shifted force Lennard-Jones (LJ) pair potential, where the standard LJ is given by [44]

$$u^{ij}_{\text{LJ}} = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$

where $i$ and $j$ denotes two different particles and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ where $\sigma_i$, $\sigma_j$ are the diameters of the particles $i$ and $j$, respectively. In the shifted-force potential both the potential and force are continuous at a cutoff radius $r_c$ and we choose a value of $r_c = 2.5\bar{\sigma}$.

The polydispersity in size is introduced by random sampling from the Gaussian distribution of particle diameters $\sigma$ [44]

$$P(\sigma) = \frac{1}{\delta \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{\sigma - \bar{\sigma}}{\delta} \right)^2 \right],$$

where $\delta$ is the width of the distribution. The standard deviation ($\delta$) of the distribution divided by its mean $\bar{\sigma}$ gives a dimensionless parameter, the polydispersity index $s = \delta/\bar{\sigma}$. The simulations are carried out here for a fixed value of the polydispersity index $s = 0.1$. The masses of the particles are varied accordingly and we assume that the mass of a particle $i$ is scaled by its diameter as $m_i = \bar{m}(\sigma_i/\bar{\sigma})^3$. The LJ energy parameter $\epsilon_{ij}$ is assumed to be same for all particle pairs and denoted as $\epsilon$.

All the quantities in this study are given in reduced units, that is, length in units of $\bar{\sigma}$, temperature $T$ in units of $\epsilon/k_B$, pressure $P$ in units of $\epsilon/\bar{\sigma}^3$, and the unit of time is $\tau = \sqrt{\bar{m}\bar{\sigma}^2/\epsilon}$. Note that if one assumes the argon units then $\tau = 2.2$ ps.

All simulations in the NPT ensemble were performed using the Nose-Hoover-Andersen method [46], where the external reduced temperature ($T^*$) is varied over a large range from 1.3 to 0.67 keeping the external reduced pressure ($P^*$) fixed at 10.0. Throughout the course of the simulations, the barostat and system’s degrees of freedom are coupled to an independent Nose-Hoover chain (NHC) of thermostats, each of length 5. The extended system equations of motion are integrated using the reversible integrator method [48]. The higher order multiple time step method has been employed in the NHC evolution operator which lead to stable energy conservation for non-Hamiltonian dynamical systems [47]. The extended system time scale parameter used in the calculations was taken to be 0.93 for $T^* \geq 1.0$ and 1.16 for $T^* < 1.0$ for both the barostat and thermostats.

A time step of 0.001 is employed for $T^* \geq 1.0$ and 0.002 for $T^* < 1.0$. The equilibration and data collection steps are also varied accordingly depending upon the temperature of the system. For $T^* \geq 1.0$, the equilibration steps are varied from $5 \times 10^5$ to $10^6$ and the data collection steps are $10^6$, whereas for $T^* < 1.0$, the equilibration steps are varied from $5.0 \times 10^5$ to $2.0 \times 10^6$ and the data collection steps from $10^6$ to $2.5 \times 10^7$. At each temperature, all the dynamic quantities are averaged over five independent runs. Diffusion coefficients ($D_j$) for the different size particles are calculated from the slope of the corresponding mean square displacements (MSD) in the diffusive limit and viscosity is calculated from the auto-correlation of the off-diagonal components of the microscopic stress tensor, via the standard Green-Kubo formula [50]. As the system is isotropic, we have taken an average over three different off-diagonal stress correlations for each of the five data sets.

III. RESULTS AND DISCUSSION

In order to make sure that there is no crystallization, we have calculated the radial distribution functions $g(r)$ which describes the average structure of the fluid. The radial distribution function calculated for $T^* = 0.67$ is shown in figure 1. The decay of correlations with increase in distance clearly reflects the absence of any long range order, a characteristic feature of the fluid.

The plot of $\ln(\eta)$ as a function of inverse temperature ($1/T^*$) in figure 2(a) clearly shows a super-Arrhenius behavior of the viscosity. In figure 2(b) we show a VFT fit to the viscosity (Eq. 1) by plotting $\ln(\eta)$ against $(1/(T^* - T^*_o))$ where $T^*_o$ is equal to 0.57. As in other fragile liquids, it shows that the divergence of viscosity is quite well described by the VFT equation. From the fitting we obtain the values of $A_\eta$ and $E_\eta$ as 2.0 and 0.81, respectively. We have also calculated the fragility parameter ($D_o = E_\eta/T^*_o$) as defined by Angell [51]. Using the values of the fitting parameters ($E_\eta$ and $T^*_o$) obtained within the temperature range investigated, its value is $\approx 1.42$. This

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Note: The above text contains mathematical and scientific content that may require specialized knowledge to fully understand.
classifies the present system into a strongly fragile liquid. Thus, the dense random packing of unequal size particles makes the present system more fragile when compared with a recent simulation study on Kob-Andersen binary mixture (D = 2.45) [4].

In a polydisperse system, all the particles are unequal in size, so their diffusion coefficients will also differ. We categorize the particles into different subsets where particles of diameters within 0.05σ are assumed to be members of the same subset. For the polydispersity index s = 0.1, we find that the minimum and maximum diameter of the particles are 0.75σ and 1.25σ, respectively. Thus subsets of particles with diameters in the ranges 0.75 to 0.8σ and 1.2 to 1.25σ corresponds to smallest and largest spheres, respectively. The diffusion coefficients for different subsets of particles are calculated at each temperature. It is well-known that in deeply supercooled liquids the diffusion coefficient shows non-Arrhenius temperature dependence and can be fitted by a VFT law

\[ D_i(T) = A_{D_i} \exp\left[-E_{D_i}/(T - T_{o}^{D_i})\right], \]  

where the index i stands for the different subsets of particles. \( T_{o}^{D_i} \) is the critical temperatures for i-th species at which the diffusion coefficients \( (D_i) \) vanishes. The diffusion coefficients for each subsets of particles have been fitted to the above equation and we show the plot of \( \ln(D_i) \) against \( 1/(T - T_{o}^{D_i}) \), for the smallest \( (D_1) \) and largest \( (D_{10}) \) spheres in figures 3(a) and 3(b), respectively, where \( T_{o}^{D_1} \) and \( T_{o}^{D_{10}} \) are 0.46 and 0.5. Thus the critical temperatures \( (T_{o}^{D_i}) \) depends on the size of the particles and increases with size of the particles \( \bar{R}_i \) \( (\bar{R}_i \) is the mean radius of the i-th subset). This is shown in figure 4. For the largest spheres, the critical temperature \( (T_{o}^{D_{10}}) \) is smaller than the corresponding critical temperature obtained from VFT fit to the viscosity \( (T_{o} = 0.57) \). This clearly signifies that near the glass transition the diffusion is partly decoupled from the viscosity and for smaller particles the degree of decoupling is more. The smaller particles remain mobile even when bigger particles are almost frozen.

In figure 5 we plot the diffusion constants \( (D_i) \) against \( 1/\bar{R}_i \) at the lowest temperature of \( T^* = 0.67 \) and compared with the well-known hydrodynamic Stokes-Einstein (SE) relation (Eq. 2 with \( C = 6 \), the stick boundary condition). It clearly shows the markedly non-Stokesian behavior of the diffusion at low temperatures. Interestingly, the fitting to the simulated data points show a highly nonlinear size dependence of the diffusion. This is a clear evidence that the breakdown of SE law is more severe for the smaller size particles. In order to get an estimate of the degree of decoupling (between diffusion and viscosity) for the smallest size particles, we have fit the inverse diffusion coefficient \( (1/D_i) \) versus \( \eta/T \). While at high T, it asymptotically satisfies the SE relation (slope is 1), the fit to the low temperature data gives the slope \( \alpha \approx 0.5 \) (that is, diffusion shows the power law behavior \( D_1 \propto \eta^{-0.5} \)). It should be noted that the dynamics of a polydisperse liquid is more heterogeneous than a monodisperse or bidisperse system due to the different time scales involved for different sizes and masses of the particles [1, 2]. The smaller particles are on average faster than others over all time scales. This becomes more prominent at lower temperatures where the relaxation time of the system is very high. At low temperature, the observed nonlinear dependence of diffusion on size is related to the increase in dynamic heterogeneity in a polydisperse system.

A more detailed analysis of the diffusion can be obtained from a closer examination of the self-part of the van Hove correlation function \( G_s(r, t) \). This gives the distribution of the displacements \( (r) \) of a particle in a time interval \( t \). We calculate \( G_s(r, t) \) for the smallest \( (\sigma = 0.75 \) to 0.8σ) and largest \( (\sigma = 1.2 \) to 1.25σ) particles for different time intervals at \( T^* = 0.67 \), the lowest temperature investigated. Figures 6(a) and 6(b) shows the correlations for the smallest and largest spheres, respectively. For the smallest particles, a gradual development of a well-defined second peak at \( r \sim 1.0\bar{r} \) is clearly visible with increase in time (figure 6(a)). However, for the largest particles, the distribution becomes bimodal at relatively longer time scales (figure 6(b)). The occurrence of the secondary peak, observed also in other model binary mixtures at low temperatures [13, 14, 15], is an evidence of the jump motion in the dynamics of the particles.

To characterize the single particle dynamics further, we have evaluated the self-intermediate scattering function \( F_s(k, t) \), the spatial Fourier transform of \( G_s(r, t) \), for different subsets of the particles for a fixed value of the reduced wave number \( k\bar{r} \sim 2\pi \) at \( T^* = 0.67 \). The long time decay of \( F_s(k, t) \) is well fitted by the Kohlrausch-Williams-Watts (KWW) stretched exponential form

\[ F_s^i(k, t) = \exp\left(-\frac{t}{\tau_i}\right)^{\beta_i}, \]  

where \( \tau_i \) and \( \beta_i \) are the relaxation time and the stretching exponent of the i-th subset. We find that both \( \tau_i \) and \( \beta_i \) increases with an increase in the size of the particles, as has been observed earlier by other authors in binary mixtures [14]. The \( F_s(k, t) \) calculated for the smallest (subset 1) and largest (subset 10) particles along with the KWW fits is shown in figures 7(a) and 7(b), respectively. Note that we fit the functions [\( F_s^i(k, t - t_0)\) \( F_s^i(k, t_0) \)] \( (t > t_0) \), to the KWW form to quantify their long time behavior [13]. For the smallest particles, the values of the fitting parameters are found to be \( \tau_1 \approx 242 \) and \( \beta_1 \approx 0.49 \), whereas for the largest particles they are \( \tau_{10} \approx 717 \) and \( \beta_{10} \approx 0.64 \). The enhanced stretching \( (\beta_1 < \beta_{10}) \) at long times is due to the more heterogeneity probed by the smaller size particles than that by the larger size particles during the time scale of decay of their \( F_s(k, t) \) [12].

In order to determine the extent of the jump-type motion more clearly we follow the trajectory of the individual particles. A close inspection of the simulated trajectory of the smallest and largest particles reveals several
IV. CONCLUSIONS

In summary, we have presented the results of large scale computer simulations for a supercooled polydisperse system with large variations in temperature at a fixed high pressure. The interparticle interaction is represented by the standard Lennard-Jones (LJ) potential and the particles in the system are considered to be polydisperse both in size and mass. Characteristic of a fragile glass former, the super-Arrhenius temperature dependence is observed for the viscosity and also for the self-diffusion coefficients of different size particles. Furthermore, within the temperature range investigated, the value obtained for the Angell’s fragility parameter (D \approx 1.4) establish the present system as a strongly fragile liquid.

In a dense polydisperse system, a wide range of time scales are involved due to the different size and mass of the particles. Thus, upon lowering the temperature, the dynamics is increasingly more heterogeneous compared to a monodisperse or bidisperse system. The increase of critical temperature for diffusion (T^{D^*}_o) with the size of the particles suggests that the dynamics is indeed heterogeneous. In addition, the critical temperature for viscosity (T^{\eta}_c) is found to be larger than that for the diffusion, indicating the decoupling of translational diffusion from the viscosity commonly observed in deeply supercooled liquids. Interestingly, a marked deviation from the Stokesian diffusion is observed where the dependence on size of the particles is highly nonlinear.

The analysis of the self-part of the van Hove correlation functions G_s(r, t) showed a clear signature of the single particle ‘hopping’ (indicated by the second neighbor peak) in the dynamics of both the smallest and largest size particles at low temperatures. However, for the larger particles, the hopping processes are found to occur at relatively longer times. The relevance of the hopping processes at low temperatures is further investigated in detail by following the trajectory of the individual particles. Crossover from continuous Brownian to hopping motion takes place at shorter time scales for the smaller size particles than that for the larger size particles.

In the present system the size of all the particles are different. It would be interesting to see whether the jump motion executed by the individual particles occurs over a single energy barrier or it takes place via a number of "intermediate" inherent structures in the potential energy landscape. A recent molecular dynamics simulations on LJ binary mixture \[13\] have shown that such a transition does not correspond to transitions of the system over single energy barriers. In addition, in a deeply supercooled liquid the jump motions are associated with strong nearest-neighbour correlations, in which several neighboring atoms jump at successive close times \[20,21,35\]. It is to be noted that similar correlations have been observed here also. Recently, a computer simulation study of a deeply supercooled binary mixture \[22\] has shown that the local anisotropy in the stress is responsible (at least partly) for the particle hopping. However, the molecular origin of the jump motions observed here (highly disordered system) is not clear and we are presently pursuing this problem.

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Figure Captions

Figure 1. The radial distribution function \( g(r) \) of the system at \( T^* = 0.67 \), the lowest temperature investigated.

Figure 2. Temperature dependence of the shear viscosity (\( \eta \)). (a) \( \ln(\eta) \) as a function of inverse of temperature \( (1/T^*) \). The simulating values given by the solid circles show super-Arrhenius behavior. The dashed line gives a guideline to the Arrhenius behavior. (b) \( \ln(\eta) \) against \( 1/(T - T^*_o) \). The solid circles are again represents the simulation results and the VFT fit is shown by the solid line. \( T^*_o \) is found to be 0.57. The slope \( (E_\eta) \) and intercept \( (\ln A_\eta) \) obtained from the fit are 0.81 and 0.69, respectively. For details, see the text.

Figure 3. Temperature dependence of the diffusion coefficients \( (D) \) for the smallest \( (D_1) \) and largest \( (D_{10}) \) particles. (a) \( \ln(D_1) \) is plotted against \( 1/(T - T^*_{D_1}) \). (b) \( \ln(D_{10}) \) against \( 1/(T - T^*_{D_{10}}) \). Solid circles are the simulation results and the solid lines are the VFT fit. The critical temperatures \( T^*_{D_1} \) and \( T^*_{D_{10}} \) obtained from the VFT fit are 0.46 and 0.50, respectively.

Figure 4. The critical temperature \( (T^*_{D_1}) \) obtained from the VFT fit to the different subsets of particles as a function of the mean radius \( (\bar{R}) \) of the subsets (in units of \( \bar{\sigma} \)). Note that \( T^*_{D_1} \) increases with the size of the particles.

Figure 5. The diffusion coefficients \( (D) \) as a function of \( 1/\bar{R} \) at \( T^* = 0.67 \). The dashed line represents the Stokes-Einstein relation (Eq. 2) with the stick boundary condition \( C = 6 \). The viscosity \( (\eta) \) value is taken from the present simulations. Solid circles are the simulated values and the solid line is the cubic polynomial fit in \( 1/\bar{R} \). The fit parameters are as follows: \( D_1 = 0.0011 - 0.00132(1/\bar{R}_i) + 0.000442(1/\bar{R}_i)^2 \). It clearly shows a highly nonlinear size dependence and a marked deviation from the Stokesian behavior of the diffusion.

Figure 6. The van Hove self-correlation function \( G_s(r, t) \) as a function of the particle displacements \( r \) (in units of \( \bar{\sigma} \)) at \( T^* = 0.67 \) for different values of time \( t \) (in units of \( \tau = \sqrt{m\bar{\sigma}^2/\epsilon} = 2.2 \) ps for argon units). (a) For the smallest size particles (subset 1). The occurrence of the second peak at \( r \approx 1.0\bar{\sigma} \) indicates the single particle hopping. (b) For the largest size particles (subset 10). Here also a second peak corresponds to single particle hopping develops but at relatively longer times.

Figure 7. The self-intermediate scattering function \( F_s(k, t) \) for \( T^* = 0.67 \) is shown with a shift in the time origin to \( t_o = 1.0 \), and normalized to the value at \( t_o \), for a fixed value of \( k\bar{\sigma} = 2\pi \). This transformation is a convenient way to eliminate the Gaussian dependence at short time \( \tau \). (a) For the smallest size particles (subset 1). (b) For the largest size particles (subset 10). Open circles represents the simulation results and the solid lines are the stretched exponential fit (Eq. 6). The time constants \( (\tau_1 \) and \( \tau_{10} \) and the exponents \( (\beta_1 \) and \( \beta_{10} \)) obtained from the fits are \( \tau_1 \approx 242, \ \beta_1 \approx 0.49, \ \tau_{10} \approx 717, \) and \( \beta_{10} \approx 0.64 \).

Figure 8. (a) Projections into x-y plane of the trajectory of a typical smallest size particle over a time interval \( t = 500\tau \). (b) Projections into x-y plane of the trajectory of a typical largest size particle over a time interval \( t = 2000\tau \). Note that the time \( (t) \) is scaled by \( \tau = \sqrt{m\bar{\sigma}^2/\epsilon} \) it is 2.2 ps if argon units are assumed. For detailed discussion, see the text.
The graph depicts the function $g(r)$ as a function of $r/\bar{\sigma}$. The function shows a peak around $r/\bar{\sigma} = 1$, with subsequent oscillations indicating a complex behavior typical in certain physical or mathematical contexts.
\[ \ln(\eta) \] vs. \[ \frac{1}{T^*} \]
\[ \ln(\eta) = \frac{1}{(T - T_o)} + \eta \]
\[ \ln(D_1) = -8 \ln(D_1) - 1/(T - T_{o_1}) \]
\[ \ln(D_{10}) = \frac{-1}{T - T_{o}^{D_{10}}} \]
$4\pi r^2 G_g(r,t)$
\[ F_s(k, t-t_0)/F_s(k, t_0) = 0.67(a) \]
\[ F_s(k, t - t_o) / F_s(k, t_o) \]

Graph showing \( F_s(k, t - t_o) / F_s(k, t_o) \) as a function of \( t - t_o \) with a peak at \( T^* = 0.67 \).
