The role of inertia on a locally favoured structure in equimolar binary mass Hard Spheres

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Abstract. Molecular dynamics simulations have been carried out to investigate the effect of inertia on both dynamics and locally favoured structures (LFS) of a supercooled liquid toward glass transition. In this work, the equimolar supercooled liquid binary mixtures of Hard Spheres with the same diameter but different masses were studied. The mass ratio of the binary system was 2:1. The simulation was performed and sampled by using the microcanonical ensemble. Both dynamics and structure changing were analysed. A cluster structure analysis was detected by topological cluster classification (TCC) based on the results of local free energy minimisation. The slowing down dynamics were found to be related to cluster structure changing in both the binary mass Hard Sphere (BMHS) and Hard Sphere (HS). The inertia affected an increasing dynamical heterogeneity and had some effects on favouring some local structures before they get crystallisation.

1. Introduction

This work was motivated by a previous Hard Sphere colloid suspension experiment [1]. In the experiment, particles were suspended in the solvent of cyclohexyl bromide mixed with cis-decalin and salt for density matching, refractive index matching and mimic effect charge between particle. In sample preparation for every state point (volume fraction), the particle and the solution need to have fine density matching. Therefore, density matching was required in every single state point. Typically, a higher volume fraction in each state point was obtained by removing the solvent. However, when the solution was repeatedly removed from the sample, the higher density salt was required to maintain density matching under gravity. Therefore, density matching was required in every single state point. Typically, a higher volume fraction in each state point was obtained by removing the solvent. However, when the solution was repeatedly removed from the sample, the higher density salt was required to maintain density matching under gravity. If solvent evaporation was mimicked, then the reasonable explanation would be that the particles are getting heavier [2]. The effect of phase separation due to a gravitational force had been well studied [3, 4]. Also mimicking the gravity effect was studied by computer simulation and the microgravity experiments [5, 6]. However, the knowledge on the effect of pure inertia on the local structure and dynamics of the Hard Sphere (HS) is quite limited. Hence, this study aims to investigate the effect of inertia on both dynamics and locally favoured structures (LFS), especially in the supercooled liquid. The supercooled liquid state had been extensively studied for tackling the glass-transition problem [7–9]. An interesting approach is that the glass transition was not only the dynamical transition but also the structural one [10, 11].

The most straightforward way to identify the structure in a liquid is to use geometric motifs. In this way, the arrangement of particles is explicitly identified and then called locally favoured structures (LFS). These LFSs have been used to identify local structures in many glass formers in simulated works [12–16] and also in particle-resolved studies in colloid experiments [17, 18]. These LFSs were also found in experiments on metallic glass formers [19,20]. Moreover, this structural motif is a better method to detect
the changes in the structure in supercooled liquids than conventional two-point correlation functions such as the static structure factor [21]. Since fivefold symmetric clusters have been found to play a role in the HS system [21–23], the investigation will focus on these structures which would reveal some insight relations of dynamics and structure in binary mass Hard Sphere (BMHS) system.

2. Simulation and analysis
To study the pure inertia effect on LFSs and the dynamics, the effect of viscosity is neglected. The molecular dynamics simulation has been chosen over Brownian dynamic simulations and Monte Carlo simulations. We used ‘DynamO’ event-driven molecular dynamics package [24] for the simulations. The investigation was carried out by using two similar systems. In the HS system, all particles had a mass of 1 (simulation unit). In BMHS half of particles had a mass of 2 and the other half had a mass of 1. The size of both systems was fixed at \( N = 5324 \). The state points of both systems were chosen to have volume fraction (\( \phi \)) of 0.1, 0.3, 0.4, 0.5, 0.55, 0.56, 0.58 and 0.60 accordingly. All samples were compressed from a density of 0.05 simulation unit to the desire volume fractions with a periodic boundary condition. Next the temperature was controlled to one in the reduced unit by using a thermostat algorithm for 30 units of simulation time. Then the thermostat was shut off. After that, the trajectories of particles were sampled with different sampling rates between several relaxation times. The number of particle in both systems, volume, and energy is constant.

3. Result and discussion
3.1. Structural measurements and analysis
The two-point correlation structure factor and the number of the high-order structures of BMHS and HS systems were compared. The high-order local structures of the HS system were identified by using the TCC algorithm with a maximum bond length of 1.4\( \sigma \) of Voronoi construction [25]. The radial distributions of the HS and BMHS systems at different fractions were determined directly from the simulated coordinates by

\[
g(r) = \frac{1}{N\rho} \sum_{i=1}^{N} \sum_{k \neq i}^{N} \delta(|\vec{r}_i - |\vec{r}_k - \vec{r}_i|) > .
\]  

From figure 1, the structures found in the BMHS system are slightly different from the structures found in the HS system at volume fraction lower than 0.6. Crystallised peaks were observed when the volume fractions of systems were higher than 0.48. At \( \phi = 0.6 \), there were some differences between structure which would be discussed later. The difference between the numbers of the cluster between HS and the BMHS liquids was investigated by determining the variation of Spearman’s cross-correlation matrix obtained from two models. The Spearman’s correlation in each matrix element was calculated by using

\[
\rho = 1 - \frac{6\sum d_i^2}{n(n^2 - 1)}.
\]  

First, fractions of certain types of clusters in various volume fractions were rank from 1 - 8. The highest cluster fraction was ranked as 1, and the lowest cluster fraction was ranked as 8. Second, we calculated the correlation between a fraction of cluster \( C_1 \) and a fraction of cluster \( C_2 \) from the summation of the different rank numbers \( d \) at several state points \( n=8 \). Lastly, a final matrix of \( \rho_{C_1,C_2} \) which represents a correlation between fraction of cluster \( C_1 \) and cluster \( C_2 \) was obtained. The highest correlation number implied that two types of the cluster were correlated positively. The lowest number meant they were negatively correlated, and zero meant they were uncorrelated. The significant difference in the number of structures was observed from the difference between the BMHS and HS matrices. Over twenty clusters were identified as low-energy clusters. There were few clusters in the BMHS system, which was changed compared to the HS system. The most considerable change belonged to 7A cluster.
(see figure 2) which highly correlated with the amount of 10W cluster. This correlation suggested that 7A cluster would be a part of the 10W cluster. From figure (2), the percentage of the difference between the two systems was high (in the order of ±1000). This huge number may indicate that the correlation between the two types of cluster was tiny. When the system was changed from HS to BMHS, the fraction detected was quite large. Therefore, it was possible to increase the correlation coefficient abruptly. The cluster which has highly related to glassy states such as icosahedral and its children such as defective icosahedral and others five-member ring clusters, reported in references [21, 26, 27], were not much related to the positive Spearman’s difference. However, the five-member ring cluster did exist at the higher volume fraction corresponding to [22, 23]. If we looked carefully to the 7K cluster, there was a similarity to 7A cluster but it had less symmetry to pentagon shape. This similarity also mentioned in reference [25]. Hence, 7K cluster was chosen to be LFSs in this context since it had a stronger change in population over the symmetric five-member ring of 7A cluster.

![Figure 1. Radial distributions at volume fraction of 0.1, 0.3, 0.4, 0.5, 0.55, 0.57, 0.58 and 0.60. Dash lines are from the regular HS system. Continuous lines are obtained from the BMHS system.](image1)

**Figure 1.** Radial distributions at volume fraction of 0.1, 0.3, 0.4, 0.5, 0.55, 0.57, 0.58 and 0.60. Dash lines are from the regular HS system. Continuous lines are obtained from the BMHS system.

**Figure 2.** The heat map represents the percentage differences of the Spearman’s correlation coefficients between 2 types of clusters. The higher differences indicate the higher changes in structures from the normal HS system.

### 3.2. Dynamical analysis

The dynamics of both systems were compared by using Angel plot obtained from fitting a self-intermediate scattering function $F_s$. We calculated the self-intermediate scattering function

$$F_s(t) = \frac{1}{N} \sum_{j=1}^{N} e^{\left(2\pi i \left(\mathbf{r}_j(t) - \mathbf{r}_j(0)\right)\right)}$$

directly from the particle coordinates. Then $F_s$ was fitted with stretch exponential $F_s(t) = Ae^{-\left(\frac{t}{\tau}\right)^b}$, where $0 < A < 1$ and $0 < b < 2$. The $\tau$ is the relaxation time for each state point. The Angel plot was obtained by plotting the relaxation time versus the volume fraction of each state point. The Angel plot was fitted with the Kohlrausch-Williams-Watts (KWW) equation for comparing fragilities between two systems. From figure 3, the relaxation time in both systems lay on the same KWW fit, which showed no significant change in whole system dynamics. However, a slight difference in the number of 7K clusters showed in figure 4 between $\phi \approx 0.5 - 0.6$ indicated that the inertia played a role in changing the structure.
The increase in amount of 7A was stopped due to crystallisation as the fraction of FCC increased. This corresponded to other reports [22, 23],

$$\tau_\alpha = \tau_\infty \exp\left[A(\phi_0 - \phi)^{-\delta}\right]$$

(4)

where $\phi_0$ could be interpreted as glass transition volum fraction. $A$, $\delta$ and $\tau_\infty$ are constant.

Figure 3. Angel plots of BMHS system and HS system and their KWW fit.

Figure 4. Fraction number of 7A, 7K, and FCC versus volume fraction. The open data point represents data from HS system. The half-open data was obtained from BMHS system (The dashed lines are used for a guide to eyes.)

3.3. Distribution analysis

To find the change which exhibited coupling between structure and dynamics, the analysis followed the ideas of references [1, 10, 11, 28]. The analysis was carried out by counting the number of time when a particle in a trajectory was found to be in the 7K cluster. This sum counts reflected a tendency of a particle to stay in a trajectory. Therefore, the dynamical heterogeneity can be indicated by a two-peaks distribution of the time-average number density of 7K particle along trajectories. The interesting results are that the distribution changes side in figure 5 b) and c) between volume fractions of 0.55 - 0.58. This change in distribution was also seen in the BMHS system (see figure 6). The signal of peak shoulder of phase separation in the trajectory space sampling, as stated above, seems to be stronger in the BMHS system. These findings need further investigation to confirm the transition.

4. Conclusion

The molecular dynamics simulation was performed to investigate the effect of the inertia on the LFS in equimolar with mass ratio 2:1. From the results, there was no noticeable change in global structure and dynamics, (the radial distribution and intermediate scattering) in the BMHS system over the HS systems. However, when investigating the change in the number of the LFS by using the difference between cross-correlation in both systems, there were some significant changes in the fraction of 7K cluster between volume fractions of 0.55 - 0.58. The distribution of average 7K fraction along the trajectories in both systems in figure 5 and 6 show a sign of two-peak distribution. This two-peak distribution indicated the phase separation between an LFS rich phase and LFS poor phase in the trajectory space. However, the two-peak signal is not strong enough to judge if there is a transition in the trajectory space. Hence, further investigation needs to be carried out. At this point, we can only conclude that both HS and BHS systems
have different local dynamics and 7K cluster had been identified as a structural motif for comparing the changing the local structure in both systems.

Figure 5. Histograms obtained from averaging counts of particle which are in 7K cluster along each trajectory of the HS system. a) at volume fraction of 0.5 b) at volume fraction of 0.55 c) at volume fraction of 0.58.

Figure 6. Histograms obtained from averaging counts of particle which are in 7K cluster along each trajectory of the BMHS system. a) at a volume fraction of 0.5 b) at a volume fraction of 0.55 c) at a volume fraction of 0.58, the black was obtained from all trajectories, the red from big particle trajectories and the green from the smaller species.

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