Collective vibrations and soft modes in hard sphere colloids
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5 Structural Rearrangements and Soft modes in a Colloidal Glass
5.1 Introduction

Supercooled liquids, amorphous polymers or atomic systems, when cooled or compressed in a way to bypass crystallization get trapped in a metastable glassy state. The characteristic of such states is accompanied with a very high viscosity ($\sim 10^{13} \text{Pa.s}$) as well as the onset of the slow dynamics. Physically, this reflects the arrested motion of individual particles in the cages formed by its neighboring particles who themselves are confined by their own neighbors. Thus evolution of the system becomes very sluggish in the configurational space leading to nonergodic behavior, as observed in glasses. Nevertheless, on longer time scales structural relaxation happens as the system undergoes thermally activated transitions from one metastable state to another in its attempt to reach the thermodynamic equilibrium. Such relaxation events which relates to the viscous flow of glasses has been studied previously in metallic glasses that measured the bulk viscosity or shear modulus in an ‘annealing’ glass [1, 2]. Recently, there are studies using confocal microscopy in an quiescent as well as sheared colloidal glasses which looked at the heterogeneous dynamics [3, 4] and the cage-arrangements [5] - [8] during long time relaxations. However, connecting such events with the excess low frequency normal modes that exist in the glasses is a relatively recent development and has only been looked at in computer simulation studies [9]-[11].

In this chapter, we study a quiescent hard sphere colloidal suspension deep in glassy phase, $\phi = 0.59$ on long time scales with the help of confocal microscopy and observe the local dynamics during $\alpha$-relaxation (cage rearrangement). Just before the system enters the $\alpha$ relaxation regimes, the mean-square displacement shows a plateau where the particles are in local equilibrium confined in their respective cages. This allows us to compute the normal modes of the system. We use the covariance matrix of displacements as described in previous chapters to obtain the normal modes of this system. The low frequency modes show quasi-localized behavior as we have discussed in chapter 4. Participation maps based on the local amplitudes further elucidate the spatial distribution of these modes. To investigate the evolution of the local dynamics we first start with the plot of the square displacements of individual particles from their initial positions over a time interval $\delta t \sim \tau_\alpha$. The spatial plots of the square displacements show a heterogeneous character where small clusters of particles show higher activity than the rest. To further gain
information about the dynamics around these particles we use a Delaunay triangulation. This gives us the neighbors of a particle in any chosen configuration at any given instant of time. We subsequently compute the number of neighbors each of the particles has lost as a function of time, eventually leading to identify the regions where the rearrangements are taking place. Our observation shows that significant changes of the neighborhood of particles are happening in the zones of higher diffusivity. We then compare the participation maps averaged over the lowest frequency modes with the spatial plots of those particle that undergo rearrangement. The superposed plot of these two shows that the re-arranging zones are correlated with the quasi-localized regions of the modes. This establishes the connection between the collective aspects of the structural relaxation with the soft localized modes present in the system.

5.2 Experiments

We have prepared a colloidal glass of volume fraction $\phi = 0.59$ following the preparation procedure as described in chapter 2. Two dimensional images are acquired using a fast confocal microscope (Zeiss LSM 5 live) in a field of view of $100\mu m \times 100\mu m$. We have imaged the particles on a plane which is $25\mu m$ away from the coverslip to avoid any possible effect of confinement. Images are acquired at a rate of 10 frames per second for a period of total 1200 secs resulting 12000 frames. The positions of the particles are identified in all the frames, and then linked to construct two dimensional trajectories of individual particles, using the standard particle tracking software (IDL).

5.3 Results and Analysis

5.3.1 Structural relaxation on longer time scales

In this section we discuss the relaxation of glassy systems at various time-scales. In colloidal glasses, close to the glass transition volume fraction there are mainly two distinct processes well studied in several dynamical light scattering experiments [12] -[14] - $\alpha$ and $\beta$ relaxation that occur over two different time-scales. The $\alpha$ relaxation happens over longer time-
scales and describes the decay of density fluctuations the \( \beta \) process exists on mesoscopic timescales in between the short time diffusion and the \( \alpha \)-relaxation. This is also reflected in the different diffusive regime observed in the mean square displacement plots of the supercooled liquids and glasses as we will see here.

The average square displacement \( < \delta r^2 > \) obtained from the displacements of the present colloidal suspension is shown in Fig.5.1 on a log-log scale as a function of time. On the shortest time scales, the increase of the average displacements is due to small scale motions of the particles where they explore the local environment without “feeling” the presence of the neighbors. However, the present system is dense (\( \phi \approx 0.59 \)) and this diffusion can only be observed at on very short time scales which is shorter than the present image acquisition rate (10 frames per sec). Thus this region is not very clearly resolved in the present data, although a few points in the beginning of the MSD curve are representative of this initial short time diffusion. Beyond this we observe a plateau in the MSD where the motion of any particle is restricted by a shell of nearest neighbors.
neighbors constituting the ‘cage’. The slow dynamics of these locally arrested structures leads to the sub-diffusive behavior that usually persists over long time in dense systems. In the present experiment this region is roughly between $0.5 sec$ up to $\sim 500secs$. On even longer timescales

at the end of this plateau, the mean square displacement shows as a systematic rise. This corresponds to a long time diffusive behavior known as the $\alpha$-relaxation regime where average displacement is linear in time $< \delta r^2 > \sim t$. This is clearly visible in Fig. 5.1 which shows that the data in this region is indeed parallel to a line of unit slope. This is where the structural rearrangements take place, the particles starts breaking away from their immediate local structures, their neighbors change, to find new local ‘equilibrium’ positions. We plot two dimensional trajectories of the particles which illustrate the nature of such cage breaking events where a particle typically undergoes a rapid shift to its new position. These rearrangements are activated by the thermal fluctuations present in the system and enable transitions from the local minima of one metastable state to another.

### 5.3.2 Normal Modes

Over the plateau of the mean square displacement we can reasonably assume that any particle is giggling around its local equilibrium position. This allows us to define a mean position $< x_i >$ for any $i^{th}$ particle.
The displacements from the mean positions are given by \( u_i = \{ x_i - <x_i>, y_i - <y_i> \} \). We then compute the co-variance matrix of displacement \( D_{lm} = < u_{mi} u_{nj} > \), as defined in chapter 3. This matrix is averaged over the configurations available on the plateau and diagonalization of which leads to \( 2N \) eigenvalues \( \lambda_m = 1, 2, 3..2N \) and corresponding \( 2N \) eigenmodes \( v(\omega_m) \). An eigenmode respective to a single frequency \( \omega_m (= \sqrt{1/\lambda_m}) \) represents a normal mode of this system. The frequency dependence and other characteristics of these modes have been discussed in detail in chapter 4. Figure 5.3 show an example of the lowest frequency modes in the system, which suggests there are smaller regions where colloidal particles apparently show higher activity than in the rest of field of view. The mode structure can further be probed by computing the local participation ratios.

**Spatial distribution of the Normal Modes**

To study the spatial distribution of the modes we compute the particle participation ratio. This is given by \( p_i(\omega) = v_i(\omega)^2 \) where the index \( i \) indicates any colloidal particle in the system and \( v_i \) is the eigenmode
amplitude projected onto it. Figure 5.4 shows a contour plot of the

![Contour map of the particle participation ratio for a single low frequency normal mode](image)

participation map corresponding to a single low frequency eigenmode (Fig. 5.3). The respective contour plot indeed shows such quasi-localized regions, where a small group of particles has higher amplitude in the background of rest of the particles with smaller amplitudes.

Now, connecting these normal modes with the structural re-arrangement regions would only be possible if these mode structures are persistent in time. To observe the evolution of the low frequency modes we study contour plots where particle participation ratios are averaged over the lowest 25 eigenmodes. Figure 5.5 shows such a plot where the covariance matrix is averaged over three different interval of times - 300, 400 and 500 secs respectively. We do not see a significant change in the mode structures for different averaging intervals, besides very slight variations in few of the quasi-localized domains.

### 5.3.3 Detection of the Zones of Structural Rearrangements

As discussed in the previous section, on short time scales the particles remain trapped in the cage constituted by their neighbors, however, they
Figure 5.5: Contour plots of particle participation ratios averaged over the lowest 25 normal modes (average participation ratio for each mode is $p(\omega) < 0.35$) shown. Normal modes are obtained by averaging the covariance matrix $D_{lm}$ over three different time intervals 300, 400 and 500 secs from left to right. Mode distribution largely remain invariant other than small variations in few of the quasi-localized regions.

Figure 5.6: Delaunay triangulation for a set of particles. The particle diameter is not shown to scale.

escape from their cages to display diffusive motion over long time scales. The cage breaking events involve a change of neighbors, leading to irreversible rearrangements in the system. Here, we identify such rearrangements by tracking the trajectories of individual particles over long time intervals. The number of neighbors each particle has changed or lost over a time interval $\Delta t \sim 1200 \text{secs}$ is determined by comparing their neighbors at time $t = 1$ and $t = \Delta t$. Given a configuration of particles, the
neighbors of each particle are identified using the technique of Delaunay triangulation. An instance of Delaunay triangulation of a set of particles is shown in Fig. 5.6; each particle is connected to its neighbors using triangles. Using this method, we have determined the number of neighbors each particle has changed or lost over a time $\Delta t$. In simulations [9], these rearrangements were identified by particles that have lost four neighbors. However, in experiments there are very few particles that lose four neighbors over the time scale of our observation. Therefore, we identify those particles that have lost three or more neighbors. An alternate measure of reorganization is the diffusive motion of a particle, which is the displacement of a particle from its initial position over whole period of observation of about $\sim 1200\text{ secs}$. We set a cut off distance $r_{c} = 0.06\mu\text{m}$, which is larger than the mean of the probability distribution function of displacements. We use both the measures: the number of neighbors lost and the diffusive motion of particles, to identify the regions of rearrangement.

5.3.4 Correlations between the Zones of Rearrangement and the Spatial Distribution of the Modes.

We track the particle motion over long time scales and determine the number of neighbors lost and the displacement of each particle. In Fig. 5.7(left), we present a spatial map of particles that have lost three or more neighbors (black circles) and particles that have diffused more than a distance $r_{c}$ (green circles), along with the rest of particles (pink circles). Clearly, the highly mobile particles (green circles) form clusters, and the particles that lose three or more neighbors occur in the vicinity of these clusters. Recent studies of supercooled liquids in computer simulations have shown that such relaxation events originate from low frequency modes in the system by comparing the spatial maps of particle participation ratios of the low frequency modes and reorganizing zones. We proceed along similar lines to understand the origin of irreversible rearrangements in colloidal glasses. A comparison of the spatial maps of the particle participation ratios, averaged over 25 lowest frequencies, and the irreversible regions is presented on the right panel of Fig. 5.7. It is worth pointing out that the normal modes in Fig. 5.7 (right) were computed by averaging the particle motion over a time interval $\delta t = 400\text{ secs}$, and the rearrangements were identified at much later stages, at around
Figure 5.7: Left: Spatial map of particles which undergo large diffusions (green circles) beyond the cut off $r_c$ in a background of particles (pink circles) which are relatively quiet is shown in a smaller section of $60 \mu m \times 60 \mu m$. Particles for which three or more neighbors change takes place indicated by the black circles. Right: Contour plots of particle participation ratio averaged over 25 lowest frequency modes superposed with highly mobile particles—white circles, as well as the particles (black circle) which lost three or more neighbors shown over the same section.

$\tau_\alpha \sim 1200 \text{secs}$. As Fig. 5.7 illustrates, the rearrangements indeed originate in the regions of high particle participation ratio.

5.4 Conclusion

In conclusion we have studied the long time dynamics of a dense colloidal glass of volume fraction $\phi = 0.59$, with the help of confocal microscopy. On longer timescale, the relaxation of the system occurs through the structural rearrangement of the particles. We have here applied normal mode analysis to understand such relaxation events. Low frequency normal modes measured show quasi-localized structures that largely remain invariant with time over the plateau of the mean square displacement. Our analysis demonstrates that these localized structures are spatially correlated with the zones of higher diffusivity where almost all the significant change of neighbors are taking place. This shows that structural
relaxation is indeed occurring along the softest available modes of the system.
Bibliography