Collective vibrations and soft modes in hard sphere colloids
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Citation for published version (APA):

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Low frequency modes in Colloidal Glasses and Supercooled Liquids
4.1 Introduction

In chapter 3 we discussed the vibrational spectra and the density of states that results from the covariance matrix of the displacements of the colloidal particles. In this chapter we present the normal modes resulting from the above analysis and discuss various aspects of their characteristics in detail. Among the vibrational spectrum over the whole range of frequencies, the lower frequency modes show "swirling motion" with the correlation extending over many particle diameters. To obtain a clearer picture we have computed an orientational order parameter as a function of the particle separation. This helps us to estimate roughly the range of correlation as well as to compare the extent of the correlated motion at different volume fractions.

The other aspect that we elaborate in this chapter are the localization properties of these modes. The present experimental samples start from the supercooled liquid suspensions $\phi = 0.54$ and go up into the dense glassy phase $\phi = 0.60$. This provides a good range of systems in which we can observe and analyze such properties. Thus, we compute participation ratios of the normal modes of the present systems, which is a well known measure for localization of collective modes in general. Below, we begin by introducing the concept of normal modes of collective motion in any system.

4.2 Normal modes

The normal modes of vibration are of fundamental importance in the study of collective oscillations. Though the motion of any single oscillator of a coupled system appears complex and may even be non-periodic, the picture is highly simplified when viewed in terms of the normal modes. Under appropriate conditions of excitations the system exhibits a simple harmonic motion with the same frequency and phase as a whole. A vibration of this kind is called a normal mode of the coupled system. The frequencies of the normal modes of a system are known as its natural frequencies or resonant frequencies. A physical object, such as a building, bridge or molecule, has a set of normal modes that depend on its structure, materials and boundary conditions. Figure 4.2 illustrates a few normal modes corresponding to different harmonics of the simplest
Figure 4.1: Normal modes of different harmonics for a rectangular drum.

Computation of normal modes in any system requires the system to be in a stable configuration say $R_0$ corresponding to one of the local minima of the potential energy surface. The potential energy $V(R)$ can be expanded around $R_0$ as,

$$V(R) = V(R_0) - F(R - R_0) + 1/2(R - R_0) \cdot K(R) \cdot (R - R_0) \tag{4.1}$$

where the dynamical matrix $K$ is given by,

$$(K)_{\alpha\beta} = \frac{\partial^2 V(R)}{\partial R_{\alpha} \partial R_{\beta}} \tag{4.2}$$

Note, that in expanding the potential energy we have considered terms up to the terms quadratic in displacement known as harmonic approximation which would be valid for small amplitude motion of the particles around the local minima. Diagonalization of the above matrix $K$ yields the normal modes (eigenvectors) and the corresponding squared frequencies $\omega^2$ which is the standard prescription in solid state $[1]$. In the present thesis we work with experimental hard sphere systems where we have direct access to the positions and displacement of the colloidal particles in time. Therefore we adopt another method to obtain the normal modes of the system by measuring the correlations in position fluctuations $[2, 3]$ leading to the matrix $D_{lm}$ as described in detail in chapter 3. The eigenvectors of this matrix $v(\omega_m)$ gives us the normal modes and corresponding frequencies are given by $\omega_m = \sqrt{1/\lambda_m}$ where $\lambda_m$ are the respective eigenvalues.
4.3 Visualization of the Normal Modes

4.3.1 Glasses

The density of states of the suspension at a volume fraction $\phi = 0.60$ is shown in Figure 4.2. The dashed line shows the limit ($\omega \sim 36 \mu m^{-1}$) up to which the spectrum is reliable and not affected by noise (chapter 3). All the results and analysis presented here remain below this frequency. Let us now see what the respective normal modes look like for this dense glassy suspension. To observe the distribution of the modes at different frequencies, we have plotted a few two dimensional eigenvector fields $v(\omega_m)$ for the different frequencies $\omega_m$ for the volume fraction $\phi = 0.60$ in Figure 4.3. The location of these chosen frequencies corresponding to

![Figure 4.2: Density of states for the volume fraction $\phi = 0.60$. The filled circles show four different locations in the spectrum corresponding to the eigenmodes shown in the figures below. The dashed line shows the frequency up to which the spectrum is reliable and not affected by noise.](image)

these eigenmodes have been indicated by the filled circles in the density of states plot. As is apparent the very lowest frequency (Fig. 4.3-a) modes shows large-scale swirling structures,
Figure 4.3: The two dimensional eigenvector fields have been plotted as function of mode frequencies in ascending order starting from the lowest ones for the volume fraction $\phi = 0.60$. The frequencies ($\mu m^{-1}$) chosen are from different part of the spectrum as indicated in Fig. 4.2. The low frequency modes shows spatially correlated motion. With the increase of frequency there is a gradual loss of such correlation. Eventually the very high frequency modes appear to be completely random.

where the motions are correlated over several particle diameters. As we go towards higher frequencies, there is a gradual loss of this extended correlation. Eventually the modes become completely random at suffi-
ciently high frequencies.

### 4.3.2 Supercooled Liquid

In Fig. 4.4, we show some of the eigenmodes as a function of frequency for the supercooled sample $\phi = 0.54$. We observe similar trends - correlated low frequency modes and a decrease in the loss of correlation in the modes as we move towards higher frequencies.

### 4.3.3 Orientational Correlation function

To quantify the order in the eigenvector fields, we calculated the orientational correlation function $c_{ij}$ defined as the scalar product of $v_i(\omega) \cdot v_j(\omega)$, where $v_i$ and $v_j$ are the eigenmode (corresponding to a frequency $\omega$) amplitudes projected onto the $i^{th}$ and $j^{th}$ particles. Fig. 4.5 shows a plot of $c_{ij}$ as a function of distance between the two particles $\delta r_{ij} = r_i - r_j$ for a single low frequency mode as shown in the right panel. Correlations over many particle diameter are reflected in the long tail of the function $c_{ij}$. The negative part in $c_{ij}$ represents an anti-correlated motion, characterizing the swirling motion.

To observe the frequency dependence of these modes, we have plotted the above correlation function in Fig. 4.6 at different parts in the spectrum (shown in inset). Each of these curves is averaged over approximately 20 eigenmodes around the chosen frequency. Low frequency modes show the same long negative tail while there is a gradual shift towards the zero axis with the increasing frequency, implying a loss of correlation at higher frequencies. In the right panel of Fig. 4.6 we have compared the correlation function $c_{ij}$ corresponding to the lowest frequency modes at different volume fractions, $\phi = 0.54, 0.57, 0.58, 0.59, 0.60$. The low frequency $c_{ij}$ nearly coincides at different volume fractions other than the fact that the negative part becomes slightly more pronounced for higher volume fractions. This shows that the correlated motions at lower frequency remain the same in the present experimental range of volume fractions from dense glassy suspensions to supercooled liquids.
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Figure 4.4: The two dimensional eigenvector fields have been plotted with increasing mode frequencies starting from the lowest ones for supercooled liquid sample, volume fraction, $\phi = 0.54$. The lowest frequency modes shows similar correlated motion as is observed with the one dense in glassy samples ($\phi = 0.60$).

4.4 Localization Phenomena

The phenomenon of localization in the presence of disorder was first introduced by Anderson [4] in 1958 while investigating the conductance of electrons in a lattice with impurity. The concept of electronic conductivity is based on the diffusive zig-zag motion of an electron multiply scattered by the impurities present in the solid. In his study of non
interacting electrons in a random potential, Anderson showed that beyond a certain critical disorder such diffusive motion is hindered due to the increasing scattering to an extent so that the motion of the electron comes to a halt giving rise to localized states. The possibility of disorder or defects resulting in the localization of the eigenmodes is quite general and extends to many systems, like gravity waves, light propagation, spin glasses as well as diffusion on disordered harmonic crystals. The concepts of “localized” or “quasi-localized” vibrations are well studied in crystalline systems with defects where localization usually happens at the high frequency ends of the normal mode spectra [5, 6]. However, the presence of localized as well as quasi-localized modes both at the higher and lower end of the spectra has also been observed in glassy systems in computer simulation studies and experiments [7]-[10]. Recently, a study [11] using video-microscopy also reports the existence of such low frequency modes in soft colloidal glasses.

Here, we have studied the normal modes in a hard sphere colloidal glass. We have studied the participation ratios to quantify the localization of these modes. Below we explain the concept of participation ratios
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Figure 4.6: Correlation function $c_{ij} = v_i \cdot v_j$ shown in different parts of the spectrum, as indicated in $D(\omega)$ in the inset. Lowest frequency modes show the usual long negative tail while there is a systematic shift of this function towards zero axis with increasing mode frequencies implying the observed loss of correlation at higher frequencies. Right: The orientational correlation function for the lowest frequency modes for different packing fractions 0.54, 0.57, 0.58, 0.59, 0.60. The general shape of the modes seems to be only very weakly dependent on volume fraction.

and discuss the present findings in more detail.

4.4.1 Localization of the Present Normal Modes

We compute participation ratios $p(\omega)$ which measures the degree of localization of the modes. Modes are normalized for each of the frequencies, so that $\sum_{i=1}^{N} v_i(\omega) \cdot v_i(\omega) = 1$. The participation ratio is defined as,

$$ p(\omega) = \left[ N \sum_i (v_i(\omega) \cdot v_i(\omega))^2 \right]^{-1}. $$

(4.3)

where, $v_i(\omega)$ is the projection of the normal mode of frequency $\omega$ onto a colloidal particle $i$ as defined previously. So, for a strongly localized mode, where the whole amplitude is concentrated over a few particles in the system, $p(\omega)$ scales as $(1/N)$, whereas for an extended mode it is of order of unity. Figure 4.7 shows the plot of this participation ratio as a function of frequency for a glass of volume fraction $\phi = 0.58$. In the present data we do not see any strong localization $p(\omega) < 0.1$ for
the low frequency modes, rather a few of the lowest frequency modes are observed to have \( p(\omega) < 0.2 \), and then a number of modes appears in between \( 0.2 < p(\omega) < 0.37 \). All the modes below \( p(\omega) < 0.37 \) apparently display quasi-localization where localized structures are superimposed on an extended wave background as observed in Fig. 4.3(a),(b). With increasing frequency, the participation ratio increases and reaches a plateau value near 0.5 indicating de-localized behavior. This relates to the homogeneous high frequency modes shown in (Fig. 4.3(d)) The very high frequency modes in glasses may show stronger localization as reported in previous studies [7, 11]. Since our access to very high frequencies are limited due to the experimental noise, we do not observe such localized modes in the present analysis.

**Participation ratio at different volume fractions**

We now compare the participation ratios for different volume fractions. Fig. 4.8 show a plot of the participation ratio \( p(\omega) \) as a function of frequency at different volume fractions. The participation ratios for the lowest frequency modes at all the volume fractions approximately show values in the same range \( \sim 0.2 < p(\omega) < 0.37 \), thus implying similar quasi-localized behavior besides the supercooled liquid sample \( (\phi = 0.54) \) that shows a little higher value of \( p(\omega) \) than the rests. The curves shifts
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Figure 4.8: Participation ratios shown at different volume fractions $\phi = 0.54, 0.57, 0.58, 0.59, 0.60$. $p(\omega)$ values corresponding to the low frequency modes are approximately in the same range ($0.2 < p(\omega) < 0.37$) at all volume fractions showing similar quasi-localization behavior. We observe a shift of these curves towards higher frequency from 0.54 to 0.60. This is related to the general shift in the spectrum towards higher frequencies due to higher pressure as the volume fractions are increased (Fig. 3.4 Chapter 3). Inset shows the same curves after smoothing the data.

to the low frequency side with the decrease of the volume fraction. This corresponds to the general shift of the spectrum towards lower frequency as can be seen in the density of states (Fig. 3.4, chapter 3) at different volume fractions.

4.5 Conclusions

In conclusion, here we observed normal modes in a hard sphere colloidal system for a range of volume fractions from supercooled liquids $\phi = 0.54$ as well as in the dense glassy suspensions $0.58, 0.59, 0.60$. Low frequency modes for all the volume fractions show spatially correlated motion over many particle diameters. This behavior of the low frequency modes remains invariant as we go from the lowest to the highest volume fractions;
only the correlation function $c_{ij}$ dips slightly more for the volume fraction $\phi = 0.60$. To quantify the localization in these modes, we have computed participation ratios. The participation values, $p(\omega) < 0.37$ for the low frequency modes display quasi-localized behavior. In the present data, approximately same range of values of $p(\omega), (0.2 < p(\omega) < 0.37)$ is observed for the low frequency quasi-localized modes at different volume fractions besides the supercooled liquid sample ($\phi = 0.54$) which shows a little higher value of $p(\omega)$ than the rests.
Bibliography