Collective vibrations and soft modes in hard sphere colloids

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Summary

Glasses and other amorphous materials show low temperature properties that significantly deviate from their crystalline counterpart. For crystalline solids, the density of states follows Debye behavior $D(\omega) \sim \omega^2$, leading to the cubic temperature ($T$) dependence of the specific heat, $C_p \sim T^3$. However, several simulation and experimental studies have reported an excess specific heat at low temperatures for amorphous solids. Related features are the existence of a plateau in the $T$-dependence of the thermal conductivity and the Boson peak observed in inelastic light or neutron scattering experiments of glasses and disordered solids. All these suggest the existence of an excess of low frequency modes in the density of states of these systems compared to the usual Debye behavior.

In the present thesis one of our main achievements is the observation of these excess vibrational contributions in the density of states of a colloidal system. In particular, we have studied glassy suspensions of hard sphere colloids. The confocal technique used to probe the structure and dynamics of the colloidal particles enables a direct visualization of these modes that helps to further understand their nature.

To prepare the hard sphere colloidal suspensions, we have suspended poly-methylmethacrylate (PMMA) particles of diameter 1.3$\mu$m in a mixture of cyclohexylbromide and decalin solvent to match both the density and index of refraction of the particles. Using confocal microscopy, two dimensional images of the suspension were recorded, from which we reconstruct the particle trajectories. To obtain the normal modes, we have constructed the covariance matrix of displacements $D_{ij} = \langle u_i u_j \rangle$, where $u_i, u_j$ are the displacement components of particles $i$ and $j$. Diagonalization of this matrix leads to the normal modes and the corresponding frequencies. A histogram of all these frequencies then gives us the density of states of the system.
We first focus on the density of states of disordered colloidal suspensions. Measurements were performed with colloidal samples of volume fractions ($\phi$) ranging from supercooled liquids to dense glassy phases $\phi = 0.54 - 0.60$. The density of states (DOS) obtained at different volume fractions from the covariance matrix shows the presence of an excess low frequency modes - a peak at lower frequencies along with a tail that decays towards high frequencies. The noise due to the finite resolution in measuring particle positions, and its effect on the DOS is also discussed. These results are complemented with Monte-Carlo simulations on hard spheres.

We subsequently investigate the spatial structure of the normal modes of the colloidal suspensions ($\phi = 0.54 - 0.60$) at different frequencies. The lowest frequency normal modes show correlated motion over several particle diameters. This correlation is gradually lost as higher frequencies are approached and the modes appear more random in nature. We have compared the extent of the correlations of the low frequency modes for different volume fractions. Spatial plots of the lowest frequency modes show localization. The degree of localization of these modes is measured by calculating the participation ratio.

We have then studied the structural relaxation of a hard-sphere colloidal glass. The dynamics of the particles exhibits spatial heterogeneity: clusters of highly mobile particles are observed. The relaxation of the system occurs through rearrangement of particles in these highly active regions. To understand the nature and origin of these rearranging regions, we have computed the low-frequency modes of the system following the above normal mode analysis. The low frequency modes have a quasi-localized character, which is evident from the contour maps of the particle participation ratios. Our analysis reveals that the regions where rearrangements occur are spatially correlated with the quasi-localized zones of the low frequency modes. This demonstrates that the system indeed relaxes along the softest available modes.

The last chapter of this thesis presents the density of states and low frequency modes of a two dimensional section of a original three dimensional hard sphere colloidal crystal. The lowest frequency modes show an extended plane wave-like character. The dispersion relations and the low frequency part of the spectrum exhibit an anomalous scaling compared to the expected Debye scaling. With the help of elasticity theory we show that such anomalous scaling is indeed the Debye behavior for a
two dimensional cut through a three dimensional system.