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

1.1 Introduction

A wave is a disturbance that travels through a medium from one location to another without any permanent displacements or mass transport of the particles in the medium. It is instead the collective vibrations of the elementary particles that enable the propagation of waves. Many different types of waves e.g elastic, electromagnetic, acoustic exist in nature depending on the types of fluctuations as well the medium in which they propagate. Thus, the study of waves has always been a universal theme nearly touching all traditional branches of physics: mechanics, thermodynamics, electromagnetism, quantum mechanics, light and sound.

In the present thesis, our focus is on the elastic response of amorphous solids to the thermal excitations. For crystalline solids, elastic wave propagation and related properties like the low frequency phonon density of states, the specific heat and conductivity are well described in solid state physics [1, 2], the predictions of which are also verified in experiments. The question we pose here whether a similar description could hold for a system with disorder. A number of papers in past decades show that the dynamical behavior of disordered solids e.g glasses and compressed granular systems deviates significantly from that of conventional solids giving rise to a new class of phenomena [16]-[18], [3]-[23]. In particular, the mechanical response as well as the thermodynamic properties of the system changes appreciably in presence of disorder. Although there are a number of simulations that investigate such dynamical response of disordered systems, not many experiments exist that complement such studies and look into the details of the collective motion.
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Here, we study the collective vibrations in colloidal systems using confocal microscopy. The time and length scales in colloids are more readily accessible in experiments compared to atomic or molecular systems characterized by very high relaxation rates. We use suspension of PMMA (polymethyl methacrylate) colloidal particles in a solvent that matches both density and index of refraction. The preparation procedure leads to hard sphere systems; the interaction potential ideally becomes infinite as soon as two adjacent particles overlap, otherwise the potential is zero. The suspension is in thermal equilibrium with the surroundings and the PMMA particles in the solvent undergo Brownian motion at very short time scales. Here, we have recorded the dynamics of the colloidal particles by taking independent snapshots with a confocal microscope of a two dimensional section of the colloidal sample. The positions of the particles are identified in each frame and subsequently linked to reconstruct their trajectories. We then obtain the density of states and the normal modes from the measured particle displacements. The spatial information obtained from the above measurements help us to visualize the wave motion as well as analyze them in microscopic detail. The different chapters of this thesis elaborate the experimental procedures as well as the relevant method and analysis we have followed. We begin with a brief description with some of the basic concepts of lattice vibrations in the following sections.

1.2 Vibrations in Solids

A solid is a state of matter characterized by its structural rigidity and resistance to changes of shape or volume. An ordered array of tightly bound atoms or molecules forms a crystalline solid, whereas in amorphous solids like glasses, the spatial arrangement of the molecules is completely disordered. The theory of the solid state has started with X-ray diffraction studies of crystals and by now well developed. However, the concepts [1]-[4] have been extended to understand noncrystalline solids and glasses as well.

Almost all the thermodynamic properties e.g specific heat, thermal conductivity of solid substances are described based on the theory of lattice dynamics [2] The general picture of vibrations in solids is that the atoms or molecules located at their equilibrium positions move back and
forth around it driven by their thermal energy and the elastic restoring force arises due to the interactions with the neighboring atoms. We continue discussing a few related concepts like the dynamical matrix and the density of states in the sections below.

### 1.2.1 Dynamical Matrix

Consider a small amplitude vibration of atoms around their mean position so that the potential energy $V$ of the lattice can be expanded in a Taylor series in powers of the atomic displacement $\mathbf{u}(\mathbf{R})$. Thus

$$V = V_0 + \sum_{\mathbf{R}} \sum_{\mu} V_\mu(\mathbf{R}) \mathbf{u}_\mu(\mathbf{R}) + 1/2 \sum_{\mathbf{R},\mathbf{R}'} \sum_{\mu,\nu} \mathbf{u}_\mu(\mathbf{R}) V_{\mu\nu}(\mathbf{R},\mathbf{R}') \mathbf{u}_\nu(\mathbf{R}') \quad (1.1)$$

where $V_0$ is the potential energy of the lattice corresponding to the equilibrium configurations of the atoms, which can be set equal to zero without any loss of generality. Further it follows from Eq 1.1, that

$$V_\mu(\mathbf{R}) = \frac{\partial V}{\partial \mathbf{u}_\mu(\mathbf{R})} \bigg|_0 \quad (1.2)$$

$$V_{\mu\nu} = \frac{\partial^2 V}{\partial \mathbf{u}_\mu(\mathbf{R}) \partial \mathbf{u}_\nu(\mathbf{R}') \bigg|_0} \quad (1.3)$$

Where the subscript zero indicates that the derivatives are evaluated at the equilibrium sites, $\mathbf{R}, \mathbf{R}'$ refers to the lattice sites and $\mu, \nu$ are the cartesian components of displacements. $V_\mu(\mathbf{R})$ implies negative of the $\mu$-component of the force on the atom situated at $\mathbf{R}$. From the definition of equilibrium, the force must be zero. Therefore,

$$V_\mu(\mathbf{R}) = 0. \quad (1.4)$$

Thus Eq 1.1 simplifies to

$$V = \sum_{\mathbf{R},\mathbf{R}',\mu,\nu} V_{\mu\nu}(\mathbf{R}, \mathbf{R}') \mathbf{u}_\mu(\mathbf{R}) \mathbf{u}_\nu(\mathbf{R}'). \quad (1.5)$$

In writing Eq. 1.5, we have neglected terms higher than order two in the displacement. This is called the harmonic approximation. To connect
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this potential energy of the lattice with the equation of motions of the atoms, let us write down the Lagrangian of the system,

$$ L = T - V = \frac{1}{2M} \sum_{R, \mu} \dot{u}_\mu(R)^2 - \frac{1}{2} \sum_{R, R', \mu, \nu} V_{\mu \nu}(R, R') u_\mu(R) u_\nu(R') $$

From the equation of motion,

$$ \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{u}_\mu(R)} \right) = \frac{\partial L}{\partial u_\mu(R)} $$

We obtain,

$$ M \ddot{u}_\mu = - \sum_{R'} V_{\mu \nu}(R, R') u_\nu(R') $$

In matrix form the above equation can be written as,

$$ \ddot{u} = Du $$

Where $D$ is the dynamical matrix$[1, 2]$ - the elements of which are given by

$$ D_{\mu \nu} = \frac{1}{\sqrt{M}} V_{\mu \nu}(R, R'). $$

Now, in Eq. 1.8 $-V_{\mu \nu}(R, R') u_\nu(R')$ represents the force exerted in the $\mu$-direction on the atom on $R^{th}$ site due to the displacement $u_\mu(R')$ of the atom on $R'^{th}$ site in $\nu$-direction. Thus $D$ contains information about the local force constants between any two interacting lattice sites. However due to the singularity in the potential energy, the dynamical matrix can not be defined in the above way for an ideal hard sphere system. In the present experiments we have access to the particle displacements at any instant of time. Therefore, we have used covariance matrix $[5, 6]$ (see chapter 3) of displacement to obtain the eigen frequencies and normal modes of the system.

The Dispersion Equation

Dispersion most often refers to frequency-dependent effects in wave propagation. The dispersion relation describes the interrelations of wave properties like wavelength, frequency, velocities, refraction index and attenuation coefficient. In the present context we consider frequency as a
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function of the wave-vectors, $\omega = \omega(q)$. Such a function can be obtained starting from the equation of motion (Eq. 1.8) of the lattice. For a $N$ atom system, it would form a set of $3N$ coupled differential equations. Because of the translational symmetry of the lattice we seek a solution of the form,

$$u_\mu(R) = \varepsilon_\mu \exp[-i(\omega t - q \cdot R)] \quad (1.11)$$

Where $\varepsilon$ determine both the amplitude as well as the polarization of the vibrations and is independent of $R$. Equation (1.11) is essentially a plane wave propagating the lattice in the direction represented by the wave vector $q$. Substituting for $u_\mu(R)$ in Eq. 1.9 and taking out the time dependence on both the sides we finally obtain an eigenvalue equation,

$$-\omega^2 \varepsilon = D(q)\varepsilon$$

where,

$$D(q) = \sum_{R'} D_{\mu\nu}(R, R')e^{-iq[R-R']}.$$ 

From the symmetry properties of the $D(R)$ it follows that, $D_{\mu\nu}^*(q) = D_{\mu\nu}(-q)$. Thus $D(q)$ is a real three dimensional symmetric matrix, diagonalization of which leads to three real orthonormal eigenvectors $\varepsilon_s=1,2,3$ as well as corresponding eigenvalues $\omega_s$, which are respectively the polarization and frequency of the normal modes with wave vector $q$. There are $3N$ such solutions for a system with $N$ allowed values of $q$ which forms the three branches of the dispersion relations and all the set of $\{\omega\}$s together constitutes the vibrational spectrum of any solid.

1.2.2 Density of Modes

We now discuss another important concept related to the spectra namely the density of states. The number of vibrations corresponding to a range $d^3q \equiv dq_x dq_y dq_z$ of the values of components of the wave vector is $\frac{d^3q}{(2\pi)^3}$ per unit volume of the crystal [4]. The density of states $D(\omega)$, gives the number $D(\omega)d(\omega)$ of vibrations whose frequencies lie in a given range between $\omega$ and $\omega + d\omega$, and is a characteristic of the vibrational spectrum of a particular lattice.

The number $D(\omega)d(\omega)$ is the volume (divided by $8\pi^3$) in $q$ space that lies between two infinitesimally close surfaces of constant frequency, $\omega(q)=$constant. At each point in $q$-space, the gradient of the function
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Figure 1.1: Phonon density of states of Iron ($\alpha - Fe$) as obtained from inelastic neutron scattering data [7]. The discontinuities in the DOS are the Van-Hove singularities as the group velocity ($d\omega/dq$) approaches vanishing limit at certain wave vectors in the dispersion curve.

$\omega(q)$ is along the normal to the constant frequency surface. Therefore the distance between the two infinitesimally close surfaces ($q$-space) measured along the normal direction is given by,

$$dq_\perp = \frac{d\omega}{\nabla_q \omega} \quad (1.14)$$

Multiplying this with the infinitesimal area $dS_\omega$ of the constant frequency surface element and integrating it over the whole surface within the first zone on which $\omega_s(q) = \omega$ yields the general expression of the frequency distribution density as

$$D(\omega) = \sum_s \frac{1}{2\pi^3} \int \frac{dS_\omega}{\nabla \omega_s(q)} \quad (1.15)$$

where the subscript $s$ indicates different branches of dispersion relation. Note, that within the first zone the function $\omega = \omega(q)$ has a few saddle points. The existence of these stationary points where group velocity vanishes leads to singularities in the structure of $D(\omega)$. As in the electronic case, these singularities are known as Van-Hove singularities.
A typical density of states as obtained from the neutron scattering experiments is shown in Fig. 1.1.

### 1.2.3 Debye Scaling

In 1912, while describing the contribution of lattice vibrations to the specific heat, Debye proposed a simple model of wave propagation in a solid medium that he assumed to be isotropic and governed by a linear dispersion up to a maximum frequency of propagation, say $\omega_{\text{max}}$. This leads to a scalar dispersion relation, $\omega = cq$, where $c$ is the velocity of sound waves. Let us now find out what would be the density of modes in this case. The number of modes for any isotropic solid lying in the interval $dq$ would simply be proportional to the volume of the shell between $q$ and $q + dq$. Thus, for a given polarization the density of modes is given by \[ V \cdot \frac{4\pi q^2 dq}{(2\pi)^3} \], where $V$ is volume of the body. Substituting for the longitudinal polarization $q = \omega/c_l$ and for the transverse ones $q = \omega/c_t$, we find that the interval $d\omega$ contains altogether, \[ V \cdot \frac{\omega^2 d\omega}{2\pi^2} \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \] vibrations. If we now define a mean velocity as, \[ \bar{c} = \frac{1}{c_l^3} + \frac{2}{c_t^3} \], then the density of states becomes, \[ D(\omega) = V \cdot \frac{3\omega^2}{2\pi^2\bar{c}^3}. \] The behavior $D(\omega) \sim \omega^2$ in three dimension does not only hold for isotropic bodies but also for crystals where the velocity $\bar{c}$ is the velocity of sound waves averaged in a certain way. This scaling of the density of states eventually leads to the famous cubic temperature dependence of the specific heat $C_p \sim T^3$, in the limit of low temperatures. The Debye behavior is established directly in few phonon or neutron scattering experiments and largely by indirect verification of the temperature dependence of specific heat [3].

### 1.3 Disordered Systems

The interest in the physics of disordered systems largely originates from the fact that the thermodynamic behavior of materials with disorder
often changes significantly and show some intriguing phenomena like localization or frustration which are otherwise absent in their ordered counterparts. To construct a general formalism to analyze such systems.

Figure 1.2: Examples of disordered systems in nature -(1) Granular soil: amorphous distribution of athermal grains [9], (2) Scanning electron micrograph of a pure polystyrene foam where different sizes of gas filled pores are dispersed in a random arrangement [10], (3) SEM image of ‘photonic glass’ made up of disordered arrangement of mixture of sub-micron sized PMMA and polystyrene spheres [11].

poses a challenge due to the lack of symmetry and periodicity as opposed to the crystalline media and remains a matter of research. Disorder could be of various types - structural, dynamic or bond disorder (spin glasses). Here, we deal with structural glasses where the spatial arrangement of the particles are disordered and consequently each particle experiences a different environment than the other ones.

1.3.1 Phenomenology of Glasses

A glass is an amorphous (non-crystalline) solid material. The most familiar types of glass we find in our everyday life are those used in windows, or drinking cups are made of silica $SiO_2$ (75%) plus some additives. In science, however, the term glass is usually used in a much wider sense, which includes all the solids that have an amorphous structure and undergo a glass transition, where the viscosity becomes very high. Some examples are metallic alloys, ionic melts, aqueous solutions, molecular liquids, and polymers.
Traditionally glasses are obtained by supercooling a liquid below its glass transition temperature. Upon cooling from high temperatures, a liquid may crystallize at melting temperature $T_m$. A liquid that is cooled below $T_m$ without crystallizing is called a supercooled liquid. As the supercooled liquid is cooled further it gets trapped in a glassy metastable state.

A qualitative description of such transitions is often based on the free energy landscape picture [8]. In this paradigm, a large number of local minima of the free energy exists. The glass transition occurs when the timescale of transitions among the glassy minima becomes so long that the system is confined in a single ‘valley’ of the landscape over experimentally accessible timescales. The characteristic of the glass transition is thus marked by the slow dynamics and the large relaxation time as well as the viscosity that can grow several orders of magnitude over a relatively small temperature interval. The temperature at which the

![Figure 1.3: Normalized intermediate scattering functions $f(q, t)$ at different volume fractions of the suspensions of colloidal PMMA spheres measured at $q \approx q_m$, where $q_m$ is the main peak in the static structure factor by Pusey et al [15]. For relatively dilute suspensions, $\phi \leq 0.528$ density fluctuations decay completely within the experimental observation time whereas for higher volume fractions $\phi \geq 0.57$ the decay remain incomplete. Finally for $\phi \geq 0.58$, $f(q, t)$ attains essentially a flat plateau value $f(q, \infty)$ showing the non-ergodic behavior of the system.](image)
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Relaxation times of the supercooled liquid becomes longer than the observation time is called glass transition temperature $T_g$. Experimentally $T_g$ is defined as the temperature at which viscosity reaches $10^{13}$ Pa.s or the relaxation time becomes larger than 100s. The slow dynamics leads also to non-ergodic behavior which is well studied in several dynamic light scattering measurements [12]-[15]. These experiments measured the decay of self intermediate scattering function $f(q,t)$ of colloidal suspensions at different volume fractions. One of those early experiments by Pusey et al [15] is shown in Fig. 1.3. For relatively dilute suspensions $f(q,t)$ decays completely within experimental observation time whereas the $f(q,t)$ at at higher volume fractions ($\phi > 0.57$) does not decay to zero on the experimental time scale. This illustrates the transition from the ergodic to non-ergodic dynamics. The emergence of such non-ergodicity is perceived as a signature of the glass transition in any system.

1.3.2 Excess Modes in Glasses

In sec 3.4 and sec 1.2.3 we have discussed the density of states and the low frequency Debye scaling $D(\omega) \sim \omega^2$ of the DOS of a crystalline solid. The above scaling leads to the Debye $T^3$ law in the limit of low temperatures where the specific heat of the solid shows a cubic dependence on temperature, $C_p \sim T^3$. However, glassy and amorphous materials exhibit low temperature properties that deviate significantly from the Debye behavior. For example, the $C_p/T^3$ as a function of temperature shows a peak at low temperature. Other features are the existence of a plateau in the $T$ dependence of the thermal conductivity [16] - [18] and the Boson peak [16] observed in the inelastic light or neutron scattering experiments [19, 20]. This suggests the existence of an excess number of low frequency modes in the density of states of these systems compared to crystalline solids. Several numerical studies have observed such enhancement of modes in the DOS of glassy systems. A recent study by Ning Xu et al [3] observed excess modes in a repulsive model glasses in which particles interact through a Lennard-Jones potential. Another study by Wyart et al [6, 23] reports similar observations in a dense system of hard discs.

In the present thesis, one of our main findings is the observation of these anomalous modes in a colloidal system. In particular, we have studied suspensions of hard sphere colloids. The confocal techniques used to
probe the structure and dynamics of the colloidal particles enables a direct visualization of these modes, which helps us further in understanding their nature.

1.4 Present Thesis

This thesis presents experimental measurement of the vibrational spectrum and normal modes in a hard sphere colloidal system. Here is a short outline of the chapters.

Chapter 2: The experimental techniques and the preparation procedure of the colloidal samples is discussed in detail. A general discussion about colloids, the hard sphere phase diagram and different aspects of confocal microscopy is given.

Chapter 3: Here we discuss the density of states of hard sphere colloidal suspensions as obtained from the measured particle displacement using confocal microscopy. A range of volume fractions from supercooled liquid up to a dense glassy phase \( \phi = 0.54, 0.57, 0.58, 0.59, 0.60 \) have been measured. The DOS shows the existence of an excess number of modes at low frequencies. The noise due to the finite resolution in measuring particle positions and its effect on the DOS is discussed. These results are complemented with Monte-Carlo simulations by Jorge Kurchan and Romain Mari on hard sphere glasses.

Chapter 4: We present the normal modes of the colloidal system at different frequencies. The lowest frequency normal modes show correlated motion. The spatial extent of the correlations is investigated for different volume fractions. The degree of localization of these modes have been measured by calculating the participation ratios.

Chapter 5: We have studied the structural relaxation of a hard-sphere colloidal glass. The dynamics of the particles exhibit 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 using normal mode analysis. The low frequency modes display 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.

Chapter 6: Here, we present the density of states and low frequency modes of a two dimensional section of an 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 shows anomalous scaling compared to the expected Debye scaling. With the help of elasticity theory (A. C. Maggs) we show that such anomalous scaling is indeed the Debye behavior for a projected two dimensional system.
Bibliography


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