CHAPTER-1
1.1. INTRODUCTION

One of the most fascinating aspects of physics is its ability to describe phenomena on vastly different length scales, from submicroscopic world of atomic nuclei ($10^{-15}$ m) to the dynamics of the universe as a whole ($10^{26}$ m). In general, different physical descriptions are associated with each distinct range of length scale. Thus, one distinguishes between microscopic, mesoscopic and macroscopic systems. The microscopic world comprises of atoms and molecules, whereas the macroscopic world ranges from objects accessible to our everyday experience to cosmological distances. Mesoscopic systems bridge the range between microscopic and macroscopic length scales and they refer to the region where microscopic behavior gradually changes into macroscopic or vice versa. The scientific interest in mesoscopic phenomena stems from this exceptional role.

Colloidal suspensions, which constitute the subject matter of this thesis, are a particular kind of mesoscopic system. These are composite systems consisting of a fluid and dispersed particles of size much larger than the molecules in the fluid. The size of these colloidal particles is typically in the range from 10 nm to 1 μm [1-4]. The lower limit in size comes from the requirement that the colloids are significantly larger than the solvent molecules, and the upper limit ensures that Brownian motion of the colloidal particles is not dominated by sedimentation effect under gravity. The multi component nature and the many-body interactions in these suspensions lead to highly complex phenomena making their scientific investigation challenging. The study of these systems is further complicated because of arbitrary size and shape of the colloidal particles. Fortunately, over the past three decades, synthesis of monodisperse spherical particles with a very narrow size distribution [1-4] has paved the way to elucidate many novel and fascinating properties of colloids under both equilibrium and non-equilibrium conditions. Under suitable conditions, these systems exhibit crystalline [5-6], liquid-like [7-9], gas-like [10] and even glass-like structural ordering [11,12], which are similar to those found in atomic systems. The striking closeness of the magnitude of the elastic constants ($E \sim U \eta_p$, where $U$ is the interparticle interaction
energy and \( n_p \) is the particle concentration) \([13, 14]\) and latent heat of melting \([15]\) of colloidal crystals (when expressed in units of “per mole”) with those of atomic solids allow one to regard colloidal suspensions as scaled-up versions of atomic solids. A colloidal dispersion with \( n_p \sim 10^{13} \text{ cm}^3 \) has \( \sim 10 \text{ dynes/cm}^2 \) as the typical value of elastic constants. On the other hand atomic solids with atomic density \( 10^{23} \text{ cm}^3 \) have elastic constants \( \sim 10^{10} \text{ dynes/cm}^2 \). The perfect scaling of the magnitudes of physical constants with particle concentration suggests that the interparticle interaction energy \( U \) in colloids must be of the same order as the interatomic interaction in atomic systems. Since the dimension of the colloidal particle is three orders of magnitude more than that of atomic dimension, the time scales of particle diffusion and all the phenomena that are governed by diffusion are also scaled appropriately. So the time scale of colloidal particle motion varies from microseconds to several seconds, which is easily accessible in experiments such as dynamic light scattering (DLS), digital video microscopy (DVM) and confocal laser scanning microscope (CLSM). Because of this fact, kinetic phenomena like nucleation and growth of crystals, which were difficult to understand through atomic systems, can now be understood through colloidal systems \([6]\). These facts led many researchers to treat colloids as a “model” condensed matter system and investigate many such effects and phenomena that are otherwise difficult to probe in atomic systems.

Colloidal suspensions fall into two categories, namely lyophilic (solvent loving) and lyophobic (solvent fearing) \([4]\). The former are thermodynamically stable and the free energy decreases on their formation from the starting component. Some examples are gelatin sol, solutions of proteins, synthetic polymers, soda and micro emulsions. On the other hand, the lyophobic colloids require extra energy in their formation due to large interfacial free energy between the particles and the solvent. These particles need a protective mechanism to prevent their agglomerations. This mechanism can be provided either by electric charge on the surface resulting in electrostatic repulsion between the particles (called charge stabilization) or by the adsorption of large molecules to the particles (called steric stabilization). Some examples of these are aqueous solution of charged polystyrene spheres, aqueous solutions of gold, AgI, Fe₂O₃ and SiO₂. Sterically stabilized suspensions are the practical realization of hard sphere systems \([11]\). Polymethyl-methacrylate (PMMA) particles serve as nearly hard sphere suspensions and have been used to study fluid-solid transition and glass
transition [11]. Apart from their fundamental interest, colloidal suspensions have technological importance. Colloidal arrays are now used in high-tech applications such as Bragg-diffraction devices [16], nano-switches [17,18], chemical sensors [19] and templates for preparing photonic band gap materials [20,21].

1.2. CHARGED COLLOIDAL SYSTEMS

Aqueous suspensions of polystyrene particles or silica particles are examples of charged colloidal systems [4,22]. In charged colloidal systems, each of the colloidal particles consists of large number of styrene polymeric chains entangled in a coil. Each of these chains starts and ends with an acidic group like \(-\text{KSO}_4\). These polystyrene spheres, when dispersed in a polar solvent like water with high dielectric constant \(\varepsilon (\sim 80)\) acquire negative charges (500 \(e\) for particles of diameter 100 nm, \(e\) = electronic charge) on the surface due to dissociation of the above acidic group [4] and the cations (\(K^+\)) liberated are known as counterions. The colloidal particles with negative charge on the surfaces are known as macroions. Similarly in the case of silica particles, the dissociation group is SiOH [22] and the counterions are \(H^+\) ions. Essentially, counterions are located around the negative charged particles forming a diffuse electric double layer.

![Schematic diagram of charged colloidal systems.](image)

As shown in Fig. 1.1, in addition to the presence of macroions and counterions, the aqueous medium also contains stray ions or salt ions (e.g. Na\(^+\), Cl\(^-\) etc.), which are known as impurity ions. Counterions and other impurity ions screen the Columbic
interaction between the negatively charged colloidal particles. The inverse Debye screening length is given by,
\[ \kappa = \frac{4\pi e^2}{\varepsilon k_B T} (n_z Z_r + C_i) \]  
(1.1)
and
\[ C_i = \sum_i n_i z_i^2 \]  
(1.2)
where \( n_z \) is the particle concentration, \( Z_r \) is the effective charge on the particle, \( C_i \) is the impurity ion concentration, \( n_i \) is the concentration of impurity ions of valence \( z_i \) (for monovalent impurity ions, \( C_i = n_i \)), \( k_B \) is the Boltzmann constant, \( T \) is the temperature and \( \varepsilon \) is the dielectric constant of the medium. In this thesis impurity ions are assumed to be monovalent. The advantage in charged colloidal systems over atomic systems is that the range and strength of the interparticle interaction energy \( U \) can be varied over a wide range by changing \( \kappa \) which can be changed by changing \( n_p, Z_r \) or \( C_i \). These systems exhibit almost all the phases that are observed in atomic systems and their phase diagrams containing liquid, crystalline [both body centered cubic (BCC) and face centered cubic (FCC)] and glassy phases have been reported in literature [23,24]. One of the most fascinating properties of charged colloids is the appearance of long-range order (colloidal crystals) even under extremely dilute volume fraction \( \phi \leq 0.001 \), \( \phi = \pi d^3 n_p / 6 \), where \( d \) is the diameter of the particle). Strong electrostatic interaction between negatively charged colloidal particles is responsible for the crystalline order.

1.3. INTERPARTICLE INTERACTIONS AND PHASE TRANSITIONS

Ordering phenomena and related phase transitions occur mainly because of the competition between the interaction energy \( U \) and thermal energy \( k_BT \). Phase transitions in atomic systems are generally achieved by varying the thermal energy \( k_BT \) relative to the interaction energy \( U \), whereas in the case of charged colloidal systems, the phase transitions are brought out by changing \( U \) relative to \( k_BT \). \( U \) can be varied over a wide range by changing the suspension parameters such as particle concentration \( n_p \), impurity ion concentration \( C_i \), charge on the particle \( Z_r \) and polydispersity in size and charge. For charged colloidal system temperature is not the appropriate parameter to study the phase transition. Since the dielectric constant of the
medium, $\varepsilon$ varies as $T^{1.5}$, temperature is a weak variable. The parameter equivalent to temperature is $C_s$. Thus by increasing $C_s$, the colloidal crystal can be melted into a colloidal liquid. Since increase in $C_s$ decreases $U$ and hence the effective temperature $T' (= k_B T / U)$ increases. In a colloidal suspension, the parameter equivalent to pressure is the osmotic pressure, which can be controlled by varying $n_p$. As mentioned in the last section, the electric double layer formed around the negatively charged colloidal particle (Fig. 1.1) can expand or shrink as a function of the impurity ion concentration.

1.3.1. DLVO Theory

Theoretical analysis of the equilibrium structure and properties of the interacting colloidal suspensions require a reliable input of the interparticle interaction potential $U$. The total interaction potential $U_I(r)$ is generally written as sum of the London-van der Waals attraction $U_d(r)$ and the screened Coulomb electrostatic repulsion $U_R(r)$, where $r$ is the distance between the centers of the macroions.

$$U_I(r) = U_R(r) + U_d(r)$$ (1.3)

This theory was developed by Derjaguin, Landau, Verwey and Overbeck [25,26] to understand the stability of colloidal suspension and is known as DLVO theory. The major underlying assumptions behind the DLVO theory are the following.

1) Motion of large size particles (macroions) can be thought of as adiabatically cut off from those of small ions (counterions).

2) Linearized Poisson-Boltzmann equation is used to calculate the total electrostatic energy.

3) A primitive model is used with the solvent treated as a continuum.

4) Debye charging process is used to charge ions.

Born repulsion, which occurs at very short separations, can be neglected as the probability of finding two colloidal particles at very close separations ($\sim \AA$) is extremely small in electrostatically stabilized suspensions. The London-van der Waal
attraction energy between two identical spheres of radius ‘\( a \)’ separated by a distance ‘\( r \)’ is given by [27],

\[
U_c(r) = \frac{H_c}{6} \left( \frac{2a^2}{r^3} \ln \frac{r^2}{4a^2} + \frac{2a^2}{r} \ln \frac{r^2}{4a^2} \right)
\]  

(1.4)

\( H_c \) is the Hamaker constant, which depends on the polarizabilities of macroions and solvent and has units of energy.

The repulsive interaction between two particles separated at a distance ‘\( r \)’ is given by,

\[
U_R(r) = \frac{Z^2 e^2}{\varepsilon} \frac{\gamma}{1 + \kappa a} \left( \frac{e^\kappa}{r} \right)
\]  

(1.5)

where \( \left( \frac{e^\kappa}{1 + \kappa a} \right) \) is the geometrical factor, which arises due to the finite size of the colloidal particle. \( U_R(r) \) without the geometrical factor is known as Yukawa potential and is given by,

\[
U_Y(r) = \frac{Z^2 e^2}{\varepsilon} e^{-\kappa r}
\]

(1.5a)

whereas Eq. 1.5 is known as Size Corrected Yukawa (SCY) potential.

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**Fig. 1.2** Total potential energy \( U_T/r_kT \) as a function of \( r/d \). Parameters are \( \phi = 0.0012 \), \( Z_e = 600 \), \( C_e = 50 \mu M \), \( d = 2a = 110 \text{ nm} \). Inset (A) shows primary minimum of the Coulomb barrier very close to the particle. Inset (B) shows the secondary minimum of extremely small depth, which occurs at a distance of \( r \approx 47d \). [adapted from the Book, edited by A.K. Arora and B.V.R. Tata, “Ordering and Phase Transitions in Charged Colloids”, VCH Publisher, ch. 1, P. 7, 1998].
Figure 1.2 shows $U(r)/k_B T$ as a function of $r/d$ for $d = 110 \text{ nm}$, $Z_e = 600$, $n_p = 1.33 \times 10^{12} \text{ cm}^3$, $C_s = 50 \text{ } \mu M$ (micro mole), $\varepsilon = 78$, $H_e = 10^{-13} \text{ erg}$. Here $d$ is the particle diameter. Here it is important to note that normally in all calculations, the effective charge $Z_e e$ on the colloidal particle is taken into account, which is different from the actual charge. If $Z$ is the total number of ionizable sites on the surface of the particle, then $Z_e = fZ$. $f$ is the degree of dissociation. Since all the sites on the surface of the particle do not dissociate, $f$ varies from 0.05 to 0.4. Effective charge, $Z_e e$ is determined from conductivity measurements [4] and $Z$ is determined from conductometric titration [4].

When the particle surfaces are less than $6A$ apart, attraction dominates. The van der Waals interaction introduces a primary minimum at very small interparticle separation and a shallow secondary minimum at a distance that is several times the diameter of the particle. The primary minimum (inset A, Fig. 1.2) near $r = d$ has a depth of more than $1000 \ k_B T$ and the repulsive barrier of height $1200 \ k_B T$ occurs at $r = 1.006 d$. Thus the particles cannot overcome the repulsive barrier and are prevented from seeing the primary minimum resulting in a stable dispersion. Since the attractive interaction falls slower ($\sim r^6$) than the repulsive interaction ($\sim e^{-r}$), the total potential energy shows a negative portion called the secondary minimum. It is shown in inset B of Fig. 1.2. The secondary minimum occurs at $\sim 47d$ with a well depth of $4 \times 10^{-9} \ k_B T$. This well depth is too small to bind the particles together. Hence in a stable suspension, $U_b(r)$ is the dominant interaction. For all practical purposes, where ordering is observed at low ionic strength, the attractive part of the DLVO potential can be ignored and the total potential energy, $U_T(r)$ is equal to the size corrected $U_b(r)$.

DLVO potential has been extensively used to explain ordering and phase transitions in homogeneous charged colloidal suspensions. A suspension is said to be homogeneous if the particles dispersed in the solvent occupy the entire volume of the suspension with uniform distribution. The average interparticle separation $d_o$ in such a suspension is given as $d_o = An_p^{-1/3}$ [where the value of $A$ depends on the type of the structural ordering of the system. $A = 1.0911$ for BCC and $A = 1.1266$ for FCC]. The screened Coulomb repulsive pair-interaction given by DLVO theory could explain the occurrence of crystalline, liquid-like, glass-like structures as well as the
melting/freezing behavior [24,28-29]. Lindmann criterion for melting and Hansen-Verlet criterion for freezing are also found to be valid in the case of charged colloidal suspensions [30-32]. Further, the phase transitions as a function of charge polydispersity have been studied extensively in the past by Tata et al. [28,32-33].

Though DLVO theory has explained all the phenomena related to structural ordering and phase transitions in homogeneous suspensions of charged colloids, it has been challenged over the last decade by experiments on dilute suspensions of highly charged colloids at low $C_s$. Reentrant transition [34], Vapor-Liquid transition (VL) [35-38], stable voids coexisting with ordered or disordered regions [39-41] have been cited as evidence for the existence of long-range attraction in the effective interparticle interaction, not captured by DLVO theory. These observations are briefly discussed below.

i) **Vapor-liquid Coexistence and Reentrant Transition**

Phase separation analogous to vapor-liquid condensation in atomic systems has been reported in dilute colloidal suspensions of polystyrene particles when either the impurity ion concentration is decreased or the volume fraction is increased [35-38]. Deionized suspensions have exhibited VL coexistence in the form of dense and rare phase below a critical volume fraction ($\phi < 1.12 \times 10^{-3}$) [37]. Dilute suspensions having a homogeneous gas-like ordering at high values of $C_s$ showed phase separation as $C_s$ is lowered. On further reduction of $C_s$, the suspension reentered a homogeneous liquid-like order. Hence as a function of salt concentrations, suspensions at dilute volume fraction show a reentrant order-disorder transition [35].

ii) **Coexistence of Voids with Ordered and Disordered Regions**

Experimental investigation on aqueous suspensions of polystyrene particles having high value of effective charge has shown coexistence of voids with ordered and disordered regions [39-41].
iii) Reentrant Solid-Liquid Transition

Recently Yamanaka et al. [22] and Toyotoma et al. [42] have investigated the phase behavior of suspensions of colloidal silica and polystyrene particles using ultra small angle X-ray scattering (USAXS) technique [28] to study the influence of effective surface charge density ($\sigma_c$). As a function of $\sigma_c$, the suspensions show a transition from liquid-like order to a crystalline order. Further at higher $\sigma_c$, the suspension once again exhibits a liquid-like disorder. This reentrant disorder state is reported to be inhomogeneous.

Using the pair potential given by DLVO theory, one cannot understand the above experimental observations. These results have been understood through Monte carlo simulations [40,43-45] using a long-range attractive potential, given by Sogami-Ise theory [46].

1.3.2. Sogami-Ise Theory

Sogami and Ise have developed a theory [46] of electrostatic interaction for charge stabilized colloidal suspensions based on Gibbs free energy. Their theory is based on the following assumptions.

1) The motion of large size particles (macroions) can be thought of as adiabatically cut off from those of small ions (counterions).
2) Linearized Poission-Boltzmann equation is used to calculate the total electrostatic energy.
3) A primitive model is used with the solvent treated as a continuum.
4) Debye charging process is used to charge ions.
5) Colloidal suspension need not occupy the entire volume of the solvent.

It can be seen that the assumptions 1-4 are same as that of the assumptions in DLVO theory except the fifth assumption. According to the fifth assumption, the solution volume is affected by the presence of highly charged macroions. So Sogami and Ise [46] derived a pair potential $U_{ij}(r)$ based on Gibbs free energy. The effective pair-potential contains a long-range attractive term that dominates at large $'r'$, in
addition to the usual screened Coulomb repulsive term given by DLVO theory. The Sogami pair-potential \( U_s(r) \) is given by,

\[
U_s(r) = \frac{Z^2 e^2}{2\epsilon} \left( \frac{\sinh(\kappa a)}{\kappa a} \right)^2 \left( \frac{A}{r} - \kappa \right) \kappa^{-\nu}
\]

(1.6)

where, \( A = 2[1 + \tanh(\kappa a)] \).

This potential has a secondary minimum at

\[
R_m = \left\{ A + [A (A + 4)]^{1/2} \right\}/2\kappa.
\]

(1.7)

and its depth is given by \( U_m = U_s(R_m) \). The primary minimum which occurs at less than 10 Å is due to the van der Walls attraction.

The dependence of \( R_m \) and \( U_m \) on \( \kappa d \) is shown in Fig. 1.3. It can be seen from Fig.1.3 (A) that \( R_m \) decreases monotonically as \( \kappa d \) increases, whereas \( U_m \) exhibits a non-monotonic dependence (Fig. 1.3 (B)). Further, \( U_s(r) \) at several values of \( \kappa d \) is shown in Fig. 1.4. It can be seen that the minimum of \( U_s(r) \) in Fig. 1.4 (curve ‘a’, ‘b’ and ‘c’) is different from that of van der Waals secondary minimum, which was, discussed earlier (inset B of Fig. 1.2). The position of average interparticle separation \( d_n \) corresponding to the volume fraction \( \phi (=0.005) \) is shown as a vertical line. At low value of \( \kappa d \), if the position of the minimum at \( r = R_m > d_n \) (curve ‘a’, Fig. 1.4), the particles essentially experience the repulsive part of the pair-potential \( U_s(r) \) given in Eq. 1.6. Hence for a homogeneous suspension, the structural ordering and phase transitions can also be explained using the pair potential \( U_s(r) \), which were earlier understood on the basis of DLVO potential. Ito et al. [47] have obtained the same values of elastic constants that had been earlier obtained using size corrected Yukawa potential \( (U_s(r)) \). It has shown that \( U_s(r) \) can also predict a solid-liquid (order-disorder) transition [48]. Tata et. al. [49] have shown using computer simulations that both \( U_s(r) \) and \( U_s(r) \) fit the structure factor of a homogeneous liquid-like ordered dispersion equally well. The photo thermal compression of colloidal crystals [50],

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which was earlier explained using $U_{\phi}(r)$, has also been understood on the basis of $U_4(r)$.

![Diagram](image)

**Fig. 1.3 (A) $R_m/d$ and (B) $U_{m}/k_BT$ as a function of $\kappa d$. $\phi = 0.005$, $d=120$ nm, $C_v = 2.0 \mu M$.**

On the other hand, at high value of $\kappa d$, $R_m < d$ (curve ‘b’ and ‘c’ in Fig. 1.4) and the attractive part of the potential (Eq. 1.6) dominates. Because of the high value of the well depth $U_m$, particles experience attraction leading to an inhomogeneous state. This inhomogeneous state can be in the form of gas-liquid, gas-solid or coexistence of voids with ordered or disordered region.

![Diagram](image)

**Fig. 1.4 $U_4(r)/k_BT$ as a function of $r/d$ with $\phi = 0.005$ for different values of $\kappa d$. (a) $\sigma_v = 0.3 \mu C/cm^2$, $C_v = 2.0 \mu M$, $\kappa d = 0.96$ (b) $\sigma_v = 0.4 \mu C/cm^2$, $C_v = 2.0 \mu M$, $\kappa d = 1.06$ (c) $\sigma_v = 0.4 \mu C/cm^2$, $C_v = 10.0 \mu M$, $\kappa d = 1.54$. The vertical line is the position of the average interparticle separation, $d_o$.**
Even though the pair potential given by Sogami and Ise [46] could explain almost all the experimental evidences of long-range attraction, this formalism has come under some criticism by Overbeek [51] and Woodward [52]. But later on these problems where sorted by Ise et al. [53], Smalley [54] and K. Schimtz [55,56].

1.3.3. Volume Term Theory

van Roji et al. [57-59] have proposed an alternative theory (called “volume term theory”) to explain the experimental observation of gas-liquid, gas-solid and coexistence of voids with ordered and disordered regions [35-41]. This theory is based on Helmholtz free energy of the system that arises from the Coulomb interaction between all species in the system. According to this theory, the potential energy between macroions in the effective one component Hamiltonian is given by

\[ V_{\text{eff}}^p (r_i) = \Phi_v + \sum_{i<j}^N U(r_{ij}) \]  

(1.8)

where \( \Phi_v \) is a state dependent term and \( N \) is the total number of particles. This \( \Phi_v \) is also called volume term, which is structure independent but state dependent. That is it does not depend on the coordinates of the macroions. The second term is the usual DLVO pair-potential. Its existence in the total interaction energy is a consequence of the reduction of multicomponent system (macroions and counterions) into an effective one-component system of dressed macroions. The volume term is given by,

\[ \Phi_v = F_{id} + k_B T \frac{\phi \bar{\sigma}} {l - \phi} V_{\text{sol}} - \frac{Z_i^2 e^2} {2 \varepsilon a} \frac{N \kappa a} {1 + \kappa a} - \frac{l \varepsilon \kappa^2} {2} (Z_e n_p)^2 V_{\text{sol}} \]  

(1.9)

\( F_{id} \) = Homogeneous ideal gas contribution from the ionic species. \( \bar{\sigma} = \frac{n^+ n^-} {n_i} \).

\( n_i = n^+ + n^- \). \( n^+ \) and \( n^- \) are the number density of the positive and negative ions present in the medium. Third term is the self-energy of the electrical double layers associated with the individual macroions or as the energy due to the potential well in which the colloidal particles reside because of the surrounding oppositely charged distribution of counterions. Fourth term is the excluded volume for the counterions, due to the hard core of the macroions. The third and fourth terms in the Eq. 1.9 are responsible for the spinoidal instability due to which phase separation occurs.

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The outcome of this theory is that the pair-potential between colloidal particles can remain repulsive as a function of interparticle distance $r$, yet a gas-liquid or gas-solid phase separation can occur due to volume terms which are responsible for the spinodal instability. Recently, Schmitz [60] has brought out a connection between the volume term theory and the long-range attraction in the Sogami pair potential between colloidal particles. Within the formalism of volume term theory, he has shown that the Sogami-Ise potential naturally arises from the screened Coulomb potential and the origin of the “attraction” which was attributed previously to the “electrostatic osmotic pressure” (in Sogami theory) is now attributed to the difference between the “Gibbs” and “Helmholtzs” free energy [60].

Recent calculations [61,62] based on Poisson Boltzmann (PB) cell model have clearly shown that the spinoidal instability prediction that arises due to volume term theory is spurious and is due to linearization of PB equation. The PB cell model shows that the non-linear PB calculations did not show any spinoidal instability.

1.3.4. Hydrodynamic Interaction

Apart from electrostatic interactions, hydrodynamic interactions are important because of the presence of intervening solvent medium. This arises because the motion of a given particle induces a flow field in the solvent, which will be felt by all the other particles and as a result these particles experience a force. It has been verified that hydrodynamic interaction in the ordered state is much stronger than in the case of disordered state [63]. Though all the phonon modes present in the ordered state of charged colloidal suspensions are overdamped because of hydrodynamic interaction, the long wavelength transverse mode can be propagative as predicted by the theory of hydrodynamic interaction [64,65]. So the lattice dynamics of a colloidal crystal presents a nice testing ground for investigating hydrodynamic interactions. A judicious choice of scattering geometry allows one to investigate these phonon modes, which can be easily accessible through dynamic light scattering method [64,65]. So far these studies are limited to only thin colloidal crystals of polystyrene suspensions at very dilute volume fractions ($\phi \sim 0.005$).
1.4. COMPUTER SIMULATIONS AND EXPERIMENTAL TECHNIQUES

In this section, various computer simulation techniques and experimental methods used for understanding the ordering and phase behavior of charged colloidal systems are briefly described.

Computer simulation provides a direct route to obtain macroscopic properties from microscopic details of a system. Computer simulations are performed in order to realize the physical properties of a system under actual experimental conditions. Mainly molecular dynamics (MD), Brownian dynamics (BD) and Monte carlo (MC) methods have been used for studying the phase behavior of colloidal systems. The following features are common to all three simulation methods.

a) Choosing a Simulation Box of Volume \( V \)

In order to simulate a system having particle concentration \( n_p (= N/V) \), where \( N = \) number of particles, \( V = \) total volume, the volume of simulation box is fixed from the \( N \). The value of \( N \) is chosen such that the equilibrium structure is independent of system size (i.e. independent of \( N \)).

b) Periodic Boundary Conditions

Periodic boundary conditions are applied to overcome the surface and finite size effects, thereby simulating more closely the behavior of an infinite system.

c) Choosing of the Initial Configuration

The initial configuration is chosen by placing the particles within the simulation box in a body centered cubic or face-centered cubic or in a random sites.

1.4.1. Molecular Dynamics Simulations

In the case of molecular dynamics (MD) simulations, one numerically solves the Newton’s equation of motion for a collection of particles [66], which interact via a
suitable interaction potential. Through the equation of motion, a natural time scale is
built in. The simulation classically samples the phase space deterministically. The
equation of motion is given by,

$$ m_i \ddot{r}_i = -\nabla \sum_{j \neq i} U(r_{ij}) $$

(1.10)

where, $U(r_{ij})$ is the interaction potential, $r_{ij}$ is the distance between the two particles $i$
and $j$, $m_i$ is the mass of $i^{th}$ particle. The right hand side of Eq. 1.10 gives the total force
acting on the $i^{th}$ particle. The starting configuration is chosen by assigning coordinates
and velocities to each particle. These velocities are usually drawn from a Maxwell-
Boltzmann distribution appropriate to the temperature of interest and selected in such a
way as to make the total linear momentum equal to zero. Subsequent particle
coordinates and velocities after a time $t + \Delta t$ are obtained by integrating the equation of
motion (Eq.1.10) using a suitable algorithm. Static and dynamic properties are obtained
as the time average over the dynamical history of the system [66]. MD simulation has
been used to simulate colloidal systems assuming the interaction to be that of Yukawa
form [67] as well that of the size corrected Yukawa (SCY) form [68]. Phenomological
criteria for melting/freezing transition, such as those of Lindemmann [69] and of Hansen
and Verlet [70] have been tested for colloidal systems using MD simulations [68,71].
The pair correlation function $g(r)$, obtained using MD simulations [72] has been
compared with that measured experimentally [73]. MD simulations also have been
used to simulate colloidal alloy and colloidal glass phases by considering binary
suspensions [74].

One disadvantage of MD simulations of colloidal system is that the effect of the
collision of solvent molecules with the large size colloidal particle is not taken into
account. In such a case, an approximate approach is adopted. The effect of solvent on
the motion of colloidal particles is represented by a combination of random forces and
a frictional term. Newton’s equations of motion are thus replaced by Langevin
equation. This is usually done in Brownian dynamics (BD) simulation.

1.4.2. Brownian Dynamic Simulations

In the case of Brownian dynamic (BD) simulations, the force acting on particles
from the background is treated stochastically. A general method for simulating the
motion of colloidal particles (in hydrodynamically dilute dispersions) in phase space is
given by Ermark [75,76]. The particle trajectories based on Ermark’s algorithm are
given by,

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{R}_i(\Delta t) + \left(\frac{D_0}{k_B T}\right)\vec{F}_i(t)\Delta t$$

(1.11)

Where $\vec{r}_i(t)$ is the position of the $i^{th}$ particle at time $t$ and $\vec{R}_i(\Delta t)$ is a Gaussian random
displacement representing the net effect of collisions of particles with the background molecules in the time interval $\Delta t$. $\vec{F}_i(t)$ is the direct force on $i^{th}$ particle due to remaining particles in the system, i.e.

$$\vec{F}_i = \sum_{j \neq i} \frac{\partial U(r_{ij})}{\partial r_{ij}} \frac{\vec{r}_i - \vec{r}_j}{r_{ij}}$$

(1.12)

and $D_0$ is the free diffusion constant. This coordinate space simulation is appropriate
only when the time step $\Delta t$ is much larger than the momentum relaxation time $\tau_R (= m_p f_r$, where $m_p$ is the mass of the particle and the frictional coefficient $f_r = 6\pi \eta a$, $\eta$ being the viscosity of the medium) and much smaller than the time $\tau_l$ over which the configuration of the particles appreciably changes. For a polystyrene particle of
diameter 100 nm in an aqueous medium ($\eta = 0.0089$ cp), the values of $\tau_R$ and $\tau_l$ are
$10^{-9}$ s and $10^{-3}$ s respectively [67]. The fundamental data available from the BD
simulations are the positions of the $N$ particles as a function time. From this
information, one may then obtain $g(r)$, $S(Q)$, mean square displacement (MSD),
$\langle r^2(t) \rangle$, van Hove space-time correlation functions and intermediate scattering function [66]. Gaylor et al. [77,78] van Megen and Snook [79] have used BD simulations to
simulate dilute as well as concentrated colloidal suspensions. Results obtained from
BD simulation have been compared with that measured using dynamic light scattering
and are found to agree well [77,78]. Tata et al. have also studied the structure factor
of charged colloidal suspension using BD [49]. Recently Wang et al. have performed
BD using Sogami potential ($U_s(r)$) to study void formation in charged colloidal
suspensions [80].
1.4.3. Monte Carlo Simulations

Monte Carlo (MC) method is used widely to simulate colloidal systems to obtain static information stochastically [81]. In the case of classical MC simulation, a system of $N$ particles interacting through some known potential is assigned a set of arbitrarily chosen initial coordinates; a sequence of configurations of the particles is then generated by successive random displacements. Not all configurations that occur are accepted, the decision whether to accept or reject a particular configuration being made in such a way as to ensure that, asymptotically, configuration space is sampled according to equilibrium probability density appropriate to the chosen ensemble. The ensemble average of a function of the particle coordinates such as potential energy is then obtained as an average over the resulting set of configurations. The particle momenta do not enter the calculation. No time scales are involved. MC simulations on colloidal systems have been discussed in detail by Castillo et al. [82] and Hirtzel and Rajagopalan [83]. Since there is no approximation involved in this, computer simulations give exact results. Here the coordinates of the $N$ particles as a function of Monte Carlo steps (MCS) are collected. These coordinates are used to calculate equilibrium quantities like pair-correlation function $g(r)$, structure factor $S(Q)$, first peak height in $S(Q)$, mean square displacement, (MSD) $\langle r^2(t) \rangle$. MC simulations have been used extensively to study structural ordering, dynamics and phase transitions in homogeneous charged colloidal suspensions using size corrected Yukawa potential [30-32]. Apart from these studies, Tata et al. have done extensive MC simulation studies using Sogami potential $U(r)$ to understand the occurrence of vapor-liquid condensation [37], reentrant transition [34], coexistence of voids with ordered and disordered regions [40] and BCC to FCC transition in homogeneous suspension [45].

1.5. EXPERIMENTAL TECHNIQUES

Scattering and microscopy are two important techniques to study the structural ordering, dynamics and phase transition in colloidal systems. These techniques are discussed briefly in this thesis.
1.5.1. Static Light Scattering and Dynamic Light Scattering

Since the interparticle separation is of the order of the wavelength of visible light and the time scale varies from microseconds to several seconds, static and dynamic light scattering are appropriate techniques to investigate structural ordering and dynamics in colloidal systems. In a static light scattering (SLS) experiment the scattered intensity $I_s$ is measured as a function of scattering angle ($\theta$), which is related to scattering wave vector $Q$ by

$$\frac{\lambda}{\mu} = \frac{4\pi\mu_m}{\lambda} \sin(\theta/2)$$  \hspace{1cm} (1.13)

where, $\lambda$ = wavelength of laser light, $\mu_m$ = refractive index of the medium. The static structure factor $S(Q)$ is calculated as a function of $Q$ after correcting for the form factor $P(Q)$ [84].

In a dynamic light scattering experiment, one measures the normalized intensity autocorrelation function, which is given by [84].

$$g^{(1)}(Q,t) = \frac{\langle I_s(Q,0)I_s(Q,t)\rangle}{\langle I_s(Q,0)\rangle^2}$$  \hspace{1cm} (1.14)

where $\langle I(Q,0)\rangle$ is the average intensity. The field correlation function, $g^{(2)}(Q,t)$ is then determined using Siegert relation [84] given by,

$$g^{(2)}(Q,t) = 1 + \delta |g^{(1)}(Q,t)|^2$$  \hspace{1cm} (1.15)

This relationship holds the Gaussian limit, i.e. where the electric field is a Gaussian random variable and $\delta$ is a factor that depends on the experimental geometry; It is roughly equal to the inverse of the number of speckles from which light is collected. Since the wavelength can be varied using different laser radiation, the range of $Q$ accessible in SLS and DLS lies between $2 \times 10^4$ cm$^{-1}$ to $3.5 \times 10^5$ cm$^{-1}$ (scattering angle lies between $10^6$ to $150^6$). SLS and DLS have been used extensively to study the ordering, dynamics and phase transitions in aqueous suspensions of polystyrene particles [28,64,65,84-88]. The disadvantage in this technique is the effect of multiple scattering, which occurs at higher volume fraction of colloidal suspensions. The effect of multiple scattering of light can be minimized either by using very dilute suspension ($\phi \leq 0.005$) or by matching the refractive index of the suspending fluid to that of the particles.
1.5.2. Small Angle X-ray and Neutron Scattering

Like SLS, Small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) techniques [89,90] are also used for studying the structural ordering in charged colloids. The usefulness of small angle scattering studies (both SASX and SANS) to colloidal systems becomes clear when one considers the length scales involved in the system. The average interparticle separation ($d_o$) is of the order of micron and the wavelength ($\lambda$) used in the case of x-ray and neutron scattering is very small ($\lambda_{x-ray} = 0.15 \text{ nm} \text { and } \lambda_{neutron} = 0.3 \text{ nm}$) compared to $d_o$. In order to probe such length, the scattering experiments are performed at small angle. The typical $Q$ range accessible in SAXS and SANS lies between $10^4$ to $10^7 \text{ cm}^{-1}$ (scattering angle lies between 0.01° to 5°). SAXS studies can be used to obtain information about structural ordering in concentrated colloidal suspension. For example, the first peak position for a suspension at $n_p = 2.3 \times 10^{16} \text{ cm}^{-3}$ occurs at $Q = 2 \times 10^5 \text{ cm}^{-1}$. This $Q$ range can be probed easily by SAXS and SANS instead of SLS. In this way, the multiple scattering can also be avoided. X-ray scattering depends on the electron density difference between the particles and the medium. If this electron density difference is small, the particles scatter poorly. So the scattering intensity is enhanced by using high-resolution synchrotron x-ray scattering. This was used to obtain the phase diagram of charged polystyrene colloids by varying $n_p$ and $C$ [23]. Using ultra small angle x-ray scattering (USAXS) method, the structural ordering can also be probed in dilute colloidal systems. Tata et al. have studied amorphous order in highly charged colloids using USAXS [40]. In SANS experiments the large difference between the scattering lengths of $^1\text{H}$ and $^2\text{H}_1$ can be used to build contrast. The contrast between the particles and the medium can be obtained by varying $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ ratio of the solvent. The energy of neutron is very small as compared to that of the X-ray. So SNAS studies are suitable for energy (heat) sensitive samples such as biological materials. Using SANS, shear induced phase transition in charged colloidal suspensions has been studied [91].

1.5.3. Digital Video Microscopy and Confocal Laser Scanning Microscopy

In suspensions of particle $d > 0.3 \mu \text{m}$, structural ordering phase transitions cannot be studied using light scattering methods because of multiple scattering effects.
This disadvantage can be overcome using optical microscope coupled with digital video imaging technique. Digital video microscopy (DVM) technique provides direct information on particle distribution in real space and real time, which is highly useful in elucidating various behaviors of particles in suspensions. Using this method one can get information about Brownian motion, ordering of particles, lattice vibrations, lattice defects, presence of stable voids in ordered and disordered colloidal suspensions. Structural parameter like pair-correlation function $g(r)$ and dynamical quantity like mean square displacement $<r^2(t)>$ are obtained from the particle coordinates. Particle coordinates are obtained by digitizing the image through an image analysis program. Ise et al [92-96] have extensively used DVM to investigate dilute charged polystyrene suspensions. Tata et al [32,33] have investigated the effect of dielectric boundary on the structural ordering of bulk charged colloidal suspensions using DVM. When the suspensions are turbid, the microscopic observation of particles deep inside the suspensions is difficult. Because of this, studies are limited to particles near the cover glass-dispersion interface or to very dilute dispersions. But the wall effect is often considered a serious problem. Another thing is that the contrast of images are poor because of the scattered light from other planes into the focal plane. Since depth resolution is not there in a conventional optical microscope, the information is limited to two dimensional (2D) only. All these problems are overcome by the use of confocal laser scanning microscope (CLSM). In a confocal microscope, the objective lens forms an image of the detector pinhole and the illuminating pinhole at the same spot in the focal plane, these are said to confocal to each other. In a CLSM, light reflected from any other parts of the sample including parts above or below the focal plane reach the edge of the detector pinhole are not detected by the detector. Hence the quality of the images are high. The selective rejection of light is responsible for formation of sharp images and increases depth resolution of confocal microscope. Since CLSM allows to image deep inside the suspension, the wall effects can be avoided. CLSM enables optical slicing and construction of three-dimensional (3D) images. Hence one can get 3D structural information. Tata et al have studied the presence of voids using CLSM in highly charged colloids [40]. The direct observation of dynamical heterogeneity in hard sphere colloids has been reported recently using CLSM [97,98].
1.6. MOTIVATION FOR THE PRESENT WORK

Colloidal Crystals (CCs) have small elastic constants (~ 10 dynes/cm$^3$) and are easily deformable by shear and compressible to a large extent by application of pressure (e.g. using a membrane permeable to solvent but not to the colloidal particles). There have been several studies on the phase behavior of colloidal suspensions under the application of shear [99-101], but pressure as a parameter has not been investigated either theoretically or experimentally. In order to investigate the structural ordering and phase transitions of charged colloidal suspensions under pressure, one needs to know the approximate range of pressure for freezing a liquid-like order suspension to colloidal crystal or in to a colloidal glass. With this as the motivation a detailed constant pressure Monte Carlo (MC) study has been carried out for different values of osmotic pressure. The transition pressures have been identified for liquid to crystal as well as liquid to glass transitions. This glass transition is analogous to that observed in the case of atomic liquids under pressure and temperature [102]. One of the striking features of liquids undergoing glass transition is that they exhibit non-exponential relaxation behavior [102-104]. This non-exponential behavior has been studied both using simulation [105-107] and experiments [108-109] in atomic systems. This non-exponential relaxation is believed to be due to the presence of 'dynamical heterogeneities' (DH) in the system [103-104]. Though simulations [105,106] on a Lennard-Jones (LJ) binary system undergoing glass transition have shown the existence of dynamical heterogeneities, the direct experimental evidence for the existence of dynamical heterogeneities has come only recently from studies on hard-sphere (HS) colloidal suspensions [97,98]. These studies have motivated us to carry out a detailed investigation close to glass transition of charged colloids under the application of pressure. The results of these investigations are reported in this thesis.

Since a colloidal particle is larger in size and heavier compared to an atom or a molecule, the time scale of a colloidal particle undergoing free Brownian motion in the medium is of the order of microseconds. In an interacting suspension, the dynamics of colloidal particles extends to several seconds due to structural rearrangement and cooperative motion. The entire range of time scales spanning over 7 to 8 orders of magnitude is accessible to dynamic light scattering (DLS) technique equipped with a multi-tau photon correlator. As discussed in section 1.4, the length scale of the spatial
ordering in interacting suspensions is of the order of wavelength of light. So SLS is the appropriate technique to characterize structural ordering in colloidal systems. Though, these techniques have been used extensively in the past to characterize structural ordering and dynamics in aqueous suspension of charged polystyrene particles [27,65,66,85-89], the domination of multiple scattering of light in aqueous polystyrene suspensions for volume fraction beyond 0.01 made these techniques seemingly unsuitable to probe the structure and dynamics. Multiple scattering can be suppressed to a large extent by dispersing the colloidal particles in a medium whose refractive index is close to the refractive index of the particle. With a motivation to study the structural ordering and dynamics in a charged colloidal suspension over a wide range of volume fraction, closely index-matched charged silica colloidal system is prepared by redispersing aqueous silica suspension in 80:20, ethylene glycol water (EGW) mixture. Since the refractive index of 80:20 EGW (~ 1.41) mixture is almost same as that of silica particle (~1.46), this suspension is found to be free from multiple scattering. So the static and dynamic light scattering studies are carried out over a wide range of $\phi$ (~ 0.0006 to 0.12) and the results are presented in this thesis.

Colloidal crystals (CCs) are known to have thermodynamic similarity to atomic crystals [64]. Electrostatic interactions are responsible for the ordering in charged colloidal suspensions. The lattice dynamics of colloidal crystals is greatly influenced by long-range hydrodynamic interactions, which arise due to the presence of the intervening fluid. Due to strong hydrodynamic friction, most of the eigenmodes (phonons) of CCs are over damped [64,65]. Dependence of the damping rates on the phonon wave vector ($q$), in other words phonon dispersion curves, were studied experimentally using DLS and also theoretically. The theory of lattice dynamics of colloidal crystals in general explains the dispersion curves of longitudinal modes observed in experiments [64,65,110]. However, disagreement remains regarding the behavior of transverse modes in the small $q$ regime. Contrary to theoretical predictions [64,65], DLS data shows that the decrement of the slow transverse mode vanishes when $q$ tends to zero. Earlier experiments are all on charged colloidal crystals of polystyrene particles contained in a thin-film cell and thin crystals were used to prevent multiple scattering of light in this system. This motivated us to study the lattice dynamics of colloidal crystals of large size (~ 3 mm) grown in a closely index matched systems (silica in ethylene-glycol mixtures) using DLS in order to verify the theoretical
prediction of the over-damped transverse modes turning propagative in long-wavelength limit. The phonon dispersion curves obtained from DLS data in the large size colloidal crystals are presented in this thesis. The measured dispersion curve for the transverse mode in the low \( q \) regime is in agreement with theory. These observations reported in this thesis provide for the first time evidence for the existence of long-wavelength propagating transverse modes in a bulk charged colloidal crystals.

As discussed in section 1.3, a purely repulsive screened coulomb repulsive pair-potential, given by DLVO theory cannot explain the observed reentrant order-disorder transition as a function of charge density on the particle [22,42]. A homogeneous liquid-like order suspension is found to undergo crystalline order upon increasing the \( \sigma_c \). Upon further increasing of \( \sigma_c \), the crystalline order is found to reenter into a disorder state once again. The latter observation has remained unexplained. This reentered disordered state is observed to be inhomogeneous. Hence it is not known under what condition, the inhomogeneous state turns homogenous once again. Motivated by their observation, detailed MC simulation studies as a function of \( \sigma_c \) and salt concentration \( C \), for the suspension parameter close to experimental condition were carried out and the results are discussed in this thesis.

MC simulations as a function of effective surface charge density, \( \sigma_c \), show that the homogeneous crystalline phase exists for a narrow range of \( \sigma_c \), whereas the ordered regions observed experimentally by Yamanaka et al. [22] and Toyotama et al. [42] exist at a relatively higher range of \( \sigma_c \). This leads to a discrepancy between experimental observations and simulations. In order to understand this discrepancy, SLS and confocal laser scanning microscopy studies are carried out on suspensions with a narrow range of charge density (\( \sigma_c = 0.24 \) to \( 0.5 \) \( \mu \text{C/cm}^2 \)) for different values of \( \phi \). These experimental studies have not only provided cause of the discrepancy but also confirmed the occurrence of gas-solid transition in highly charged colloids. These experimental results are reported in this thesis and the comparisons with MC simulation are also presented.
1.7. THESIS OVERVIEW AND IMPORTANT RESULTS

This thesis deals with the study of structural ordering, dynamics and phase transitions in charged colloidal suspensions induced by pressure, effective charge density and salt concentration. Apart from this, this thesis also reports static light scattering, dynamic light scattering and confocal microscope studies on homogeneous and inhomogeneous suspensions of charged colloids. Pressure induced phase transitions are investigated using constant pressure MC simulation techniques. Phase transitions as a function of charge density and salt concentration are investigated using constant volume MC simulation method. Further SLS and confocal microscope studies are performed on inhomogeneous phase of charged polystyrene suspensions. SLS and DLS experiments are carried out for a wide range of volume fraction in a silica ethylene glycol-water mixture. Further using DLS technique, the phonon dispersion curves are measured in charged silica colloidal crystals. The chapter wise break up is as follows:

Chapter 2 deals with the details of MC simulations and experimental methods used to investigate structural ordering, dynamics and phase transitions in charged colloidal suspensions. Constant volume (NVT), constant pressure (NPT) MC simulations are performed to simulate monodisperse charged colloidal systems. Computation details of structural parameters like pair correlation function, $g(r)$, structure factor, $S(Q)$, coordinate averaged pair correlation function, $g_c(r)$, height of the first peak in structure factor $S_{max}$ etc are presented. The calculation procedure of mean square displacement (MSD), $\langle r^2(t) \rangle$, which describes the diffusion of particles, is also reported. Apart from the simulation study, the theory and experimental methods of static and dynamic light scattering employed for investigating the structural ordering and dynamics of various phases in charged colloidal suspensions are explained. Details of the light scattering instrument, which is used to measure the structure as well as dynamics of the colloidal suspensions, are described in this chapter. Sample preparation and characterization of suspension parameters used for light scattering and CLSM studies are described.

Chapter 3 deals with the effect of pressure (osmotic pressure) on the phase behavior of charged colloids [111-113]. Constant NPT MC simulation program has
been developed to study the effect of pressure. Freezing of a colloidal liquid to a colloidal crystal under the application of pressure is studied by increasing the pressure sequentially. When subjected to a sudden pressure, the same colloidal liquid is found to undergo a glass transition. The dependence of $g(r)$ on pressure is investigated to identify structural ordering in different phases. Freezing into a crystalline state as well as into a glassy state is identified from the pressure dependence of $S_{\text{max}}$ and mean square displacement (MSD) [112]. The freezing transition is found to occur at $P_c = 4.8 \text{ dynes/cm}^2$. Knowledge of transition pressure $P_c$ is essential to identify the supercompressed liquid state and glass transition. Glass transition pressure is identified using the well-known Wendt-Abraham parameter $R_g = \frac{g_{\text{min}}}{g_{\text{max}}}$, where $g_{\text{min}}$ is the value of the first minimum of $g(r)$ and $g_{\text{max}}$ is height of the first peak in $g(r)$ and is found to occur at $P = 27 \text{ dynes/cm}^2$. For the first time, the glass transition is found to occur at a very low volume fraction ($\phi \approx 0.003$) as compared to the experimental observation of glass transition ($\phi \geq 0.2$) in monodisperse charged colloidal suspensions. Particle dynamics is studied from the behavior of MSD as a function of Monte Carlo Steps (MCS) at different pressures. In the supercompressed state (at $P = 20 \text{ dynes/cm}^2$), the MSD shows three stages in time. The characteristics of these three stages are discussed. This glass transition is analogous to that observed in the case of atomic liquids under pressure and temperature. One of the striking features of liquids undergoing glass transition is that they exhibit non-exponential relaxation behavior. This non-exponential behavior is due to the superposition of different relaxation processes or 'dynamical heterogeneities' (DH) present in these systems. Dynamical heterogeneities near a glass transition can be detected by investigating the time dependence of van Hove self-correlation function, $G(r, t)$. To a first approximation, $G(r, t)$ has a Gaussian form, referred to as $G_d(r, t)$, but deviation from this at intermediate times reflects the presence of dynamical heterogeneities. Such deviations are characterized by the non-Gaussian parameter, $\alpha_2(t)$. The procedure for calculating $\alpha_2(t)$ and its time dependence at different pressures is discussed in this chapter. Structural relaxation and cooperative motion of particles in the supercompressed liquid state of charged colloids are investigated by identifying the mobile ('fastest moving') and immobile ('slowest moving') particles. The criteria for identification of both the mobile and immobile particles are described in detail. It is found that number of both mobile and immobile particles are 5% of the total number of particles. Spatial
correlations of mobile as well as the immobile particles are investigated by calculating respective pair-correlation function. These mobile and immobile particles form clusters and are found to have strong spatial correlations. Cluster size distributions, \( I(h) \) are obtained and their dependence on the pressure is discussed [112].

Chapter 4 deals with the experimental study of structural ordering and dynamics in the silica ethylene glycol-water charged colloidal system over three orders of magnitude in volume fractions (\( \phi \approx 0.0006 \) to 0.12) [114,115]. Samples were prepared in 8 mm optical path length light scattering cells, by diluting the mother suspension with ethylene glycol/water mixtures at a ratio of 80:20. SLS and DLS measurements have been carried out on samples with different values of \( \phi \). Light scattering studies revealed that the suspension at \( \phi = 0.0006 \) is found to be gas-like. Suspensions with \( \phi < 0.02 \) is found to have liquid-like order and a crystalline order beyond this \( \phi \). The structure factors \( S(Q) \) as a function of scattering wave vector \( Q \) in each of the above phases are obtained from the angular dependence of scattered intensity \( I_s(Q) \). The particle dynamics in gas, liquid, and crystalline states is studied by measuring the intensity-intensity autocorrelation function, \( g^{(2)}(Q,t) \) at a given \( Q \). The electric field autocorrelation function, \( g^{(1)}(Q,t) \) is extracted from \( g^{(2)}(Q,t) \) using the Siegert-Relation [84]. The diffusion coefficients \( D_S \) and \( D_L \), which characterize the particle motion in a liquid-like ordered suspension at short and long times respectively are obtained by analyzing \( g^{(1)}(Q,t) \). The details of these calculations are reported in this chapter. For the crystalline state, \( g^{(1)}(Q,t) \) measured at peak position is found to exhibit very slow decay extending up to several seconds. The calculated MSD, \( \langle r^2(t) \rangle \) from \( g^{(1)}(Q,t) \) also shows saturation at long times. A shear melted liquid-like ordered suspension at \( \phi = 0.04 \), when subjected to a sudden compression by centrifuge, is found to freeze into a glassy state and the \( \phi \) obtained from the first peak position (\( Q_{max} \)) is found to be 0.12. The measured \( g^{(1)}(Q,t) \) at \( Q_{max} \) exhibits very slow decay and the estimated \( \langle r^2(t) \rangle \) shows tendency towards saturation as a function of time \( t \) [115]. These results are compared with those reported for aqueous latex suspensions.

Chapter 5 describes the measurement of phonon dispersion curves using dynamic light scattering technique on charged colloidal crystals of silica EGW system [115-117]. As already stated, in order to minimize the effect of multiple scattering and
also to grow relatively large size crystals, suspensions of silica particle dispersed in solvent of EGW mixture at ratio of 90 10 have been prepared. The use of 90 10 EGW mixture not only helped in matching the refractive index of the particle with the solvent, but also caused slower diffusion of the particles due to increase in the viscosity (viscosity of EGW mixture is 14 times higher than that of water). Samples are prepared over a wide volume fraction range ($\phi = 0.0006$ to 0.1) in 8 mm optical path light scattering cells. Crystallization is observed in samples with $\phi > 0.02$. Samples with $\phi = 0.05$ showed large size crystals (~3 mm) with (110) planes oriented perpendicular to the scattering plane. This sample is used for studying the phonon dispersion measurement. The sample cell is mounted on a home built xyz-stage, which has provision for rotation of the sample. By appropriately orienting the sample, the scattering wave vector $Q_{110}$ is made parallel to the phonon wave vector $q$. $g^{(2)}(Q,t)$ is measured at different values of $q$. $g^{(1)}(Q,t)$ is extracted from $g^{(2)}(Q,t)$. The longitudinal and transverse mode dispersion curves have been obtained by analyzing $g^{(1)}(Q,t)$. The transverse mode dispersion curve exhibited a shallow peak structure at small values of reduced wave vector ($q/Q_{110}$) as predicted by the theory of lattice dynamics with hydrodynamic interactions. This observation provides unambiguous evidence over the damped transverse modes turning propagative in the range of small wave vectors (long-wave length limit) in agreement with the theory of hydrodynamic interaction in charged CCs.

Chapter 6 describes the MC study of charged colloids as a function of effective surface charge density, $\sigma_e$ and salt concentration, $C_s$ [118]. $\sigma_e$ is varied over a range (0.05 $\mu$C/cm$^2$ to 0.6 $\mu$C/cm$^2$) where, as already stated, a reentrant solid-liquid transition in suspensions of silica and polymer latex particles has been reported. Simulations as a function of $\sigma_e$ show a homogeneous liquid-like order at a low $\sigma_e$, a homogeneous crystalline order at increasing $\sigma_e$ and a reentrant disordered state at high $\sigma_e$. The structural ordering in these states is identified by calculating the pair correlation function $g(r)$ and coordinate averaged pair correlation $g_c(r)$. In the reentrant disordered state, the disorder is found to be glass-like and is found to coexist with voids. The transitions from homogeneous liquid to homogeneous crystalline state (freezing) and homogeneous crystalline state to inhomogeneous disordered state are identified from the dependence of $S_{max}$ as a function of $\sigma_e$. The sudden increase in $S_{max}$ at
$\sigma_c = 0.23 \, \mu C/cm^2$ corresponds to the freezing transition and the sudden drop in $S_{max}$ at $\sigma_c = 0.33 \, \mu C/cm^2$ corresponds to the transition from homogeneous crystalline state to inhomogeneous state. The reentrant disordered phase is identified as a gas-solid coexistence state. These results are understood from the dependence of $U_c(r)$ on $\sigma_c$. These simulation results are found to be in agreement with the observed experimental results. Furthermore, in order to know under what conditions, the reentered disordered state would go to a homogeneous disordered state, MC simulations are carried out over a wide range of $C_i$. As the value of $C_i$ increases, structural correlation in $g(r)$ extends up to a few times the diameter of the particle. The first peak position in $g(r)$ is found to vary and matches exactly with $R_m$ (position at which the $U(r)$ shows a minimum).

Formations of dense phase clusters are also observed. In order to identify the nature (solid-like or liquid-like) of these clusters, $g(r)$ $g_2(r)$ and $\langle r^2 \rangle$ of particles within the clusters are calculated. From the analysis of these quantities, the clusters are identified to be solid-like in nature. At very high salt concentration ($C_i = 1000 \, \mu M$) $g(r)$ showed only a single peak at $r = R_m$ and the projection of particles in the MC cell are distributed uniformly. These observations suggest that the suspension with $C_i = 1000 \, \mu M$ is homogeneous and non-interacting (gas-like). Thus the reentrant disordered state undergoes a transition to a homogeneous disordered (gas-like) state as $C_i$ increases.

Chapter 7 deals with light scattering and confocal laser scanning microscopy (CLSM) studies on suspension of highly charged colloids [119,120]. It starts with the brief introduction to the past experimental and simulation results on the inhomogeneous state of suspensions at a high charge density. MC simulations study as a function of charge density show that the homogeneous crystalline phase exists for a narrow range of $\sigma_c$, whereas the crystalline region observed by Yamanaka et al. [22] and Toyotama et al. [42] exists at a relatively higher range of $\sigma_c$. Simulations have predicted the existence of an inhomogeneous crystalline state in the form of voids coexisting with ordered region. This has not been confirmed experimentally. Hence static light scattering studies have been performed with polystyrene suspensions with effective charge densities in the range of $\sigma_c = 0.24 - 0.5 \, \mu C/cm^2$. The concentration of the mother suspension is determined by the drying method. Samples are prepared between the above ranges of $\sigma_c$ for a wide range of volume fraction ($\phi = 0.0005$ to
(0.005) under denatured condition. The samples prepared between \( \sigma_r = 0.24 \) to \( 0.41 \, \mu C/cm^2 \) showed iridescence to naked eye due to Bragg diffraction of the visible light, whereas the samples with \( \sigma_r > 0.4 \, \mu C/cm^2 \) showed no iridescence to naked eye. These observations are in qualitative agreement with those of Yamanaka et al. [22] and Toyotoma et al. [42], which show that at higher \( \sigma_r \), the charged colloidal suspension is in the disordered state. Static light scattering (SLS) measurements on samples, which exhibited iridescence, show a shift in the first peak position of the structure factor \( S(Q) \). This suggests that the crystalline state is inhomogeneous. The measured volume fraction in the crystalline phase is found to be more than the original volume fraction. This observation indicates that crystals do not occupy the full volume in the suspension. The volume that is not occupied by the particles is expected to appear as particle-free regions (voids). CLSM study on the same sample confirmed the existence of voids, which coexist with ordered regions. MC simulations using \( U_c(r) \) close to the suspension parameters used in experiments also showed coexistence of ordered regions with voids. The SLS measurements on the sample with \( \sigma_r = 0.5 \, \mu C/cm^2 \) also show a shift in the position of the first peak \( S(Q) \). The CLSM study as well as MC simulations confirmed the coexistence of voids with glass-like disordered regions. Further, samples with volume fraction, \( \phi \) below 0.001 show macroscopic phase separation in the form of a dense phase at the bottom of the sample cell and a rare phase on the top. The dense phase shows iridescence and SLS measurements in the rare phase region indicate gas-like disorder. These studies provide unambiguous evidence for the occurrence of gas-solid transition in highly charged colloids. The agreement between experimental results and MC simulation results indicate the existence of long-range attraction in the effective interparticle interaction of like-charged colloids. These results are discussed in detail in this chapter.

The thesis ends with the chapter 8 consisting of a brief summary of the results obtained and the conclusions drawn.
REFERENCES


D Y C Chan, P Linse and S N Petris, *Lanmuir* 17, 4202 (2001)


Gen.* 8, 664 (1975).
83 C.S Hirtzel and R. Rajagopalan, in *Micellar Solutions and Microemulsions*,
Eds. Chen and R. Rajagopalan, (Spring-Verlag, New York, 1979), p. 1
85. B.J. Berne and R. Pecora *Dynamic Light Scattering with Applications to
86. F. Gruner, and W. P. Lehmann in *Light Scattering in Fluids and
Macromolecular Solutions*, Eds V. Degiorgio, M Corti and M. Gigho,
87 P.N. Pusey and R.J.A Tough in R Pecora in *Dynamic light Scattering
Applications of Photon Correlation Spectroscopy*, (Plenum, New York, 1985),
ch. 5.
113. P.S. Mohanty, B.V.R. Tata and M.C. Valsakumar (*communicated*).


120. P.S. Mohanty, B.V.R. Tata, J. Yamanaka and T. Sawada (*communicated*).