Two Dimensional Colloidal Assembly under an Alternating Electric Field: from Introduction to Structure

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Summary

The lateral assembly of charged, monodispersed colloidal particles into two dimensional (2D) ordered structures in the presence of an alternating current (AC) electric field has evoked much interest in the past two decades both experimentally and theoretically.

In this work, the transverse two-dimensional assembly of colloidal particles is studied by varying the frequency and field strength, in the absence and presence of an added electrolytes. The variation of the translational and bond-orientational correlation functions with frequency suggests the existence of a hexatic phase in which the particles retain the remnants of the crystalline long-range orientational order, but has a liquidlike translational order. The electrohydrodynamic (EHD) flow is analyzed in the light of the existing theoretical models put forward by Trau [16,43], and Sides [48,81] et al. It follows that the equilibrium distribution $r_{eq}$ of particles is considered to be the resultant of mainly two opposing forces-Stoke’s attractive force due to EHD flow, the repulsive screened Coulomb interaction, and dipole-dipole repulsions between the colloidal particles. The EHD flow is found to affect directly the particle aggregation, the equilibrium interparticle separation $r_{eq}$, which was also considered as functions of ionic strength and $\zeta$-potential.
In this aspect, the kinetics and equilibrium distribution ($r_{eq}$) of colloidal particles under an AC electric field are investigated by varying the frequency, field strength, and salt concentration. The variation of the aggregation rate constant as well as the order/crystallinity of the lattice can be correlated to the variation of the equilibrium interparticle separation $r_{eq}$ within the frequency window for the 2D assembly. Particle size, ionic concentration, and field strength also affect the mean equilibrium distance between neighboring particles, thus establishing that $r_{eq}$ can be used as a new criterion to examine the degree of perfection of a 2D colloidal assembly and the self-assembly process of colloidal particles. The understanding gained may be found useful in the design of self-assembled templates using colloidal particles.

The effect of temperature on the transverse 2D colloidal assembly was also examined. The dependence on temperature of the phase diagram of the equilibrium distance ($r_{eq}$) of the particles as a function of frequency was investigated which could be explained with the existing theoretical models based on electrohydrodynamic (EHD) flow. Furthermore, a facile method was developed to reversibly modulate the lattice space of 2D colloidal assembly over a wide range of temperature and the frequency and strength of AC electric field. Once the desired colloidal assembly formed, it could be permanently fixed by simply switching to a direct current (DC) electric field. The technique presented may find important applications in the field of photonic devices, chemical and biological sensors.
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Chapter 1

Introduction

1.1 Colloidal System

In general, a colloid or colloidal dispersion is a substance with components of one or two phases, a type of mixture intermediate between a homogeneous mixture (also called a solution) and a heterogeneous mixture with properties also intermediate between the two. Colloids are ubiquitous in nature and can be found in natural occurring materials such as blood, mud, sea or tap water, butter, milk or everyday consumer products such as toothpaste, paint and ink. (Table 1.1) This field of study was initiated by Scottish scientist Thomas Graham in 1861. [1–3]

The size of dispersed phase particles in a colloid ranges from nanometers to micrometers. Dispersions where the particle size is in this range are referred to as colloidal aerosols, colloidal emulsions, colloidal foams, or colloidal suspensions or
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Table 1.1: Classification of Colloids

<table>
<thead>
<tr>
<th></th>
<th>Gas</th>
<th>Liquid</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>NONE (All gases are soluble)</td>
<td>Liquid Aerosol Examples: Fog, mist</td>
<td>Solid Aerosol Examples: Smoke dust</td>
</tr>
<tr>
<td>Liquid</td>
<td>Foam Examples: Whipped cream</td>
<td>Emulsion Examples: Milk, hand cream</td>
<td>Sol Examples: Paint, pigmented blood</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid Foam Examples: Aerogel, styrofoam</td>
<td>Gel Examples: Jelly, cheese</td>
<td>Solid Sol Examples: Cranberrey glass, ruby glass</td>
</tr>
</tbody>
</table>

dispersions.

Overbeek [4] points out that monodisperse (or homodisperse or isodisperse) systems have allowed colloid science to make essential contributions to our understanding of the behavior of matter. The large family of colloidal particles exhibit many kinds of morphologies and different properties. [5–8]

From a colloidal point of view, flocculation, clouding, ordering and related phenomena may be interpreted in terms of the interaction forces acting between the particles in the system. In general, the following forces play an important role in the interaction of colloid particles:

van der Waals forces: This is due to interaction between two temporary and
induced dipoles. Even if the particles do not have a permanent dipole, fluctuations of the electron density gives rise to a temporary dipole in a particle. This temporary dipole induces a dipole in particles nearby. The temporary dipole and the induced dipoles are then attracted to each other. This is known as van der Waals force and is always present, short range and attractive.

**Zeta potential and Electrostatic interaction:** Colloidal particles often carry an electrical charge and each colloidal particle is surrounded by an electrical double layer [9]. [Figure 1.1] One layer is formed by the charge on the surface of the particles. The second layer is formed by the counterions. Within the double layer there is a notional boundary inside which the ions and particles form a stable entity. When a particle moves (e.g. due to gravity), ions within the boundary move with it, but any ions beyond the boundary do not travel with the particle. This boundary is called the surface of hydrodynamic shear or slipping plane. The potential that exists at this boundary is known as the Zeta potential.

In the locality of a charged colloidal particle there is a balance between the electrical forces which are tending to attract counterions and repel co-ions and thermal motion which tends to produce a uniform distribution of these ions. [10] The combined effect of electrical effect of electrical forces and thermal agitation is to create a ‘diffuse’ electrical double layer. The thickness of this diffuse layer is of colloidal dimensions. The charge of both the continuous and the dispersed phase, as well as the mobility of the phases are factors affecting this interaction.

Excess counterions near to the charged particle surface screen the electrostatic attraction for counterions further away from the particle surface, with the result that
Figure 1.1: Schematic illustration of the electrical double layer around a colloidal particle. The counterions (positively charged ions) are shown by red dots; the negatively charged ions are shown as blue dots.

The concentration rapidly at first and then more slowly with increasing distance. An increase in the electrolyte concentration or an increase in the valency of the counterions magnifies the screening effect and leads to compacting of the diffuse double layer. When two macroions approach each other, overlap of their double layers causes a repulsive force (‘electrical double layer force’) which can stabilize the particles against aggregation (‘charge stabilization’).

**Depletion force:** Depletion forces arise when small particles (polymer, small colloidal particles) are added to a suspension of large colloidal particles. [11,12] These forces result from the excluded-volume interaction between a large and a
small particle. When two large particles approach each other, the smaller particles are expelled from the gap. The difference between the osmotic pressure in the gap and in the bulk induces the attraction.[Figure 1.2]

Figure 1.2: Depletion mechanism. (a) When far apart, a uniform osmotic pressure is exerted on the bigger colloidal particles. (b) Smaller colloidal particles cannot enter the region between the closely spaced larger particles. The result is net attraction between larger colloidal particles.

Entropic forces: According to the second law of thermodynamics, a system progresses to a state in which entropy is maximized. This can result in effective forces even between hard spheres.

Steric forces: At very small interparticle distances, close to contact, there arises
a strong repulsive force that determines how close the two particles can ultimately approach each other. These repulsive forces are referred to as hard core repulsion, steric repulsion. The hard core repulsion represents the excluded volume effect due to finite size of particles.

**DLVO theory:**

The classical DLVO theory is named after Derjaguin, Landau, Verwey and Overbeek who developed it in the 1940s. [13, 14] Previously, the DLVO theory, which accurately describes the behavior of isolated pairs of spheres, was widely used to interpret particle behaviors among different systems. According to this theory, the stability of a colloidal system is determined by the sum of the van der Waals attractive ($V_A$) and electrical double layer repulsive ($V_R$) forces that exist between particles as they approach each other due to the Brownian motion they are undergoing. (Figure 1.3) This theory proposes that an energy barrier resulting from the repulsive force prevents two particles from approaching one another and adhering together. But if the particles collide with sufficient energy to overcome that barrier, the attractive force will pull them into contact so that they adhere strongly and irreversibly together. Therefore if the particles have a sufficiently high repulsion, the dispersion will resist flocculation and the colloidal system will be stable. However if a repulsion mechanism does not exist then flocculation or coagulation will eventually take place. Thus in a system that holds identically charged colloidal particles, particles should have repulsive forces between each other and will not flocculate or form aggregation under normal circumstances. However, under an alternating electric field, it has been observed that a long-range attractive force exists, [15, 16] which the DLVO theory alone cannot account for.
Figure 1.3: Schematic diagram of interaction between a pair of colloidal particles with particle separation according to DLVO theory.

\[ V_{DLVO}(r) = V_C(r) + V_A(r) \]  

The interaction curves can be used to judge the stability of the system at rest and under external force.

1.2 Implications and Applications

Colloids are often used as an interesting model system to investigate physical behaviors for atoms. [17–23] This is because firstly at the “atomic scale”, colloidal particles are large enough to be observed by optical microscopy. Secondly, many of the forces that govern the structure and behavior of colloidal suspensions are similar to those among atoms and molecules. For example, the same techniques that can be used to model ideal gases can be used to model the behavior of a hard
sphere colloidal suspension. Thirdly, phase behaviors of colloidal systems are found very similar to those of atomic or molecular systems. In this sense, phase transitions in colloidal suspensions can be studied in real time using optical techniques and are analogous to phase transitions in liquids.

Apart from the above, when dispersed in liquid media, colloidal particles display a rich phase behavior and a complex rheology that has made the use of colloidal structures advantageous in a diverse assortment of technological applications ranging from food stuffs, cosmetics, and pharmaceutical. [24] Ordered colloidal systems have lattice spacings ranging from nanometers to micrometers and can therefore diffract ultraviolet, visible, and near-infrared light. One can take advantage of this for a variety of applications, including sensors [25, 84], narrow-band optical filters [27], optical switches, photonic band gap materials, waveguides [28], and other types of optical and electrooptical devices [29]. Photonic crystals could allow significant advances in the miniaturization and high-speed performance of integrated circuits and have profound applications for telecommunications, lasers, fiber optics, data processing, and display technologies [30, 31]. Significant research has also focused on incorporating colloidal structures in emerging technologies such as nanotechnology and biotechnology. [32, 33] To develop novel materials, the structural organization of colloids in these applications can be tailored by a number of ways including: manipulating the magnitude and nature of interparticle interactions; varying the concentration, size, shape and polydispersity of particles; and/or applying an external field.
1.3 Self-Assembly Strategies for Colloid Arrays

As mentioned earlier, colloidal particles dispersed in various solvents are influenced by many kinds of interactions including van der Waals forces, steric repulsions, Coulombic repulsions and forces exerted by external fields. Since the dispersion stability and the crystallization of colloidal dispersion are governed by these interactions, intensive studies on colloidal interactions have been conducted both experimentally and theoretically. [35] Derjaguin-Landau-Vervey-Overbeek (DLVO) theory describes successfully the interactions between colloidal particles and has been used to predict the stabilization of dispersions. [36] However, during the fabrication of colloidal templates or masks, other mechanism may become dominant in leading the colloidal assemblies. Figure 1.4 illustrates some typical strategies for fabricating a 2D colloidal array including dip-coating, floating on an interface, electrophoretic deposition, physical and chemical template-guided self-assembly and spin-casting [37].

Figure 1.4a shows the dip-coating method. In this case, capillary forces and controlled evaporation induce colloidal self-organization. [38] The quality of the ordered arrays is determined by the evaporation rate, and the assembled structure usually has domains throughout the entire area. A large-scale polycrystalline monolayer of a colloidal array with a diameter ranging from a few tens of nanometers to a few micrometers can be obtained with this method.

Figure 1.4b shows the lift-up process of a colloidal array floated on an interface. The quality and packing sequence of the array can be controlled by changing the concentration of the particles or electrolytes, the particle size, the surface charge,
Figure 1.4: Some typical self-assembly strategies to create ordered colloid arrays: a) dip-coating, b) lifting up a colloid array from an interface using the substrate, c) electrophoretic deposition, d) chemical or electrochemical deposition with a patterned array, e) physical template-guided self-organization, f) spin-coating in which shear and capillary forces drive the colloidal self-organization.
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and the hydrophobicity of the particles. [39–42] Colloidal particles can be trapped at the liquid interface as a result of electrostatic and capillary forces. Compared to evaporation-induced self-assembly, the particles at the interface are able to form a monolayer without variation in the layer thickness. An ordered particle array can be transferred to various substrates by lifting up the colloidal film or by controlled evaporation of the solvent. [39]

Figure 1.4c shows electrophoretic deposition of colloidal particles utilizes the movement of the particles that is driven by applied electrical fields. Electrophoretic movement in a dc field [15, 32, 43, 44] or ac field [45, 47, 79] has been studied and applied for rapid and precisely controlled deposition of particles. Particle assembly generally takes place inside a thin layer of a colloidal suspension sandwiched by conducting substrates such as indium tin oxide (ITO) coated glass slides. An electric field is then applied across the electrodes. The driving force assembling the particles into 2D crystals are the electrohydrodynamic interactions between the microspheres. [15, 32, 43, 44, 48] Electrophoretic movement not only accelerates the sedimentation speed of small colloids but also guides the growth of a colloidal crystal over a large area in a controlled manner.

Figure 1.4d and e are examples for selective deposition of colloids on a substrate patterned with chemicals or charges, [49–53] and physically patterned substrate, [54] respectively. Template-assisted self-assembly of colloid particles is usually employed for suppressing defect formation in colloidal crystals. [55–57]

Spin-coating of particle suspension is also available for preparing the colloidal
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layer. [58] Figure 1.4f illustrates the organization of colloidal particles into a hexagonal array during centrifugal spreading of a suspension on a wetttable substrate, more rapidly compared to evaporation methods such as dip-coating, drop-dripping, and electrolyte adsorption.

AC electric fields outstands among these techniques due to several advantages. Firstly, AC electric field has the ability to precisely tune the forces exerted on the particles by the field and the field-induced particle-particle interactions. The parameters characterizing an AC signal applied to electrodes include magnitude, frequency, wave shape, wave symmetry, and phase (when multiple electrodes are involved). All of these parameters can be controlled electronically and all can influence in different ways the behavior of particles between the electrodes. This allows precise adjustment of driving forces to an extent that is hardly possible with any alternative technique using liquid flow, evaporation, sedimentation or mechanical manipulation. The second major advantage of using electric fields on a chip is the relative simplicity and availability of experimental cells and equipment needed. The microlithography facilities used in electronic circuit fabrication allow facile fabrication of any kind of “chips” with microelectrodes for this type of research. [87] Although techniques were developed to form three-dimensional (3D) colloidal crystal with tunable interactions [60, 61], the detailed understanding of the mechanism in the ordering of these systems remains elusive, however, and has motivated the detailed examination of simpler two-dimensional (2D) analogues.
1.4 Review on 2D Colloidal Assembly under an Alternating Current Electric Field

Harvesting the convenience of electrical particle manipulation, however, requires knowledge and prediction of the response of the particles and liquid inside the experimental cells to the fields applied to the electrodes. That response is often quite complex, as generally, electric fields drive motion of both particles and liquid as will be explained in more detail below. Rich varieties of field-driven effects have been revealed and are the subject of active investigation.

In the previous decade, investigators of electrophoretic deposition have noticed that particles not only are deposited but also aggregate laterally and self-order in some cases. [15, 16, 32, 43, 44, 63, 65, 66, 68–70, 90] Particles have moved in a variety of circumstances including direct current (DC) and alternating current (AC) polarization, frequency variation from zero to megahertz, particle size variation from nanometric to micrometric, and particle composition variation from dielectric to metallic. Experimental parameters associated with reported phenomena are collected in reference [48]; some features are summarized as follows. (1) Micron-size particles move in fields of order 0.1 kV/m under DC polarization [16,44,90] but aggregate at fields >1 kV/m in AC polarization [16,63,68]. (2) Aggregation in AC fields occurred at higher frequencies for smaller particles (compare reference [68] to reference [63]). (3) Particles stopped or became repulsive as the frequency was increased [16,63,68]. (4) Particles moved more quickly as they approached each other in DC polarization but moved more slowly as they approached in AC polarization [68]).
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The mobility of the particles can be a result of forces acting directly on them or of the drag from the moving liquid around them. The electric field driven mobility of the particles and of the liquid can be classified in several broad categories. [84]

The electrophoretic mobility of charged particles in constant electrical fields has been a major topic in colloidal science for a long time. [85] Charged particles in suspension are surrounded by a cloud of counterions, and the particle-counterion complex is electroneutral. The ions in the fluid layer closest to the interface are strongly attracted to the substrate and are hence immobile. This layer is known as the Stern layer. The application of external field, however, can “shear” away some of the ions outside this layer, which begin moving towards the electrode of opposite charge. The particle surface below the plane of shear is characterized with a potential in that plane called zeta potential, $\zeta$. This potential is involved in nearly all electrokinetic flows. [86] The particles of effective potential $\zeta$ move towards the electrode of opposite sign [84].

A common complication in using DC fields to move particles in ionic media (such as water) is the electrophoretic mobility of the liquid adjacent to the walls of the experimental cell. The dielectric walls of chips and containers in contact with suspension nearly always develop a surface charge, with the corresponding counterionic double layer in the water phase. The ions in this layer move towards the oppositely charged electrode, dragging the liquid, and resulting in electroosmotic water motion. [84]

The application of an AC field across particle suspensions leads to emergence of dielectrophoretic (DEP) force. As the sign of the electrode polarization changes
constantly, the particles are not attracted by direct charge-electrode electrostatic interactions (apart from oscillations at low frequencies on the order of tens of Hertz). Instead, the DEP force arises via interaction of the induced dipoles with the gradient of the (inhomogeneous) field. [84] The DEP effects become much more complex when large numbers of particles are present between the electrodes. The processes of interaction and assembly of the particles can be explained in an intuitively clear, albeit simplified, way by assuming that the field induces a dipole within each particle. These induced dipoles interact not only with the external field, but also with each other if the particles are close enough.

Dielectrophoresis might account for other observations such as a change of behavior with frequency. Yeh et al. [63] mentioned dielectrophoresis for its potential as a source of normally directed force on the particles but did not examine it as a potential cause of aggregation. The dielectrophoretic (DE) force arises from the interaction of a nonuniform electric field and the dipole moment induced in the particle by a field. Lateral electric field gradients arise because the dielectric particles deflect current around them, which produces gradients in the plane of the electrode. Since the dielectrophoretic interaction of two adjacent particles in a field applied normally to the electrode depends only on the lateral field, the factor of 0.1 must be applied twice to give an estimate of the field strength. The complex polarizability depends on the permittivities and conductivities of the particles and the medium. [72]

Uniform AC fields applied normally or tangentially to a charged wall do not engender fluid flows as the DC fields. Fluid flows, however, are generated in areas near the electrodes where a strong electric field gradient exists across a solid-liquid
interface. The interaction of the ions collected in the high field intensity areas and
the field leads to liquid drag near the dielectric wall adjacent to the electrodes.
These flows, referred to as AC electrokinetic, [44,68–70] are strongly dependent on
the field frequency and electrolyte concentration because of their dependence on
the capacitive charging of the double layer. The counterions farther away from the
interface than the shear plane are loosely bound and have the ability to move in
both the transverse as well as parallel directions. The external applied voltage at
electrode surfaces modifies the native charge on the surface thereby leading to an
“induced” zeta potential different from the intrinsic zeta potential. Furthermore,
for AC fields the induced double layer charge changes sign synchronously with the
electric field frequency. The counterions in the double layer move in and out of
the layer during the subsequent half-cycles of the electric field frequency. This
leads to induced zeta potentials that may be different for the positive and negative
half-cycles of the AC field, but are always of sign same as that of the electrode field
applied to the electrodes. [87] There is no net flow, unless the field has a compo-
nent tangential to the surface. The ions in the double layer then react to tangential
electric fields leading to bulk liquid flow along the interface. Notably even though
an AC field is applied, the bulk flow in different half cycles points in the same
direction along the field gradient resulting in a net fluid flow. This phenomenon
is referred to as AC electroosmosis or AC electrohydrodynamic (EHD) flow. [84]
As the applied electric field induces double layer formation and then leads to bulk
fluid flow by acting on its own induced charge, these flows are also referred to as
“induced-charge electroosmosis (ICEO)”. [88,89] AC EHD and electroosmosis are
types of ICEO flows.
The dynamics of the electrophoretic assembly of latex particles suspended between conductive electrodes have been reported by Trau et al. [16, 43] and Böhmer. [90] The latex particles are attracted to the oppositely charged electrode and the counterionic atmosphere around the particles disturbs the concentration polarization layer at the electrode surfaces. This leads to electrohydrodynamic flows around the particles that in effect pull them together to form 2D colloidal crystals at the electrode surface. [16, 44, 48, 70, 73, 90, 91] The electrohydrodynamic flows generated around the particles are a function of the electrolyte concentration and the frequency of applied field. Depending on these parameters, the electrohydrodynamic flows in the vicinity of the particles can aggregate them or separate them. Sides and co-workers have treated these phenomena theoretically and demonstrated experimentally how the critical frequency for the change in electrohydrodynamic flow direction depends on the particle size. [81, 92–96]

Since our project selected the system with colloidal particles suspended between two parallel electrodes, we will mainly review the mechanism and work carried out in this kind of system in the following paragraphs.

Establishment of Electrohydrodynamic (EHD) Mechanism in the system where particles suspended between conductive electrodes

In order to interpret the long-range attractive force under AC field, an electrohydrodynamic mechanism was proposed by Trau, Saville and Aksay and Yeh, Seul and Shraiman. [16, 43, 63] They independently reported their observations that colloidal spheres can spontaneously self-assemble into crystalline aggregates near
electrodes under AC applied fields and proposed somewhat similar electrohydro-
dynamic mechanisms for this aggregation.

Attraction between electrophoretically deposited particles is unexpected due to
the strong repulsion arising from electrostatic interparticle forces. The particles
are similarly charged and possess a diffuse ion cloud (double layer), polarized by
the applied field. Thus, nearby particles experience electrostatic repulsion from
monopole and dipole interactions (Figure 1.5(a)). Evidently, the migration of one
particle toward another or toward a raft of particles is not the result of interparticle
forces.

In the proposed mechanism, concentration polarization adjacent to the electrode
produces a finite free charge in the diffusion layer; the charge interacts with any
lateral electric field arising from nonuniformities to produce a distributed body
force on the liquid within the region of concentration gradients (Figure 1.5(b)).
This is the first establishment of EHD mechanism and it provided a foundation for
the further studies in this field. However, they did not address the need to provide
quantitative interpretations of the behaviors of spheres.

**Quantitative Development of EHD Mechanism**

Further efforts have been made by different groups to establish a quantitative
model to account for the behaviors of colloidal particles under an AC field. [48, 73–
82, 91, 109] Sides [48, 81] established a model to predict the behaviors of colloidal
particles and attributed the colloidal behaviors under AC field to the kind of ions
added into the solution, conductance effects from the introduced ions, particle sizes,
Figure 1.5: Schematic of particles near electrode surface: (a) polarization of double layer; (b) flow pattern expected to give rise to particle attraction.
field strength, and frequency-influenced double layer. According to him, beyond a certain range of frequency, the thickness of an electrode double layer is influenced by the frequency. In the low frequency range, the particles are immersed in the double layer and the movement of fluid flow within the double layer helps the spheres to assemble together, while above a certain frequency, the double layer becomes so thin that the particles no longer stay in the double layer, and hence the fluid flow can no longer helps particles to assemble together. This consideration can account for the fact that colloidal particles stopped to form 2D assembly above a certain frequency. However, it fails to predict the cut-off frequencies accurately, [82] and did not consider the factors that could influence the cut-off frequency even for the same kind of particles, for example, the salt concentration.

Effect of conductance of present ions on colloidal assembly was also studied by Sides. In his study, [48] he concluded that the sum of conductance of different ions will influence the direction of fluid flow and will finally determine whether the particles will assemble or not. His theory has been proved right in some two-particle systems. For example, colloidal particles in presence of potassium chloride will form assembly, while in the presence of potassium hydroxide they disperse. [48] However, this prediction was only proved in a two-particle system. [91] It has not been proved in an identically charged multi-particle system, in which the particle behaviors are likely to be different from those for a two particle system because the interactions for a multi-particle system are more complicated. [82]

Another noteworthy aspect of Sides’ model is that he considered the size effect of colloidal particles. According to him, smaller particles will assemble at relatively higher frequencies compared with larger particles, and requires high field
Chapter 1. Introduction

strength to form assembly. This is the first prediction about size effect, but again failed to offer accurate values quantitatively because not enough parameters were considered; for example, salt concentration, and zeta potential were omitted.

Apart from the above theoretical predictions, detailed measurements were carried out by Nadal et al. [82] to test both the attractive (electrohydrodynamic) and repulsive (electrostatic, dipole-dipole) interactions between the spheres. For the first time they identified the cut-off frequencies experimentally for different sizes of spheres, and provided further evidence that EHD flow is dominant for colloidal assembly by tracing the fluid flow with small spheres around a larger sphere, and measuring the change of distance caused by dipole interactions. However, they only focused in the high frequency range and did not extend their study towards low frequencies nor studied the phase behaviors.

Since both the theoretical predictions and interpretations of experimental results are based on the interaction forces among particles and these forces are closely related to the direction and strength of the assembly velocity, it is important to quantify this velocity. This was first achieved by Ristenpart et al. [83]. They derived the EHD velocity, which is proportional to the square of field strength. Furthermore, they carried out a series of measurements, and the results agreed well with theoretical predictions. However, they only focused on the assembly in the higher frequency range and did not investigate the behaviors at low frequencies. A possible reason why they all tend to omit the study at low frequencies is that at low frequencies, the double layer at electrode becomes very thick and the fluid flow that drives the motion of particles is difficult to predict. Also for some of the groups, the experimental setups had limitations so that they could not run to low
Chapter 1. Introduction

frequencies.

The mechanism of colloidal assembly under AC field is still not clear. Colloidal assembly under AC field is a very complicated system, and it involves interactions among thousands of particles and between particles and fluid flow. There are a lot of parameters that play a role in the colloidal assembly, such as field strength, frequency, particle size, kind of salt, salt concentration, zeta potential, and temperature. Yet each study focused on only several parameters. No phase diagrams that include all the parameters have been presented, and hence the mechanism of colloidal assembly under AC field has not been fully investigated. Besides, the phase transitions from disorder to order, the mechanisms that dominate at different conditions and the degree of perfection for the assembly have not been studied so far. These are also important because a lot of promising applications, such as micro-sensor and optical material design, can only be developed based on a clear understanding of these aspects.

1.5 Objectives

In this thesis, the two-dimensional colloidal assembly under an AC field will be studied. To obtain a comprehensive understanding of this process, the objectives of this thesis are summarized as:

(1) To identify phase behaviors (order/disorder, structures of aggregation formed/degree of perfection) of colloidal particles under AC field with change of parameters (field strength, frequency, particle size, kind of salt, salt concentration, zeta potential,
temperature etc.) and figure out their phase diagrams.

(2) To further develop the mechanism for colloidal assembly under alternating electric field by analyzing the results of several measured parameters and improve the existing EHD models, to make them more comprehensive.

(3) To study the phase transition by applying pair correlation function, orientational correlation function, local orientational bond etc.

(4) To characterize the degree of perfection of colloidal assembly by using structure factor and equilibrium distance in order to control the degree of perfection of colloidal assembly obtained.

(5) To establish a method to modulate the interactions among colloidal particles so that the desired patterns can be formed for further use as templates.

1.6 Scope and Summary

The results should contribute to future study in applications such as optical material design and bio-sensor. Investigation of the mechanism should be important for a better understanding of phase behaviors of colloidal particles. The control of colloidal assembly as well as of degree of perfection should offer useful information on promising applications such as micro-sensor and optical material design.

Research activities we carried out were only limited to two dimensional (2D) systems because 2D is the basis of 3D, and a sufficient understanding of 2D assembly
is necessary before further development in either the mechanism or applications of 3D colloidal assembly can be made.

In this thesis, we used polystyrene colloidal particles in the experiments and measurements. The reason for the choice of polystyrene is that it is one of the most typical kinds of colloidal particles which have been studied in model systems widely, and it has clear advantages. In particular, polystyrene particles are very stable over a large range of temperature (-192°C – 800°C) for a long time of storage (above 3 years), while the properties (charge density, conductivity etc.) remain almost constant.

To achieve the objectives listed above, we need to set up a 2D colloidal system under an alternating electric field. Also to identify the effects from different parameters, we need to adjust either the conditions of solution (such as particle size, salt concentration) or system setup (temperature control). In the following chapter we will introduce the materials used and the experimental setups.
Chapter 2

Techniques, Materials and Data Analysis

2.1 Experimental Techniques

2.1.1 Experimental Setup

The experimental set up was similar to that described in Figure 2.1. The cell consisted of two parallel ion tin oxide (ITO) electrodes (glass substrate 1 cm in diameter; thickness of coating 15 – 30 nm; sheet resistance 100 Ω/cm²) separated by glass spacers \( H = 120 \mu m \). The sample suspension was sealed in the cell with UV cured adhesive (Norland Industries, Type 88) before the experiment.

An alternating electric field was applied to the sample suspension, and a series
Figure 2.1: Experimental Cell.
of experiments were conducted changing frequency $f$ and field strength $E_0$. A digital imaging camera (CoolSNAP cf, Photometrics) mounted on an Olympus BX51 microscope was used to monitor the colloidal assembly. (Figure 2.2)

The colloidal dispersion used in the experiment consisted of negative charge stabilized polystyrene (PS) spheres (diameter 1.8, 3 and 5 $\mu$m, Duke Scientific; the size distribution of all the particles is smaller than 5%). The polystyrene particles were dispersed either in deionized water (resistivity 18.2 M $cm^{-1}$) or 0.02, 0.05 or 0.1 mM sodium chloride (NaCl), or 0.1 mM potassium hydroxide (KOH) solution. Figure 2.3 shows example pictures taken by the microscope for colloidal assembly.
of 5 µm in diameter with time.

2.1.2 Zetasizer

The occurrence of a net charge at the particle surface affects the distribution of ions in the surrounding interfacial region, resulting in an accumulation of counter ions close to the surface. Thus an electrical double layer exists around each particle. The liquid layer surrounding the particle exists as two parts; an inner region, called the Stern layer, where the ions are strongly bound, and an outer, diffuse, region where they are less firmly attached. Within the diffuse layer there is a notional
boundary inside which the ions and particles form a stable entity. When a particle moves (e.g. due to gravity), ions within the boundary move with it, but any ions beyond the boundary do not travel with the particle. This boundary is called the surface of hydrodynamic shear or slipping plane. The potential that exists at this boundary is known as the Zeta potential. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there is no tendency to flocculate. However, if the particles have low zeta potential values then there is no force to prevent the particles coming together and flocculating.

Charged particles in a liquid suspension can be made to move by applying an electric field to the liquid through two electrodes. By alternating the charge between the electrodes, the particles move back and forth between the electrodes at a velocity related to their surface charge and the electrode potential. This velocity can be determined by measuring the doppler shift of laser light scattered off of the moving particles. The Doppler shift is the change in the frequency of the peak in the power spectrum when compared to the reference spectrum in the absence of an electric field. Using the Smoluchowski equation, the zeta potential $\zeta$ is determined:

$$\mu = \frac{\zeta \varepsilon}{\eta}$$  \hspace{1cm} (2.1)

where $\mu$ is the electrophoretic mobility, $\varepsilon$ is the dielectric permittivity of the liquid and $\eta$ is the viscosity.

A zeta potential measurement system comprises of six main components. First
of all a laser is used to provide a light source to illuminate the particles within the sample; for zeta potential measurements this light source is split to provide an incident and reference beam. The reference beam is also ‘modulated’ to provide the doppler effect necessary. The laser beam passes through the center of the sample cell, and the scattering at an angle is detected. On insertion of the cell into the cell holder, the cell terminals allow the system to recognize the type of zeta potential cell fitted, and configures the software to use the correct measurement sequence.

When an electric field is applied to the cell, any particles moving through the measurement volume will cause the intensity of light detected to fluctuate with a frequency proportional to the particle speed. A detector sends this information to a digital signal processor. This information is then passed to a computer, where the Zetasizer software produces a frequency spectrum from which the electrophoretic mobility and hence the zeta potential information is calculated. The intensity of the scattered light within the cell must be within a specific range for the detector to successfully measure it. If too much light is detected then the detector will become overloaded. To overcome this an “attenuator” is used to reduce the intensity of the laser and hence reduce the intensity of the scattering. For samples that do not scatter much light, such as very small particles or samples of low concentration, the amount of scattered light must be increased. The attenuator will automatically allow more light through to the sample. To correct for any differences in the cell wall thickness and dispersant refraction compensation optics are installed within the scattering beam path to maintain alignment of the scattering beams.
2.1.3 Temperature Control System

The TMS 94 has been specifically designed to give precise temperature control of the Linkam range of heating/freezing Stages. Digital Linearisation of the Stage’s sensor gives accurate temperature values whilst the function keys have been carefully chosen to allow rapid changes in data values.

The temperature under which to obtain colloidal assemblies was controlled by a Linkam THMS 600 Heating and Freezing stage (T can be controlled within 0.1°C from the range of −192°C − +600°C) where the cell was mounted.

2.1.4 Scanning Electron Microscope

The Scanning Electron Microscope, or SEM, is an incredible tool for seeing the unseen worlds of microspace. Conventional light microscopes use a series of glass lenses to bend light waves and create a magnified image. The Scanning Electron Microscope creates the magnified images by using electrons instead of light waves. The SEM shows very detailed three-dimensional images at much higher magnifications than is possible with a light microscope. As the best known and most widely-used of the surface analytical techniques, SEM, accompanied by X-ray analysis, is considered a relatively rapid, inexpensive, and basically non-destructive approach to surface analysis. It is often used to survey surface analytical problems before proceeding to techniques that are more surface-sensitive and more specialized. High resolution images of surface topography, with excellent depth of field
are produced using a highly-focused, scanning (primary) electron beam. The images created without light waves are rendered black and white. Samples have to be prepared carefully to withstand the vacuum inside the microscope. Because the SEM illuminates them with electrons, they also have to be made to conduct electricity. SEM samples are coated with a very thin layer of gold by a machine called a sputter coater. The sample is placed inside the microscope’s vacuum column through an air-tight door. After the air is pumped out of the column, an electron gun (at the top) emits a beam of high energy electrons. This beam travels downward through a series of magnetic lenses designed to focus the electrons to a very fine spot. Near the bottom, a set of scanning coils moves the focused beam back and forth across the specimen, row by row. As the electron beam hits each spot on the sample, secondary electrons are knocked loose from its surface. A detector counts these electrons and sends the signals to an amplifier. The final image is built up from the number of electrons emitted from each spot on the sample. The Scanning Electron Microscope is revealing new levels of detail and complexity in the amazing world of micro-organisms and miniature structures.

2.2 Data Analysis

The first step of image processing is to identify the location of each colloidal particle in the series of pictures. The basic idea is to group all the pixels with brightness within a certain range of value, into clusters of next neighbors. Then the center of mass of the cluster can be determined using standard procedure [97–99].
The assembly of colloidal particles under AC field is not necessarily limited to two-dimension, but our study focuses on the conditions when colloids can form 2D hexagonal crystal phase. Thus in the study of phase transition, we introduce both radial pair correlation function $g^{2D}(r)$, and bond-orientational correlation function $g_6(r)$.
Chapter 2. Techniques, Materials and Data Analysis

Figure 2.5: Illustration of Radial Pair Correlation Function.
2.2.1 Radial Pair Correlation Function $g^{2D}(r)$

The translational correlation function can be expressed as:

$$g_G \equiv \langle \rho_G(0)\rho_G(r) \rangle$$  \hspace{1cm} (2.2)

where $\rho_G(r)$ is the probability of finding a particle at a distance $r$ away from the particle at the origin. From the microscope image, the extent of 2-D translational ordering can be calculated by the radial pair correlation function as described by Bongers et al. [99]:

$$g^{2D} = \frac{n_d}{2\pi r \Delta r \rho}$$  \hspace{1cm} (2.3)

where $n_d$ is the number of particles found in a ring with an inner radius of $r - 0.5 \Delta r$ and an outer radius of $r + 0.5 \Delta r$, $\Delta r$ being the width of a histogram channel, and $\rho$ is the mean number density of spheres. The first peak of $g^{2D}(r)$ corresponds to the nearest center-center equilibrium distance $r_{eq}$ in the assembly. Accuracy in the determination of requires areas of assembly to be as large as possible.

2.2.2 Bond-orientational Correlation Function $g_6(r)$

The bond-orientational correlation function offers information about the rotational symmetry of the crystal assembly, and can be expressed as [100]:
where the bond-orientational order parameter is defined as:

\[ g_6(r) = \langle \psi_6(r) \psi_6^*(r) \rangle \] (2.4)

\[ \psi_6(r_i) = \frac{1}{N} \sum_j \exp(6i\theta_{ij}) \] (2.5)

Here the sum \( j \) runs over all neighbors of particle \( i \) within the first coordination shell, and \( \theta_{ij} \) is the angle between the bonds linking particles \( i \) and \( j \) with a fixed reference axis. This formula can also be redefined as [101]:

\[ \psi_6(r_i) = \frac{\sum_j l_j \exp(6i\theta_{ij})}{\sum_j l_j} \] (2.6)

where \( l_j \) is the length of line joining two adjacent neighbors \( j \) and \( j - 1 \). The weighting with respect to length ensures that an infinitesimal distortion from perfect triangular lattice gives rise to continuous change in \( \psi_6 \).
Chapter 3

Investigation of The Mechanism of 2D Colloidal Assembly under an AC Field

3.1 Introduction

The lateral assembly of charged, monodispersed colloidal particles into two dimensional (2D) ordered structures under an alternating electric field has evoked much interest in the past two decades both experimentally and theoretically. [16, 43, 48, 63, 81–83, 91, 102–104] The manipulation of the assembly on patterned electrode surfaces by electrical forces has several applications in photonic materials, biotechnology etc. [32, 72, 105] The transverse motion of identical, charged colloidal particles leading to the formation of crystalline aggregates above the electrode surface
suggests the existence of attractive interaction between the particles that enables them to overcome the repulsive Coulombic and induced dipole interactions. Trau et al. [16, 43] and Yeh et al. [63] attributed the attractive forces as due to the electrohydrodynamic (EHD) mechanism wherein gradients in current density, caused by the presence of particles near the electrode surface, generate localized fluid flow that carries the particles towards each other. Sides [48, 81] proposed a quantitative model of the electrohydrodynamic flow that could explain the experimental results of Nadal et al. [82] Existence of a critical frequency for the colloidal assembly of identical particles was demonstrated by Nadal et al. [82] They suggested that below the critical frequency the attractive forces due to EHD flow dominate leading to particle aggregation, while above the critical frequency the domination of the repulsive dipole-dipole interactions disintegrate the tightly organized structures. Recently, Ristenpart et al. [83] derived expression for the EHD velocity that brings particles together, and showed that it scales with the square of the applied electric field strength and inversely with frequency, their experimental results providing support to this scaling theory.

To further investigate the complex mechanism of colloidal assembly driven by an alternating electric field, we determined phase diagrams representing the mean equilibrium distance of separation of the particles in the assembly as a function of frequency and electric field strength. We observed the existence of two critical frequencies at a given field strength, one below and another above the frequency window corresponding to 2D crystalline aggregates. The range of this frequency window was found to depend not only on the ionic strength of the solution but also on the type of the electrolyte used.
Chapter 3. Mechanism of 2D Colloidal Assembly under an AC Field

3.2 Experiments and Data Analysis

The experimental set up is shown as in Figure 2.2. The cell consisted of two parallel ITO electrodes (glass substrate 1 cm in diameter; thickness of coating 15 – 30 nm; sheet resistance ≈ 100 Ω/cm²) separated by glass spacers (H = 120±5 μm). The sample suspension was sealed in the cell with UV cured adhesive (Norland Industries, Type 88) before the experiment. An alternating electric field was applied to the sample suspension, and a series of experiments were conducted changing frequency $f$ and field strength $E_0$. From the voltage applied, $V$, the field strength was calculated as $E_0 = V/H$. The selected voltage range was 0.4 – 3.3V. For $V < 0.4V$ the particle movement was negligible and for $V > 3.3V$ part of the ITO electrode starts burning. The colloidal dispersion used in the experiment consisted of negative charge stabilized polystyrene (PS) spheres (diameter 5 μm, Duke Scientific). The polystyrene particles with a volume fraction $\varphi = 0.15\%$ at pH ≈ 6.00 and of $\zeta$-potential, $\zeta ≈ −101$ mV (measured by Malvern $\zeta$-sizer) were dispersed either in deionized water (resistivity $\sim 18.2 M\Omega cm^{-1}$) or 0.1 mM sodium chloride (NaCl) or 0.1 mM potassium hydroxide (KOH) solution. A digital imaging camera (CoolSNAP cf, Photometrics) mounted on an Olympus BX51 microscope was used to monitor the colloidal assembly.

The first step of image processing is to identify the location of each colloidal particle in the series of pictures. The basic idea is to group all the pixels with brightness within a certain range of value, into clusters of next neighbors. Then the center of mass of the cluster can be determined using standard procedure. [97–99]
Figure 3.1: A sample area illustrating the selection of particles for equilibrium distance measurement in a single frame. In this case, $\psi_6$ is set to be 0.7. Dots correspond to the center-of-mass locations of the particles which have $\psi_6 > 0.7$ and six nearest neighbors, while the crosses represent particles that do not satisfy one or both requirements.

The assembly of colloidal particles under ac field is not necessarily limited to two-dimension, but our study focuses on the conditions when colloids can form 2D hexagonal crystal phase. Thus in the study of phase transition, as introduced in Chapter 2, we introduce radial pair correlation function $g^{2D}(r)$, and bond-orientational correlation function $g^{2D}(r)$ to quantitatively carry out our study. $g^{2D}(r)$ offers information of the translational order of the assembly and $g^{2D}(r)$ offers information of orientational information. In particular, the first peak of $g^{2D}(r)$ corresponds to the nearest center-center distance between the particles among the assembly.
An issue arises: The boundary particles are sometimes loosely spaced or randomly distributed and hence some standardization is required to select the particles in an area for calculating the equilibrium distance. For this, only those particles are selected which have six nearest neighbors (to ensure hexagonal assembly and to exclude particles at the boundaries) and a local bond-orientational order parameter $\psi_6$ larger than a certain threshold value. For example, Figure 3.1 shows that if we set the condition for particles with $\psi_6 > 0.7$ and six nearest neighbors, the particles occupying the dotted positions only will be selected for calculation. Another issue arises: Since we carried out a number of measurements under different circumstances to obtain a proper trend of data, we focused on several small areas (so that the whole area was inside one image) for the study of equilibrium distance $r_{eq}$ and tracked the change associated with the same areas under different conditions. (Figure 3.2) During the change of either frequency or voltage, the assemblies may change shape or join with each other, so the selected areas should not be too near each other.

3.3 Colloidal Assembly under an AC Field

3.3.1 Phase Behaviors of Colloidal Particles at different Zeta Potentials, Field Strengths and Frequencies

As discussed by several authors, [16, 43, 48, 63, 81–83, 91, 102–104] application of alternating electric field of certain frequency and strength drives the uniformly
dispersed charged colloidal particles to move in a transverse direction to the field and form densely assembled 2D structures separated by voids near the electrode surface. We selected several areas of particle assembly of width $\geq 20a$, where $a$ is the particle radius and determined $g^{2D}(r)$ and $g_6(r)$. The position of the first peak of $g^{2D}(r)$ corresponds to the equilibrium center-to-center distance $r_{eq}$ between the nearest neighbors. In Fig 3.3, the $r_{eq}$ values, normalized to the particle diameter $2a$, are plotted as a function of frequency $f$, for the colloidal dispersion in deionized water under an applied field strength of $E_0 = 1.5 \times 10^4$ V/m. The points are representative of a few areas selected for the study. Results for other areas fall within the range of representative points shown in figure. Tight assembly of the particles with least gap between them was observed for $f$ in the range of 150 – 350 Hz. Above 400 Hz, smaller areas melted away first and merged into the larger
Figure 3.3: For four typical areas, the variation with frequency of the equilibrium center-to-center separation $r_{eq}$ normalized to particle diameter, $2a = 5 \, \mu m$, is shown. $E_0 = 1.5 \times 10^4 \, V/m$. Dispersion in de-ionized water; pH = 6.0; $\zeta = -101 \, mV$.

areas. No crystalline assembly could be detected for $f > 500 \, Hz$. For the same dispersion adjusted for pH = 4.6 by the addition of 0.1M HCL ($\zeta = -60 \, mV$), the particles assembled closer together and the upper critical frequency shifted to a higher value[Figure 3.4].

When the electric field strength $E_0$ was varied keeping frequency constant for the dispersion in de-ionized (DI) water (pH = 6.0; $\zeta = -101 \, mV$), it was observed that in the frequency range of 150 – 350 Hz, $r_{eq}$ was almost independent of $E_0$ but with a slight increase for large field strengths. At lower frequencies, $r_{eq}$ showed larger variations with $E_0$ as shown in Figures 3.5 and 3.6.
Chapter 3. Mechanism of 2D Colloidal Assembly under an AC Field

Figure 3.4: For four typical areas, the variation with frequency of the equilibrium center-to-center separation $r_{eq}$ normalized to particle diameter, $2a = 5 \mu m$, is shown. $E_0 = 1.5 \times 10^4 \text{ V/m}$. Same dispersion as for Figure 3.3 mixed with 0.1 M HCl; $pH = 4.6$; $\zeta = -60 \text{ mV}$.

Figure 3.5: For a typical single area, the variations of the equilibrium particle separation $r_{eq}/2a$ with electric field strength $E_0$ at a fixed frequency (100 Hz). Particle diameter= 5 $\mu$m; $pH = 6.0$; $\zeta = -101 \text{ mV}$.
Figure 3.6: For a typical single area, the variations of the dimensionless equilibrium particle separation $r_{eq}/2a$ with electric field strength $E_0$ for different frequencies are shown. Particle diameter $= 5 \mu m$; $pH = 6.0$; $\zeta = -101 mV$.

### 3.3.2 Effects of Ionic Strength and Salt Specificity

In order to investigate the influence of ionic strength and salt specificity, we determined the phase diagrams in the presence of 0.1 and 1.0 $mM$ sodium chloride and 0.1 $mM$ potassium hydroxide, respectively. These phase diagrams are shown in Figures 3.7, 3.8 and 3.9 for PS particles of diameter of 5 $\mu m$. The added electrolyte of 0.1 $mM$ concentration [Figures 3.7 and 3.9] gives rise to a tighter assembly of the colloidal particles with the gap between the particles extremely small (2% of the particle diameter) in the frequency range of 80 – 250 Hz. The overall frequency range for crystalline assembly is wider than in the absence of the added electrolyte, with the upper critical frequency being larger for potassium hydroxide than for sodium chloride (the upper critical frequency is the upper cut-off frequency...
Figure 3.7: In the presence of sodium chloride, the variation with frequency of the dimensionless equilibrium particle separation $r_{eq}/2a$ is shown. $E_0 = 1.5 \times 10^4 V/m$; particle diameter = 5 $\mu m$; $pH = 6.0$; $\zeta = -101$ mV for 0.1 mM sodium chloride; the dotted line corresponds to the calculated values of $r_{eq}/2a$ obtained by balancing $F_h$ [Eq. 3.13] with $F_c$ [Eq. 3.14] in the experimental range of frequencies.

above which colloidal particles cannot form 2D assembly; even though without further measurement to a higher frequency, a smaller value of $r_{eq}$ indicates a wider frequency window in this case, considering the assembly changes with frequency in a continuous way). For the same electrolyte (sodium chloride), increase in salt concentration from 0.1 to 1.0 mM shifts the upper critical frequency to a higher value as can be seen from Figures 3.7 and 3.8.
Figure 3.8: In the presence of sodium chloride, the variation with frequency of the dimensionless equilibrium particle separation $r_{eq}/2a$ is shown. $E_0 = 1.5 \times 10^4 \text{ V/m}$; particle diameter = 5 \( \mu \text{m} \); pH = 6.0; $\zeta = -101 \text{ mV}$ for 1 mM sodium chloride.

Figure 3.9: In the presence of 0.1 mM potassium hydroxide, the variation with frequency of the dimensionless equilibrium particle separation $r_{eq}/2a$ is shown. Particle diameter = 5 \( \mu \text{m} \); pH = 6.0; $\zeta = -101 \text{ mV}$; $E_0 = 1.5 \times 10^4 \text{ V/m}$. The dotted line corresponds to the calculated values of $r_{eq}/2a$ obtained by balancing $F_h$ [Eq. 3.13] with $F_c$ [Eq. 3.14] in the experimental range of frequencies.
3.3.3 The Role Played by the Particle Size on Colloidal Assembly

To elucidate the effect of particle diameter on the 2D colloidal assembly, we selected a smaller particle diameter of 3 µm and ionic strength of 0.1 and 1.0 mM sodium chloride (Figures 3.10 and 3.11). While the lower critical frequency is almost the same, the upper critical frequency shifts to a far higher value with the decrease in particle diameter. The equilibrium inter-particle separation is larger for smaller particles, the ionic strength being the same. With increase in ionic strength, the range of frequency for the 2D crystalline assembly becomes broader with the particles getting packed closer to each other.

To further obtain a clearer and general picture of the phase diagram of colloidal assembly under an AC field, we performed another series of experiments. Figure 3.12 shows the variation of $r_{eq}$ with frequency at different field strengths ($0.33 \sim 2.5 \times 10^4 V/m$) for 3 µm particles in presence of 0.1 mM NaCl ($pH \approx 5.70$ and $\zeta \approx -86 mV$). For 3 µm PS particles, at low field strengths ($0.33 \times 10^4 V/m$ and $0.5 \times 10^4 V/m$ in Figure 3.12), the frequency windows which corresponds to the colloidal assembly are much narrower compared with those at higher field strengths ($2 \times 10^4$ and $2.5 \times 10^4 V/m$ in Figure 3.12). While the lower critical frequency is almost the same, the upper critical frequency shifts to a far higher value with the increase in field strengths. The equilibrium inter-particle separation $r_{eq}$ is larger for smaller field strengths, the frequency being the same. With increase in field strength, the range of frequency for the 2D crystalline assembly becomes broader with the particles getting packed closer to each other.
Figure 3.10: Variation with frequency of the dimensionless equilibrium particle separation $r_{eq}/2a$ in the presence of sodium chloride of concentration of 0.1 mM. Particle diameter= 3 $\mu$m; $E_0 = 0.8 \times 10^4 \text{ Vm}^{-1}$.

3.4 Discussions

The lateral assembly of colloidal particles in an alternating electric field has been observed for a wide range of frequencies, particle composition and sizes, electrolyte composition and ionic strengths. [16,43,48,63,81–83,91,102–104] Concerted efforts of several groups such as Trau et al. [16, 43], Yeh et al. [63], Nadal et al. [82], Sides [48,81], Kim et al. [91], indicate that electrohydrodynamic (EHD) flow is the
Chapter 3. Mechanism of 2D Colloidal Assembly under an AC Field

Figure 3.11: Variation with frequency of the dimensionless equilibrium particle separation \( r_{eq}/2a \) in the presence of sodium chloride of concentration of 1.0 mM. Particle diameter= 3 \( \mu \)m; \( E_0 = 0.8 \times 10^4 \) Vm\(^{-1}\).

most likely mechanism responsible for the two dimensional fluid and crystalline structures formed on the electrode surface subjected to AC polarization. According to this model, dissolved ionic species build up a concentration polarization adjacent to the electrode surface, which is disrupted by the presence of colloidal particles. Lateral variations in the amount of concentration polarization induce a spatially varying free charge; the charge interacts with the lateral electric field caused by the distortion of the applied field by the colloidal particles and sets up fluid motion. The EHD flow causes lateral migration of the colloidal particles and enables them to assemble into ordered structures, overcoming the electrostatic repulsion. Based on their experiments on 2D colloidal aggregation of carboxylated polystyrene particles of various size and surface charge, as well as isolated particle pairs, Nadal et al. [82] suggested that the competition between the EHD force, \( F_h \) and the electrostatic dipole-dipole repulsive force, \( F_e \) is the cause of the observed behavior of the colloidal
Figure 3.12: For a typical single area, the variations of the dimensionless equilibrium particle separation $r_{eq}/2a$ with frequency for different field strengths $E_0$. Particle diameter= 3 $\mu$m; $pH = 5.70$; $\zeta = -86$ mV.
particles under an alternating field of varying frequency, $f$ and amplitude, $E_0$. The attractive force $F_h$ can be approximated as the Stoke’s force:

$$F_h \sim 6\pi \eta \nu(f, r)$$  
(3.1)

where $\eta$ is the viscosity of the solvent and $\nu(f, r)$ is the frequency dependent fluid velocity at a distance $r$ from one of the particles or radius, $a$. The repulsive force

$$F_e \sim 3\pi \varepsilon_0 \varepsilon_s a^6 E_0^2 / r^4$$  
(3.2)

is due to the instantaneous dipole moment induced in the colloidal particles subjected to a slowly oscillating field $E(t) = E_0 \cos(2\pi ft)$, where $\varepsilon_0$ is the permittivity of free space, $\varepsilon_s$ is the dielectric constant of the solvent, with $\varepsilon_s > \varepsilon_p$, the dielectric constant of the particles. At frequencies below a critical frequency, the Stoke’s forces dominate and aggregate the particles, while above the critical frequency the dipole forces dominate and the particles repel each other. Thus the equilibrium distribution of the particles can be considered as due to the balancing of these opposing forces.

A quantitative model of hydrodynamic flow near a dielectric sphere on an electrode subjected to AC polarization was first derived by Sides [48]. The combined effect of electrode kinetics and capacitance, the diffusion of electrolyte (ion transference numbers) and frequency of the applied field was shown to result in a fluid velocity, $\nu$, that would aggregate (for $-\nu$) or separate (for $+\nu$) the suspended colloidal particles.
The theory correctly predicted that the interparticle velocity was independent of electrolyte concentration and ζ-potential and became smaller for larger frequencies or smaller amplitudes of the applied field [91]. Depending on the particle size and other electrochemical parameters, the theory predicted a frequency window within which the fluid velocity was negative, enabling aggregation. Individual ionic conductances of the binary electrolyte were predicted to play a decisive role in the aggregation behavior. The difference in ion transference numbers ($t_+$ or $t_-$ for the two ions),

\[
\hat{t} = \frac{t_+}{z_+} + \frac{t_-}{z_-} \quad (3.3)
\]

\[
t_i = \frac{z_i^2 D_i}{z_+^2 D_+ + z_-^2 D_-} \quad (3.4)
\]

Here, $z_i$ and $D_i$ are respectively the valence and diffusion coefficient of the ion of type $i$ (+ or -). A positive value of $\hat{t}$ gives rise to particle aggregation. However, contrary to the theoretical predictions, even in alkaline solutions like sodium and potassium hydroxide with negative values particle aggregation has been observed (Ref. [82] and [91] and the present work).

For our study, we dispersed the colloidal particles in three different solvents: (i) deionized water, (ii) 0.1 mM sodium chloride and (iii) 0.1 mM potassium hydroxide. The ionic strength and composition for solution condition (i) is unknown. Since the solution is slightly acidic ($pH \simeq 6.0$), the hydronium ion ($H_3O^+$) and other ions released by the electrochemical reactions at the electrode surface must
cause the concentration polarization leading to the EHD flow. However, no quantification is possible, though the colloidal aggregation behavior is similar to that in the presence of added electrolyte. When 0.1 M HCl is added to solution (i) to change the pH to 4.5, the particles form a tighter assembly and the frequency range becomes wider. (Figure 3.3 and 3.4) The addition of H\(^+\) ions can cause a change in the concentration polarization; the reduced surface charge on the particle due to pH change can also play a role in modificaion the interparticle interaction and hence the equilibrium distribution of the particles. Since both the effects are coupled, it is difficult to ascribe the cause to one or the other. The other electrolytes used by us, namely, sodium chloride and potassium hydroxide, have negative values for \(i\) (-0.21 and -0.46 respectively). But their presence leads to a broader frequency window for 2D crystalline aggregates as well as gives rise to tighter assembly of the particles (Figures 3.7, 3.8 and 3.9 vis-à-vis Figures 3.3 and 3.4). Extending the earlier work on EHD flow in the vicinity of a colloidal particle, Sides [81] solved the Stokes equations, the diffusion equation, and Laplace’s equation simultaneously to obtain a numerical solution. For relatively slow electrode kinetics and small particles such as micron size particles on indium-tin oxide (ITO), the theory predicts a critical frequency, \(f_c\), below which aggregation is possible. \(f_c \approx 0.44D/a^2\) or \(0.64D/a^2\), where \(D\) is the diffusion coefficient of the electrolyte. With \(D\) values of \(1.61 \times 10^{-9} m^2/s\) for sodium chloride and \(2.85 \times 10^{-9} m^2/s\) for potassium hydroxide, the highest critical frequency values predicted by the theory for the colloidal particles used by us \((a = 2.5 \mu m)\) are respectively 165 Hz and 290 Hz, far less than the observed value of over 500 Hz. However, our observation that the critical frequency for potassium hydroxide is larger than that for sodium chloride is well supported by the theory. Since \(f_c \propto a^{-2}\), for smaller particles, the upper critical
frequency should be larger. This is verified for $a = 1.5 \, \mu m$ (Figures 3.10 and 3.11). However, the dependence of $f_c$ on ionic strength that is experimentally observed cannot be accounted for.

Ristenpart et al. [103] derived scaling expressions for the EHD fluid velocity that leads to particle aggregation. Assuming perfectly polarizable electrode with an alternating potential and using point dipole approximation to describe perturbation in the field near the electrode due to the particles, taking into account mobile charge in the particle double layer, the tangential velocity due to EHD forces is shown to scale as

$$\nu \sim \frac{3\varepsilon_0\varepsilon_s}{\eta k} E_0^2 \left[C_0' + \frac{D\kappa^2}{\omega} C_0''\right]$$

(3.5)

Here $\omega = 2\pi f$. The Debye length, $\kappa^{-1} \sim 30nm$ for 0.1 mM electrolyte solution. $C_0'$ and $C_0''$ are respectively the real and imaginary parts of the dimensionless dipole coefficient, $C_0$ which is a complex function of frequency and the properties of the particles such as $\zeta$-potential and radius. It also depends on the solution properties such as ionic strength, ion valences and mobilities, and the dielectric constant. Mangelsdorf and White [106] investigated the dielectric response and electrical conductivity of spherical colloidal particles in an oscillating field and obtained numerical solution to the dipole coefficient using standard electrokinetic model [107]. Ristenpart et al. [103] based their calculations on this standard electrokinetic model. However, for our system with large $\kappa a (= 82.6$ for 0.1 mM salt) and low frequencies such that $\omega/\kappa^2 D \ll 1$, Hinch et al.’s [108] analytical solution for $C_0$ can be used. For $f > 300 \, \text{Hz}$, the formula of Hinch et al. [108] agrees closely.
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with the numerical solution of Ristenpart et al. [103], while for \( f < 300 \text{ Hz} \), it underestimates \([C_0' + (D\kappa^2/\omega)C_0'']\) by a factor less than 2. For an electrolyte with two ionic species, the formula of Hinch et al. [108] can be written as,

\[
C_0(\omega) = -\frac{1}{2} + \frac{3\beta'}{2[1 + \gamma' + \beta'(1 + \gamma'\delta')]} \tag{3.6}
\]

where

\[
\beta' = \frac{\sqrt{2}}{\kappa_2a} (1 + \frac{3\lambda_2\bar{\mu}}{z_2^2\epsilon}) \exp(-\frac{ez_2\zeta}{2k_BT}) \tag{3.7}
\]

\[
\gamma' = -\frac{z_1\lambda_2}{z_2\lambda_1} \tag{3.8}
\]

\[
\delta' = \frac{1 + \lambda'a}{1 + \lambda'a + \frac{1}{2}(\lambda'a)^2} \tag{3.9}
\]

\[
\lambda' = \left[-\frac{i\omega}{k_BT}(\frac{z_2\lambda_1 - z_1\lambda_2}{z_2 - z_1})\right]^{1/2} \tag{3.10}
\]

Here subscript 1 refers to the co-ion and 2 refers to the counter-ion.

\[
\lambda_i = \frac{N_A e^2|z_i|}{\Lambda_i^\infty}, \quad i = 1, 2 \tag{3.11}
\]
\[
\bar{\mu} = \frac{2\varepsilon_0\varepsilon_s k_B T}{3\eta e}
\]  \hspace{1cm} (3.12)

\(N_A, k_B, e, \zeta\) and \(T\) are respectively the Avogadro number, Boltzmann constant, electronic charge, \(\zeta\)-potential of the particle and absolute temperature of the solution. The ionic conductance is \(\lambda_i^\infty (i = 1, 2)\).

The particles will be entrained towards each other due to EHD flow if \(C_0' + (D\kappa^2/\omega)C_0'' < 0\). According to Eq. 3.5, the velocity and hence the kinetic rate of aggregation scale as \(E_0^2\) and \(\omega^{-1}\). This prediction has been verified by Ristenpart et al. [103] and also observed by other authors [82, 91]. However, this model does not predict a limiting frequency above which the velocity reverses direction for the experimental conditions used by Ristenpart et al. [103] as well as by us for 0.1 mM sodium chloride and potassium hydroxide. Nevertheless, we calculated the EHD velocity using Eqs. 3.5 and 3.6 and determined Stoke’s force,

\[
F_h = 6\pi \eta av(f)
\]  \hspace{1cm} (3.13)

The average interparticle separation \(r_{eq}\) depends on the balance of several forces including electrostatic repulsion, van der Waals attraction, EHD forces, gravity etc. The van der Waals forces being short-ranged, the balance can be considered as due to dominant electrostatic repulsion and EHD forces. The dipole-dipole interaction varies as \(r^{-4}\), and for the range of frequencies used and the corresponding \(F_h\) values obtained using Eq. 3.13, the dipole interaction, \(F_e = 3\pi \varepsilon_0 \varepsilon_s a^6 E_0^2/r^4\) was at least an order of magnitude less at the equilibrium distances obtained experimentally.
Also $F_e$ varies marginally with inter particle distances around $r_{eq}$. In contrast the screened Coulomb force $F_c$ exhibits larger variation with $r$ near close contact. From the expression of screened Coulomb potential [14], $F_c$ can be derived as:

$$F_c = \frac{Z_p e^2}{4\pi \varepsilon_0 \varepsilon_s (1 + \kappa a)^2} \frac{(\kappa a + 1) \exp[-\kappa (r - 2a)]}{r^2}$$

(3.14)

where $Z_p e$ is the surface charge on the colloidal particle that can be related to the $\zeta$- potential by,

$$Z_p e = 4\pi \varepsilon_0 \varepsilon_s a (1 + \kappa a)\zeta$$

(3.15)

The equilibrium distances $r_{eq}$ calculated by balancing $F_h$ with $F_c$ in the experimental range of frequencies are also plotted on Figures 3.7 and 3.9. Though the calculated values agree closely with the experimental values for some frequencies, the de-aggregation beyond a cut-off frequency cannot be predicted by this theory. Inclusion of dipole interaction, namely, balancing $F_h$ with $F_e + F_c$ does not cause much change in the theoretical curve. Another limitation is that the forces derived for the interaction between a pair of particles cannot be expected to account for a multi-particle assembly.

The existence of a lower and an upper cutoff frequency has been predicted and verified experimentally by Nadal et al. [109, 110] for the EHD flow in the vicinity of a dielectric stripe deposited on a conducting plate subjected to ac polarization. The stripe is modeled as a small change in surface capacitance of the plate and
the EHD coupling is treated in the limit of a thin double layer. The presence of
the dielectric stripe results in a rectified electro-osmotic slip along the surface that
leads to a set of counter-rotating rolls whose size decreases with frequency and the
strength of flow increases with the applied voltage amplitude. The rectified slip
velocity of the fluid decreases to zero in both the limits of the applied frequency,
f \rightarrow 0 and also \( f \rightarrow \infty \). The lower cutoff frequency \( f_L \) is essentially the cutoff
frequency of an equivalent resistance-capacitance circuit formed by the electrolyte
and the electrodes.

\[
\omega_L = 2\pi f_L = \frac{2D(1 + \alpha_0)}{\lambda_D L} \tag{3.16}
\]

where \( D \) is the diffusion coefficient of the electrolyte, \( \lambda_D \equiv \kappa^{-1} \) is the thickness
of the Debye layer, \( L \) is the distance between the electrodes, and \( \alpha_0 = \lambda_c \varepsilon / \lambda_D \varepsilon_c \).
The dielectric constant of the electrolyte is \( \varepsilon \) and that of the oxide layer of the
thickness \( \lambda_c \) on the electrode surface is \( \varepsilon_c \). The upper cutoff frequency \( f_a \) depends
on the width of the stripe, \( 2a \).

\[
\omega_a = 2\pi f_a = \frac{D(1 + \alpha_0)}{a\lambda_D} \tag{3.17}
\]

For \( \omega < \omega_a \), the fluid velocity at the edge of the stripe

\[
\nu_{typ} \propto \varepsilon \varepsilon_0 \frac{a}{\eta} \left( \frac{\phi_0}{L} \right)^2 \tag{3.18}
\]
where $\phi_0$ is the amplitude of the applied AC voltage and $\eta$ is the solvent viscosity. For $\omega > \omega_a$, the velocity decreases to zero and varies as $\omega^{-2}$. Though these discussions pertain to a rectangular dielectric stripe on a conducting plane of the electrolyte cell (later extended to a circular stripe in Ref. [110]), they seem to at least qualitatively explain our observations on the spherical dielectric colloidal particles in a similar situation. Our observations of the existence of an upper and a lower cutoff frequency for the 2D colloidal assembly, the lower cutoff frequency being $\sim 100$ Hz and independent of particle size, and the upper cutoff frequency being inversely related to the particle diameter, agree well with the above model. Since $I/\lambda_D \equiv \kappa \propto \sqrt{I}$, where $I$ is the ionic strength, the upper cutoff frequency $f_a \propto \sqrt{I}$. Thus for higher ionic strength, the frequency range of colloidal assembly is widened, consistent with our observation. If the fluid velocity is $\propto a$, as in Eq. 3.18, then the EHD force of attraction $F_h$ [Eq. 3.13] will be larger for bigger particles. From Eq. 3.14, it is obvious that the equilibrium distance obtained by balancing the Coulomb force $F_c$ with $F_h$ will be smaller for larger particles, other parameters remaining comparable. This again is concurrent with our observation. Increase in ionic strength decreases the range of Coulomb interaction which should enable a tighter assembly of particles. Decrease in $\zeta$ potential decreases the Coulomb repulsion which again would decrease the equilibrium interparticle distance. Our experimental results support these predictions of the model wherein the equilibrium distribution of the particles in the colloidal assembly is the resultant of the two opposing forcesethe attractive force due to EHD flow and the repulsive screened Coulomb interaction between the spherical colloids.
3.5 Summary

The two-dimensional assembly of colloidal particles near an electrode surface subjected to AC polarization is studied by varying the frequency and field strength in the absence and presence of added electrolyte. The equilibrium centre-to-centre particle separation, $r_{eq}$, does not show remarkable variation with voltage within the frequency window for crystallization. The added electrolyte strength and salt-specificity affect the range of the frequency window, with the range being wider in the presence of salt. The electrohydrodynamic flow, suggested by several authors to be the most likely mechanism for the 2D fluid and crystalline structures, is analyzed in the light of the existing theoretical models. The equilibrium distribution of the particles is considered to be the resultant of the two opposing forces - the Stoke’s force due to EHD velocity and the screened Coulomb interaction between the colloidal particles. The existence of a lower and upper cut-off frequency for colloidal aggregation cannot be explained by the existing theoretical models. However, the decrease in EHD velocity and hence the increase in inter-particle separation at high frequencies can be explained. Also, several features of the experimental results can be accounted for, such as the role played by the EHD flow in the particle aggregation, the dependence of the equilibrium inter-particle separation on ionic strength and $\zeta$-potential.
Chapter 4

Colloidal Phase Transition Driven by Alternating Electric Field

4.1 Introduction

Suspensions of monodispersed colloidal particles are a rich model experimental system for understanding the fundamental mechanism for melting of two-dimensional crystals, and for searching for the elusive hexatic phase, with order intermediate between that of a perfect crystal and disordered fluid. By performing imaging experiments on colloidal systems, one can surmount a number of problems that have plagued either past experiments on atomic scale systems or computer simulations. The colloid experiments share some useful features with computer simulations. In particular, the colloids can be made very rigidly two-dimensional, so that promotion to a second layer may not occur. The particle-particle interactions can be
adjusted from short- to long-range. The interparticle separation and particle di-
ameter can be chosen for optimum video imaging with visible light so that one can
obtain direct visual evidence of lattice defects, dynamics and of bond-orientational
order in real space in the system on relevant timescales.

In this chapter, we studied the phase transition of colloidal particles under AC
field driven by the frequency. Under an alternating current (AC) electric field,
colloidal spheres can be driven to aggregate laterally and form 2D assembly by
tuning frequency and field strength. Especially, this behavior is more sensitive to
the modulation of frequency. However, not all frequencies can produce a crystalline
assembly of particles. There exist a finite frequency range with well defined lower
and upper cutoff finite frequency values characteristic of particle size, charge, etc.

4.2 KTHNY Theory

Between the crystalline and the isotropic liquid many liquid crystal compounds
exhibit two or more distinct mesophases with various degrees of translational and
orientational order. These materials provide new thermodynamically stable phases
and are excellent systems for studying melting processes, phase transitions, and
critical phenomena. Considerable experimental and theoretical effort has been
aimed toward understanding the variety of physical phenomena related to various
mesophases.

Among theories of two-dimensional melting transition, the Kosterlitz-Thouless-
Halperin-Nelson-Young (KTHNY) theory has led to a large number of experimental
and simulation studies of the 2D melting transition and no discussion of 2D melting would be complete without mention of this seminal theory.

The most interesting prediction of the KTHNY theory is that melting in two dimensions can occur via two continuous phase transitions, associated with the successive unbinding of dislocations and declinations. The KTHNY theory also predicts a novel intermediate phase, the hexatic phase, having short-range translational order and quasi-long-range bond orientational order. Both the solid-hexatic and hexatic-liquid transition can be continuous.

The nature of a continuous phase transition can be characterized by a set of characterizations related to the ordering such as radial pair correlation function $g^{2D}(r)$, which corresponds to the translational order, and bond-orientational correlation function $g_6(r)$, which corresponds to the orientational order.

4.3 A Frequency-driven KTHNY Phase Transition

Most of the two-dimensional melting experiments done to date have used as samples monodisperse charge-stabilized colloidal polystyrene latex spheres which range from $\sim 0.1 - 10 \mu m$ in diameter. By adjusting the parameters of the specific colloidal suspension, one can create a model system of interacting microparticles with forces of interaction that vary between short- and long-range.

In our study, the crystal to liquid-like phase transition driven by frequency was
Figure 4.1: For 5 µm particles, the correlation functions \( g^{2D}(r) \) and \( g_6(r) \) as functions of dimensionless interparticle distance \( r/2a \) are plotted at different frequencies at fixed field strength \( E_0 = 1.5 \times 10^4 \) V/m.
studied by evaluating $g^{2D}(r)$ and $g_6(r)$ as functions of the interparticle distance, $r$, for different frequencies keeping field strength constant. These results are shown in Figure 4.1. At $f = 800\text{ Hz}$, both $g^{2D}(r)$ and $g_6(r)$ are representative of a liquid-like distribution of particles with no long-range translational or orientational order (Figure 4.1 (a)). At $600\text{ Hz}$, the bond orientational correlation function $g_6(r)$ remains at the lower cut-off value of 0.8 set for crystalline assembly, whereas the translational correlation function is uncharacteristic of a crystalline structure (Figure 4.1 (b)). In the frequency range $150 - 400\text{ Hz}$ the correlation functions were characteristic of crystalline structure as shown in Figure 4.1 (c). At $120\text{ Hz}$ the structure melted into liquid-like with loss of translational order (Figure 4.1 (d)), while orientational order still retained a high value. Further, decrease in frequency resulted in the loss of both translational and orientational order. The out-of-plane motion of the particles complicated a systematic analysis of $g^{2D}(r)$ and $g_6(r)$ at low frequencies. The behavior of the translational and orientational correlation functions shows that the alternating electric field can produce a frequency driven 2D crystal-liquid phase transition in the colloidal assemblies, with an intervening hexatic phase in which the particles retain the remnants of the crystalline long-range orientational order, but has liquid-like short range translational order. This is similar to the KTHNY phase transition observed in several systems. [100,111–114].

To our knowledge this is the first systematic observation of the frequency-driven KTHNY transition in colloidal aggregates near the electrode surface subjected to ac polarization.
For $3 \mu m$ particles in the presence of 0.1 $mM$ sodium chloride, the correlation functions $g_{2D}(r)$ and $g_6(r)$ as functions of dimensionless interparticle distance $r/2a$ are plotted at different frequencies at fixed field strength $E_0 = 0.8 \times 10^4 V/m$. 
To further testify the crystal to liquidlike phase transition, a similar series of experiments were performed for 3 \( \mu \)m colloidal particles (pH = 5.7, \( \zeta = -86 \) mV) in presence of 0.1 mM NaCl driven by frequency by evaluating the translational correlation function \( g^{2D}(r) \) and bond-orientational correlation function \( g_6(r) \) as functions of the interparticle distance \( r \) for different frequencies, keeping field strength constant. These results are shown in Figure 4.2. At 2500 Hz, both \( g^{2D}(r) \) and \( g_6(r) \) are representative of a liquidlike distribution of particles with no long-range translational or orientational order [Figure 4.2]. In the frequency range of 1800 – 2200 Hz, the bond-orientational correlation function \( g_6(r) \) remains at cut off value of 0.85 set for crystalline assembly, whereas the translational correlation function is uncharacteristic of a crystalline structure [Figure 4.2 (b), (c)]. In the frequency range of 100 – 1800 Hz, the correlation functions were characteristic of crystalline structure as shown in Figure 4.2 (d), (e) and (f). At 40 Hz the structure melted into fluidlike with loss of translational order [Figure 4.2 (g)]. The phase transition was characterized with an intervening hexatic phase in which the particles retain the remnants of crystalline long-range orientational order but has liquidlike short-range translational order. Figure 4.3 show some illustration pictures of assembly at different frequencies which correspond to Figure 4.2. This is similar to the KTHNY phase transition observed in several systems, including our previous work on larger colloidal particles. We believe this is a strong support for our previous conclusion that colloidal phase transition driven by frequency is a KTHNY-type phase transition.
Figure 4.3: Comparison of the colloidal assemblies obtained under different frequencies: 500 Hz, 1900 Hz and 2500 Hz. The field strength was fixed at $E_0 = 0.8 \times 10^4$ V/m.

4.4 Summary

Altogether, for a given field strength, a frequency window can be identified within which the assembly has a crystalline structure, namely, a long-range bond-orientational and translational order. Outside this frequency window, the structure undergoes a crystal-liquid transition. The variation of the translational and bond-orientational correlation functions with frequency suggests the existence of a hexatic phase in which the particles retain the remnants of the crystalline long-range orientational order but has a liquidlike translational order. This suggests a frequency-driven KTHNY transition in 2D colloidal assembly, which we believe is the first systematic observation of its kind.

However, frequency is not the only way to drive 2D colloidal phase transition under an AC field. Our later study showed that field strength and temperature etc. can also cause 2D colloidal phase transition in our system. This work is an initial study of its kind and should provide useful information for further work. Further
study is suggested to be carried out to explore the mechanism of 2D colloidal phase transition driven by other parameters such as field strength and temperature etc.
Chapter 5

Kinetics and Equilibrium

Distribution under AC Field and

Correlation to Degree of

Perfection of Colloidal Crystals

5.1 Introduction

Close packed arrays of uniform colloidal particles form templates for deposition of films of metals, semiconductors or polymers which find important and diverse applications in photonic materials, nanotechnology, and biotechnology. [32,33] Further improvement of crystal quality depends on the understanding of the assembly
mechanism, technology, or structure characterizations as well. The quality of the colloidal 2D assembly is closely related to the growth rate, which depends on the interactions among particles. In this chapter, by studying the 2D colloidal crystal under an alternating current (AC) electric field, we will establish the correlation between the center-to-center distance $r_{eq}$ between the neighboring particles obtained from the steady state and the degree of perfection of the colloidal crystals or colloidal assembly. Apart from this, we will also relate $r_{eq}$ to the kinetics of colloidal aggregation at different frequencies and salt concentrations to establish the correlations between the assembly rate and $r_{eq}$. Further investigation of $r_{eq}$ as a function of particle size, salt concentration and field strength is used to elucidate the influence of these parameters on the kinetics of aggregation and the EHD flow.

In contrast to electrophoretic deposition under a dc field, an ac field offers an additional parameter to control the assembly, namely, the frequency. [16, 43, 63] However, not all frequencies can produce a crystalline assembly of particles. There exists a finite frequency range with well defined lower and upper cut-off values characteristic of particle size, charge, ionic strength of the solution, pH etc. In the previous chapters, we investigated the influence of these parameters on the equilibrium distribution of colloidal particles. [116] The attractive force which can overcome the interparticle electrostatic repulsion and enable 2D colloidal aggregation is widely suggested to be due to electrohydrodynamic (EHD) flow. [16, 43, 63] The dissolved ionic species build up an electric double layer adjacent to the electrode surface, which is disrupted by the presence of colloidal particles leading to spatially varying free charge. Fluid motion is set up by the interaction between this free charge and the lateral electric field, which is caused by the distortion of
Chapter 5. Kinetics, Equilibrium Distribution, and Degree of Assembly Perfection

the applied field by the colloidal particles. Kinetic experiments and scaling analysis for EHD flow were performed by Ristenpart et al. [83] Their study shows that the EHD velocity is proportional to the square of applied field strength and varies inversely with frequency. This conclusion is well supported by the experiments carried out by Solano [136]. However, the detailed mechanism remains unclear as regards the role played by ionic concentration and particle size in the kinetics, and the existence of boundary frequencies for the 2D assembly. Detailed study of the kinetics of particle assembly under various experimental conditions is rather difficult as compared with the steady-state particle distribution. Hence establishing a correlation between the two and also characterizing the order/crystallinity of the assembly would be helpful in understanding the mechanism of the 2D colloidal assembly.

5.2 Degree of Perfection of Colloidal Assembly and Equilibrium Distance

A detailed description of the experimental setup, image processing and data analysis have been reported.(Ref. Chapter 2 and 3) The colloidal dispersion used in the experiment consisted of negative charge stabilized polystyrene (PS) spheres (diameters of 1.8, 3 and 5 µm, Duke Scientific). The polystyrene particles of diameter of 3 µm with a volume fraction \( \varphi = 0.04\% \) at \( \text{pH} = 5.7 \) and \( \zeta \) potential \( \approx -86 \text{ mV} \) (measured by Malvern \( \zeta \) sizer) were dispersed in 0.1 mM/0.02 mM sodium chloride (NaCl) solution. Experiments were also conducted on PS particles of diameter
Chapter 5. Kinetics, Equilibrium Distribution, and Degree of Assembly Perfection

Figure 5.1: Variation of $r_{eq}/2a$ and $W$ for 3 µm particles under a fixed field of $1.5 \times 10^4$ V/m in the presence of 0.1 mM NaCl, averaged for 5 typical single areas. Also shown are the video micrographs of the assembly.

of 1.8 µm of $\varphi = 0.02\%$ at pH=5.7 ($\zeta$ potential $\approx -75$ mV) and of diameter of 5 µm of $\varphi = 0.15\%$ at pH= 5.7 ($\zeta$ta potential $\approx -100$ mV), both dispersed in 0.1 mM NaCl.

The criteria to be established is to examine the quality of 2D colloidal crystals in terms of the equilibrium distance, $r_{eq}$. Following the method described in Chapter 2 and 3, the radial pair correlation function, $g^{2D}(r)$ and $r_{eq}$ were determined for particles of diameter 3 µm under a fixed field strength of $E_0 = 1.5 \times 10^4$ V/m in the presence of 0.1 mM NaCl. The full width at half maximum (fwhm) $W$ at the
first peak of $S(Q)$, which is the Fourier transform of $g^{2D}(r) - 1$, was obtained using the relation,

$$S(Q) = 1 + 2\pi \rho \int_0^\infty [g^{2D} - 1] J_0 Q(r) r dr$$  \hspace{1cm} (5.1)$$

where $S(Q)$ is the structure factor, $Q$ is the wave vector, $\rho$ is the particle number density and $J_0$ is the zeroth order Bessel function. A small value of $W$ represents persistent oscillations in $g^{2D}(r)$ and hence a well ordered crystal lattice with large correlation length. Figure 5.1 shows that the variations of $r_{eq}$ and $W$ with frequency have the same trend, which implies that smaller values of $r_{eq}$ represent better crystalline assemblies. Also shown in Figure 5.1 are the video micrographs of the assembly. It is worth mentioning here that $S(Q)$ and hence $W$ can also be obtained from the intensity of the radiation scattered by the colloidal crystal. However, obtaining $r_{eq}$ is much easier than obtaining $S(Q)$ from scattering studies. Thus $r_{eq}$ can be used as a parameter to judge the quality of the 2D assembly.

## 5.3 Kinetics and Equilibrium Distribution

### 5.3.1 Method to Perform Kinetics Measurements

The rate of singlet disappearance is used to quantify the aggregation process. [83] The first step is to set a threshold to identify singlets. According to Ristenpart et al.’s method, [83] they separated individual particles (and higher order aggregates)
from the background by identifying the number of pixels in the clusters. Singlets have a relatively narrow distribution of “detected” size. A cluster that subtended \( p \) pixels \( (p_{\text{min}} < p < p_{\text{max}}) \) was identified as a singlet; cluster with \( p > p_{\text{max}} \) were identified as higher order clusters. We used a slightly different image analysis method for determining whether the particles are singlets. Instead of judging this by the pixel number in the cluster, we simply used the center-of-mass location of the particles. A threshold was set \((1.3 \times 2a)\) so that a particle that does not have a neighboring particle within the range of \(1.3 \times 2a\) is treated as a singlet. Both methods should be equally effective, but ours involves less data processing.

A very large number of particles were chosen to analyze their behaviors under AC field. At the outset, the majority of the particles were isolated and undergoing Brownian motion. Upon application of the field, “singlets” moved together or toward larger aggregates to form clusters (Figure 5.2, 5.3, 5.4, 5.5). The observed motion was approximately two-dimensional and the rate of singlet disappearance served as a measure of the rate of aggregation introduced by the electric field. Since this method focuses on the initial rate of particle aggregation, the crystallites are relatively small; it is clear from the previous work that they will assemble into larger two- or three-dimensional crystals. [43]

In order to obtain the singlet disappearance, images were recorded at one frame every two seconds. Then standard image process were applied to each image. The rate of singlet disappearance has been expressed as \([83]\) \( \frac{dn_1}{dt} = -k_E n_1^2 \), and hence
Figure 5.2: Illustration picture of assembly for 3µm colloidal particles at fixed field strength and frequency: $E_0 = 0.8 \times 10^4$ V/m; $f = 350$ Hz. $t = 0s$.

Figure 5.3: Illustration picture of assembly for 3µm colloidal particles at fixed field strength and frequency: $E_0 = 0.8 \times 10^4$ V/m; $f = 350$ Hz. $t = 10s$. 
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Figure 5.4: Illustration picture of assembly for 3µm colloidal particles at fixed field strength and frequency: $E_0 = 0.8 \times 10^4$ V/m; $f = 350$ Hz. $t = 20s$.

Figure 5.5: Illustration picture of assembly for 3µm colloidal particles at fixed field strength and frequency: $E_0 = 0.8 \times 10^4$ V/m; $f = 350$ Hz. $t = 30s$. 
\[ \frac{n_1^0}{n_1} = 1 + k_E n_1^0 t \]  

(5.2)

where \( n_1 \) is the singlet concentration (number per unit area), \( k_E \) is the aggregation rate constant and \( n_1^0 \) is the initial particle concentration. A plot of the inverse singlet concentration normalized on \( n_1^0 \) as a function of time \( t \) is used to determine the rate constant \( k_E \).

The reproducibility were tested as well by Ristenpart et al. [83] Reference [83] shows the rate constant obtained in a sequence of 52 experiments with a 500 Hz and 4 V applied potential. [83] The apparent rate of aggregation will be correspondingly larger due to higher order encounters if particles are closer to one another at the onset of the electric field. In order to minimize this effect, the particles were moved into a widely separated configuration prior to each experiment using a 10 kHz, \( 2.0 \times 10^4 V/m \) applied field. This provided a reproducible random initial condition for each experiment. However, it was difficult to precisely control the initial singlet concentration, which varied between experiments due to random aggregation and de-aggregation via Brownian motion. This partially accounts for the scatter in the measured rate constants, since contributions from higher order clusters are neglected in the analysis. [83]

Rescaling the data as \( n_1^0/n_1 \) shows that the inverse concentration increases linearly with time, consistent with Eq. 5.2. (Figure 5.6) Note that theoretically the line should go through \((0, 1.0)\). However, for our experimental system where within the observation area around 500-1000 particles move around, even at the very beginning there are some particles that are very near to others. Thus not all the
Figure 5.6: Scaled (inverse) singlet concentration data in our system for 3 \( \mu m \) PS particles in presence of 0.1 \( mM \) NaCl. \( E_0 = 0.8 \times 10^4 \) V/m. The slopes of the lines yield the aggregation rate constants.

... particles are singlets in the beginning and the lines do not exactly go through (0, 1.0). However the experimental results are still statistically meaningful considering only very small amount of them are not singlets.

5.3.2 Kinetics and Analysis

It is generally accepted that electrohydrodynamic (EHD) flow is the most likely mechanism for the formation of 2D fluid and crystalline structures by colloidal particles near the conductive surface of an electrode subjected to an alternating electric field. [15, 16, 48, 63, 81–83] The EHD flow is engendered by field inhomogeneities near the polarization layer. The presence of particles near the electrode surface cause gradients in current density and generate localized fluid flow that carries the particles towards each other. The competition between two kinds of antagonist forces (repulsive and attractive) determines whether the particles would
assemble or disperse. The dominant attractive force is the Stokes force

\[ F_h \sim 6\pi\eta v(f, r) \tag{5.3} \]

Here \( \eta \) is the viscosity of the solvent and \( v(f, r) \) is the frequency \( (f) \)-dependent EHD velocity at a distance \( r \) from one of the particles of radius \( a \). The repulsive forces are due to the electrostatic screened Coulomb interaction and the dipole-dipole interaction between the particles. [82, 116] At frequencies within a certain range, the EHD velocity is negative, leading to an attractive Stokes force that causes particle aggregation while outside this frequency window, the velocity either diminishes or becomes positive giving rise to predominantly repulsive forces that cause disintegration of the ordered assembly. The scaling expression for the tangential velocity due to EHD forces that leads to particle aggregation has been derived by Ristenpart et al. [83] The tangential aggregation rate constant is shown to scale as:

\[ k_E \approx \frac{2\pi a}{\eta \kappa} \frac{3\varepsilon \varepsilon_0 E_0^2}{\kappa} |C_0'| + \frac{D \kappa^2}{\omega} |C_0''| \tag{5.4} \]

Here \( \varepsilon \) is the fluid dielectric constant, \( \varepsilon_0 \) is the permittivity of free space, \( \kappa \) is the reciprocal Debye length, \( D \) is the ionic diffusion coefficient, and \( \omega = 2\pi f \) is the angular frequency. \( C_0' \) and \( C_0'' \) are respectively the real and imaginary parts of \( C_0 \), the dimensionless dipole coefficient which is a complex function of frequency, and particle properties such as the \( \zeta \)-potential and the radius. It also depends on the solution properties such as ionic strength, ion valences and mobilities, and the
dielectric constant. In the frequency range of interest for the colloidal assembly, $C'_0$ is a weak function of frequency and it is almost constant. Thus the rate constant is proportional to the square of the field strength $E_0^2$, and inversely proportional to the frequency $f$. Ristenpart et al. [83] verified these scaling relations for 2.7 μm polystyrene particles in a 1.0 mM potassium chloride solution. We undertook a similar study on 3 μm polystyrene particles in a 0.02 and 0.1 mM sodium chloride solution.

Figure 5.7: Variation of aggregation rate constant $k_E$ with frequency for 3 μm particles under a fixed field of $8 \times 10^4$ V/m and in the presence of NaCl of concentrations of 0.02 mM (inverted triangles) and 0.1 mM (squares). The inset shows typical scaled singlet concentration data in the presence of 0.1 mM NaCl. Solid lines are linear fits to the data; the slope of the line is $k_E n_1^0$.

Figure 5.7 shows the variation of the aggregation rate constant $k_E$ for two ionic concentrations (0.02 and 0.1 mM NaCl) over the frequency range in which the 2D assembly can be formed at fixed field strength. The assembly rate constant reaches
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its maximum between 200 − 500 Hz, and then decreases towards zero. For a given frequency, \( k_E \) turns out to be larger in the presence of a higher ionic concentration. It is noteworthy that Ristenpart et al. \[83\] have reported a linear variation of \( k_E \) with \( \omega^{-1} \); however, we observe that \( k_E \) passes through a maximum when plotted as a function of frequency, the reason being that our investigation is extended over a wider range of frequencies (70 − 1300 Hz). As \( k_E \) is directly related to the EHD velocity, \[83\] it can be inferred that the EHD velocity decreases to zero at lower and upper cut-off frequencies, exhibiting a peak with a broad shoulder, especially toward higher frequencies. Unfortunately, neither Eq. 5.4, nor any other theoretical expressions for the EHD velocity found in the literature \[81,118\] can predict (with regards the observation of a peak) two cut-off frequencies for the EHD velocity in a 2D colloidal assembly. However, a similar prediction has been given by Nadal et al. \[82\] for EHD flow in the vicinity of a dielectric stripe deposited on an electrode subjected to an alternating electric field.

We further investigated the equilibrium distribution of the particles in the assembly under the same experimental conditions as in the kinetics study. The frequency range of the maximum assembly rate is found to correspond to the range in which the colloidal particles form a tight assembly. Figure 5.8 shows the phase diagram of \( r_{eq} \) as a function of frequency in the presence of two ionic concentrations at fixed \( E_0 \). From Figure 5.7 and 5.8 we find that an increase in salt concentration corresponds to larger EHD velocity and gives rise to a tighter assembly of colloidal particles. These observations agree with Eq. 5.4, which predicts that, in the approximation of a negligible \( C'_0 \), \( k_E \) is linear with respect to \( \kappa \). Since a higher ionic concentration leads to an increase in \( \kappa \), the aggregation rate \( k_E \) should increase with
Figure 5.8: Variation of equilibrium distance $r_{eq}$ with frequency for 3 $\mu$m particles under a fixed field of $0.8 \times 10^4$ V/m and in the presence of NaCl of concentrations of 0.02 mM (inverted triangles) and 0.1 mM (squares).

Ionic concentration, which is consistent with our observation. Another outcome is that when $k_E$ becomes larger, the attractive EHD force $F_h$, which is proportional to $v(f, r)$, should increase as well. Since the equilibrium distribution corresponds to the balance between attractive and repulsive forces, the increased attraction can overcome a larger electrostatic repulsion, thereby bringing the particles into a tighter assembly. This is consistent with our observation in Figure 5.8 that $r_{eq}$ decreases when the ionic strength increases.
5.4 Investigation of the Effect of Field Strength and Particle Size on Colloidal Assembly

According to Eq. 5.4, the aggregation rate constant $k_E$ should be proportional to the square of field strength, $E_0$. A similar conclusion is arrived at by the theory developed by Sides. [81] This implies that when $E_0$ increases, $F_h$, which is proportional to fluid velocity, would also increase to overcome stronger repulsive forces, so as to produce a tighter assembly of colloidal particles. This is consistent with our result for 1.8 $\mu$m particles as shown in Figure 5.9, implying that $r_{eq}$ becomes smaller as $E_0$ increases. However, a trend was observed for $r_{eq}$ to become larger beyond a certain value of $E_0$, for 3 $\mu$m particles at frequencies near the lower cut-off value. Although this result is hard to interpret using existing models, it is consistent with our earlier result for 5 $\mu$m particles [Figure 3.6] that at all frequencies $r_{eq}$ tends to increase with increasing $E_0$ beyond a certain value. This may imply that above a certain field strength, another mechanism becomes dominant besides the EHD flow. We expect that for 1.8 $\mu$m particles also a similar trend may be present above a certain value of $E_0$, which is beyond our range of experimentation due to limitations in the setup.

Another deduction that we can draw from Eq. 5.4 is that the aggregation rate constant $k_E$ and hence $F_h$ are proportional to the particle size. Thus larger particles can form tighter assembly compared with smaller particles. This conclusion is confirmed by Figure 5.11, which shows that fixing $pH$ and the ionic strength of the solution while allowing a slight variation of the $\zeta$-potential, the minimum value of $r_{eq}$ for 5 $\mu$m particles is much lower than for 3 and 1.8 $\mu$m particles. We also
find that the frequency window for crystal-like assembly shifts to larger values for smaller particles.

5.5 Summary

In conclusion, we have established that the equilibrium center-to-center particle separation $r_{eq}$ can be a new criterion for characterizing 2D assembly, since it can be used as a measure of the crystalline order in the lattice and it can also be correlated to the kinetic rate constant for aggregation of colloidal particles under an alternating electric field. Taking a particular case as an example, at the frequency where $r_{eq}$ reaches its minimum, colloidal particles form a tight assembly and the
attractive interactions are much stronger than repulsive ones. Meanwhile at this point, the quality of the assembly becomes almost perfect and the rate constant $k_F$ is largest due to the overwhelmingly attractive forces. The roles played by frequency, field strength, salt concentration and particle size on the 2D assembly have been investigated. Based on this work, we hope that the complicated mechanism of colloidal assembly driven by an alternating electric field could be further understood and our experimental results might enable further refinement of theoretical models. This understanding will benefit future study of binary or multi-component systems of colloidal dispersions, as well as in the design of optical materials, biotechnology, etc.
Figure 5.11: Variation of $r_{eq}/2a$ with frequency for colloidal particles of three different diameters in 0.1 mM NaCl. Field strength $E_0$ was kept constant at $1.5 \times 10^4$ V/m.
Chapter 6

Fine Tuning of Equilibrium Distance of Two-dimensional Colloidal Assembly under an Alternating Electric Field

6.1 Introduction

The two-dimensional (2D) assembly of colloidal spheres has been used in a variety of applications, such as photonic crystals, biosensors, and nanofluidic devices. [119–124,126–128] Recently, the 2D colloidal assembly has attracted increasing interest in the context of an emerging technique known as colloidal lithography,
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because it can be used as a template to fabricate various functional nanostructures
in an inexpensive and simple way. [37,128,129] Colloidal assemblies exhibiting pre-
dominantly hexagonal close packed arrays are easy to obtain as they are favored
thermodynamically and have a robust mechanical stability. However, non-close
packed structures are preferable, as they exhibit more flexibility for creating pat-
terns with a tunable separation distance, which is important for the application
in nanoparticle optics and sensors. [130–132] Moreover, the spherical colloids of
non-close packed arrays are not interconnected so that further deposition of ma-
terials can form continuous films rather than distinct islands. [128,133] However,
up to now, non-closed packed arrays of colloidal assemblies are mainly constructed
by means of lithographic techniques, which are expensive, time consuming and
difficult to apply for a large area of construction. [134]

A simple strategy for the fabrication of a 2D colloidal array is the application of
an alternating current (AC) electric field to a solution of charged colloidal spheres.
[16,43,48,63,81–83,93–96,104,116,136–141] Upon application of the AC field, col-
loidal spheres can be driven to aggregate laterally and form a 2D assembly of crys-
talline ordering. Various theories and models have been proposed to explain this
phenomenon, such as the electrohydrodynamic (EHD) model [16,43,48,63,81–83]
and the Faradaically coupled electroosmosis (FCEO) model. [93–96,136] However,
the exact mechanisms responsible for the net motion have been difficult to discover,
and the effect of temperature on the colloidal assembly remains unexplored. Be-
sides, the research carried out in this field so far focuses mainly on the mechanism
and lags behind in the exploration to the correlated applications.
In this chapter, we report on the study of the effect of temperature on the equilibrium separation distance $r_{eq}$ of the 2D colloidal assembly under an AC field. We show that the dependence of the equilibrium separation distance $r_{eq}$ of the particles on the temperature is different in different frequency ranges, providing evidence that different mechanisms are present over the frequency window corresponding to colloidal assembly. Moreover, based on the understanding gained here, we establish an effective method to finely tune the equilibrium separation distance $r_{eq}$ of the assembly over a wide range. This method can be used to form large areas of either close packed or non-close packed patterns of colloidal assemblies for practical applications.

6.2 Non-Close Packed Arrays by the Combination of Frequency, Field Strength, and Temperature

6.2.1 Effect of Temperature on Colloidal Assembly

The experimental details, image processing and data analysis have been reported elsewhere. [104,116,137–142] For this study, the sample cell was kept in a Linkam THMS 600 Heating and Freezing stage in which the temperature $T$ could be controlled within 0.1°C in the range of -192°C to + 600°C. [142] The colloidal dispersion consisted of negatively charge stabilized polystyrene (PS) spheres (diameter $2a$ of 3 µm, Duke Scientific). The dispersion with a volume fraction $\varphi$ of 0.05 % at a
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Figure 6.1: Variation of dimensionless equilibrium distance $r_{eq}/2a$ with frequency at different temperatures in the presence $0.05 \text{ mM NaCl}$ at a fixed field strength $E_0 = 1.5 \times 10^4 \text{ V/m}$.

$pH$ of 5.7 and $\zeta$ potential $\approx -86 \text{ mV}$ (measured by a Malvern $\zeta$ sizer) was dispersed in a $0.05 \text{ mM}$ sodium chloride (NaCl) solution. To permanently fix the 2D colloidal assembly for practical applications, a direct current (DC) electric power supply was connected in parallel to the AC power supply. The scanning electron microscope (SEM) images of the permanently fixed colloidal assembly were obtained using a field emission scanning electron microscope (FE-SEM, JEOL_6500F).

Figure 6.1 shows the variation of normalized equilibrium distance $r_{eq}$ with frequency $f$ for different temperatures $T$ at a fixed field strength and ionic concentration. As the temperature increases, the frequency window corresponding to the 2D
colloidal assembly widens, and the upper cutoff frequency $f_H$ in the high frequency range ($> 500 \text{ Hz}$) becomes much larger. According to the theoretical electrohydrodynamic (EHD) model based on an induced charge electroosmotic flow proposed by Sides, [81] for relatively slow electrode kinetics and small particles such as micron size particles on indium tin oxide, the critical upper cutoff frequency $f_H$ below which aggregation is possible can be expressed by:

$$f_H \propto \frac{D}{a^2}$$

(6.1)

Here $D$ is the diffusion coefficient of the electrolyte expressed by the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\eta a}$$

(6.2)

where $\eta$ is the viscosity of surrounding medium which becomes smaller as temperature increases. Eqs. 6.1 and 6.2 indicate that an increase in temperature $T$ results in an increase of $D$, thus causing $f_H$ to become larger. (Figure 6.1) The EHD model [81] can explain well our observations in the high frequency range ($> 500 \text{ Hz}$). It can also be inferred that the increase of temperature has a similar effect on $f_H$ as the reduction of the particle size $a$. Our previous results (Figure 3.6) show that the reduction of particle size leads to a higher $f_H$. [116,140]

In the low frequency range ($< 500 \text{ Hz}$), however, the dependence of $r_{eq}$ on temperature $T$ is complicated. To determine precisely the change of $r_{eq}$ with temperature
Chapter 6. Fine Tuning of Equilibrium Distance of 2D Colloidal Assembly

We performed another set of systematic temperature-dependence experiments at various frequencies while the field strength was kept fixed. As shown in Figure 6.2a, in the high frequency range (≥ 300 Hz), \( r_{eq} \) does not show any significant change with temperature. Whereas in the low frequency range (for example, 150 Hz and 100 Hz), \( r_{eq} \) is strongly dependent on the temperature and shows a clear increase as the temperature increases. The competition between the attractive forces and the repulsive dipole-dipole forces determines the equilibrium particle separation distance. The apparent change of the behavior of the temperature dependence suggests that the mechanism generating these forces changes when the frequency is decreased.

Recent work [95, 96, 104, 136] suggests that multiple mechanisms are responsible for the net motion of the particles over all frequency ranges. On the basis of an observation of the vertical response of a single particle in an AC field near an electrode, Fagan et al. [96] demonstrated that for frequencies below about 200 Hz, a FCEO mechanism dominates the particle behavior, while for frequencies above \( \sim 500 \) Hz, as increasing frequency short circuits the faradic channel, the EHD mechanism takes over and can account for the experimental observations of the lateral motion at those frequencies. Our experimental results show that in the high frequency range (> 500 Hz) the observations can be explained by the EHD model, whereas in the low frequency range, a transition of the behavior occurs at \( \sim 300 \) Hz, consistently with Fagan’s demonstration. Experiments of the field-strength dependence of \( r_{eq} \) also show an apparent change of the field-strength dependence when the frequency is decreased (Figure 6.2b). In the high frequency range (> 300 Hz), \( r_{eq} \) decreases as the field strength increases, in accord with the
Figure 6.2: Variation of dimensionless equilibrium distance of $r_{eq}/2a$ at different frequencies with the temperature at a fixed field strength $E_0 = 1.5 \times 10^4 V/m$ (a), and with the field strength at a fixed temperature $T = 25^\circ C$ (b).
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EHD model. [83] Whereas in the low frequency range (100 Hz and 200 Hz), $r_{eq}$ increases with the field strength, contrary prediction of the $E^2$ dependence obtained from the EHD model. [83] This further confirms that a change of the origin of the EHD mechanism occurs at $\sim 300$ Hz.

6.2.2 Non-Close Packed Arrays by the Combination of Frequency, Field Strength, and Temperature and Formation of Permanent Template

Based on the understanding gained above, we establish an effective method to finely tune the equilibrium distance of the 2D colloidal assembly by a combination of the temperature and the AC field for a directed assembly. According to Figure 6.2, the close-packed colloidal assembly can be modulated to become a non-close-packed assembly by decreasing the frequency range to low frequency range. In the low frequency range ($< 300$ Hz), an increase in the field strength gives rise to a significant increase in $r_{eq}$. Moreover, we observed that in two-dimensions the particles are more readily restricted in two-dimension at lower temperatures probably due to a weaker Brownian motion. Thus at low temperature and low frequency, one can tune the $r_{eq}$ over a wide range by increasing the field strength to obtain non-close packed colloidal arrays with large interparticle separations. Figure 6.3 shows that at low temperature and at a very low frequency (40 Hz), $r_{eq}$ has been modulated over a wide range from $1.05 \times 2a$ to $2.23 \times 2a$ by increasing the field strength.
Figure 6.3: Representative Optical images of sample areas illustrating the adjustment of $r_{eq}$ over a wide range from 1.18 to 2.23 for 3 μm PS particles. (a) Tight assembly area obtained under the frequency of 200 Hz, $E_0 = 1.5 \times 10^4$ V/m, and 25 °C. For (b), (c) and (d), temperatures were fixed at 5 °C and frequencies were kept constant at 40 Hz. The field strengths which were applied to adjust were $5.8 \times 10^4$, $7.5 \times 10^4$, and $8.3 \times 10^4$ V/m, respectively.
Figure 6.4: Representative SEM images of 2D colloidal assemblies fixed by the application of DC field. Close packed assembly with $r_{eq}$ around 1.

The assembly/disassembly is reversible on reversing the change in the parameters - field strength, frequency and temperature. Furthermore, the assembly can be permanently fixed by a sudden switch to a DC field due to the strong electrophoretic force. [143] Figure 6.4 and 6.5 shows representative SEM images showing the fixed patterns of both close and non-close packed arrays with $r_{eq}/2a = 1$ and $r_{eq}/2a = 1.66$, respectively. Following this method, we can first tune conditions such as temperature, field strength and frequency to form a large area of a 2D colloidal assembly, modulate $r_{eq}/2a$ to the a desired value, and then fix it permanently for further practical applications, such as use as template for colloidal lithography. [37]
In this regard, we would also like to point out that, upon the strong application of a DC field, the colloidal particles are tightly bonded to the charged electrode. The tight bond can even overcome the later capillary force when the fluid is drained away. As a result, the colloidal pattern can remain after drying.

6.3 Summary

In conclusion, we have investigated the effect of the temperature on the equilibrium separation distance $r_{eq}$ of the 2D colloidal assembly under an alternating electric...
field. In the high frequency range (> 500 Hz), an increase of temperature leads to a wider frequency window of the colloidal assembly, consistent as with the EHD mechanism. In the low frequency range (< 300 Hz), we have observed a crossover in frequency at which the behavior of the temperature dependence changes, suggesting a change in the origin of the EHD mechanism. By tuning various process parameters including temperature, frequency and field strength for a directed assembly, colloidal arrays with a wide range of $r_{eq}$ ($\sim 1.0 \times 2a$ to 2.2 $\times 2a$) have been obtained. Such electrically switchable colloidal arrays may find use in a variety of practical applications, including optical switches, waveguides, chemical or biosensors, and templates for colloidal lithography.
Chapter 7

Conclusions and Future Work

7.1 Conclusions

In this thesis, the phase diagrams of polystyrene colloidal particles near an electrode surface subjected to AC polarization were examined by varying frequencies, field strengths, kinds of salts, salt concentrations, particle sizes, and temperatures.

For a given field strength, a frequency window can be identified within which the assembly has a crystalline structure, namely, a long range bond-orientational and translational order. Outside this frequency window, the structure undergoes a crystal-liquid transition. The variation of the translational and bond-orientational correlation functions with frequency suggest the existence of a hexatic phase in which the particles retain the remnants of the crystalline long-range orientational order, but has a liquid-like translational order. This suggests a frequency driven
KTHNY transition in 2D colloidal assembly.

The equilibrium centre-to-centre particle separation, \( r_{eq} \), does not show remarkable variation with voltage within the frequency window for crystallization, but may exhibit variation at boundary frequencies (Figures 3.6, 5.10). The strength of added electrolyte and salt-specificity affect the range of the frequency window, with the range being wider in the presence of salt. The electrohydrodynamic flow, suggested by several authors [16,43,63] to be the most likely mechanism for the 2D fluid and crystalline structures, was analyzed in the light of the existing theoretical models [16, 43, 48, 63, 81–83, 104, 109, 118]. The equilibrium distribution of the particles is considered to be the resultant of the two opposing forces - the Stoke’s force due to EHD velocity and the screened Coulomb interaction between the colloidal particles. The existence of a lower and upper cut-off frequency for colloidal aggregation cannot be explained by the existing theoretical models. However, the decrease in EHD velocity and hence the increase in inter-particle separation at high frequencies can be explained [48,81,83,118]. Also, several features of the experimental results can be accounted for [82,83,109,118], such as the role played by the EHD flow in the particle aggregation, the dependence of the equilibrium inter-particle separation on ionic strength and \( \zeta \)-potential.

We have also established that the equilibrium center-to-center particle separation \( r_{eq} \) can be a new criterion for characterizing 2D assembly, since it can be used as a measure of the crystalline order in the lattice and it can also be correlated to the kinetic rate constant for aggregation of colloidal particles under an AC electric field. Taking a particular case as an example, at the frequency where \( r_{eq} \) reaches
its minimum, colloidal particles form a tight assembly and the attractive interactions are much stronger than repulsive ones. At the same time, the quality of the assembly becomes almost perfect and the rate constant $k_E$ is largest because the attractive forces are much larger than repulsive forces. Establishing the correlation between the kinetic rate constant and the equilibrium particle distribution is important for two reasons: the study of the equilibrium particle distribution becomes easier and less prone to error. In addition, a kinetics is study not feasible under all experimental conditions. In our study, the attempts to systematically study particles of diameter of 1.8 and 5.0 $\mu m$, as well as 3.0 $\mu m$ particles at a higher salt concentration, were not successful. Nevertheless, we can use the equilibrium particle distribution to further explore the parameters that influence the kinetics of the colloidal assembly. Furthermore, by applying this criterion, the role played by particle size on the 2D colloidal assembly have been investigated. The deduction from the theoretical model [48, 81, 83] that smaller particles has smaller aggregation rate constant $k_E$ was testified in the experiments: Larger particles form tighter assemblies (smaller $r_{eq}$), which implied larger $k_E$.

The effect of temperature on colloidal assembly under an AC field was firstly examined in our system as well. The increase of temperature can lead to a wider frequency window of colloidal assembly. Besides, for lower boundary frequencies at low temperature, the equilibrium distribution $r_{eq}$ becomes larger with increase of temperature. The results are analyzed with existing models based on electro-hydrodynamic flow. Apart from the illumination of theoretical models, another striking point is that by utilizing the properties of colloidal assembly at different
conditions, we can tune \( r_{eq} \) over a wide range (\( \sim 1.0 \times 2a \) to \( 2.0 \times 2a \)). Furthermore, an effective method has been established to fix the 2D colloidal assembly for further use as templates by a sudden switch to a DC field.

In conclusion, we have investigated the effect of the temperature on the equilibrium separation distance \( r_{eq} \) of the 2D colloidal assembly under an alternating electric field. In the high frequency range (\( > 500 \) Hz), an increase of temperature leads to a wider frequency window of the colloidal assembly, consistent as with the EHD mechanism. In the low frequency range (\( < 300 \) Hz), we have observed a crossover in frequency at which the behavior of the temperature dependence changes, suggesting a change in the origin of the EHD mechanism. By tuning various process parameters including temperature, frequency and field strength for a directed assembly, colloidal arrays with a wide range of \( r_{eq} \) (\( \sim 1.0 \times 2a \) to \( 2.2 \times 2a \)) have been obtained. Such electrically switchable colloidal arrays may find use in a variety of practical applications, including optical switches, waveguides, chemical or biosensors, and templates for colloidal lithography.

### 7.2 Future work

Based on the experimental results and the discussion and conclusions presented, the following recommendations may be interesting for the future investigation to this topic.

The frequency driven KTHNY phase transition, to our best knowledge, is the first systematic observation of its kind, and also an initial work in this field. Numbers
of parameters can lead to colloidal phase transition under AC field such as temperature, volume fraction etc. To study the phase transition driven by different parameters, further work need to be carried out by tuning these parameters.

The mechanism of colloidal assembly under an AC field developed so far is still far from complete because there are too many parameters needed to be considered. Our establishment of phase diagrams by tuning field strength, frequency, kinds of salts, salt concentration, particle size, ζ-potential, and temperature would benefit the further improvement of the existing models and could be a good reference to test the models as well.

The investigation of the different size of colloidal particles under AC field, and the observation that the frequency ranges corresponding to their assembly are different, will benefit future study of binary or multi-component systems of colloidal dispersions, as well as in the design of optical materials, biotechnology, etc. Based on our work, a further study can be focused on binary system and is expected to be able to obtain supper lattices by modulating parameters properly.

Even though we have demonstrated the interpretations of the colloidal assembly under change of temperature based on the existing theoretical model [81], it should be pointed out that further theoretical work needs to be done as several parameters change with temperature and hence temperature effect is difficult to explain.

Various combinations of frequency, field strength and temperature are likely to find applications in more elaborate techniques for precise assembly of ordered
structures. Such electrically switchable colloidal arrays may find use in a variety of photonic applications, including optical switches, waveguides, and chemical or bio-sensors. Other applications include the creation of patterned arrays in lithographic techniques, as masks to fabricate regular arrays of micro- or nano-structures. Since we can tune the equilibrium distribution \((r_{eq})\) over a wide range and then permanently fix the assembly by a sudden switch of DC field, the pattern could be precisely controlled and formed for further use as templates.

Another aspect is that the particle sizes selected for study were all in micro-scale: 1.8, 3 and 5 \(\mu m\). Further study could also be carried out for particles with smaller size (nano-scale). Nano-scale particles should share similar properties with micro-scale particles, as well as with even smaller particles. In addition, bio-molecules fall in the domain of colloidal particles. This implies that further extension of the study of colloidal particles of smaller scale may shed a light on the study of assembly of bio-molecules. We hope that the complicated mechanism of colloidal assembly driven by an alternating electric field could be further understood and our experimental results might enable further refinement of theoretical models.

Although this study addressed the study of 2D assembly in details and provides important information for further study in 3D colloidal assembly (2D is the basis of further development of 3D study), the system we used cannot be directly applied to extend the study to 3D study. This is because the assembly is mainly directed by the electrohydrodynamic flow which drives the colloidal particles to form 2D assembly, and this flow is caused by disturbance of uniform electronic field due to existence of colloidal particles near the electrodes. However, once 2D assembly forms above the electrodes, because the particles are not conductive, there is no electric double layer
above the 2D assembly. Hence even if there are particles above the assembly, there is no electric fluid flow that can drive them to form assembly above the formed 2D assembly. One possible way to solve this problem is to apply conductive particles so that after one layer of assembly forms, the layer can serve as an electrode for the other particles above the first layer and then form 3D assembly. Another way is to apply other external fields together. For example, it has been reported that magnetic field could also lead colloidal particles to form assembly [32, 33, 144]. Therefore after making the mechanisms of colloidal assembly under different external fields clear, certain combination of external fields [32, 33, 144, 145] may lead to 3D assembly or provide more flexible control of both 2D and 3D colloidal assembly.
References


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Two Dimensional Colloidal Assembly under an Alternating Electric Field: from Introduction to Structure

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