# DIELECTROPHORETIC ASSEMBLY OF COLLOIDS IN TOGGLED AC FIELDS

by

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A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering with Distinction

Spring 2017

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#### ACKNOWLEDGMENTS

First and foremost, I would like to thank my advisor, Eric Furst, for everything he has done for me over the last two years. His enthusiasm for teaching and learning was what sparked my initial interest in research. He has provided me with numerous learning opportunities and his guidance has helped me become a better researcher. He always pushed me to fill gaps in my understanding and persevere in solving challenging problems. I will use the skills I have learned from this experience for the rest of my career.

I would also like to thank the other members of my thesis committee, Norman Wagner and Emily Day. My conversations with Professor Wagner about my academic and career plans throughout my undergraduate education have been greatly appreciated. Professor Day's feedback on my presentations was extremely helpful for preparing for my thesis defense.

Finally, I would like to thank the members of the Furst Group for their continual help and support throughout my research. Particularly, I would like to thank Tamás Prileszky for taking me under his wing and answering my numerous questions, brainstorming with me, and showing me how to use equipment in the lab. I would also like to thank Hojin Kim for our discussions about self-assembly experiments and for spending innumerable hours in the lab with me troubleshooting and overcoming the obstacles we faced before achieving successful results. Many thanks go to the rest of the current and past group members, Kimberly Dennis, Jill Emerson, Lilian Lam Josephson, Seyeon Park, Mahlet Woldeyes, and Caitlin Wood, for their various contributions to my success and for making the basement a much less dreary place to spend my days.

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#### ABSTRACT

The dielectrophoretic directed self-assembly of colloidal particles is a rapid, tunable, and simple method for the production of materials with phononic and photonic band gaps. However, under the application of a constant AC electric field, particles become kinetically trapped in non-equilibrium structures containing numerous defects which interfere with the desired phononic and photonic properties. This problem is amplified by anisotropic particles as they must translationally and rotationally align to assemble into equilibrium structures. To resolve this limitation of dielectrophoretic self-assembly, a method to anneal kinetically trapped configurations to an equilibrium state is needed.

Before exploring an approach to improve the order of structures formed by dielectrophoretic directed self-assembly, a well-documented method for producing planar electrodes, and their use in the construction of a dielectrophoretic sample cell is presented. Furthermore, the high voltage circuit used to generate the applied AC electric field is introduced and thoroughly characterized.

This experimental setup is then used to investigate the use of toggled AC electric fields to assemble polystyrene colloids into crystalline structures free of defects. The time evolution of the macroscopic structures and the long-time microscopic structures formed under the influence of toggled AC electric fields are discussed for three colloidal suspensions: 1  $\mu$ m polystyrene spheres dispersed in a density mismatched H<sub>2</sub>O-based medium, in a density matched H<sub>2</sub>O/D<sub>2</sub>O-based medium, and polystyrene dicolloids in a density mismatched H<sub>2</sub>O-based medium. The first of these suspensions suggests toggling is not necessary to construct equilibrium structures from isotropic particles with weak interactions. When the 1  $\mu$ m particles are suspended in a density matched solution, only localized ordering is observed indicating gravity is an integral force in the formation of macroscopic colloidal crystals through dielectrophoretic self-assembly. Finally, the dicolloidal suspension exhibits an increase in order when a toggled field is applied at a frequency of 0.1 Hz rather than a constant field. This suggests toggled fields make it possible to improve the order of these particles, which are particular difficult to assemble due to their anisotropy.

## Chapter 1 INTRODUCTION

The term "colloid" describes a stable dispersion of particles, droplets, or bubbles between approximately 1 nm and 10  $\mu$ m within a continuous medium. Particles in this size range are subject to both macroscopic and microscopic forces including gravity, thermal motion, van der Waals interactions, and electrostatics [1]. The interplay of these forces results in unique properties absent at both the molecular and bulk scale which make colloids useful for numerous applications. For instance, colloids are used to enhance drug delivery [2], purify water [3], and clarify smoke emitted by plant chimneys [4]. In a related area of research, the Brownian motion of colloidal particles is measured to study the rheology of solutions [5]. New ways to exploit the properties of colloids are being found nearly every day.

The assembly of crystalline structures from colloidal particles has long been of considerable interest. At sufficiently high volume fractions, colloids spontaneously form crystalline structures [6]. However, this process is kinetically limited by the glassy characteristics of concentrated dispersions. The process of crystal formation can be accelerated by applying external fields or forces to dilute suspensions, a process known as directed self-assembly. Numerous driving forces can induce self-assembly, including: concentration via gravitational sedimentation [7] or solvent evaporation [8], large amplitude oscillatory shear [9], spin-coating [10], and the application of magnetic [11] or electric fields [12]. The latter of these is the primary focus of this thesis and will be described in more detail later.

The interest in creating colloidal crystals was spurred by the discovery of photonic and phononic band gap materials. There is a wealth of applications for these crystals. Several examples include displays visible even under intense direct lighting [13, 14], materials capable of guiding light through 90° angles [15], and optical cloaking materials [16]. Photonic band gaps are observed in materials containing a periodic variation in permittivity at approximately half the wavelength of light (200 - 500 nm). These materials inhibit the propagation of light waves within the band gap [17]. Photonic band gaps are observed naturally in opals which consist of regularly packed silica spheres [18]. Directed self-assembly enables the rapid, tunable production of structures exhibiting these properties. The size of colloidal particles makes them ideal building blocks for man-made photonic crystals.

Phonoic crystals are similar to photonic crystals, but they block the propagation of phonons rather than electromagnetic waves. A phonon is a quasiparticle description of the collective motion of atoms or molecules, such as sound. Phononic band gaps are observed in materials containing a periodic variation in density at the same characteristic length as mechanical waves [19]. Although postulated by physicists prior, the first experimental evidence for phononic band gaps was found in the sculpture Organo by Eusebio Sempere. Researchers were able to demonstrate the structure exhibited a partial phononic band gap in the frequency regime of audible sound (kHz) [20]. Similar structures exhibiting audible sound band gaps can be used in sound isolation applications [21]. Additionally, defects in the structure can guide and trap sound waves within the structure [22]. However, the large wavelength of audible sound, and consequently large size of these structures, limits their practical applications. Microscopic structures, like those formed by colloids, exhibit phononic band gaps in the ultrasonic to hypersonic (MHz - GHz) regime [23]. These structures simultaneously interact with mechanical and electromagnetic waves [24]. At even smaller length scales, band gaps in the THz regime are expected but such structures have not yet been realized experimentally [25]. Such structures could be useful for thermal cloaking and manipulation as phonons in this frequency regime are partially responsible for the transmission of thermal energy [26].

Magnetic or AC electric field directed self-assembly are attractive methods for rapidly assembling crystalline structures from colloidal building blocks. However, in many cases these methods lead to kinetically trapped defects in the crystalline structures, even when using simple spherical colloids as building blocks [11, 27]. Directed self-assembly is further complicated when anisotropic colloids, such as ellipsoids and dicolloids, are used as the building blocks [28]. The production of structures exhibiting photonic and phononic band gaps requires a method capable of creating nearly defectfree crystal structures as defects can partially or fully destroy the band gaps. Recent work by Swan et al. demonstrated it is possible to anneal kinetically trapped defects in paramagnetic colloids assembled under the influence of a magnetic field by toggling the field [11]. These findings are outlined further in Section 1.2. The primary goal of this work is to extend these findings to both spherical and anisotropic polystyrene colloids assembled via dielectrophoresis in an effort to produce structures with improved ordering compared to those assembled with a constant field.

In this chapter, the polarization of colloids in AC electric fields is introduced and two models to describe the polarization of colloidal particles are discussed. Then, AC electroosmotic flows are described and finally parameters relevant to toggled field directed self-assembly are introduced.

#### 1.1 Dielectrophoretic Ordering

To induce dielectrophoretic ordering of colloids in this work, an AC field is applied to a dispersion of polystyrene colloids which causes the particles to self-assemble through dielectrophoresis (DEP). This method makes it possible to create ordered structures on the order of seconds to minutes and, given sufficient time, the formation of these structures is fully reversible. In comparison, crystals formed spontaneously in concentrated suspension take minutes to hours to form [6]. Additionally, undesirable electrophoresis, electroosmotic flows, and faradaic reactions present under DC driven self-assembly can be suppressed at sufficiently high AC frequencies [29]. Consequently, much higher field strengths can be applied to the suspension, inducing stronger interparticle attractions. AC electric fields also have the advantage of being able to direct the self-assembly of any polarizable particle while magnetic fields are only useful for the assembly of paramagnetic particles. The following section discusses the various polarization mechanisms responsible for dielectrophoresis in colloidal particles.

#### 1.1.1 Polarization

When an electric field is applied to a neutral body it becomes polarized and, if the field is non-uniform, a net force acts upon the particle. There are five polarization mechanisms and the magnitude of their influence depends on the physical and chemical properties of the polarized body. Electronic polarization is the first of these mechanisms and although its magnitude is relatively small, it occurs in all matter. It is caused by the distortion of the positive and negative charges within the atoms making up a material. The second mechanism, atomic polarization, is caused by movement of charged atoms with respect to one another to opposite sides of the electric field. This mechanism is negligible in organic solids due to the absence of charged atoms. In bodies containing molecules or functional groups exhibiting a permanent dipole, polarization occurs by reorientation of the dipoles in the electric field. This polarization mechanism is responsible for the exceptionally high dielectric constant of water. The fourth possible mechanism of polarization is nomadic polarization. This is limited to specific chemistries and does not occur in the colloidal particles considered in this work. These four polarization mechanisms only depend on the molecular makeup of a body occur due to a dielectric mismatch between an object and its surrounding medium.

The final polarization mechanism, interfacial polarization, is typically the most important for colloidal particless due to their enormous specific interfacial area and ionic double layers. This polarization mechanism occurs via the movement of charge carriers through the double layer. At low applied field frequencies, the charges associated with the particle are free to migrate to opposite ends of the particle leading to strong interfacial polarization. As the electric field frequency increases, the magnitude of interfacial polarization decreases, eventually becoming negligible compared to the four molecular polarization mechanisms [30]. This leads to a change in the direction of polarization of colloidal particles, as interfacial polarization occurs parallel to the applied electric field while the other polarization mechanisms occur anti-parallel to the electric field.

The decrease in double layer polarization with increasing frequency can be understood by defining two characteristic polarization frequencies. The frequency associated with the migration of charges to opposite ends of the particle is

$$\omega_p = \frac{D_{CI}}{a^2} \tag{1.1}$$

where  $D_{CI}$  is the diffusivity of the counterions in the double layer. At frequencies greater than this, the ions in the double layer are no longer able to migrate the distance of the particle but some residual polarization is observed because charges are able to move across the double layer. The characteristic frequency for this process is

$$\omega_{DL} = \frac{D_{CI}}{\kappa^{-2}} \tag{1.2}$$

where  $\kappa$  is the inverse Debye length,

$$\kappa^{-1} = \sqrt{\frac{k_B T \varepsilon_m}{2I e^2}} \,. \tag{1.3}$$

In this expression,  $k_B$  is the Boltzmann constant, T is the absolute temperature,  $\varepsilon_m$  is the dispersing medium permittivity, e is the fundamental charge, and I is the ionic strength given by

$$I = \frac{1}{2} \sum_{i=1}^{N} z_i^2 n_i^{\infty}$$
(1.4)

where  $z_i$  is the valence of the  $i^{\text{ith}}$  ion and  $n_i^{\infty}$  is the bulk density of the  $i^{\text{th}}$  ion. As the frequency is increased beyond  $\omega_{DL}$ , charges effectively remain immobile and interfacial polarization is negligible. Figure 1.1 shows depictions of each of the polarization regimes.

Although these relationships are useful for understanding the general time scales the polarization of the double layer occurs over, more rigorous models make it possible to quantitatively model the complete polarization behavior of colloidal particles and understand the implications of the change in the dominant polarization mechanism. The polarization behavior of colloids can be described phenomenologically with the Maxwell-Wagner-O'Konski model or mechanistically with the standard electrokinetic model (SEKM). The SEKM is more rigorous and provides better agreement with experimental results [31]. However, the simplicity of the Maxwell-Wagner-O'Konski model is useful for generally understanding the behavior of colloids within the influence of an AC electric field. In the subsequent sections, the Maxwell-Wagner-O'Konski model is presented and analyzed first, then the governing equations of the SEKM model are given.

#### 1.1.2 Maxwell-Wagner Polarization and Field Induced Forces

Consider the application of an electric field in the z-direction of a laboratory reference frame. A spherical particle in this field experiences an effective dipole phasor given by [32]

$$\boldsymbol{p}^* = 4\pi\varepsilon_m E_{RMS} a^3 f_{CM}^* \boldsymbol{\hat{z}}$$
(1.5)

where  $\varepsilon_m$  is the permittivity of the surrounding medium,  $E_{RMS}$  is the root mean squared amplitude of the electric field, a is the radius of the sphere,  $\hat{z}$  is the z-direction unit vector. The asterisk indicates the quantity is a complex variable. The term  $f_{CM}^*$ is the Clausius-Mossotti factor [33]

$$f_{CM}^* = \frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*} \tag{1.6}$$

where the subscript p indicates the particle and the subscript m indicates the medium. The complex permittivities can be expressed as

$$\varepsilon_j^* = \varepsilon_j - \boldsymbol{i} \frac{\sigma_j}{\omega} \,, \tag{1.7}$$



Figure 1.1: The effect of electric field frequency on the polarization of the diffuse portion of the double layer  $(\vec{p}_{DL})$ . At low frequencies (left), the ions are given enough time to diffuse to opposing ends of the particle leading to strong polarization of the Stern and diffuse layers. At intermediate frequencies (middle), the ions are no longer able to transport across the entirety of the particle. The double layer remains somewhat polarized by diffusion of ions to portions of the double layer closer to the oppositely charged region of the electric field. At sufficiently high frequencies (right), the ions remain approximately stationary and the double layer remains unpolarized. Only counter ions are shown for clarity.

where  $\sigma_j$  is the conductivity of component j and  $\omega$  is the frequency of the AC field. The fully expanded form of the Clausius-Mossotti factor is

$$f_{CM}^{*} = \frac{\omega^{2}(\varepsilon_{p} - \varepsilon_{m})(\varepsilon_{p} + 2\varepsilon_{m}) + (\sigma_{p} - \sigma_{m})(\sigma_{p} + 2\sigma_{m})}{\omega^{2}(\varepsilon_{p} + 2\varepsilon_{m})^{2} + (\sigma_{p} + 2\sigma_{m})^{2}} + \frac{i\frac{3\omega(\sigma_{m}\varepsilon_{p} - \varepsilon_{m}\sigma_{p})}{\omega^{2}(\varepsilon_{p} + 2\varepsilon_{m})^{2} + (\sigma_{p} + 2\sigma_{m})^{2}}.$$
 (1.8)

Due to the double layer surrounding most colloids in polar solvents,  $\sigma_p$  cannot be taken as the bulk conductivity ( $\sigma_{\text{bulk}}$ ), rather, the Maxwell-Wagner model is modified by calculating  $\sigma_p$  according to the relationship originally proposed by O'Konski, [34]

$$\sigma_p = \sigma_{\text{bulk}} + 2\frac{K_s}{a} \,, \tag{1.9}$$

where  $K_s$  is the surface capacitance of the particle. Equation 1.9 results in  $\sigma_p > \sigma_m$ , the implications of which can be realized by developing an expression for the force exerted on a particle in the electric field.

Based on the instantaneous force exerted on a dipole [30]

$$\boldsymbol{F} = (\boldsymbol{p} \cdot \nabla) \boldsymbol{E}_{\boldsymbol{ext}}, \qquad (1.10)$$

where  $E_{ext}$  is given by

$$\boldsymbol{E_{ext}} = \boldsymbol{E_{RMS}}\sqrt{2}\cos(\omega t) = E_{RMS}\sqrt{2}\cos(\omega t)\hat{\boldsymbol{z}}$$
(1.11)

for an AC electric field with angular frequency  $\omega$ . The time averaged dielectrophoretic (DEP) force exerted on a spherical particle in this AC field is

$$\langle \mathbf{F}_{\mathbf{DEP}} \rangle = 2\pi \varepsilon_m a^3 \Re \left( f_{CM}^* \right) \nabla \left| \mathbf{E}_{\mathbf{RMS}} \right|^2 .$$
 (1.12)

The real component of the Clausius-Mossotti factor can be rearranged to [33]

$$\Re\left(f_{CM}^{*}\right) = \frac{\varepsilon_{p} - \varepsilon_{m}}{\varepsilon_{p} + 2\varepsilon_{m}} + \frac{3(\varepsilon_{m}\sigma_{p} - \varepsilon_{p}\sigma_{m})}{\tau_{MW}(\sigma_{p} + 2\sigma_{m})^{2}(1 + \omega^{2}\tau_{MW}^{2})}$$
(1.13)

where  $\tau_{MW}$  is the Maxwell-Wagner time

$$\tau_{MW} = \frac{\varepsilon_p + 2\varepsilon_m}{\sigma_p + 2\sigma_m} \,. \tag{1.14}$$

The Maxwell-Wagner frequency is

$$\omega_{MW} = \frac{1}{\tau_{MW}}.\tag{1.15}$$

Each component of the Clausius-Mossotti factor as a function of field frequency for polystyrene particles is shown in Figure 1.2. The plot of the real component exhibits two limiting cases at low and high frequencies. Expressions for these limiting cases are found by taking the limit of  $\Re\left(f_{\underline{CM}}\right)$  as  $\omega \to 0$  and as  $\omega \to \infty$ .

$$\lim_{\omega \to 0} \Re \left( f_{CM}^* \right) = \frac{\sigma_p - \sigma_m}{\sigma_p + 2\sigma_m} \tag{1.16}$$

$$\lim_{\omega \to \infty} \Re \left( f_{CM}^* \right) = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m} \tag{1.17}$$

These expressions provide mathematical insight to the two primary polarization regimes discussed in the previous section. At low frequencies, polarization is conductivity dominated due to polarization of the double layer and results in a positive value of  $\Re(f_{CM}^*)$ . Consequently, the particle polarizes parallel with the electric field and experiences a time averaged force in the direction of the electric field gradient. At high frequencies, polarization becomes permittivity dominated as polarization of the double layer is lost. In this limit, the value of  $\Re(f_{CM}^*)$  becomes negative, corresponding to polarization of the particle antiparallel to the electric field. As a result, the particle experiences a force opposing the electric field gradient. Based upon this analysis,  $\omega_{MW}$ can be considered the frequency at which polarization switches from being conductivity to permittivity dominated. This roughly corresponds to the frequency at which the field oscillates faster than charges within the double layer are able to migrate and interfacial polarization is no longer the dominant polarization mechanism. For polystyrene particles, this occurs on the order of 1 MHz [34]. A schematic representation of the two polarization behaviors is shown in Figure 1.3a and the resultant DEP force on a particle between two planar electrodes is shown in Figure 1.3c. Typically, directed self-assembly using AC electric fields is performed well below the crossover frequency,



Figure 1.2:  $\Re(f_{CM})$ ,  $\Im(f_{CM})$ , and  $|f_{CM}|$  as a function of electric field frequency for a polystyrene sphere. The parameters used to produce this plot were:  $\varepsilon_m = 78.5\varepsilon_0$ ,  $\varepsilon_p = 2.55\varepsilon_0$ ,  $\sigma_m = 1.5 \times 10^{-4}$  S/m,  $\sigma_{bulk} = 0$ ,  $K_s = 2.56 \times 10^{-9}$  S [34], and  $a = 1 \ \mu m$ . The particles exhibit a crossover from positive to negative polarization at approximately 2.7 MHz.

in the kHz frequency range, and this effect is of little significance. However, other areas have developed methods to take advantage of this behavior. For example, living and dead cells can be sorted based upon differing values of  $\omega_{MW}$  [35].

In addition to the force exerted on the particle by the external electric field gradient, the particles also exert a force on one another due to local field gradients around the particle [30]. The electric field in the vicinity of an polystyrene colloidal particle in water is shown in Figure 1.4 These gradients result in the formation of the higher order structures which are the primary area of interest for this work. For dipoles that are parallel and aligned with the electric field, the interaction energy between two particles is

$$U_{12} = 4\pi\varepsilon_m \left| f_{CM}^* \right|^2 a^6 E_{RMS}^2 \left[ \frac{3\cos^2\theta - 1}{r^3} \right] , \qquad (1.18)$$

where the quantities r and  $\theta$  are defined in Figure 1.3b. The interaction force can be calculated by

$$F_{12} = -\frac{dU_{12}}{dr}, \qquad (1.19)$$

which gives

$$F_{12} = 12\pi\varepsilon_m \left| f_{CM}^* \right|^2 E_{RMS}^2 a^6 \left[ \frac{3\cos^2\theta - 1}{r^4} \right] \,. \tag{1.20}$$

At a separation distance of r = 2a and at  $\theta = 0$ , where the attractive force is strongest, the following relation is obtained [36]

$$F_{12} = \frac{3}{2} \pi \varepsilon_m \left| f_{CM}^* \right|^2 E_{RMS}^2 a^2 \,. \tag{1.21}$$

Additionally, Equation 1.18 can be used to define a unitless measure of the interaction as the ratio of dipole interaction energy to thermal energy [37]

$$\Lambda = \frac{U_{12} \left( r = 2a, \theta = 0 \right)}{k_B T} = \frac{\pi \varepsilon_m \left| f_{CM}^* \right|^2 a^3 E_{RMS}^2}{k_B T}$$
(1.22)

For values of  $\Lambda > 1$ , the suspension will overcome thermal fluctuations and achieve selfassembly by the induced dipolar interactions. This parameter is used numerous times in this work to compare the self-assembly driving force in different colloidal dispersions.

#### 1.1.3 Standard Electrokinetic Model (SEKM)

The SEKM is used to describe the behavior of a single colloidal particle at the limit of infinite dilution in an electric field. The full model is described a set of coupled electrostatics, momentum balance and flux balance equations [38]. The electrostatics is described by the non-dimensional Poisson-Boltzmann equation,

$$\nabla^2 \psi = \sum_{i=1}^N z_i \left( n_i - n_i^f \right) \,. \tag{1.23}$$

 $z_i$  is the valence of the  $i^{\text{th}}$  ionic species. The equation is non-dimensionalized by scaling the potential,  $\psi$  by  $k_B T/e$  where e is the fundamental charge. The counter-ion and fixed-ion,  $n_i$  and  $n_i^f$ , respectively are scaled by twice the ionic strength. Finally, all lengths are scaled by the Debye length.



Figure 1.3: (a) Visual representation of the net particle polarization as a function of frequency. Below  $\omega_{MW}$  (left) the particles are polarized parallel to the electric field and above  $\omega_{MW}$  (right) the particles are polarized anti parallel to the electric field. The vectors indicate the relative magnitude of each polarization. (b) Schematic depicting the quantities r and  $\theta$  in Equation 1.18. (c) The direction of the DEP force on a particle above and below  $\omega_{MW}$ . The dashed lines represent the electric field lines and the solid lines show the direction of the DEP force.



Figure 1.4: Local modification of the electric field by (a) a conductive particle, corresponding to  $\omega \ll \omega_{MW}$  and (b) an insulating particle, corresponding to  $\omega \gg \omega_{MW}$ .

For each ionic species, there is a transport equation given in dimensionless form

by

$$\frac{\operatorname{Pe}_{j}(\boldsymbol{u}-\boldsymbol{v}_{i})}{u^{*}}-z_{i}\nabla\psi-\nabla\ln(n_{i})=0. \qquad (1.24)$$

Here,  $\boldsymbol{u}$  is the fluid velocity,  $\boldsymbol{v_i}$  is the ion velocity,  $\operatorname{Pe}_i$  is given by

$$\operatorname{Pe}_{i} = u^{*} \kappa^{-1} / D_{i} \tag{1.25}$$

where  $D_i$  is the diffusivity of ionic species *i*, and  $u^*$  is given by

$$u^* = \frac{\varepsilon_m (k_B T/e)^2}{\eta a} \,. \tag{1.26}$$

In this expression,  $\eta$  is the dynamic viscosity of the fluid. As defined,  $Pe_i$  provides an indication of the degree of deformation of the double layer.

The ion, momentum, and mass balance equations are

$$\Omega_i \frac{\partial n_i}{\partial t} + \operatorname{Pe}_i \nabla \cdot (n_i \boldsymbol{v}_i) = 0, \qquad (1.27)$$

$$\Omega \frac{\partial \boldsymbol{u}}{\partial t} = \nabla^2 \boldsymbol{u} - \nabla p - B(r)(\boldsymbol{u} - \boldsymbol{V}) - \kappa a \sum_{i=1}^N n_i z_i \nabla \psi, \qquad (1.28)$$

and

$$\nabla \cdot \boldsymbol{u} = 0, \qquad (1.29)$$

respectively. Here, t is scaled by  $\omega^{-1}$ , the particle velocity, V is scaled by  $u^*$ , and the pressure, p, is scaled by  $\eta u^* \kappa$ ,  $\Omega_i = \omega \kappa^{-2}/D_i$ , and  $\Omega = \omega \kappa^{-2}/v$  where v is the kinematic viscosity.  $\Omega_i$  is the ratio of the electric field frequency to the ionic diffusion time and  $\Omega$  is the ratio of double layer thickness to the viscous penetration length. The Brinkmann function, B(r), is used to model polymer coatings, such as surfactants, and is expressed as

$$B(r) = \left(\frac{\kappa^{-1}}{l_B(r)}\right)^2 \tag{1.30}$$

where  $l_B$  is the Brinkman screening length.

Equations 1.23, 1.24, 1.27, 1.28, 1.29 are then solved simultaneously using numerical solvers. Commonly used boundary conditions include constant surface charge density

$$\frac{\partial \psi}{\partial r}|_{r=\kappa a} = -\sigma \tag{1.31}$$

or constant surface potential

$$\psi|_{r=\kappa a} = \zeta \tag{1.32}$$

in conjunction with

$$\psi|_{r=\infty} = 0. \tag{1.33}$$

The resultant solution can then be used to calculate the polarizability of the particle much more accurately than with the Maxwell-Wagner-O'Konski model.

Although the SEKM provides excellent agreement with experimental results for dilute colloidal dispersions, both the SEKM and the Maxwell-Wagner-O'Konski models fail when the particle volume is increased above infinite dilution. In this work, the effective volume fraction of the particles is well above this limit. As neither model is particularly accurate, the Maxwell-Wagner-O'Konski model is used rather than the SEKM to calculate the unitless interaction number,  $\Lambda$ , according to Equation 1.22 to simplify calculations. Additionally, due to the inaccuracy of these models at high volume fractions, the values of  $\Lambda$  presented in this work should be considered order of magnitude estimates rather than exact values. More accurate measurements for  $\Lambda$  can be obtained experimentally by dielectric spectroscopy [31].

#### 1.1.4 Field Induced Flows

In addition to dielectrophoretic forces, AC fields generate electroosmotic and electrothermal flows that subject particles to drag forces. Of the two, electrothermal flows are slower, on the order of  $1 - 10 \ \mu m/s$  and therefore exert less force on the particles. This class of flows is caused by temperature gradients within a medium exposed to an electric field. The temperature gradients are the result of power dissipation and in turn lead to gradients density, conductivity, and permittivity causing convection via

buoyancy, electrophoresis, and dielectrophoresis, respectively. The power dissipation within the electrode is given by [39]

$$W = \sigma_m E_{RMS}^2 \,. \tag{1.34}$$

Based upon this expression, power dissipation, and electrothermal flows, can be suppressed by minimizing the conductivity of the solution, which has the added benefit of increasing the interaction strength between particles and reducing the second class of flows, AC electroosmotic flows.

AC electroosmotic flows have a higher velocity than electrothermal flows, typically ranging from  $0 - 50 \ \mu m/s$  [40] for planar electrode geometries. Non-planar electrodes exhibit AC electroosmotic flows an order of magnitude higher [40]. Consequently, AC field directed self-assembly is performed using planar electrodes to minimize the disturbances introduced by these flows. In a closed sample cell, electroosmotic flows create a convective pattern shown in Figure 1.5 [36]. AC electroosmotic flows are caused by the force exerted on the ions in the double layer around an electrode edge by the tangential component of the applied electric field. The velocity of these flows is proportional to  $E^2$  and electroosmotic flows disappear in the limit of very high and low frequencies [41].



**Figure 1.5:** The experimentally observed AC Electroosmotic flow profile. This flow profile creates three areas of particle concentration: in the middle of the sample cell and near the two electrode edges. At sufficiently high flow velocities, well defined flow patterns are no longer observed and vortices form.

The movement of the suspending medium then gives rise to a drag force on the particles given by Stoke's Law

$$\boldsymbol{F_d} = 6\pi\eta a \boldsymbol{v} \tag{1.35}$$

where  $\eta$  is the dynamic viscosity of the suspending medium and v is the fluid velocity. If  $||\mathbf{F}_d|| > F_{12}$ , the suspension is unable to form ordered structures. While the velocity of electrothermal flows is not typically of a large enough magnitude to cause this AC electroosmotic flows can prevent the occurrence of self-assembly.

The magnitude of electroosmotic flows can be reduced through the addition of a non-ionic polymer surfactant to the solution. The brush layer created on the surface of the particles by the surfactant reduces the mobility of the ions in the diffuse double layer around the colloidal particles [42]. Consequently, the fluid motion around the particles is reduced. This effect is shown schematically in Figure 1.6.

#### 1.2 Toggled Field Directed Self-Assembly

Under the application of a constant external field, crystallization is thermodynamically favored. However, kinetically arrested rather than crystalline phases are observed at experimental time scales because strongly polarized particles form glassy structures and trap particles in local rather than global energy minima. One method for realizing the thermodynamically favored structure is the application a toggled rather than constant field. During the periods when the field is switched off, the particles regain translational and rotational freedom and escape energetically unfavored positions at random via Brownian motion. Recent work by Swan et al. demonstrates this effect using paramagnetic colloids: under magnetic fields toggled at frequencies between 0.5 and 1 Hz, particles form coarse ellipsoidal structures not observed in a static field or toggled fields at frequencies outside the optimal range. Microscopic observation of the coarsened structures revealed a higher degree of crystallinity than the structures formed outside the optimal toggling frequency range [11].



Figure 1.6: The brush layer on the particle created by surfactant (right) reduces the mobility of ions near the surface of the particle when compared to the uncoated particle (left).

In Swan's work, a magnetic field capture radius is defined to provide a metric for determining the optimal toggling frequency [11]. In a dielectrophoretic experiment, an analogous time can be defined as

$$r_c = 2a\Lambda^{1/3} = \left(\frac{8\pi\varepsilon_m |f_{CM}^*|^2 a^6 E_0^2}{k_B T}\right)^{1/3}.$$
 (1.36)

At this distance, the attractive energy between particles is equal to the thermal energy of the system. Thus, at  $r > r_c$  Brownian motion dominates and at  $r < r_c$  dielectrophoretic forces dominate. This serves as an approximation of the distance necessary to fully escape an energetically unfavored state. Based on this, a capture time can be defined as the time required for a particle to diffuse a distance of  $r_c$ . Using the Stokes-Einstein-Sutherland relation, this is given by

$$\tau_c = 4 \left(\frac{3\pi\eta a^3}{k_B T}\right) \left(\Lambda^{1/3} - 1\right)^2 \,. \tag{1.37}$$

#### 1.3 Summary

In this chapter, an overview of AC electric field self-assembly, the effect of toggled fields, and the applications of colloidal crystals were introduced. Chapter 2

presents an overview and characterization of the experimental setup used to drive selfassembly and the method used to characterize the structures formed. Next, Chapter 3 presents the experimental results and conclusions. Finally, Chapter 4 discusses overall conclusions and future research opportunities based upon this work.

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## Chapter 2 MATERIALS AND METHODS

In this chapter, the production and setup of the materials used to drive DEP self-assembly are presented. This includes the DEP cell and the electric circuit it is placed into. Additionally, the data collection and analysis methods are outlined.

Several obstacles had to be overcome to obtain successful self-assembly results. The primary challenge was producing the planar electrodes used in the DEP sample cell outside of a clean room. In the past, these electrodes were made in the DuPont Hall clean room but, in the interest of saving money, the production was moved to a conventional lab fume hood. This required complete redevelopment of the photolithography process which is outlined in Section 2.1.1. Additionally, preliminary experimental results exhibited unacceptable AC electroosmotic flow velocities and particle migration to the ground electrode. This warranted more thorough characterization of the electric circuit which is shown in Section 2.2.

#### 2.1 Dielectrophoretic Cell

The dielectrophoretic cell consists of parallel planar electrode attached to a microscope slide with a spacer to create a channel for loading colloidal suspensions in the gap between the electrodes. The production of each of the cell components as well as the assembly of the cell are outlined in the following sections.

#### 2.1.1 Electrode Fabrication

Planar parallel electrodes were patterned onto new, precleaned 22 mm x 22 mm (Fisherbrand Cat. No. 12-542-B) cover slips using photolithography. Generally, photolithography consists of the following key steps, each of which is described individually
in this section: spin coating, soft-baking, UV exposure patterning, hard-baking, development, metal deposition, and photoresist removal. First, the spin coating procedure outlined in Table 2.1 is performed on a spin coater (Laurell Technologies WS-650MZ-23NPP/LITE) with a 20 mm x 20 mm high porosity vacuum chuck adapter. To ensure successful results, a set of cover slips purchased within the last 6 months is reserved to be used exclusively for electrode production. This precaution is necessary as surface contaminants, even if they are not visible, can result in poor photoresist and metal adhesion. The cleaning step in Table 2.1 only removes dust and light organic contaminants and is not sufficient for cleaning heavily soiled coverslips.

In the silanization step in Table 2.1, hexamethyldisilazane (HMDS) (Sigma-Aldrich 440191) silanizes the glass to promote wetting of the glass by the photoresist. HMDS is highly reactive with water, including humidity in the air, and must be handled carefully to ensure adequate modification of the glass surface chemistry. To achieve the best results, the HMDS is deposited onto the coverslip using a 1 mL syringe (Norm-Ject Tuberkulin 1 mL) with a needle (BD PrecisionGlide Needle  $21G \times 1 1/2$ ) and allowed to rest for approximately 5 seconds before spinning dry. The brand of syringe is critical as syringes with rubber stoppers degrade quickly in the presence of HMDS. In addition, the syringe used to withdraw HMDS from the bottle is replaced approximately every 30 minutes, to dispose of reacted HMDS in the syringe. After several months, enough of the HMDS in the container reacts with moisture in the air that the photoresist no longer wets the glass surface. When this occurs, the HMDS is discarded and a fresh

Step	Chemical & Amount	Spin Speed (RPM)	$egin{array}{c} { m Acceleration} \ { m (RPM/s)} \end{array}$	Duration (s)
Cleaning	0.5  mL IPA	500 4000	$100 \\ 1500$	10
Silanization	0.3 mL HMDS	500	100	10
		4000	1500	40
Photoresist	0.5 mL Futurrex	500	100	10
	NR71-1500PY Photoresist	5000	1500	40

 Table 2.1: Spincoating process for production of cover slip electrodes

bottle is purchased. To prevent the premature degradation of the HMDS, it should be stored in a desiccator. A comparison between poor and good photoresist wetting is shown in Figure 2.1 for reference.

Prior to applying the photoresist in the final spin coating step, 10 - 20 mL of photoresist from the original bottle is poured into a vial wrapped with several layers of label tape. This reduces the number of particulates introduced into the primary container. The vial is wrapped in label tape to reduce UV exposure. The photoresist is then withdrawn from the vial using a 1 mL syringe and deposited onto the cover slip. Before spinning, any air bubbles in the photoresist are removed using the syringe and the photoresist is gently spread across the surface of the cover slip using the syringe tip. The selected spin speed results in a film thickness of  $1.1 - 1.3 \mu m$ , the thinnest achievable thickness using this photoresist. Generally, using the thinnest possible film for a given photoresist results in the smallest edge bead and therefore the best end result. The complete manufacturer documentation is provided in Appendix A.3.

After the spin coating process is completed, the cover slips are soft-baked in a petri dish on a hot plate at 150 °C for 1.5 minutes. The temperature is based upon the manufacturer specifications and the steady-state temperature of the surface of the petri dish is verified to be within 10 °C of the desired temperature using a infrared thermometer for each bake step. Excessively high soft-bake temperatures result in degradation of the photoresist while low temperatures cause poor solvent evaporation and resist adhesion. The cover slips are baked for slightly longer than the manufacturer specification to account for the reduced heat conduction caused by baking in a petri dish rather than directly on the hot plate surface. Both longer and shorter bake times produce unusable results.

After baking, a UV mask with the dimensions shown in Figure 2.2 is placed onto the coated cover slips and placed under a high intensity UV lamp (Uvitron International Intelli-Ray 400) for 30 seconds ( $390 \text{ mW/cm}^2$  at 365 nm). The exposure energy is based upon the manufacturer specifications and the exposure time is based upon a 365 nm light intensity meter measurement. The UV intensity should be remeasured annually



Figure 2.1: Comparison of (a) poor glass wetting by photoresist and (b) good wetting. In (a) there are areas which have not been covered by photoresist due to improper modification of the glass surface chemistry by HMDS.

and the exposure time should be recalculated as the intensity of the UV lamp will degrade slowly over time.

After exposure, the cover slips are hard-baked at 100 °C for 1.5 minutes. Once again, the bake time is slightly longer than the manufacturer specification for the same reason mentioned previously. After 1.5 minutes has elapsed, the hot plate is shut off but the cover slips are kept on the hot plate until the hot plate has cooled to room temperature. This step is by far the most crucial for producing usable electrodes. If the cover slips are immediately removed from the hot plate, the cured photoresist will either be removed in the development step due to poor adhesion to the glass or the film will exhibit stress fractures due to the difference in thermal expansion coefficients between the glass and the photoresist. If the first occurs, it is immediately obvious that the coverslip is unusable. However, stress fractures are not visible to the naked eye and therefore the patterned photoresist should be inspected for fractures using a microscope before metal is deposited onto them. If any stress fractures are present, the patterned areas will not effectively block metal when it is evaporated onto the surface of the coverslip rendering the electrode unusable. This step is time consuming as it takes upwards of an hour for the hot plate to cool to room temperature. To save time, five



Figure 2.2: Photomask used to expose pattern the photoresist for electrode production. The top left mask was used for this work.

coverslips are spincoated, soft-baked, UV exposed, and stored in an opaque container. Then, all five coverslips are placed onto the 100 °C petri dish and hard-baked using the outlined procedure.

After reaching room temperature, the cover slips are sprayed with developer (Futurrex Resist Developer RD6) using a wash bottle for 12 s then rinsed with MilliQ water for 30 s. Finally, the coated cover slips are dried using filtered nitrogen. The glass is then inspected for visible residues. If residue is present, the development step is repeated. Any residual surface contaminants lead to poor adhesion of the metal after deposition. In an attempt to reduce the amount of resist developer used, several attempts were made to develop the coverslips in a 3:1 water/developer solution via submersion for 60 s, according to manufacturer specifications. However, this resulted in unacceptable amounts of surface contamination and as a result, spray development must be used.

The patterned coverslips are then taken into the Nanofabrication Facility at the University of Delaware for deposition. ~100 nm of aluminum are deposited onto the coverslips in an e-beam/thermal evaporative deposition chamber (PVD Products). Extensive training on how to load and operate the chamber is provided by the staff of the nanofabrication facility. In the past, electrodes were coated with gold but aluminum is now used in the interest of saving money. The Pourboix diagrams for aluminum is shown in Figure 2.3 [1]. At neutral pH the electrodes do not degrade into ionic species and therefore there is no reason to be concerned with sample contamination. Additionally, the conductivity of aluminum (36.9 S/m) is comparable to that of gold (44.2 S/m). One attempt was made to use titanium but the melting point of titanium is high enough that the photoresist pattern was destroyed by the heat.

Several other evaporation chambers have been used in the past but moving forward this chamber should be used. The chamber in the ISE lab is newer and therefore more reliable and each deposition takes approximately an hour while other chambers take all day to perform one deposition. If the ISE lab chamber is not accessible, another chamber is available in DuPont Hall which is owned by Professor Keith Goossen. This



**Figure 2.3:** Pourbaix Diagram of aluminum from *The Aqueous Chemistry of the Elements* [1].

chamber is not capable of doing aluminum depositions but can do chromium and gold. The mounting and evaporation procedure for this chamber is outline in Panczyk's dissertation [2]. Additionally, there is a chamber which is occasionally available in the Institute for Energy Conversion (IEC) owned by Professor William Shafarman. This chamber is capable of doing aluminum depositions and the IEC staff is familiar with the mounting procedure.

After deposition, the cover slips are placed in a bath of isopropyl alcohol for an hour then mildly sonicated in isopropyl alcohol to remove the remaining photoresist. The coverslips are then rinsed with MilliQ water and dried using filtered nitrogen. Finally, the cover slips are plasma cleaned for 5 minutes on high power (Harrick Plasma PDC-32G plasma cleaner) to remove any remaining surface contaminates and restore the hydrophilicity of the surface. The etch rate of this plasma cleaner is low enough that plasma cleaning to does not appear to have any adverse affects on the deposited metal. The resultant electrodes exhibit extremely smooth, parallel edges, even when imaged using microscopy. An image showing the edge smoothness taken using a  $10 \times$  objective is shown in Figure 2.4.

## 2.1.2 Cell Construction

Images showing the steps involved in constructing the sample cells used for experiments are provided in Figure 2.5. Prior to cell assembly, a glass microscope slide (Fisherbrand Cat. No. 12-550-A3) is cut to 75mm  $\times$  15mm, rinsed with isopropyl alcohol, then ethanol, then nanopure water and dried with filtered nitrogen gas. In the final cleaning step, the slides are plasma cleaned (Harrick Plasma PDC-32G Plasma cleaner) on high for 5 minutes to remove any remaining organic contaminates. Next, to create a channel for loading the colloidal suspension into the sample cells, approximately 5 mm wide strips of 100 µm thick latex is soaked with UV glue (Norland Optical Adhesive 81). Excess glue is removed and then the strips are placed on either side of the electrode gap. The cut slide is then placed on top of the strips and the glue is cured for 10 minutes under a UV lamp (UVP UVL-56).

The colloidal suspension is then loaded into the channel using a micropipette and the ends of the channel are sealed using more UV glue which is cured for 10 minutes. Finally, to create leads for connecting the electric circuit, copper tape is placed on the exposed metal edges of the coverslip. A cross-sectional diagram of the resulting sample cell is shown in Figure 2.6.

#### 2.2 Electric Circuit

A schematic of the electric circuit used to drive self-assembly is shown in Figure 2.7. A function generator (Agilent 33220A) is used to generate a sinusoidal AC potential. The waveform is then passed through an amplifier (Trek PZD700A or Tegam 2340) to increase the input voltage to the levels required to drive self-assembly, 40-100 V<sub>RMS</sub>. The manufacturer specifications for each amplifier are provided in Table 2.2. The signal is carried through the circuit using coaxial cables except at the connection to the sample cell. Here, a coaxial to alligator clamp adapter cable is used. Both a



Figure 2.4: Optical microscopy image of an electrode edge taken with a  $10 \times$  objective. There is no visible roughness.

multimeter (Keithley 2001) and an oscilloscope (Tektronix TBS 1052B) are used to monitor the signal waveform. The multimeter displays the RMS voltage being applied to the sample cell which is used to calculate the applied electric field strength according to

$$E_{RMS} = V_{RMS} / w_{cell} \tag{2.1}$$

where  $w_{cell}$  is the width of the gap between the planar electrodes.

# 2.2.1 DC Filtering

The signal outputted by the function generator has an immeasurablely small DC component which is increased to levels capable of inducing electrophoresis by the amplifiers. For these experiments, the DC component must be removed to prevent

Table 2.2: Manufacturer specifications for each of the high voltage amplifiers.

Specification	Trek PZD700A	<b>Tegam 2340</b>
Output Voltage	0 to $\pm 700$ V DC or peak AC	0 to $\pm 200$ V DC or peak AC
Bandwidth	DC to $> 125$ kHz	DC to 2 MHz
Slew Rate	$> 380 \text{ V/} \mu \text{s}$	$> 250 \text{ V/} \mu \text{s}$
Gain	$25 \mathrm{V/V}$	0 to $300 \text{ V/V}$ , adjustable



Figure 2.5: 1. Completed electrode, 2. with UV glue soaked latex strips placed on top to create a spacer. 3. A microscope slide cut to 75 mm  $\times$  15 mm is placed on top of the latex spacers to create a channel. 4. The completed sample cell with the ends of the channel sealed and copper tape to create connection leads.



Figure 2.6: Cross-sectional diagram of the sample cell used to perform experiments.



Figure 2.7: Electric circuit used to generate electric field. The components are the AC voltage function generator, amplifier, capacitor, resistor, oscilloscope (denoted by O), the multimeter (denoted by V), and the sample cell (denoted by SC).

particle migration by electrophoresis. Previously, a 1  $\mu$ F capacitor (Illinois Capacitor 105MABA05KJ) was added to the circuit to create a high pass RC filter and remove the DC component of the signal [3, 2]. A polypropylene film capacitor was selected to due to its low equivalent series resistance (ESR) [4]. In this setup, the sample cell acts as the resistor in the RC circuit. This is problematic because the resistance of the sample cell, and thus the characteristics of the RC circuit vary based upon the conductivity of the solution. This variance can be calculated using Kohlrausch's Law,

$$\Lambda_m = \Lambda_m^o - K\sqrt{c} \,, \tag{2.2}$$

which gives the molar conductivity of strong electrolyte solutions at low ionic strengths.  $\Lambda_m$  is the molar conductivity,  $\Lambda_m^o$  is the limiting molar conductivity (149.8 S cm<sup>2</sup> mol<sup>-1</sup> for KCl), K is the Kohlrausch coefficient (94.50 S cm<sup>2</sup> mol<sup>-1</sup> M<sup>-1/2</sup> for KCl), and c is the molar concentration [5]. The molar conductivity can then be converted to the sample cell resistance using

$$R = w_{cell} / (\Lambda_m cA) \tag{2.3}$$

where A is the cross sectional area of the sample cell.

To reduce this undesirable variability, a 10 k $\Omega$  resistor (Ohmite 20J10KE) is now connected between the outlet of the capacitor and ground. A resistor with a resistance approximately an order of magnitude less than typical sample cell resistances is used, as this results in the total resistance of the circuit being approximately independent of the ionic strength of the suspension. For example, using Equations 2.2 and 2.3 a 1.25 mm wide, 100  $\mu$ m thick, and 20 mm cell containing a 0.1 mM KCl solution has a resistance of 420 k $\Omega$ . If this cell is connected to the circuit, the total resistance of the circuit can be calculated using the relationship for resistors in parallel

$$1/R_{total} = 1/R_{cell} + 1/R_{resistor} \,. \tag{2.4}$$

This results in  $R_{total} = 9.77 \ k\Omega$ . Thus, connecting the sample cell to the circuit changes the total resistance by only 2.4%. As a result, experimental repeatability is improved. This setup has the additional benefit of allowing the capacitor to discharge when the sample cell is disconnected to prevent accidental shocks.

The capacitor and resistor combination has a cutoff frequency of

$$f_c = \frac{1}{2\pi RC} = 15.9 \text{ Hz}$$
 (2.5)

and a time constant of

$$\tau = RC = 0.01 \text{ s.}$$
 (2.6)

Prior to performing experiments, the DC offset within the circuit was quantified to ensure it was reduced to acceptable levels by the RC circuit. To perform this measurement, waveform data was exported by an oscilloscope (Tektronix TBS 1052B) to a computer. The oscilloscope was set to average 128 waveforms to reduce the effect of noise. This data was then fit to a sine wave and the resultant y-intercept was taken to be the DC offset of the signal. To quantify what an "acceptable" DC offset is, a Péclet number for a colloidal particle in the cell can be calculated. The Péclet number for this is given by

$$Pe = \frac{\text{rate of advective transport}}{\text{rate of diffusive transport}} = \frac{\text{rate of transport due to electric field}}{\frac{\text{rate of transport due to electric field}}{\text{rate of diffusion due to Brownian motion}} = \frac{a^2}{D} \frac{v}{a} \quad (2.7)$$

where a is the particle radius, D is the diffusivity is given by

$$D = \frac{k_B T}{6\pi\eta a} \tag{2.8}$$

and v is the particle velocity due to the electric field given by

$$v = \mu E_{DC} \,. \tag{2.9}$$

Here,  $\mu$  is the particle electrophoretic mobility (4.6  $\mu$ m cm s<sup>-1</sup> V<sup>-1</sup> for a 1  $\mu$ m polystyrene sphere in 0.1 mM KCl) [6] and  $E_{DC}$  is the DC electric field strength. Values of Pe > 1 mean advective transport due to the DC offset is dominant for each particle while Pe < 1 indicates particle movement is dominated by diffusive transport. Substitution of Equations 2.8 and 2.9 into Equation 2.7 gives

$$Pe = \frac{6\pi\eta\mu a^2 E_{DC}}{k_B T} \,. \tag{2.10}$$

The above expression is not strictly accurate as the larger structures formed under the application of an electric field have much lower diffusivity than dilute colloids, but this is still a useful metric for quantifying the effect of the DC offset on the suspension. The magnitude of the DC component of the signal and the corresponding Péclet number, as well as values for the circuit without the 10 k $\Omega$  resistor and without any filtering, are shown in Table 2.3.

For the capacitor only filter used previously and the new resistor-capacitor circuit, the Péclet number is less than one. This suggests the DC offset is reduced to levels that do not have a noticeable experimental effect. Addition of the resistor appears to have increased the DC offset slightly, but based upon the measurement uncertainties, this increase cannot be considered statistically significant. **Table 2.3:** DC offset and corresponding Péclet numbers for the no filter circuit, the capacitor only circuit used previously, and the newly implemented resistor-capacitor circuit. In all cases, a voltage of  $12.4 \text{ V}_{\text{RMS}}$  with f = 150 kHz was applied to the sample cell. The Péclet numbers were calculated assuming a 1 mm electrode gap.

Circuit	$\mathbf{V_{DC}} (\mathrm{mV})$	$\mathbf{Pe}$
No Filter	$92.9\pm0.2$	$4.370 \pm 0.009$
Capacitor Only	$-9.7 \pm 1.6$	$0.46\pm0.08$
Resistor + Capacitor	$-11.0 \pm 1.6$	$0.52\pm0.08$

# 2.2.2 Circuit Dynamics

The time and frequency dynamics of the circuit were also studied and documented. First, the time required for the amplifiers to approach steady-state was measured. Voltage measurements were taken every 5 minutes for 70 minutes immediately after turning all components in the circuit on. A plot of the results is shown in Figure 2.8. Both amplifiers require approximately 65 minutes to reach steady-state, however the initial voltage is less than 1% different from the steady-state value and therefore warm-up times can generally be neglected.

To further characterize the circuit, the gain of each amplifier as a function of frequency was measured. Data with and without the sample cell connected for each of the amplifiers is shown in a Bodé diagram in Figure 2.9. For both amplifiers, the response of the circuit is identical with and without the sample cell connected with the exception of very low frequencies using the Tegam amplifier. This provides additional support for the previous assertion that the addition of the resistor causes the circuit to exhibit properties independent of the sample cell resistance.

The gain of the Tegam amplifier is essentially independent of frequency at the frequencies measured while the gain of the Trek amplifier varies significantly with frequency. The Trek amplifier exhibits a maximum amplitude of 230 at 50 kHz which then quickly tails off at higher frequencies. This behavior is somewhat different than



Figure 2.8: Measured voltage (V) relative to the stead-state voltage (V<sub>SS</sub>) of the circuit as a function of time immediately after turning all elements of the circuit on. It takes approximately 70 minutes to achieve a steady voltage measurement.

that reported previously due of the inclusion of the resistor [2, 3]. No plot is shown for the phase lag because no phase lag was observed at the frequencies studied.

Finally, as this work is primarily concerned with toggling the field, the toggle response of the circuit was quantified. To ensure the response time of the circuit is adequate, the toggle response of the circuit was examined by setting the function generator to output 9 cycles at 75 mV<sub>pp</sub> and 50 kHz every 2 seconds. This output setting represents a worst case scenario as the capacitor is given a short charging period and a long discharging period. The output response of the circuit to this input, with the input waveform as reference, is shown in Figure 2.10. The output signal is purely an amplified version of the input signal suggesting the amplifier and RC circuit do not impart additional dynamics onto the circuit and the transient component of the response can be neglected.



Figure 2.9: Bodé diagram of the response of the electric circuit for each amplifier. The amplitude ratio given by, A.R. =  $V_{out}/V_{in}$ , is plotted against the signal frequency. The sample cell connected data was obtained using a 100 µm thick cell with a 1 mm electrode gap loaded with a solution containing 0.12 wt% Pluronic F108, 10 µM KCl, and  $\phi = 0.56\%$  1 µm polystyrene spheres.

#### 2.3 Optical Microscopy

The time evolution of the structure of the colloidal dispersions is observed using a 10× objective (Zeiss A-Plan 10×) on an inverted microscope (Zeiss Axio Observer A10). Time lapse images of the structure are taken every 5 s for 3 hrs using a DSLR (Canon EOS Rebel T2i) with a shutter speed of 1/1250 s at ISO 400. To observe the micro-structures, a 63× oil immersion objective (Zeiss Plan-Apochromat 63×) is used to observe the 1 µm spherical particles and a 40× objective (Zeiss Plan-Neofluar 40×) is used to observe the dicolloidal particles. These high magnification images are taken with a shutter speed of 1/250 s at ISO 400 after at least 3 hours had elapsed.

#### 2.4 Summary

In this section, the methods for preparing the materials required for driving the colloidal self-assembly were discussed. Additionally, the characterization methods used in this thesis were presented. In the next chapter, the experimental results collected using these methods are presented and discussed.



Figure 2.10: Short toggle response of the electric circuit. The input voltage is shown for comparison. The function generator was set to output 9 cycles at 75 mV<sub>pp</sub> at 50 kHz every 2 seconds. Data was collected after several toggle cycles had completed.

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# Chapter 3

# TOGGLED FIELD RESULTS

### 3.1 Introduction

This chapter presents the results of the dielectrophoretic directed self-assembly of colloids in toggled fields. First, experimental results are shown for suspensions of 1  $\mu$ m polystyrene spheres in both density mismatched and density matched mediums. The particles dispersed in the density mismatched solution are then discussed in terms of the findings of the analogous magnetic field experiments [1]. The density matched results are compared to the findings of simulation work by Sherman and Swan [2]. Finally, the results of assembling anisotropic polystyrene dicolloidal particles in toggled fields are presented and analyzed.

## 3.2 Materials and Methods

#### 3.2.1 Dispersion Stability

In most cases, particle aggregation in colloidal dispersions is undesirable and therefore dispersions must be prepared in such a way that they are kinetically stable against aggregation. Stability can be determined experimentally by trial and error, however, without some starting point, this is a daunting task. Development of interaction energy curves using the Derjaguin-Landau-Verwey-Overbeek (DLVO) Theory of Colloidal Stability allows for *a priori* prediction of the stability of a dispersion. This makes it possible to quickly determine a set of preparation conditions which give rise to a stable dispersion.

DLVO Theory states the interaction energy between two particles is given by the sum of the attractive and repulsive interaction energies. For a colloidal dispersion to be kinetically stable against aggregation, the energetic barrier created by the repulsive force between particles must be greater than the thermal energy in the system  $(k_BT)$ . The polystyrene latex dispersions used in this work generally have an attractive van der Waals interaction and a repulsive electrostatic interaction. The attractive van der Waals interaction energy between two spherical particles is given by

$$U_{\rm VDW} = -\frac{A_{212}}{6} \left[ \frac{a^2}{2f_1(a,d)} + \frac{a^2}{2f_2(a,d)} + \ln\left(\frac{f_1(a,d)}{f_2(a,d)}\right) \right]$$
(3.1)

where d is the particle separation distance,

$$f_1(a,d) = d^2 + 2ad, (3.2)$$

$$f_2(a,d) = d^2 + 2ad + a^2, (3.3)$$

and  $A_{212}$ , the effective Hamaker for a particle (1) surrounded by a medium (2), is calculated by

$$A_{212} = \left(A_{11}^{1/2} - A_{22}^{1/2}\right)^2 \,. \tag{3.4}$$

In this expression,  $A_{11}$  is the Hamaker constant of the particle and  $A_{22}$  is the Hamaker constant of the medium. Next, the repulsive electrostatic interaction energy can be found by the Derjaguin approximation,

$$U_{\rm ES} = 32\pi a k_B T n_\infty \kappa^{-2} \Upsilon_0^2 \exp\left(-\kappa d\right) \,, \tag{3.5}$$

which is applicable when  $\kappa R_s > 10$ . Here,  $n_{\infty}$  is the number bulk ion concentration and

$$\Upsilon_0 = \frac{\exp\left(\frac{ze\zeta}{2k_BT}\right) - 1}{\exp\left(\frac{ze\zeta}{2k_BT}\right) + 1}$$
(3.6)

where  $\zeta$  is the zeta potential of the particle. The total interaction energy at a given particle separation distance is therefore

$$U_{\text{total}} = U_{\text{VDW}} + U_{\text{ES}} \,. \tag{3.7}$$

These expressions were used to develop interaction energy curves for the dispersions used in this work. To simplify calculations, the dicolloids were approximated as spherical particles. The parameters used to create these curves are shown in Table 3.1 and the resultant curves are shown in Figure 3.1.

The results of these plots show both suspensions should be kinetically stable under the given conditions as there is a maximum interaction energy two orders of magnitude greater than  $k_BT$  at a separation distance of 2 – 7 nm. However, the stability of these dispersions is somewhat more complicated as the energy driving dielectrophoretic self-assembly is one to two orders of magnitude higher than  $k_BT$ . To maintain the kinetic stability of the suspension, even under the application of an electric field, surfactant is added to create steric repulsion between particles. To achieve this, Pluronic F108 was added to the suspension medium. Pluronic F108 adsorbed to polystyrene creates a steric boundary approximately 10 nm thick [3]. As shown in Figure 3.1, this effectively makes it impossible for the particles to achieve a separation distance where van der Waals forces, which drive aggregation, dominate.

#### 3.2.2 Solution Preparation and Loading

For the experiments performed with suspensions of spherical particles, 1  $\mu$ m polystyrene spheres (Spherotech PP-10-10, 5.1 wt%, 1.0-1.4  $\mu$ m nominal size) are rinsed 3 times in Milli-Q water (18.2 M $\Omega$  cm<sup>-1</sup> minimum resistivity) by centrifuging at 1,800 RCF for 5 minutes, removing the supernatant, and re-suspending. Particles to be density matched are diluted to  $\phi = 0.56\%$  in a solution of 11  $\mu$ M KCl and 0.01% w/v Pluronic F108 surfactant and particles to be dispersed in a density mismatched medium

**Table 3.1:** Parameters used to generate interaction energy curves, shown in Figure3.1 for the colloidal particles used in this work. [4, 5]

Parameter	1 µm Spheres	Dicolloids
$a \ (\mu m)$	1	3.9
$A_{212} \times 10^{20} (\mathrm{J})$	0.76	0.76
z	1	1
$I \ (\mu M)$	10	10
$\zeta~({ m mV})$	-41.8	-18.2



Figure 3.1: Interaction energy vs. separation distance for (a) 1 μm polystyrene particles and (b) dicolloidal particles. Plotted using the parameters listed in Table 3.1. Dashed lines indicate the approximate location of the steric boundary formed by Pluronic F108 [3].

are diluted to the same volume fraction in a solution containing 10  $\mu$ M KCl and 0.01% w/v Pluronic F108 ( $\kappa^{-1} = 97$  nm). The salt concentration is increased by 10% for the particles to be density matched because D<sub>2</sub>O has a conductivity approximately 20% lower than H<sub>2</sub>O [6]. The surfactant concentration corresponds to the plateau of the adsorption isotherm of F108 onto polystyrene latex [7]. The particles are then rinsed in this solution 5 times by centrifuging at 1,800 RCF for 5 minutes, removing the supernatant, and re-suspending in fresh solution. For the density-matched samples, the particles are suspended in a solution of 50 vol. % H<sub>2</sub>O, 50 vol. % D<sub>2</sub>O, 11  $\mu$ M KCl and 0.01% w/v Pluronic F108 ( $\kappa^{-1} = 97$  nm) after the final centrifugation. Particles suspended in this solution showed minimal sedimentation after 20 mins of centrifugation at 20,000 RCF.

Dicolloids prepared by methods described by Panczyk are used for the experiments performed with dicolloidal dispersions [5]. Dried dicolloidal particles (D1 = 3.23  $\mu$ m, D2 = 3.38  $\mu$ m, L = 4.5  $\mu$ m) are placed in in a 1 wt% F108 solution which is then gently sonicated for 3 hours. To remove the majority of the aggregates, the suspension is centrifuged at 50 RCF for 30 s and the supernatant is removed, added to a new centrifuge tube, and mixed. This procedure is performed a second time and then the same procedure is completed a third time at 100 RCF for 30 s. The particles are then evaporatively dried and resuspended in a solution containing 10  $\mu$ M KCl and 0.01% w/v Pluronic F108 at  $\phi = 1.9\%$ . The particles were then rinsed in this solution 5 times using the same procedure described above.

The resulting suspensions are then loaded into the sample cells using the method described in Chapter 2.1.2. The density mismatched 1  $\mu$ m polystyrene spheres and the dicolloids are allowed to sediment for at least 8 hrs before experimental results are collected. The volume fraction of the spheres is selected to match the work done previously with toggled magnetic fields [1]. When sedimented, the dispersed volume fraction ( $\phi = 0.56\%$ ) corresponds to a volume fraction just below random close packing of spheres ( $\phi = 0.64$ ). The dicolloid volume fraction is selected to provide the same surface area coverage as the spherical particles.

## 3.2.3 Circuit Toggling

The loaded sample cells are connected to the electric circuit and a field of 700 V/cm at a frequency of 150 kHz. For the toggled field experiments, the output of the primary function generator is toggled using a secondary function generator (Agilent 33220A). The primary function generator is set to output the desired sinusoidal signal then the "burst" mode is enabled. Next, the primary function generator is set to "gated" mode. The output of the secondary function generator is attached to the trigger input of the primary function generator. Finally, the secondary function generator is set to output a square wave alternating between 0 V and 1 V at the desired toggle frequency and duty cycle.

## 3.3 Results for Density Mismatched 1 µm Spheres

Low magnification time lapse images are shown in Figure 3.2, and higher magnification images are shown in Figure 3.3. In Figure 3.2, the structures formed at short times under the application of a constant field appear similar to the suspension spanning chain structures formed in previous work with toggled magnetic field directed self-assembly [1]. At toggling frequencies from 0.1 to 1 Hz the formation of suspension spanning structures at short times does not occur. Application of frequencies 2 Hz and greater is equivalent to applying a field with approximately half the strength. Swan et al. observed similar behaviors at toggling frequencies greater than 2 Hz with magnetic field directed self-assembly [1]. In all cases, it appears the suspension takes approximately 45 minutes to reach a quasi steady-state where further ordering does not occur. The low magnification images also reveal the colloids do not coalesce into elliptical structures under any toggling frequency, unlike the paramagnetic colloids.

Images taken using the 63x objective reveals toggling is detrimental to ordering at all frequencies. The constant field image shown in Figure 3.3 has a nearly defect-free hexagonal structure. At 0.1 Hz, the suspension organizes into small crystallites but no long range order is observed. At 0.33 and 0.5 Hz, the particles only forms chains and no larger order structures are observed. The suspension appears to most disordered at a toggling frequency of 0.66 Hz where no structures are apparent. Order returns to the suspension at toggling frequencies of 1 and 2 Hz where crystalline structures are once again observed, but numerous defects are present. The discrepancy between the results observed in the paramagnetic colloidal suspension previously and this suspension likely stems from the difference in the interaction energy between the colloids. The time scales required for self-assembly to occur are significantly longer in the dielectrophoretic experiments as a result of weaker particle interactions. A comparison between the parameters introduced in Section 1.2 is shown in Table 3.2. To achieve a similar value of  $\Lambda$  in these dielectrophoretic experiments, a field strength of 3800 V/cm would need to be applied to the suspension. However, the field strength is limited to approximately 700 V/cm as higher voltages lead to unacceptable electroosmotic flow velocities and disruption of particle ordering.

Although  $\Lambda$ ,  $r_c$ , and  $\tau_c$  only serve as rough estimates of the behavior of the suspension, they suggest the field off period is too long and the particles are able to return to a fully disordered state prior to the field being reapplied. It may be possible



**Figure 3.2:** Density mismatched toggled field time lapse images. The dark areas of the images are the colloidal particles. Field conditions are 700 V/cm at 150 kHz.



Figure 3.3: High magnification images of the 1  $\mu$ m sphere density mismatched colloid suspension. The dark regions outline the colloidal particles. Field conditions are 700 V/cm at 150 kHz.

**Table 3.2:** Comparison between  $\Lambda$ ,  $r_c$ , and  $\tau_c$  for this work and the work done with paramagnetic colloids by Swan [1].

Variable	1 µm Polystyrene Spheres	1 µm Paramagnetic Spheres
Λ	2	69
$r_c \; (\mu \mathrm{m})$	1.3	3.8
$ au_c$ (s)	0.12	8.7

to circumvent this limitation by increasing the duty cycle above 50% such that the field off time is much shorter than the field on time to prevent the suspension from returning to a fully disordered state. However, pursuing this method as a means to obtain more ordered structures is not be worthwhile as the application of a constant field results in essentially defect free structures. Despite this, it may be worthwhile to explore the effect of varying the duty cycle as a means of improving the kinetics of assembly. In the magnetic field experiments, toggling the field revealed equilibrium structures were formed more rapidly at optimal toggling frequencies. Additionally, recent simulation results suggest it may be possible to achieve different crystal and fluid-crystal structures by varying the duty cycle [2].

One possible cause of the formation of crystalline structures under the application of a constant electric field may be the presence of flows within the sample cell. In the magnetic field experiments, large system-spanning chain structures are formed. When this occurs, diffusional freedom within the suspension is effectively lost as the chain structures are too large to readily diffuse and the individual particles interact with their neighbors so strongly that they can no longer move freely. In these dielectrophoretic experiments, individual colloids retain some diffusional freedom as the thermal energy of the system is of the same order of magnitude of the interaction energy between particles. Consequently, particles have some ability to escape energetically unfavorable states. Additionally, the larger structures formed retain their mobility due to flows in the sample cell exerting drag forces on the structures. This induces the continuous movement seen in Figure 3.2. This may make it possible for chains to coalesce into larger, lower energy, crystalline structures. Unfortunately, it is impossible to isolate the suspension from these flows experimentally but it may be possible for simulations to reveal the role of flows in dielectrophoretic self assembly.

#### 3.4 Results for Density Matched 1 µm Spheres

The low magnification time lapse images are shown in Figure 3.4 and higher magnification images of each experiment are shown in Figure 3.5. The low magnification images reveal long range ordering does not occur. With the exception of the constant and 2 Hz toggled field images, there is not a system spanning orientation in the direction of the electric field.

The high magnification images show similar trends to those observed in the density mismatched suspension. The constant field results exhibit the highest degree of ordering where long chains are observed. The 2 Hz toggled images also exhibit ordered structures although the chains are not as long as the constant field again demonstrating that toggling frequencies  $\geq 2$  Hz are equivalent to applying a weaker constant field. The intermediate frequencies exhibit very little ordering with only 2 – 3 particle chains forming.

The results of these experiments demonstrate gravity is integral for the formation of crystalline structures. Recent simulation work by Swan et al. suggests that gravity exerts a downward pressure on the suspension that aids in the formation of crystalline structures in dilute suspensions [2]. It is difficult to compare this simulation work to these experimental results as the simulation applied a toggled field to particles which were initially packed into a multilayer FCC structure. However, these results provide some experimental support for the simulation predictions.

Based upon the results of these experiments, it appears the density mismatched suspension is capable of producing macroscopically ordered structures because gravity creates a highly concentrated particle region at the bottom of the sample cell approaching that of random close packed spheres. As a result, all of the particles within the







Figure 3.5: High magnification images of the 1 µm density matched colloid suspension. The dark regions outline the colloidal particles. Field conditions are 700 V/cm at 150 kHz. suspension are within the attractive influence of one another. In the absence of gravity, the particles remain dilute and are far enough away from one another the particles behave essentially independently of one another. Under equilibrium conditions, the particles should eventually coalesce into one large structure but due to mixing by the electroosmotic flows in the sample cell, the kinetics of the process make this state practically unrealizable. However, it may be possible for ordering to occur in more concentrated density matched solutions where particles are closer to their neighbors an able to exert a stronger attractive influence on one another

To conclusively determine the role of gravity in AC field directed self-assembly, more experiments need to be performed. Particularly, the self-assembly of higher volume fraction density-matched suspensions needs to be studied. In previous work, Fermigier and Gast characterized the effect of particle volume fraction on the kinetics of self-assembly and the long-term structures of paramagnetic particles under the application of magnetic fields using image processing algorithms [8]. Similar methods could be employed to study the dielectrophoretic self-assembly of suspensions, although the analysis may be complicated by AC electroosmotic flows causing particles and higher order structures to move in and out of the area being imaged. These characterization methods are also limited to somewhat dilute volume fractions as multiple scattering makes it effectively impossible to use optical microscopy to obtain information about the state of the suspension at high volume fractions. However, small angle neutron scattering (SANS) is capable of characterizing the structure of colloidal dispersions at any volume fraction. Using SANS in conjunction with the methods employed by Fermigier and Gast would make it possible to characterize the role of volume fraction in the dielectrophoretic self-assembly of density matched suspensions.

# 3.5 Dicolloid Assembly

Recently, there has been interest in using directed self-assembly to created ordered structures with anisotropic colloids. The resultant structures are intriguing as they exhibit properties not found in crystals produced using spherical colloids. For instance, dicolloids have been assembled into structures with a volume fraction higher than FCC or HCP sphere packing arrangements [9]. However, the assembly of structures from dicolloids provides unique challenges. Spherical particles only need to achieve an energetically favored spatial positioning. Due to their anisotropy, dicolloids must achieve both an energetically minimum spatial position and rotational orientation. Consequently, the diffusion time provided by toggling the external field used to direct self-assembly may provide benefits not observed in the spherical suspensions. Additionally, owing to their increased size, the dicolloids used for these experiments experience two orders of magnitude stronger interactions. Thus, they may become kinetically trapped in unfavorable positions more easily due to stronger localization.

## 3.5.1 Microscopy Results

The low magnification time evolution images are shown in Figure 3.6. Unfortunately, the hard drive used to save the images ran out of space part way through the 0.5 Hz experiment and a small bubble formed in the sample cell during the constant field experiment. With the exception of the constant field experiment, which was disturbed by the bubble, these images do not change significantly with time. Although they do not provide much insight into the kinetics of assembly, the time lapse images do reveal AC electroosmotic flows were nearly absent in these experiments. This difference may be due to differing surface chemistries of the spherical and dicolloidal particles. The spherical colloids are initiated using a persulfate initiator and thus have highly charged surface. The dicolloids are initiated with AIBN and as a result their surface charge is significantly lower. Thus, the dicolloids are less influenced by ions moving past their surface. The high magnification images of the long term structures are shown in Figure 3.7. The high magnification images were taken as far as possible for the bubble in the sample cell and this image does not appear significantly different from the other images suggesting it is still comparable to the other results.

The images in Figure 3.7 indicate toggling is an effective means of improving the ordering of the suspension. The ordering of the particles improves notably between







**Figure 3.7:** High magnification images of the dicolloid suspension after at least 3 hours of field application. Field conditions are 700 V/cm at 150 kHz.

the constant field and 0.1 Hz toggled images. The other toggling frequencies studied do not appear to be significantly more or less ordered than the constant field images. This suggests there is an optimal toggling frequency between 0 and 0.33 Hz that produces maximal ordering. This result is consistent with the mechanism proposed previously for paramagnetic colloids [1]. These particles are larger and have stronger interactions than the paramagnetic particles. Thus, they require approximately an order of magnitude longer time scales to escape kinetically trapped states compared to paramagnetic spheres. The presence of an optimal toggling frequency in this suspension and the absence of one in the 1  $\mu$ m sphere density mismatched suspension suggests there may be some minimum size or interaction potential required for toggling to have a positive impact on the ordering of the particles.

The difference between the optimal toggling frequency observed for the paramagnetic particles and for the dicolloids do not agree well with Equation 1.37. This relationship suggests time scales approximately 2 orders of magnitude longer than the paramagnetic spheres are required for the dicolloids to escape from a trapped state while the experimental results reveal only one order of magnitude longer is required. This suggests there is a more complex relationship between diffusion and attraction than described by Equation 1.37. Regardless, these results suggest toggling should be explored further as a means of obtaining enhanced ordering in anisotropic dispersions.

## 3.5.2 Fast Fourier Transform (FFT) Image Analysis

Quantitative support for the qualitative observations made from the microscopy images was obtained by performing Fast Fourier Transforms (FFTs) on the high magnification optical microscopy images of each toggling frequency studied in ImageJ. Performing an FFT on an image is the mathematical analog of Bragg scattering. Thus, for disordered particles, an isotropic ring appearing at a q-vector (q) at low q. As the particles align with the field, the ring is expected to elongate in the direction perpendicular to the applied field due to the asymmetry of the particles. The formation of periodic crystals is expected to give rise to Bragg peaks in the FFT. FFTs of each of the high magnification microscopy images are shown in Figure 3.8. Qualitative analysis of the FFTs agrees with the conclusions drawn from the microscopy images. With the exception of the 0.1 Hz field, the low q rings are nearly isotropic indicating long-range disorder in the suspension. At very low q, a line perpendicular to the applied field appears except under the application of a constant and 0.66 Hz toggled field. This line indicates there is some degree of long-range alignment in the suspension. This once again suggests there is an optimal toggling frequency between 0 and 0.1 Hz that leads to maximized ordering in the suspension. Bragg peaks do not appear in any of the FFTs indicating there is no long range crystalline structure in the structures formed.

The FFTs of the images were more quantitatively analyzed by calculating the ratio of the long to short dimension of the low  $\boldsymbol{q}$  ring. A visual depiction of this analysis is shown in Figure 3.9a and the resultant values are shown in Figure 3.9b.

These results agree well with the qualitative analysis of the microscopy images and their corresponding FFTs. The 0.1 Hz FFT is considerably more anisotropic than the other FFTs and there is a general decrease in anisotropy as the toggling frequency is increased above 0.1 Hz indicating the suspension becomes progressively more disordered.

## 3.6 Summary and Conclusions

The effect of toggling on the ordering of both spherical and dicolloids was studied by systematically varying the toggling frequency. For the spherical particles, no improved ordering was observed at any toggling frequency. In fact, near perfect ordering was observed under the application of a constant field. This is most likely a consequence of the weaker interaction between particles assembled via dielectrophoresis. However, improved ordering was observed in the larger, dicolloidal particles at a toggling frequency of 0.1 Hz.

Additionally, the dynamics of assembly of spherical particles dispersed in a density matched medium were studied. These results revealed gravity plays an integral



Figure 3.8: FFTs of the long-time, high magnification images of the dicolloidal particles. Images are shown in false color to highlight intensity differences.



Figure 3.9: (a) Visual depiction of the quantities a and b used to characterize the degree of anisotropy in the FFTs. (b) Plot of a/b for each of the FFTs shown in Figure 3.8.
role in the formation of two and three dimensional structures. In the absence of gravity, particles are only able to form chains and the average chain length is shortened at all toggling frequencies. This result supports previous simulation results which showed gravity was necessary for the crystallization of the particles [2].

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# Chapter 4

# FUTURE DIRECTIONS

# 4.1 Scaling Relationship for Optimal Toggling Frequency

The results obtained in this work suggest Equation 1.37 does not provide an accurate description of the optimal toggling frequency. The ability to predict of the optimal toggling frequency would be useful for future experiments with different particles. This would be particularly useful to predict the behavior of sub-micron particles which are not easily observable with optical microscopy. Highly ordered structures of these particles are more desirable than micron sized particles as they are capable of forming photonic crystals. The key variables in this study would be particle diameter and applied field strength.

#### 4.2 Suppression of AC Electroosmotic Flows

The field strength used for these experiments was limited by the magnitude of the AC electroosmotic flows in the sample cell. Increasing the field strength beyond these levels is desired as it improves the kinetics of self-assembly. One possibility for reducing the velocity of the electroosmotic flows is to use a thinner spacer to construct the sample cell. Flow velocity could be characterized by loading the cell with a dilute suspension of fluorescent particles in conjunction with fluorescence microscopy and particle tracking algorithms.

# 4.3 Small Angle Light Scattering (SALS)

Quantifying the kinetics of self-assembly in the suspensions studied proved to be difficult optical microscopy. When toggled magnetic fields are used to drive selfassembly of paramagnetic colloids, they coalesce into elliptical structures. This makes it possible to characterize the kinetics of assembly using this size of the structures formed as a quantitative metric for the kinetics. Neither the density mismatched 1  $\mu$ m spherical or the dicolloidal suspensions exhibited the same behavior and quickly formed on large crystalline structure, the order of which is not distinguishable in the low magnification microscopy images. SALS provides an alternate method for characterizing the kinetics of self-assembly in these suspensions. Images of the scattering patterns can be collected and then the Bragg peaks can be fit with 2-D Gaussian curves. The full-width at halfmaximum (FWHM) then serves as a measurement for the degree of ordering in the suspension [1]. In addition, this would serve as a better metric for characterizing the order of the suspension than FFTs of microscopy images as the area probed by SALS is several orders of magnitude larger than the area visible through the high magnification objectives.

# 4.4 Small Angle Neutron Scattering (SANS)

The results using the density matched solution were limited to very dilute volume fractions because they were only studied using optical microscopy. Higher volume fractions would lead to multiple scattering rendering optical microscopy useless. Using SALS, it is possible to study somewhat higher volume fractions but even this method would be limited to  $\phi < 0.05$ . However, there is practically no upper concentration limit for SANS which would make it possible to study significantly more concentrated dispersions. Results at higher volume fractions would force the particles closer to one another leading to stronger attractive forces between one another and would be more comparable to the simulation work done by Sherman et al. [2].

# 4.5 Duty Cycle Variation

The experimental work performed to date with toggled fields has limited itself to applying a field with a 50%-50% duty cycle giving the particles equal times to diffuse and order. However, these two processes do not occur on the same time scales. As a result, better results may be obtained by varying the duty cycle to increase or decrease the relative time for diffusion to occur. Recent simulation results suggest different phases may be observed depending on the toggling frequency used during assembly [2].

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# Appendix

# SUPPORTING INFORMATION

#### A.1 Small Angle Light Scattering Results

Some small angle light scattering results for a different dicolloidal dispersion than the one studied in the main body of this thesis are presented in Figure A.1. Dicolloids (D1 =  $3.10 \pm 0.02 \ \mu$ m, D2 =  $3.36 \pm 0.03 \ \mu$ m, L =  $4.3 \pm 0.1 \ \mu$ m) were dispersed at  $\phi = 0.07$  in a solution containing 2 wt% Pluronic F108 and 10 mM KCl. These experiments were performed prior to optimizing the dispersion medium which is why the salt and surfactant concentrations are significantly different from the solution used in the main body of this work. Interestingly, these scattering results show a different pattern than the results obtained by Panzcyk [1]. One example of a scattering image he obtained is shown in Figure A.2. He focused primarily on monolayer structures and therefore worked at  $\phi = 0.02$ . In addition, he used particles with slightly different dimensions: D1 = D2 =  $3.45 \pm 0.06 \ \mu$ m and L =  $4.63 \pm 0.06 \ \mu$ m. The multilayer sturctures formed at  $\phi = 0.07$  and the slightly different particle aspect ratio may account for the difference in scattering patterns. In the future, it may be interesting to study the effect of particle geometry and volume fraction on the resultant structures and scattering patterns.

# A.2 Non-Planar Electrodes and Electroosmotic Flows

For quite some time, there were no available evaporative deposition chambers making it impossible to fabricate planar electrodes. During this time period, numerous attempts to create non-planar electrodes using copper tape were made. This turned out to be a fruitless pursuit as AC electroosmotic flows are amplified by several orders of magnitude in non-planar electrode geometries [2]. In the future, it is crucial that



Figure A.1: (a) Constant field SALS result and (b) 1 Hz toggled field result presented in false color to accentuate color differences. Each image is an average of five images taken in the same location to remove the effect of time fluctuations. Field conditions are  $E_{RMS} = 735$  V/cm and f = 50 kHz.



Figure A.2: SALS pattern obtained by Panczyk for dicolloidal particles [1].

planar electrodes are used otherwise it is impossible to obtain usable results. Additionally, the Trek amplifier appears to produce higher velocity electroosmotic flows than the Tegam amplifier at the same field strength. The cause of this is not known and seems to disagree with the notion that the electroosmotic flows are only a function of the electric field strength and electrode geometry.

# A.3 Photoresist Manufacturer Documentation



**TECHNICAL INFORMATION** 

# TECHNICAL INFORMATION

# Futurrex, Inc.

12 Cork Hill Road Tel: (973) 209-1563 Franklin, NJ 07416 Fax: (973) 209-1567 www.futurrex.com E-Mail: info@futurrex.com

#### Processing

- 1. Application of resist by spin coating at selected spin speed for 40 s.
- 2. 150°C hotplate bake for 60 s\*; 165°C hotplate bake for 240 s\*\* (softbake)
- 3. Resist exposure with a tool emitting 365 nm wavelength.
- 4. 100°C hotplate bake for 60 s\*; 110°C hotplate bake for 240 s\*\* (post-exposure bake)
- 5. Resist development in Resist Developer RD6 by spray or immersion. Development time for 1.5  $\mu$ m thick film, for example, is 12 s. To increase development time to 60 s combine RD6/water 3:1.
- 6. Resist rinse in deionized water until water resistivity reaches prescribed limit.
- 7. Drying of resist.
- 8. Removal of resist in Resist Remover RR41.

\*For good conductors of heat such as Si, GaAs, InP, etc. \*\*For 1mm thick glass substrate.

#### **Handling Precautions**

Negative Resist NR71-1500PY is a combustible liquid. Handle it with care. Keep it away from heat, sparks and flames. Use adequate ventilation. It may be harmful if swallowed or touched. Avoid contact with liquid, vapor or spray mist. Wear chemical goggles, rubber gloves and protective coating.

2

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