The Response of an Ellipsoidal Colloid Particle in an AC Field

Cornelius Adebowale Obasanjo

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THE RESPONSE OF AN ELLIPSOIDAL COLLOID PARTICLE 
IN AN AC FIELD

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Submitted in Partial Fulfillment of Requirements for the Degree
MASTER OF SCIENCE IN CHEMICAL ENGINEERING
at the
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DEDICATION

I dedicate this work to my parents, Mr. and Mrs. Matthew Obasanjo Odetunde.

Through their prayers, labor of love and hard work; I found my path to greater blessings.
ACKNOWLEDGEMENT

To the only wise God, through Jesus Christ, be the glory forever. Amen

“Per aspera ad astra… - through difficulties to the star”

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The quest for new smart materials with engineered properties and desired functionalities has driven scientists into the domain of nanotechnology over the past 30 years.\textsuperscript{1} Particles with anisotropic properties as a result of their geometry, chemical patterning or surface functionality have been envisioned as building blocks for advanced materials. By tuning the anisotropic interactions engendered by anisotropic particles, one potentially could manipulate the dynamic pathways for assembly.

The work described in this thesis considers the response of an ellipsoidal colloid particle to a nearby AC electrode polarized at $\sim 0.1 – 4$ kV/m and $\sim 0.1 – 3$ kHz. The ellipsoidal particle, which had a surface sulfate functional group, was dispersed in $10^{-6}$M NaCl. The particle experienced typical electric-field induced responses, including electro-rotation and electro-orientation at low frequency - 100Hz - with an electric field intensity of 2500Vm$^{-1}$. For instance, the particle (lying) was observed to frequently try to align its longer axis parallel to the electric field. We quantified the ellipsoid’s response by tracking its position and orientation with and without an electric field. The translational diffusion coefficient without and with electric field was calculated to be in the range of $(7.625 – 39.2750) \times 10^{-3} \mu m^2/s$ and $(0.725 – 305.525) \times 10^{-3} \mu m^2/s$ respectively. Surprisingly, the ellipsoid was also observed to propel in the direction normal to the electric field, which we believe to be a first for such a system. We proposed that the propulsion is a result of broken symmetry in the electrohydrodynamic (EHD) flow due to non-symmetric ellipsoid shape of our particle.
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CHAPTER I
INTRODUCTION

Nano- to micrometer scale particles (i.e. “colloidal” particles) are regularly found in natural and synthetic applications. The quest for new smart materials with engineered properties and desired functionalities has driven scientists into the domain of nanotechnology over the past 30 years.\textsuperscript{1} One approach in nanotechnology is that of bottom-up assembly, in which engineered building blocks are used to create new materials by either their self-assembly (driven by thermodynamics) or directed-assembly (driven by an external field). Substantial consideration, therefore, has been devoted to the preparation of various types of building blocks for the self-assembly process. Colloidal particles have been identified as one of the preferred choices for creating complex structures via directed assembly.\textsuperscript{1} The substantial research efforts in the preparation of colloidal particles are driven by their potential applications in fields such as drug delivery, separation technology, and developing intricate and complex colloidal crystals. These particles often show physical properties dominated by their surfaces because of their small size and enormous surface-to-volume ratios.
The classic colloidal system for a “bottom-up” directed assembly processes is that of isotropic spherical particles. An isotropic spherical particle typically engenders isotropic interactions, meaning that spherically shaped particles are capable of ordering into a limited number of arrangements as a result of their shape. More complex microstructure is possible with an extra degree of freedom via introducing an anisotropy in either shape or surface chemistry. For instance, an extra degree of freedom could be achieved by tuning the aspect ratio of simple isotropic spherical colloidal particles, hence creating more complex arrangements and observing how such a change in microstructure are capable of influencing macroscopic properties, especially optical properties. Anisotropic colloidal particles with directionally dependent interactions or interfacial functionality have drawn enormous attention due to their potential in materials engineering, from the nano- to the macro-scale. Recent scientific and technological development require materials with technically diverse properties that could find application in photonic material fabrications, self-assembly, emulsion stabilization, separation of biological cells from other particles and molecular probes amongst others, through careful study of mechanisms such as self and directed assembly of this particles. The use of external fields, electrical or magnetic, to drive assembly processes may help to engineer tailored, long-range inter-particle forces with tunable intensity and directionality that can generate well-ordered and programmable multi-dimensional assemblies. Impressive efforts have been made towards assembly of spherical colloids, but much interest rises for non-spherical anisotropic particles through externally or induced directed and self-directed assemblies.

This thesis focused on the response of an anisotropic colloid very near a polarized electrode. Our goal was to experimentally observe the response of the particle to a nearby
electrode and subsequently determine the underlying mechanism for the particle’s response. We were motivated by previous studies on the response and assembly of spherical colloidal particles (we also achieved assembly of spherical particles in our lab using AC field) and also (more recently) doublets by Ning Wu’s group at Colorado School of Mines.\(^8\) We fabricated symmetric and asymmetric doublets as well as ellipsoids, but the main body of this work focused on the response of ellipsoidal colloidal particles very near an electrode responding to an ac electric field at varying electric field strength and frequency. The main conclusions of this thesis includes that:

- We observed that non-symmetric ellipsoids were associated with some propulsion speed made along the long axis at angles to the electric field.
- We observed a critical frequency and electric field intensity (2500V/m, 100Hz) where the particle’s translational diffusion coefficient was found to be maximum (0.3055μm\(^2\)/s)
- We observed a non-linear (quadratic) relationship in the Mean Square Displacement (MSD) for the Brownian motion of our particles in AC fields, which indicates the particle is experiencing directional propulsion at certain conditions.

Furthermore, we determined the translational diffusion coefficient of the particles with changing experimental conditions.
CHAPTER II
LITERATURE REVIEW AND THEORY

2.1 The emergence of anisotropic colloidal particles

Colloidal particles are solid particles with a characteristic size between 0.01μm and 10μm. Solid particles of this size appear frequently in synthetic and biological applications, and are often used as a building block for advanced materials, with one example being colloidal crystals. Colloidal crystals, which have attracted more attention over the past two decades, have unique optical properties that make them candidates for applications in photonics. Colloidal crystals interact with visible light in unique ways because the spacing and individual components of the crystal have length scales that are comparable to the wavelength of light. Significant effort in this area was initially focused on crystals comprising spherical particles.\textsuperscript{9-13} However, spherical particles limit the attainable microstructure to hexagonally packed arrays. Applications would benefit from more intricate and complex structures assembled by anisotropic colloidal particles; one way to achieve such microstructure is to tune the particle shape because of the potential to influence the packing patterns obtained from colloidal assembly. Building blocks with non-
spherical shapes offer different symmetries, packing densities and directionalities. Therefore, a greater variety of possible assembled structures is expected compared to their isotropic counterparts.\textsuperscript{14} Consequently, advances in synthesizing particles that feature both desirable shapes and directional interactions are now setting the stage for the assembly of more complex structures.

Over the past decade, colloidal particles of exotic shape and functionality have been fabricated.\textsuperscript{15} New synthesis and fabrication techniques are being pioneered to make nanoparticles and colloidal particles whose asymmetric shapes and anisotropic interactions provide a variety of crystal polymorphs and assembled structures unprecedented in colloid science. Glotzer S. C. et al\textsuperscript{15} stated that the urgent question for engineers today is: “to what extent may the richness of molecular crystal structures be imparted to suspensions of nanoparticles and colloidal “molecules”?”. A great amount of research has been done towards fabricating profound colloidal particles and hence molecules, in a way of addressing the question stated above.

2.2 Fabrication and classification of anisotropic colloidal particles

Anisotropic particles fall into a variety of categories, depending on the nature of the anisotropy. Classifications of anisotropy includes geometry, surface chemistry, and composition.

2.2.1 Geometrically anisotropic particles

These are particles with non-spherical shapes, such as ellipsoids, rods, and clusters of spheres (colloidal dimers, trimers, tetramers etc.). Geometrically anisotropic particles
have found great application in studying anisotropic interactions in colloids. Shape has a fundamental role in self-assembly as it can regulate particle recognition, control the density and the structure of particle packings and also help binding of ligand molecules\textsuperscript{16}. Several methods of fabrication such as seeded emulsion polymerization\textsuperscript{17} amongst others has made it possible for more diverse particle shapes, such as ice cream cone-like or popcorn-like particles\textsuperscript{4}. Similarly, complex shapes have been achieved by stretching spherical polymer particles that are embedded in a flexible matrix\textsuperscript{14}, deforming them by light irradiation or ion beam irradiation, microfluidic synthesis, controlled precipitation of sol-gel precursors in the solution phase, and by several other approaches that have been reviewed in the past.\textsuperscript{14} Furthermore, Kim et al (2006), successfully fabricated cone, diamond triple rod and triangle particles in a well-controlled manner with high yield. It was also shown through experiment that anisotropic (non-spherical particles) have a higher packing density as compared to their spherical counterparts.\textsuperscript{18}

2.2.2 Chemically anisotropic particles

Particles with chemically patterned surfaces are similarly anisotropic colloidal particles which include Janus and patchy particles amongst others. These particles have at least two components of different chemistry, functionality, and/or polarity\textsuperscript{19}. Some examples include polymer-polymer, inorganic-inorganic, or organic-inorganic hybrid particles with chemical/physical properties and tunable morphological structure.\textsuperscript{19,20} Chariya K. et al (2013) in his paper also listed several methods for fabrication of Janus particles which includes but not limited to emulsion polymerization, solvent evaporation, controlled nucleation and growth. Not until recently have microfluidic-based system been
considered as one of the most important methods used for fabrication of Janus colloidal particles. This method involves controlling of liquid flow in microfluidic channels followed by solidification, generating monodisperse emulsions or Janus droplets.

2.2.3 Compositionally anisotropic particles

Morphology plays a significant role in the self-assembled structure and performance of microspheres. The chemically patterned anisotropic particles as well as the shape or geometric nature of anisotropic particles places much focus on the control of external morphology of particles. However, many research groups have demonstrated the preparation of hollow spheres using templating methodology.\textsuperscript{7,17} Core-shell particles are first prepared from colloidal particles such as polymer latex, silica, gold, and ZnS.\textsuperscript{3,21} Typically, templated particles are coated with various materials to prepare core-shell composite particles by controlled surface precipitation of inorganic materials,\textsuperscript{17} layer-by-layer adsorption of a polyelectrolyte and of charged nanoparticles, or direct surface polymerization using functional groups on the surfaces.

2.3 Fabrication techniques for anisotropic colloidal particles

Multifunctional colloidal particles have recently attracted increasing attention due of their promising properties for various applications. This impulsion for colloidal particles with precisely engineered properties has inspired material scientists to develop or fabricate novel synthetic routes towards colloidal particles with multiple functionalities.\textsuperscript{22}

Fabrication of colloidal particles with well-controlled anisotropy is quite challenging.\textsuperscript{23} Nonetheless, technologies have been devised to fabricate colloidal particles
with controlled shapes, structures, dimensions, and very attractive functional properties for
the development of new generations of nanosystems.\textsuperscript{24} An example of such is the Janus
particle, which is capable of forming monovalent or multivalent bonds that lead to well-
defined colloidal clusters.\textsuperscript{23} However, fabrication of anisotropic micro and nanoparticles,
such as rods, disks, fibers, tubes, dumbbell-shapes, acorn shapes, sheets and ellipsoids\textsuperscript{22}
have been realized by a myriad of different fabrication processes and/or technologies.
Amro K. F. et al (2009)\textsuperscript{25} in his paper stated that a range of procedures for fabrication of
anisotropic micro- and nanoparticles have been developed, which includes micro-contact
printing, lithography-based micro-stamping, clusterization of microspheres or partial
coating of particle monolayers, micro-fluidics, electro-hydrodynamic jetting, and
controlled nucleation and precipitation. Kyung J. L.(2010)\textsuperscript{22} also added that some other
approaches such as, stretching methods and methods using seeded polymerization have
been particularly successful in creating well defined particle shapes of which many have
been adopted from other areas of material processing. Seed polymerization, a method that
can yield substantially smaller non-spherical particles\textsuperscript{22} also provides potential access to
compositionally anisotropic particles. Similarly, Weitz and coworkers\textsuperscript{22} have since shown
that particle shapes can be effectively tuned by varying either the crosslinking density or
the degree of phase separation between the seed polymers and the newly made polymers.

2.4 Particle interactions in colloids

The interaction forces acting between colloidal particles in suspension play an
important part in determining the property of a variety of materials. Yuncheng L.et al
(2007)\textsuperscript{26} in his paper stated that this interaction forces play an important role in determining
properties such as the shelf life, stability, rheology amongst others. This arises due to the dependence of the behavior of the suspensions/emulsions on the magnitude and range of the surface interactions. There have been well-built theories that describe the interparticle interactions in colloidal suspensions, most of which can be resolved either analytically or numerically in terms of the underlying fundamentals.26

The DLVO (Derjaguin-Landau-Verwey-Overbeek) theory remains the starting point to describe the interaction between colloidal particles assuming only two types of forces, repulsive electrostatic forces - as a consequence of electric double layer overlap - and attractive van der Waals forces.27 The van der Waals attractive forces are negligible when the separation distance between colloidal particles is more than a hundred nanometers (>100 nm). Van der Waals forces are forces that they are larger than kT at distances somewhat smaller than the particle size, and they decay as an inverse power of the distance between the surfaces. The electrostatic double layer forces can be more understood for colloidal particles in water and in other media which favors electrolytic dissociation, colloidal particles are usually charged. The suspension as a whole, however, is electroneutral. A charge opposite to that of the particles is carried by small ions in the solution and forms a more or less diffuse electric double layer around each particle, rather similar to the ionic atmosphere known from the Debye and Huckel theory. When colloid particles approach one another the interaction of these double layer causes a repulsion. However, there are additional surface forces in aqueous solutions associated with the other two forces mentioned earlier, which includes solvation or hydration (in case of water) force, hydrophobic force and steric force. These are equilibrium forces in the sense that the surface is not responding to an external field (such as an electric field).
These forces are important to the formation of structure in colloidal materials. In cases where these interparticle forces are sufficiently balanced in a colloidal system, self-assembly can occur. For example monodispersed nanometer and micrometer sized spheres in a suspension can spontaneously form closed-packed colloidal crystal arrays if their free volume is restricted below a certain level.\textsuperscript{14} The surface charge of the particles must be sufficiently repulsive to discourage random aggregation but not large enough to prevent close packing.

On the other hand, just like cars in an assembly plant, colloidal particles could potentially be arranged via the manipulation of external fields. Use of external fields to drive the assembly processes is able to induce tailored, long range inter-particle forces with tunable intensity and directionality that can generate highly ordered and programmable multi-dimensional structures\textsuperscript{6}. Electrokinetics, the use of external fields to exert electrostatic forces on charged or polarizable fluids and suspended particles, which in turns induces the motion of fluids and particles. Mechanisms of electrically driven particle and fluid motion includes; electrophoresis, electroosmosis, electrohydrodynamics (EHD), and induced dipole interaction. Electric field assisted directed assembly has found great application in the manipulation of the interparticle interaction forces due to this mechanism. Applying the theoretical and experimental concepts learned from these model systems for a simple isotropic particle to more complex colloidal systems,\textsuperscript{28} as involved in this research work is expected to generate interesting results due to the orientation involved for anisotropic particles.
2.5 The concept of electric double layer

Most substances tend to gain surface charges when brought into contact with an aqueous medium. Surface charge arises mainly from the adsorption or dissociation of chemical groups. The stability of colloidal dispersions is very sensitive to the addition of electrolytes and to the surface charge of the colloidal particle. The electrostatic interaction between the charged surface and the surrounding ions attracts counterions and repels co-ions from the charged surface. Consequently, a layer predominantly occupied with more counterions is formed in the vicinity of the charged surface. This layer is referred to as the Electric Double Layer (EDL) – as shown in the figure 2.1. The EDL consists of the two layers namely; the stern and diffuse layers. Within this diffuse layer is a notional boundary, known as the slipping plane. This particle acts as a single entity within this boundary – the potential at this boundary is the zeta potential.

Figure 2.1: An illustration of the electric double layer. (Nanocomposite.com, 2016)
In the absence of fluid motion and at steady state; the Debye length, characterizing the EDL thickness is given as:

\[ \lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon_f RT}{\sum_{i=1}^{n} e^2 z_i^2 C_i}} \]  

(1)

\( \varepsilon_0 \) and \( \varepsilon_f \) are, respectively, the absolute permittivity of vacuum and the relative permittivity of the fluid, \( F \) is the Faraday constant; \( z_i \) is the valence of the \( i \)th ionic species, \( C_i \) is the bulk concentration of the \( i \)th ionic species, \( n \) is the total number of ionic species.

2.6 Electrokinetics Mechanism

Electrokinetics is the relative motion between two charged phases. Electrokinetic phenomena occurs when one attempts to shear off the mobile part of the electric double layer. As the charged surface tends to move in the appropriate direction, the ions in the mobile part of the electric double layer undergo a net migration in the opposite direction, carrying solvents along with them, thereby causing movement of the solvent. Amongst many types of phenomena that might occur as a result of relative motion between charged phases and electrolytes, electrophoresis, electro-osmosis, dielectrophoresis and induced dipole interactions will be reviewed.

2.6.1 Electrophoresis

Electrophoresis is the migration of charged particles suspended in an aqueous solution subjected to an external field. The negatively charged colloidal particle migrates towards the anode. The particle’s electrophoretic velocity is given as,

\[ U_p = \eta E \]  

(2)
Where $\eta$ is the particle’s electrophoretic mobility. Many particles of interest in microfluidic applications, such as biological entities, synthetic nanorods\textsuperscript{29} are non-spherical, that is, anisotropic in micro-channels. Hence, increased attention has been given to the electrophoresis of non-spherical particles.

### 2.6.2 Electro-osmosis

Movement due to applied electric field of an electrolyte solution relative to a stationary (parallel) charged surface can be referred to as electro-osmosis. The excessive counterions within the EDL of the charged surface migrate towards the oppositely charged electrode, dragging the viscous fluid with them.\textsuperscript{29} The pressure necessary to counterbalance electroosmotic flow is termed the electroosmotic pressure.

### 2.6.3 Dielectrophoresis

Dielectrophoresis (DEP) is the motion of a particle produced by the interaction of a non-uniform electric field with the induced effective dipole moment of the particle.\textsuperscript{31} The interaction of dipoles induced in the particles with a non-uniform electric lead to the emergence of the DEP force. DEP is typically conducted with an AC electric field (as opposed to a DC electric field) because oscillatory fields have the advantage of permitting high field strengths without water electrolysis. The forces that an AC electric field exerts on particles during DEP can be efficiently controlled by adjusting field parameters such as magnitude, frequency, wave shape, wave symmetry and phase. The ratio of the polarizability of the particles to that of the electrolyte solution determines the direction of the DEP force. The DEP force is proportional to the square of the electric field, indicating
nonlinear electrokinetics. Also, the DEP force, is proportional to the third power of the
particle size. A positive (negative) dielectrophoresis refers to the DEP force directed
towards (away from) the region with a higher electric field.\textsuperscript{29}

The time averaged force on each homogeneous particle, $F_{DEP}$, in the AC field
\( (Ee^{i\omega t}) \) is dependent on the gradient of the field squared, $\nabla E^2$, and the radius cubed
(effectively volume) of the particle, $r^3$.

\[
F_{DEP} = 2\pi \varepsilon_1 \text{Re} |K(\omega)| r^3 \nabla E^2_{\text{rms}}
\]  

The sign and magnitude of the dipoles induced in the particle are given by the real
part of the Clausius-Mossotti function, $K$,

\[
\text{Re}|K| = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} + \frac{3(\varepsilon_1 \sigma_2 - \varepsilon_2 \sigma_1)}{\tau_{MW}(\sigma_2 + 2\sigma_1)^2(1 + \omega^2 \tau_{MW}^2)}
\]  

Where $\varepsilon_1$ and $\sigma_1$ are the dielectric permittivity and conductivity of the media, and,
$\varepsilon_2$ and $\sigma_2$ – of the particles. The frequency-dependent polarizability response of dielectrics
is given in their complex permittivity (which is a function of AC field frequency, $\omega$, $\varepsilon_r =
\varepsilon_0 \varepsilon_r - \frac{i\sigma}{\omega}$) where $\varepsilon_0$ is the dielectric permittivity of vacuum ($8.854 \times 10^{-12}$ C$^2$ N$^{-1}$ m$^{-2}$), $\varepsilon_r$
is the relative permittivity, $i$ is the imaginary unit and $\sigma$ is the electrical conductivity. $\tau_{MW}$
is the Maxwell-Wagner charge relaxation time $\tau_{MW} = \frac{\varepsilon_2 + 2\varepsilon_1}{(\sigma_2 + 2\sigma_1)}$.

\section{2.6.4 Electrohydrodynamics}

This is the motion of the fluid arising from the action of electric fields on small
charge imbalances that exist in the diffusion layer, that is, outside the diffused part of the
double layer. The gradient of the electric field strength normal to the lower electrode arises
from concentration variations which is necessary to generate unbalanced charge\textsuperscript{32}. Lateral
electric field components exert force on the unbalanced charge in the diffusion layer, thereby moving the fluid along the particle and the electrode.

2.7 Brownian motion of anisotropic particles

In addition to equilibrium and electric field induced forces, a colloidal particle experiences a random force as a consequence of thermal agitation. This random force is called Brownian motion.\textsuperscript{33} The analysis of the Brownian motion of anisotropic particles is considerably more complicated compared to the spherical particles due to the coupling of rotational and translational motion.\textsuperscript{33,34} The dependence of the instantaneous translational diffusion coefficient on the current orientation of the particle leads to anisotropic motion for short times.

The coefficient of diffusion, D, is an important transport property of a colloidal particle and it represents the role of Brownian motion on the movement of the particle. With increasing time, the colloidal particle will diffuse due to Brownian motion within the medium\textsuperscript{30}. The mean square displacement (MSD) of the diffusing particle proportional to the lapsed time $t$, for a 1D is

\[ \langle x^2 \rangle = 2Dt \] \hfill (5)

Therefore, for a 2D, we can extract an ensemble of particle trajectories starting at different times $\tau_0$ (the lag time), and ending at a time $t$, later. The total positional and angular displacements in these trajectories are, respectively,\textsuperscript{34} $\Delta \bar{x}(t) = \bar{x}(t + \tau_0) - \bar{x}(\tau_0)$, $\Delta \bar{y}(t) = \bar{y}(t + \tau_0) - \bar{y}(\tau_0)$ and $\Delta \bar{\theta}(t) = \bar{\theta}(t + \tau_0) - \bar{\theta}(\tau_0)$. Therefore,

\[ \langle MSD \rangle = \langle [\Delta x(t)]^2 \rangle + \langle [\Delta y(t)]^2 \rangle = 2D_a t + 2D_b t \] \hfill (6)
Where the translational diffusion coefficient, $D_T = (D_a + D_b)$, is the sum of the parallel and perpendicular translational diffusion coefficients for an ellipsoid (that is, along the short and long axis for an ellipsoid). The mean square angular displacement is given as,

$$\langle MSD \rangle = \langle [\Delta \bar{\theta}(t)]^2 \rangle = 2D_\theta t$$  \hspace{1cm} (7)
CHAPTER III

EXPERIMENTAL PROCEDURE AND INSTRUMENTATION

3.1 Procedure for the preparation of samples with varying pH

Zeta potentials are best understood with specific pH references. We had to prepare different pH samples to help us understand better the behavior of our particles in different salt concentration. For best results, standardization (or calibration) of the Fisher Scientific accumet basic (AB) Benchtop meter AB200, is recommended prior to measurement. The AB200 was turned meter on, while the measurement was selected for pH mode. The pH and ATC electrodes were rinsed carefully (it is advised that if the pH electrode has not been hydrated, place in solution for more than one hour) with deionized water then submerge in a beaker containing the pH 7.00 standard buffer. (Allow the electrode to soak in buffer for 10 minutes prior to standardization). The meter was standardized, carrying out the same procedure for buffer solutions samples of pH 4.01 and 10.01. Dilute samples of NaOH and HCl with concentrations of approximately 0.1mM and 1mM respectively were prepared in two separate volumetric flasks. 400ml of the 0.1mM NaOH solution was taken
apart in a clean beaker and its pH value measured, 10ml of the sample was then measured into a 20ml disposable scintillation vial for each of the five separate particles sample to be prepared and the pH labelled (9.52, in this case) on the vial. Dropwise addition of 1mM HCl to the remaining solution from previous step was the followed until a next desired pH value was obtained. This procedure was repeated for seven other pH values ranging from 9.52 to 2.19; with the scintillation vials being carefully labelled for each pH value and for five particle samples. The particle samples (white suspension) were acquired from Molecular Probes, Life technologies which includes carboxyl latex particles suspension; 4% w/v 3µm (C1) and 4% w/v 2µm (C2) and sulfate latex particles suspension; 8% w/v 3µm (S1), 8% w/v 2µm (S2) and 4% w/v 6µm (S3) (see certificate of analysis for each sample in the appendix). 20ml empty scintillation vial was measured on an ML analytical balance (by Mettler Toledo). Few drops of the sample were then transferred into the vial from the sample dropper. Calculated quantity (relative to the concentration, particles/ml, as prescribed by the manufacturer) of each particle sample from the vial was then added to the prepared pH solution so as to attain a desired concentration of \( \sim 4.5 \times 10^6 \frac{\text{particles}}{\text{ml}} \) for each particle sample from pH 9.52 to pH 2.19. The resulting solution was agitated for 2 minutes; this becomes the base sample to be measured. This procedure was also repeated for the other four particle samples.

### 3.2 Zeta potential measurement

The equipment used for the zeta potential and electrophoretic mobility measurement is the Malvern DLS (Dynamic Light Scattering) Zetasizer Nano ZS from Malvern Instrument Limited, UK. The instrument uses micro-
electrophoresis/electrophoretic light scattering technology to measure electrophoretic mobility. An electric field is applied to a solution of molecules or a dispersion of particles, which the moves with a velocity related to their electrophoretic mobility. The velocity is measured using a laser interferometric technique called M3-PALS (Phase Analysis Light Scattering). This enables the measurement of electrophoretic mobility, and from this, the zeta potential and zeta potential distribution are calculated.

The fluid (“zeta”) cell used for the measurement can accommodate a minimum sample volume of 0.75ml. Some of the sample was taken using a 1ml disposable syringe, dislodging any air bubbles, and the syringe inserted into one of the ports in the zeta cell. The zeta cell was filled by gently depressing the syringe plunger and carefully checking for any air bubbles in the fluid cell prior to measurement. Both ports were simultaneously capped to ensure even sample levels on both side of the zeta cell. The zeta cell contains a weld line (a small notch along the top of the cell on one side; which is the front of the zeta cell) and should be facing the front of the instrument. The temperature of the fluid cell was controlled and measured with a precision of 0.3°C or better. An equilibration time of 2 minutes was used prior to starting measurement. A minimum of three runs were performed per sample to establish measurement repeatability. Measurement duration, that is, number of sub-runs per run, was set according to the instrument manufacturer’s recommendations. The applied voltage was set to automatic (the best voltage is set by the software). This procedure was then repeated for different pH samples. The instrument conditions were as follows:

- Dispersant – Water (Temperature - 25°C, Viscosity – 0.8872cp, Refractive index – 1.330, Dielectric constant – 78.5)
• Smoluchowski model - F(κa) value of 1.5
• Temperature - 25°C
• Equilibration time – 120 seconds
• Delay between measurements – 20 seconds
• Cell type – Disposable folded capillary cells (DTS1070)
• Automatic attenuation selection and automatic voltage selection
• Number of measurement – 3

Figure 3.1 below shows the experimental set-up for the electrophoretic mobility measurement.
3.3 Particle fabrication

3.3.1 Fabrication of Symmetric and Asymmetric Dimers

The method used for the synthesizing of the colloidal dimers for this experimental was a modification of the procedure from Allison M. Yake, et al (2006)\textsuperscript{35} paper; “Fabrication of Colloidal Doublets by a Salting Out – Quenching – Fusing Technique”. This is a simple, rapid, scalable method for producing colloidal homodoublets or heterodoublets, which are similarly referred to as symmetric and asymmetric dimers respectively.

Different samples of symmetric and asymmetric particles were synthesized; S1-S1, C1-C1, S1-C1, S2-C2; the symmetric dimers and S1-S2, C1-C2, S1-S2, S2-C1; the asymmetric dimers, corresponding to sample 1 through 6 respectively. 200µL of a 500mM Sodium Chloride (NaCl - MW 58.44, was purchased from ARCOS Organics, New Jersey, USA) was added to 200µL of a mixture of the combinations as listed above (with careful calculations made to keep particle concentration of each combining mixture approximately equal for the asymmetric dimers and symmetric dimers with different surface groups, that is, sample 3 and 4) into separate beakers. The beakers were slowly swirled by hand so as to ensure the particles and NaCl solution mixed well. At 250mM NaCl, our particles aggregated quickly and consequently were being salted out. After 60s, the aggregation process was quenched by adding 30ml of deionized water (with a specific resistance of 18.2 MΩ·cm and -25°C) to the beaker, the concentrations finally stepped down to approximately 3.2895mM. At this point, the electrostatic repulsion between the similarly charged particles prevented further aggregation. The final colloidal suspension contained
singlet, doublets (symmetric and asymmetric as the case may be) and larger particles aggregate (trimers, tetramers, etc).

Severe agitation (such as sonication, vortexing or high-speed centrifugation) are capable of causing doublets aggregates to break apart. In an effort to avoid this degradation, the particles in their salt suspension were heated above their glass transition temperature \( T_g \) for 15mins and the doublets allowed to permanently fuse to each other; thereby allowing the polymer chains in the touching particles (in this case, the dimers) to diffuse together. \( T_g \) of polystyrene particles is approximately 93°C. We used an autoclave (120°C, 18 psi) to exceed this temperature without boiling. After cooling, the particles were viewed under the Field Emission Scanning Electron Microscopy (FESEM) at the Physics Laboratory, Cleveland State University.

### 3.3.2 Fabrication of Ellipsoidal particles

Two clean glass bottles with a total volume of 1000ml were rinsed a few times with distilled water. Afterwards the bottles were filled approximately 80% with distilled water and 20% ethanol (allowing a small air gap). They were then ultra-sonicated for 30mins, the bottle was then emptied and rinsed with mQ-water to remove all ethanol leftovers; making sure no ethanol remains in the bottle (which is capable of screwing up the film). The bottle was allowed to sit in an oven (opened) for about an hour; making it completely dry and to absolutely make sure no ethanol is left inside. Afterwards, the bottle was allowed to cool down (capping it so as to prevent dust falling in). The bottle was then placed on a scale (zero scale) where 300g mQ of water was added and measured. 7.5g of Polyvinyl Alcohol (PVA - POVAL 40-88 Kuraray polyvinyl alcohol – Lot No. DE13022363) was the
separately measured out on a clean glassware (using a clean spoon). The bottle containing the water was then placed on a stirring plate; while a magnetic stirrer (properly cleaned with ethanol and mQ) was dropped inside the glass bottle. The stirring speed was kept steady at 400rpm. The PVA was then added bit-by-bit to avoid forming a big lump, and was allowed to stir for at least 24hrs.

The resulting solution was the filtered into the second cleaned bottle using filter paper, clamp and funnel. The bottle containing the filtered solution was then placed on a scale and 1g of 6μm polystyrene (PS) particles was then added to the solution. The PVA solution and the PS sample was gently mixed by swirling the bottle. A 32x32cm square boundary was formed on a mirror using caulk; while the mirror was initially cleaned with ethanol - produced by Decon Labs, International (DSP-MD.43) - 4 to 5 times, until a squeaking sound when rubbing the tray for the fifth time was clearly heard. The glass (mirror) tray was then severally cleaned with just mQ using some Kleenex (this is crucial, so as to remove all ethanol). At the stretching area, the mirror tray was then levelled. The resulting suspension was then poured into the 32×32cm boundary right from the middle onto the mirror tray (if levelled correctly, the spreading should form a nice circle). Making sure every part was filled (with edges and corners of tray). The tray was then covered so as to prevent dust particles from falling into the drying film but also exposed enough to dry. The solution was then allowed to 2-3 days to dry. The entire film was then removed from the tray carefully along it edges.

A fraction of the film was then cut-out and measured, while the fraction was sandwiched between a top and bottom metal bars using screws, see figure 3.2. The entire setup was then placed in an oven (which has constantly been kept at 150°C) for about 10
minutes. The entire set-up was removed from the oven and allowed to cool, before the iron bars were being disengaged. The film was then cut into smaller rectangles. The stretched film was then place in a beaker (which has been severally cleaned with ethanol and water and dried in the oven) containing a magnetic stirrer (severally cleaned with ethanol and water) adding a 3:7 mixture of isopropyl alcohol (Isopropyl alcohol (99.8% pure IPA, produced by Techspray)/water. The resulting solution is then allowed to stir for 12 hours. The resulting mixture is then centrifuged and washed with IPA/water in the proportion 3:7 for three more times allowing all remaining PVA adsorbed to surface of the prepared ellipsoids to be removed significantly. Thereafter, the particles were further washed with mQ, 5-6 times before dispersing them in salt concentration of $10^{-6}$M NaCl.

Figure 3.2: Experimental set-up for Stretching of PVA film (wherein spherical particles were dispersed)
3.4 Setup and apparatus for electric field experiments

Experiments were conducted in a parallel plate electrochemical cell as shown in figure 3.3. The cell consists of Indium tin oxide coated glass electrodes (with surface resistivity of 30-60Ω/sq) used in this experiment were purchased from Sigma Aldrich. Silver conductive epoxy adhesives (A and B) were used in attaching the conducting wire (obtained from cerrowire) to the electrodes and was allowed to dry (for almost 24hrs). After the epoxy adhesives were fully dried, the electrodes were sonicated in acetone and IPA for 10mins each. The electrodes were further exposed to plasma oxygen (air) for 5mins (so as to increase the amount of negative surface charges, since our colloidal particles bear negative charges) using plasma cleaner PDC-32G. Note that we tried cleaning the electrodes before using with several methods as suggested by Ning Wu et al (2015) and also by Scott C. Bukosky et al (2015) amongst others.

The spacer used in the experiment was purchased from molecular probes, life technologies (Secure seal spacer, eight wells, 9mm diameter, 0.12mm deep). One end of the spacer was then placed and sealed on the conducting surface of one of the electrodes while the other surface protecting the secure seal spacer was carefully peeled off. 8µL of the colloidal suspension was then introduced onto the open spaces provided on the spacer and was then sandwiched between the two parallel pieces of ITO glasses.
This entire setup was then carefully assembled on a 3D printed stage holder before it was then placed on the microscope (Fixed Stage Upright Microscope System (Olympus BX51W1) with Hamamatsu ORCA-R2 digital deep cooled CCD camera (C10600) from Olympus Microscopy through B&B Microscopy Limited.). The holder was securely sealed onto the stage to avoid movement during the experiment. The two electrode ends having the conducting wires were then connected to a function generator (Reference 600+...
Potentiostat/Galvanostat/ZRA) obtained from Gamry Instruments (to apply AC field between the ITO glasses).

Video sample were then taken for a given potential difference with varying frequencies. Potential difference considered during this experiment are 0.1, 0.2, 0.3, 0.4 and 0.5V with each potential difference kept constant for varying frequencies for 100Hz, 200Hz, 500Hz, 1000Hz, 2000Hz and 3000Hz. These potential differences correspond to electric field strengths of 833V/m, 1667V/m, 2500V/m, 3333V/m, and 4167V/m. Samples after being assembled onto the microscope stage and carefully held down with tapes to avoid uneven balance of the fluid cell are allowed to settle for at least 5-10mins before the start of the experiment. The function generator supplying the potential difference, is configured using the sine wave signal type for the AC field to be applied, where the acquired frequency was at least three times the acquisition frequency, and the amplitude, which is the potential difference to be measured across the ends of the electrodes. The device control mode was set to potentiostat, where the voltage is being regulated and the current being monitored. The video was allowed to record for initial 100 seconds, where particles were allowed to undergo Brownian motion before the electric field is being turned on. The field was then allowed for 10mins where video was being captured at 8 frames per seconds.

3.5 Image processing and particle tracking

The video captured were then analyzed using ImageJ. Particles were tracked using the software provided by ImageJ for particle tracking. Video captured during the experiment were then imported onto the ImageJ application platform in the “.avi” video
format. Each image in the stack was made binary. The binary thresholding is a way of partitioning an image into foreground and background. The particle to be tracked was made black, while the background of the image was white. White reflections (also called holes in ImageJ) on the particle image was filled before tracking. Coordinated X and Y were recorded as well as the angle of orientations. The figures below show the image processing steps.

Furthermore, after the particle were tracked, we used a Matlab code (see appendix, A1) provided by my supervisor, to calculate the positional and rotational mean square displacements of the particles and the lag time. The Matlab code calculates the frames in the first hundred seconds of the video, which it uses to calculate the MSD without field and the remaining frames is being computed for the MSD with field. We allowed the max lag time to be 10% of the total number of frames with and without field, which helps us to calculate the number of lag times per regime (frames with field and frames without field). Since our frame rate was 8 frames per seconds, the lag time for the first 100 seconds would compute the data (X, Y coordinates and angle of orientation) of the first 80 lag times for the MSD of the ellipsoid when it was undergoing Brownian motion. We converted the lag times to actual time in seconds, by multiplying the lag time with the frame rate. MSD plot were then made for the two regimes and are shown in the result section.
Figure 3.5(A-P) – Image processing and particle tracking steps for the ellipsoidal particles. From figure A-J, image conversion to a binary image. From figure K–P, particle tracking in 2d.
4.1 Introduction

In this chapter we discussed the results as were obtained from our experiment. The particles used for the experiment were first characterized. This is to help us have a better understanding of the interfacial properties of our particles prior to further experiments. Thereafter, we synthesized anisotropic particles such as dimers – symmetric and asymmetric (also referred to as doublets) and ellipsoids. However, this thesis primary focus was on the ellipsoidal particles. The ellipsoid synthesized was then used in the AC field experiments. Colloidal sample specifications with their symbols; Carboxyl latex particles; 4% w/v 3μm (C1), 4% w/v 2μm (C2) and Sulfate latex particles; 8% w/v 3μm (S1), 8% w/v 2μm (S2), 4% w/v 6μm (S3)

4.2 Particle characterization

In an effort to understand the nature of the particles acquired from the manufacturer, we needed to characterize the particles prior to further experimental procedures. The table
4.1, below shows values of zeta potential and electrophoretic measurement for the five samples as acquired from molecular probes. Zeta potential is a measure of charges carried by particles suspended in a liquid (water or salt solution). Generally, for colloidal particles that are small enough, a high zeta potential will confer stability. When the potential is small attractive forces may exceed the electrostatic repulsion and the dispersion may break and flocculate.

The electrophoretic mobility of our five (5) different colloidal samples was measured using Malvern Nano ZS. The zeta potential is related to the electrophoretic mobility by the Henry equation for values of $\kappa a$ between $0.01 - 100$.

$$U_e = \frac{2\varepsilon zf(\kappa a)}{3\eta}$$  \hspace{1cm} (8)

$U_e$ is the electrophoretic mobility, $z$ is the zeta potential, $\varepsilon$ is dielectric constant, $\eta$ is the viscosity, $f(\kappa a)$ is the Henry’s function. The unit of $\kappa$, termed the Debye length, are reciprocal length and $\kappa^{-1}$ is often taken as a measure of the “thickness” of the electrical double layer. The parameter “$a$” refers to the radius of the particle and therefore $\kappa a$ measures the ratio of the particle radius to electrical double layer thickness.

For this experiment the value of $\kappa a$ is 0.3119, which means the value of $f(\kappa a)$, becomes 1.5, and this is referred to as the Smoluchowski approximation (when $f(\kappa a)$, becomes 1, then it is referred to as the Huctel approximation). Hence, the zeta potential is then calculated from the equation. For our set of samples, the calculated zeta potential was as high as -124mV (pH 5.08) for sample S3 and as low as -48.60mV (pH 3.27) for sample S1 in the negative regime (both with the sulfate functional group on the surface of the polystyrene microspheres). While in the positive regime, the zeta potential was measured to be as high as 67.4mV (pH 2.19) for sample S2, and as low as 12.70mV (pH 3.27) for
sample C2. Particles with a large magnitude in zeta potential will tend to be more stable than those with a smaller magnitude in zeta potential. In other words, zeta potential is a key indicator of the stability of colloidal dispersions.

The graph of electrophoretic mobility against pH (figure 4.1) was used to identify the isoelectric point of the particles. The isoelectric point (IEP) is the point at which there is no net surface charge on the particle. The particles will have an electrophoretic mobility of zero at the IEP. This means at this point the particles would not respond to an electric field. The pH at which this phenomenon occurs is called the isoelectric pH. The microspheres with the sulfate functional groups (S1, S2 and S3) had IEPs with pH between 2 and 3. The microspheres with the carboxyl functional groups (C1 and C2) had IEPs with pH between 3 and 4. The understanding of the IEPs helped in the fabrication of the doublets and more importantly, to know the zeta potential at the conditions of the electric field experiment.
Table 4.1: Electrophoretic mobility (Mob), Zeta potential (ZP), Conductivity (Cond), of Carboxyl latex particles; 4% w/v 3μm (C1), 4% w/v 2μm (C2) and Sulfate latex particles; 8% w/v 3μm (S1), 8% w/v 2μm (S2), 4% w/v 6μm (S3) against pH in the range of 2.19-9.52 (Where Mob (SD) and ZP (SD), means Standard Deviation of electrophoretic mobility and zeta potential respectively)
The table above can be used as a handy tool for characterization of our particles at the experimental conditions. Also, it gives a wider range of pH values which could be useful for further experimental purposes.

4.3 Particle fabrication

Dimers (symmetric and asymmetric) and ellipsoids were synthesized in the course of this research. However, our focus was on the ellipsoids. This is as a result of much interest placed on anisotropic particles over the past few years. Figures 4.2, 4.3, and 4.4 show images of particles fabricated in our lab.
Figure 4.2: Scanning Electron Microscopy (SEM) images of (a) Single particles (S2), Symmetric (S3-S3) and Asymmetric (S3-C2) dimers and higher aggregates formed during the dimers synthesis (b) Symmetric dimers C1-C1 after Salting out and Quenching (without fusing)
Figure 4.3: Scanning Electron Microscopy (SEM) images of (a) Symmetric dimers S3-S3 after Salting out - Quenching and Fusing (SQF) (b) extent of fusing of a symmetric dimer after autoclaving for 15mins (120°C, 18psi)
Figure 4.4: SEM images of uniaxially stretched ellipsoid (prolate ellipsoids) synthesized in our lab with aspect ratio in the range of 1.84 – 1.95

The figures 4.2 (A) and (B) are images of the particles obtained after the Salting out – Quenching and Fusing (SQF) procedures has been carried out. In figure 4.2 (A) after the SQ procedure, particles were observed to form dimers (symmetric and asymmetric), trimers (not shown in the figures) and higher aggregates. The figure 4.5, below shows the amount (number of particles) that were obtained as a result of varying the quenching times. It helped us to know how the formation of the dimers varies. We observed that as the time increased, the numbers of single particles aggregating to form dimers increased, while dimers also aggregated forming even more larger aggregates. However, these aggregates can be redispersed when the sample is sonicated.
Figure 4.5: Histogram of particle yields for S3-S3 at various time scales after the SQ process and at varying quenching times.

Furthermore, in figure 4.2(B) dimers formed were observed to be touching (kissing spheres). However, these touching spheres were then permanently fused (figure 4.3), under the conditions (15mins, 120°C, 18psi). Figure 4.4, is the SEM image of the ellipsoid that were prepared in our lab. Particles with different aspect ratio can be obtained by varying parameters such as the weight of the bar used while stretching, the temperature at which the film is being exposed to and the time its allowed to stay in the oven. This can help to establish a standard protocol for further fabrication of ellipsoids with desired aspect ratio and with precise process conditions.

We also found out that the washing steps involved in the synthesis of the ellipsoid was crucial to the particle stability when redispersed in salt solution after washing. One of
the challenges we had were ellipsoidal particles irreversibly sticking to electrodes before or early on in an experiment. However, we observed that, after the PVA film has been allowed to dissolve in IPA:water mixture in the ratio 3:7 for 12hours, it is very important that the resulting ellipsoid harvested from the PVA film is rewashed 2-3 times using fresh IPA:water mixture in the same proportion as stated above. However, we chose to focus on ellipsoids because purification of doublets, which were highly polydisperse as can be observed from figure 4.5, was too laborious.

4.4 Particle response in AC fields

In the course of this research, we endeavor to manipulate ellipsoid particles, whereby the AC electric field exerts a force on the particles and thereby evaluating the response by adjusting field parameters such as electric field intensity, \( E(V/m^{-1}) = \frac{v}{d} \), (where \( v \) is the potential difference across the ends of the electrodes, \( d \), is the thickness of the spacer between the electrodes 120μm) and frequency of the AC field; for 833V/m, 1667V/m, 2500V/m, 3333V/m, 4167V/m (for 0.1V to 0.5V) at frequencies of 100Hz, 200Hz, 500Hz, 1000Hz, 2000Hz and 3000Hz respectively.

4.4.1 Translational and Rotational Mean Square Displacements (MSD)

After the experiment was concluded, movies recorded were then tracked using ImageJ. We extracted the x and y coordinates as well as angle of displacement with respect to the x-axis as a function of time as well as the frame numbers. We used a MATLAB code (provided by my supervisor) to calculate the translational and rotational mean square displacements with and without external field. The movies were taken in the first 100
seconds without external field and the next 10 minutes after the electric field had been
turned on at 8 frames per second. The number of frames without field (fwoF) was obtain
by computing the product of the first 100 seconds with the frame rate. While frames with
field (fwF) is the difference between the total frames and that calculated for fwoF.

Figure 4.6: Mean Square Displacements (MSD) for the 2D translational motion of
ellipsoids in (a) AC field (833V/m, 200Hz) and (b) when particle undergoes Brownian
motion without external field.
We used a basis to calculate the lag time, such that, the lag time was 10% of the fwoF and fwF. We had 80 lag times for the fwoF and the number of lag times for the fwF was depended on the total number of frames taken for a particle experiment.

![Graph A](image1)

![Graph B](image2)

Figure 4.7: Mean Square Displacements (MSD) for the 2D translational motion of ellipsoids in (a) AC field (4167V/m, 200Hz) and (b) when particle undergoes Brownian motion without external field.
The code then uses the input supplied to generate the translational and rotational MSD (using equation 6 and 7) data as well as the lag time. The figures 4.6 and 4.7 shows a typical MSD graph obtained for the translational motion without and with electric field.

The presence of an external field causes an additional motion with a velocity superimposed on the random motion. From figure 4.6, it was observed that the linear relationship between the MSD and time, crosses from linear to non-linear as we introduced an external force. For sufficiently short times the second term in equation (12) is very small compared to the first one and the mean squared displacement satisfies $MSD = 4D_e \Delta t$. Now for a particle undergoing a random Brownian motion, in this time regime, the dependency of MSD on time is linear. However, for an externally induced force imposed on the particle undergoing the free random movement, that is, under the influence of the AC field, the particle acquires a velocity, which is related to the MSD. This quadratic equation results in a non-linear relationship as observed in figure 4.6(A). The slope of the relationship between time and MSD, results in the diffusion coefficient of the particle under study.

The translational and rotational diffusion coefficients were then calculated from the slopes of the graphs; however, we placed our primary focus on the translational diffusion coefficient. The MSD of the translational motion transitioned from linear to quadratic as the electric field intensity and the frequency increased. We were able to fit the nonlinear MSD into an equation which was first proposed by Howse et al\textsuperscript{5}, where the mean square displacement (MSD) is plotted as a function of time, this was to allow us account for the apparent velocity which we observed. When $\Delta t$ is much less than the inverse rotational
diffusion coefficient of the anisotropic particle $\tau_R$, the curve can be fitted with a quadratic function of $\Delta t$:

$$MSD = v^2 \Delta t^2 + 4D_e \Delta t$$

(9)

where $v$ and $D_e$ are the propulsion speed and the effective diffusion coefficient of the ellipsoids respectively.

### 4.4.2 Effect of AC field on particle translational diffusion coefficient

The table 4.2 below are values that were obtained by normalizing the translational diffusion coefficient (under the influence of the AC field) by the translational diffusion coefficient of the ellipsoid before the external field was turned on. We normalized the diffusion coefficient so as to remove the impact of changing ellipsoids between experiments.

<table>
<thead>
<tr>
<th>Electric field intensity (V/m)</th>
<th>Frequency (Hz)</th>
<th>100</th>
<th>200</th>
<th>500</th>
<th>1000</th>
<th>2000</th>
<th>3000</th>
</tr>
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<tbody>
<tr>
<td>833</td>
<td></td>
<td>1.4695</td>
<td>0.8757</td>
<td>1.2253</td>
<td>1.0690</td>
<td>0.0866</td>
<td>0.0683</td>
</tr>
<tr>
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<td></td>
<td>0.7279</td>
<td>0.7461</td>
<td>1.6799</td>
<td>0.8411</td>
<td>0.7581</td>
<td>0.3763</td>
</tr>
<tr>
<td>2500</td>
<td></td>
<td>7.9668</td>
<td>6.6620</td>
<td>2.1472</td>
<td>0.6397</td>
<td>0.9744</td>
<td>0.5907</td>
</tr>
<tr>
<td>3333</td>
<td></td>
<td>0.0744</td>
<td>0.0464</td>
<td>1.2807</td>
<td>1.8153</td>
<td>1.2168</td>
<td>0.9770</td>
</tr>
<tr>
<td>4167</td>
<td></td>
<td>1.5544</td>
<td>1.6209</td>
<td>1.3009</td>
<td>0.4316</td>
<td>0.7168</td>
<td>0.6330</td>
</tr>
</tbody>
</table>

Table 4.2: Dimensionless translational diffusion coefficient of ellipsoids at different electric field intensity and different frequencies.
Figure 4.8: Dimensionless translational diffusion coefficient versus electric field intensity at different frequency.

The translational diffusion coefficient of the ellipsoidal particle - with little variations in aspect ratios as a result of non-symmetry of our ellipsoidal particle – was calculated before and after the electric field was initiated. The translational diffusion coefficient without and with electric field was calculated to be in the range of $(7.625 \times 10^{-3} \text{μm}^2/\text{s})$ and $(0.725 \times 305.525) \times 10^{-3} \text{μm}^2/\text{s}$ respectively for the entire sets of experiment. Although we measured a wind range of the diffusion coefficient, this is as a result of steady height variations relative to the polarized electrode. Our result agreed with previous experiments (Mukhija, 2009), the experimental value of colloidal rod, without external field, was found to be $2.57 \times 10^{-4} \text{μm}^2/\text{s}$ (aspect ratio of 3.1, 6μm particle).

In figure 4.8 above, at electric field strengths of 2500V/m and above and as well as frequencies above 1000Hz, the dimensionless translational diffusions coefficient was
observed to be below 1, which implies that, as the electric field strength and frequency increases, there is some steady height variations – as a result of the competition between the hydrodynamic, electric and Brownian torques – which alters the diffusion of the ellipsoidal particle. This also can be observed in figure 4.9 below, where an exponential decay in the dimensionless translational diffusion coefficient was observed as frequency increased. At frequencies above 500Hz, the dimensionless translational coefficient was observed to be below 1, when 2500V/m was applied. Consequently, the ellipsoidal particle translational diffusion coefficient changes (see trend for 100Hz and 200Hz, at various electric field intensity) in an AC field as electric field intensity and frequency increases (critical points may exist – for these parameters - above and/or below which particle can behave in an unprecedented pattern) which can also lead to directed assemblies as well.

Furthermore, the range of the dimensionless translational coefficient of the ellipsoid particle at lower electric field intensities were observed to be lower as compared to the intensities from 2500V/m and above. Interestingly, at this electric field intensity (2500V/m and 100Hz, see figure 4.9), the ellipsoidal particle was observed to rotate along its short axis and tries to reorient at an angle (fluctuating between 0° to 360°), both clockwise and anti-clockwise with the electric field; which competes with thermal fluctuations to orient the particle, therefore resulting in an increase in the translational diffusion coefficient in electric field at that point.
Figure 4.9: Dimensionless translational diffusion coefficient versus frequency at different electric field intensity.

4.4.3 Effect of frequency and electric field intensity

It was observed that at various frequencies – between 0.1kHz to 3kHz - considered during the experiment the effect of the electric field at 833V/m and 1667V/m; was not as pronounced as can be observed for other electric field intensities of 2500V/m, 3333V/m and 4167V/m. However, it was observed that for various frequencies of our experiment and at 2500V/m, the ellipsoidal particle began to rotate along the short axis of the ellipsoid. This rotation of the ellipsoid occurred when it makes an angle (reorient) between $90 > \theta \geq 0$ (the figure 4.10 below illustrates what $\theta$ stands for), and when the long axis is parallel with the electric field.
Energetically, the ellipsoidal particle will seek to align one of its principle axes with the applied field to minimize the field dipole interaction energy. It was observed that only one of these alignments – the one where the longest axis is parallel to the field – tends to be stable. Therefore, for our experiment, the rotation, alignment and stability assumes a frequency-dependent aspect. As other frequencies were reached, but yet with field intensities above 2500V/m were these phenomena observed, though the maximum effect...
(as observed) of the rotational torque occurred at the 2500V/m. Consequently, at low
frequency regime, as considered in our experiment and for very dilute salt concentrations
our “lying” ellipsoidal particle tries to align the longer axis parallel to the field while it also
aligns its axis through angle $\theta = 0^\circ$ to $\theta = 180^\circ$ (as well as angles in the opposite direction)
to the field at higher frequencies. However, it was observed that as the frequency increased,
the longer axis tries, more frequently, to orient at an angle $\theta = 0^\circ$ or $\theta = 90^\circ$; when the short
axis is $\theta = 90^\circ$ and $\theta = 0^\circ$ (but preferably when the longer axis aligns parallel to the field
direction) respectively. This depicts the effect of the particle’s anisotropic shape, as
compared to their spherical counterpart.

Furthermore, as electric field increased with increasing frequency, the particle was
observed to make even further displacement of angle with the field beyond $180^\circ$ (which
could be termed to be in the region of $\theta = 0^\circ$ and $\theta = -180^\circ$). The particle goes through all
this orientation displacement in order to balance the forces acting on it. It was observed
that the orientation varied with frequency (as well as salt concentration, which was not
varied in this experiment) under the same electric field strength.

4.4.4 Apparent Velocity

We also observed that the ellipsoidal particle moved with an apparent velocity as
tabulated in table 4.3 below. At lower frequencies (100Hz and 200Hz) the velocity was not
observable as at when compared with higher frequencies. The field intensities also played
a crucial role in affecting the particle velocity. At higher field strength, the electric torque
initiates a stronger fluid flow around the ellipsoid particle close to the electrode. This flow
results in a velocity of the particle. At lower frequencies, there appears to be no apparent
velocity. However, at frequency between 2000Hz and 3000Hz, for electric field intensity of 833V/m, 1667V/m and 2500V/m, there was a non-zero velocity fluctuations. (see figure 4.11).

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Electric field intensity (V/m)</th>
<th>Apparent Velocity (μm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>833</td>
<td>1667</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3000</td>
<td>0.0142</td>
<td>0.0200</td>
</tr>
</tbody>
</table>

Table 4.3: Apparent velocity of ellipsoidal particle in AC field as a function of frequency

Furthermore, expressing the velocity in relations to the electric field intensities (see figure 4.13), there exists a similar relationship as well for frequencies between 100Hz and 500Hz. However, at higher electric field strength and frequency, the electric torque and thermal fluctuations of the colloidal system becomes prevailing, and we observed a non-zero velocity relationship (Figure 4.13)
Figure 4.11: Apparent velocity of ellipsoidal particle as a function of frequency in AC field at different electric field intensity.

Figure 4.12: Apparent velocity of ellipsoidal particle as a function of frequency in AC field at electric field intensities of 3333V/m and 4167V/m.

This velocity which arises as a result of particle displacement mostly within the range of $90 > \theta \geq 0$ and $180 \geq \theta > 90$ with respect to the long axis, that is, in a direction
parallel to the field and also at an angle with the field. This seems to agree with the results of previous experiments. Where two approaching ellipsoids were observed to chain at an angle to one another.

Though, we believe that irregularities in the symmetry of the ellipsoidal particle, that is, the non-uniform shape of the prolate ellipsoid (in this case) would impact the field gradient around the ellipsoidal particle. Consequently, this would affect the overall direction of the velocity of the particle that was observed.

Figure 4.13: Apparent velocity of ellipsoidal particle as a function of electric field intensity in AC field at different frequencies
CHAPTER V
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Our experiments, for the first time, measured the response of an ellipsoidal particle very near a polarized electrode. Perhaps the most surprising result from our experiments was that we observed a non-linear (quadratic) relationship in the Mean Square Displacement (MSD) with respect to time, indicating that the particle was propelled along the long axis at angles of $90 > \theta \geq 0$ and $180 \geq \theta > 90$ with the direction of the electric field. A critical frequency and electric field intensity (2500V/m, 100Hz), where electro-rotation about the particle short axis became apparent - at this point the particle translational diffusion coefficient was found to be maximum (0.3055μm$^2$/s). Also, translational diffusion coefficient without and with electric field was calculated to be in the range of $(7.625 - 39.2750) \times 10^{-3}\mu m^2/s$ and $(0.725 - 305.525) \times 10^{-3}\mu m^2/s$ respectively, which agreed with previous results.
5.2 Recommendations

We faced a challenge as to particle sticking onto the substrate, which we later overcame. We observed that washing the ellipsoids after dissolving the stretched film with IPA/water is a very important step. This limited the time available to us for further studies as regards particle-particle interactions and particle assembly. However, it is highly recommended that further experiments should be conducted with varying parameters such as signal type, salt concentration, aspect ratio as well as other shapes and forms of anisotropic particles.

Finally, the overall success of this research area would be to fabricate particles with complex anisotropies as well as achieve 2D and 3D crystals through directed assembly.
REFERENCES


Appendix

A1. MATLAB code for the calculation of positional and orientational Mean Square Displacement (MSD) with and without electric field

```
function MSD(file,fr,Etime);

% MSD calculates the positional and orientational MSD
% 'file' = file name saved in same folder as function
% 'fr' = frame rate of movie
% Etime = time electric field was turned on in second

% file should have following format:
% Column (1) = frame
% Column (2) = x position
% Column (3) = y position
% Column (4) = Voltage in mV
% Column (5) = Frequency in Hz

data = xlsread(file);
[L W] = size(data);
x = data(:,2);
y = data(:,3);
Theta = (data(:,4)).*(pi/180);
V = data(1,5);
omega = data(1,6);

fwoF = Etime*fr;
fwF = L-fwoF;
LagTwoF = 0.1*fwoF;
LagTwF = 0.1*fwF;
MSDTimewoF = 0:1:LagTwoF;
MSDTimewF = 0:1:LagTwF;

for n = 1:LagTwoF
    for i = 1:fwoF-n
        dx(i+1) = x(i+n)-x(i);
        dy(i+1) = y(i+n)-y(i);
        TDsd(i+1) = (dx(i+1).^2)+(dy(i+1).^2);
    end;
    TDmsdwoF(n+1) = mean(TDsd);
end;

for n = 1:LagTwoF
    for i = 1:fwoF-n
        dT(i+1) = Theta(i+n)-Theta(i);
    end;
end;
```
sad(i+1) = (dT(i+1).^2);
end;
msadwoF(n+1) = mean(sad);
end;
DatawoF(:,:,:) = [MSDTimewoF(:) TDmsdwoF(:) msadwoF(:)];

for n = 1:LagTwF
    for i = 1:fwF-n
        dx(i+1) = x(i+n)-x(i);
        dy(i+1) = y(i+n)-y(i);
        TDsd(i+1) = (dx(i+1).^2)+(dy(i+1).^2);
    end;
    TDmsdwF(n+1) = mean(TDsd);
end;

for n = 1:LagTwF
    for i = 1:fwF-n
        dT(i+1) = Theta(i+n)-Theta(i);
        sad(i+1) = (dT(i+1).^2);
    end;
    msadwF(n+1) = mean(sad);
end;
DatawF(:,:,:) = [MSDTimewF(:) TDmsdwF(:) msadwF(:)];
csvwrite(['Voltage_', num2str(V), 'mV_Frequency_', num2str(omega), 'hz_MSD_withoutEField.dat'], DatawoF);
csvwrite(['Voltage_', num2str(V), 'mV_Frequency_', num2str(omega), 'hz_MSD_withEField.dat'], DatawF);