The Impact of Stern-Layer Conductivity on the Electrohydrodynamic Flow Around Colloidal Motors under an Alternating Current Electric Field

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Particles under a perpendicularly applied alternating current (AC) electric field assemble into complex structures and exhibit tunable locomotion. Although they possess very similar physical properties, silica particles form two-dimensional (2D) close-packed crystals in deionized water, whereas polystyrene (PS) spheres repel each other. Using nanoparticle tracers, it is shown that the electrohydrodynamic (EHD) flow around silica particles is contractile, whereas it is extensile around PS particles. The Stern-layer conductivities of PS and silica spheres are further measured experimentally and used in theoretical models to calculate the EHD flow surrounding them, which matches well with experiments. Therefore, the incorporation of Stern-layer conductivity resolves the puzzle that EHD flow surrounding a particle with moderate zeta potentials is extensile. The impacts of zeta potential, Stern-layer conductivity, salt concentration, and particle size on the EHD flow are examined herein. It is found that particles with high zeta potential, small diameter, or immersed in low salt concentration solutions tend to have extensile EHD flow surrounding them because the enhanced surface conductivity in the double layer makes the particles effectively more polarizable than the solvent. Herein, it is further shown that asymmetric EHD motors made from PS and silica particles exhibit behaviors that are consistent with the model predictions.

1. Introduction

Directed motion of microscopic objects is fundamental to both understand the locomotion of living organisms and fabricate synthetic microrobots.[1] Among various actuating techniques, the electric field shows distinguished versatility and scalability in regulating both individual and collective behaviors of micromotors.[2] Under an alternating current (AC) electric field that is applied perpendicularly across two electrodes, an electrohydrodynamic (EHD) flow is generated around an isotropic spherical particle. Such kind of flow, acting with other field-induced particle interactions such as the dipolar interaction, can lead to a rich variety of structures such as face-centered cubic crystals, hexagonal arrays,[3] non-close-packed lattices, and colloidal oligomers.[4] In addition, we have recently found that particles with asymmetry in geometry, surface charge, or chemical compositions can all propel along the substrate which is perpendicular to the applied field direction[5] due to the unbalanced EHD flow surrounding the particles. When particles are assembled into chiral clusters, they can also spin in either clockwise or counterclockwise directions depending on their handedness.[6]

The key to understanding the motion of individual colloids and assembly between multiple particles is to understand the EHD flow surrounding an isolated spherical particle near the electrode. Back in 1984, Richetti et al.[7] reported that 2D hexagonal arrays of 2 μm polystyrene (PS) particles were formed under a kHz AC electric field, which was unexpected as the particles experienced strong dipolar repulsion from each other. Later, Trau et al. found that micro- and nanosized PS particle suspension with added ionic surfactants exhibited long-range attraction and aggregated into layers of ordered structures under both direct current (DC) and AC electric fields.[8] They suggested that the ionic current flow through the solution may result in this EHD flow. Yeh et al. imaged the flow field around individual particles and proposed that this flow was induced by the distortion of electric field because of inhomogeneities of ions in the double layer near the electrode.[9]

Ristenpart et al.[8] developed a scaling law to explain the origin of this EHD flow, that is, the flow stems from the local distortion of the applied electrical field by the presence of particles, whose tangential component acts on the induced charges near the electrode. The direction of the EHD flow is dictated by the sign of the particle polarizability. They later solved a simplified version of the standard electrokinetic model with decoupled equations for electric potential and fluid flow.[9] The obtained quantitative solutions compared favorably with experiments performed on a 50 μm spherical particle,[9] where the EHD flow is contractile and directed toward the particle. Interestingly, the same particles
behave differently in different types of salt solutions such as potassium chloride versus potassium hydroxide.[8,10] It was recently proposed that an asymmetric rectified electric field might explain the anomalous behavior of particles in solutions where counterions and coions have a large difference in mobilities.[11]

As the tangential electric field that drives the electro-osmotic flow of induced charges near the electrode arises from the dipole moment of the particle, being able to correctly calculate the induced dipole moment is crucial. In a previous study,[9] where the type and concentration of salt are the same, the existing EHD differs in different types of salt solutions, is a baf

One of the key conclusions from Ristenpart et al.[8,9] is that the direction of EHD flow is determined by the sign of the real part of particle polarization coefficient $K$. When $\text{Re}(K) > 0 (<0)$, the flow is extensile (contractile), that is, being directed away from (toward) the particle. However, the imaginary part of the polarization coefficient, which characterizes the phase lag between charge relaxation and the imposed field, is also important for evaluating the EHD flow around particles.[13] Theoretically, the particle zeta potential needs to be unrealistically high (e.g., $\approx 150 \text{ mV}$) to yield an extensile EHD flow around it. However, our recent experiments[14] showed that the EHD flow might be extensile for particles with moderate zeta potentials ($\approx 40–60 \text{ mV}$). More interestingly, we found that PS and silica microspheres, although they possess similar sizes, dielectric constant, and zeta potential, behave quite differently under the same field condition and within the same solution. In deionized (DI) water and low salt concentration ($<10^{-4} \text{ M KCl}$), silica particles aggregate into 2D hexagonal crystals, whereas PS particles are separated from each other. However, in higher salt concentrations, both types of particles form close-packed crystals. Such a phenomenon, although it looks similar to another long-observed phenomenon where the same type of particle behaves differently in different types of salt solutions, is baffling because the type and concentration of salt are the same. The existing EHD theory cannot explain this phenomenon.[10,15] To reconcile the discrepancy between theory and experiments, we here propose to incorporate the Stern-layer conductivity into the current EHD model developed by Ristenpart et al.[9] In principle, the mobile charges associated with a colloidal particle consist of counterions and coions in the diffusive layer and charges behind the shear plane, that is, within the Stern layer. In electrokinetics, particle surface conductivity $\sigma_p$ is used to account for high conductivit y of $\sigma_p$ because of the excess surface charges around the particle. The particle surface conductivity, $\sigma_p^d$, is expressed as the sum of two parts, $\sigma_p^{d,1}$ and $\sigma_p^{d,2}$, where $\sigma_p^{d,1}$ is the surface conductivity of counterions and coions within the diffusive layer, whereas $\sigma_p^{d,2}$ is the surface conductivity of counterions within the Stern layer, that is, the inner part of the double layer. Therefore, it is often called the Stern-layer conductivity. The diffusive layer conductivity $\sigma_p^{d,1}$ attracts far more attention than the Stern-layer conductivity $\sigma_p^{d,2}$ and charges in the Stern layer are traditionally perceived as immobile. Experiments and theories,[17] however, have suggested that the inclusion of the Stern-layer conductivity is necessary to model and interpret the experimental measurement of dielectric properties of the colloid solution,[18] dipolar interaction between particles,[17a] and electrokinetic potential of particles.[16] Indeed, $\sigma_p^{d,1}$ is a significant part of the total surface conductivity: although the mobility of counterions in the Stern layer might be smaller than those in the diffusive layer, the ion concentration is higher. Simple calculation shows that the surface conductivity of the diffusive layer, $\sigma_p^{d,2}$, is $1–100 \text{ pS}$. However, it has been reported that the Stern-layer conductivity $\sigma_p^{d,1}$ is one order of magnitude larger than the diffusive layer conductivity $\sigma_p^{d,2}$, that is, in the range of $0.1–10 \text{ nS}$,[17a,19] depending on the particle properties and methods used. As shown later, the inclusion of Stern-layer conductivity in the EHD model can resolve the puzzle why EHD flow is extensile for particles with moderate zeta potentials. Silica and PS particles have very different values for Stern-layer conductivity.

As an exemplary model with distinct assembly behaviors under AC electric fields, we have performed experiments to track the EHD flow around PS and silica particles using nanoparticle tracers and measured the crossover frequencies of PS and silica particles, from which, we obtained their Stern-layer conductivities. With the incorporation of Stern-layer conductivity, we computed the EHD flow around the particles and validated the theoretical model with our experimental data. We further investigated the impacts of zeta potential, salt concentration, and particle size on the EHD flow around a charged dielectric sphere with variable Stern-layer conductivities. Our combined experimental and theoretical studies revealed the impacts of Stern-layer conductivity on both direction and magnitude of the EHD flow, which can quantitatively describe experimentally observed different assembly behaviors of dielectric spheres. The deepened understanding of EHD flow surrounding an isotropic particle will facilitate the investigation of the in- and far-from-equilibrium behaviors of both individual and an ensemble of anisotropic particles.

2. Experimental Section

2.1. Material and Methods

Electric field experiments were performed with two types of electrode arrangements: the parallel and the coplanar quadrupolar electrode setups (Figure 1). The parallel electrode setup (Figure 1a) consisted of a chamber formed between two indium-tin-oxide (ITO) glass slides (Diamond Coating, West Midlands, UK) that were separated by a pair of 50-µm-thick plastic spacers. To prevent irreversible adhesion of particles on the
substrate, the ITO glasses were coated with a thin film (13 nm) of silicon dioxide. They were then thoroughly cleaned by sequential rinse of acetone, isopropyl alcohol, and DI water before being treated under oxygen plasma for 2 min. Next, the ITO glass slides were immersed in a mixture of 0.5 M sodium chloride (NaCl) and 5 mg mL⁻¹ poly(sodium 4-styrenesulfonate) solution for 10 min under sonication. All slides were thoroughly rinsed with DI water before use. About 2 μm PS microspheres (ζ_p = -43.8 ± 3.8 mV; Life Technology) and 2 μm silica microspheres (ζ_p = -41.5 ± 3.1 mV; Bangs Laboratories) were cleaned with DI water four times before use. A total of 3–10 μL particle suspension was pipetted onto the bottom substrate. To obtain the Stern-layer conductivity of PS particles, we measured their electrophoretic mobility and crossover frequency under AC electric fields. The electrophoretic mobility of particles was measured using a commercial zeta potential analyzer (90Plus PALS Brookhaven) with dilute particle suspension. To obtain the crossover frequency f_c, a total of 3–10 μL colloidal solution was added to the center of coplanar quadrupolar electrodes,[20] and a glass slide was put on top of the suspension to reduce the solvent evaporation. Four signals of the AC electric field were applied to the quadrupolar electrodes with a 180° phase difference between neighboring electrodes (Figure 1b). The crossover frequency f_c was obtained when the particles changed their dielectrophoretic behaviors, that is, when the frequency was low, PS particles aggregated in the peripheral regime near the quadrupolar electrode (where the field gradient was maximal) due to positive dielectrophoresis. Beyond f_c, they aggregated near the central regime (where the field gradient was minimal) enclosed by the quadrupolar electrode due to negative dielectrophoresis. In contrast, silica microspheres exhibited negative dielectrophoresis within the full frequency range of 100 Hz–10 MHz.

To observe the particle assembly, an AC electric field was applied across the parallel electrode setup by a function generator (RIGOL DS1054Z) and a voltage amplifier (TREK 2100HF). All experiments were performed on an inverted microscope (Olympus IX71) equipped with a color camera (QImaging Retiga-2000R) and a high-speed black/white camera (Silicon Video 642).

In the EHD flow-tracing experiments,[21] we quantified the displacement of nanoparticle tracers against time around immobilized PS and silica microspheres on the substrate. About 1 μL dilute particle suspension was first smeared evenly on an ITO substrate. After solvent evaporation, the particles stuck onto the ITO substrate due to van der Waals attraction. About 10 μL fluorescent PS nanosphere suspension (500 nm in diameter, ≈0.067 wt/vol%, Life Technology) was then added onto the substrate as tracers. Videos were captured at 25 frames per second (fps) and they were analyzed in ImageJ by tracking the x–y coordinates of individual tracers at different times.

3. Experimental Results and Discussion

3.1. Assembly of PS and Silica Microspheres and the Associated EHD Flow

Among a few puzzles of EHD flow surrounding colloidal particles under electric fields, the different assembly behaviors of PS and silica (SiO₂) microspheres is an intriguing one.[16] In DI water, when 2 μm PS and 2 μm SiO₂ microspheres with similar zeta potentials (ζ_p = -43.8 ± 3.8 mV for PS and ζ_p = -41.5 ± 3.1 mV for SiO₂) were subjected to a perpendicularly applied AC electric field, the PS spheres were separated from each other (Figure 2a). With high particle concentrations, they assembled into nonclose-packed hexagonal crystals.[22] Under the same field condition, silica spheres, however, formed into close-packed hexagonal crystals (Figure 2b). Indeed, the field-induced layering of silica spheres has been reported in the early investigation of the EHD flow.[16,23] The different assembly behaviors of PS and silica spheres under the same field and solution conditions are somehow unexpected, especially considering the fact that the difference in their dielectric constants is very small (1/40 and 1/20 of water). Here, we hypothesize that this difference in assembly is because the EHD flow around PS spheres is extensile, whereas it is contractile surrounding silica spheres. As a result, silica particles aggregate due to hydrodynamic attraction, and PS spheres are separated from each other due to hydrodynamic repulsion.

To test our hypothesis, we purposely immobilized the PS and silica microspheres on the conducting substrate and then added nanoparticle tracers to track the hydrodynamic flow under the same electric fields. As shown in Figure 3a,b, the tracer particles were ejected away from the PS microspheres when they are adjacent to the substrate, whereas tracers moved toward the silica microspheres. This provides direct evidence that an extensile flow is engendered surrounding a PS microsphere and a contractile flow is generated around the silica microsphere.
We can further quantify the magnitude of flow by tracking the position of each tracer as a function of time. As shown in Figure 3c,d, we plotted the displacement of individual tracers from the center of the PS and SiO$_2$ microspheres against time, where $t_0$ was set as the moment when tracers appear from (or reach) the edge of the particle. We have also calculated the dipolar interactions between tracers and the PS and SiO$_2$ microspheres and concluded that the tracer velocity due to dipolar interactions is on the order of 1.5 $\mu$m s$^{-1}$, which is $\approx$10% of the observed maximum tracer velocity. Moreover, we purposely moved the focus plane to the top of the immobilized microspheres, where the tracers disappeared (emerged) from the top of the PS (silica) microspheres. There is hardly any accumulation of tracers either near the pole or equator of the microspheres. This indicates that the motion of the tracers is primarily due to EHD flow. The experimental data can then be fitted with the scaling law\cite{14} for the EHD flow velocity

$$\mathbf{U} \propto \frac{(r/a)}{[1 + 4(r/a)^{2}]}^{1/2}$$

Figure 3. EHD flow tracking by nanoparticle tracers surrounding PS and silica microspheres under a perpendicularly applied AC electric field at 200 Vpp mm$^{-1}$ and 800 Hz. a) A snapshot of tracer particles surrounding PS (top left one) and silica (bottom right two) microspheres. Scale bar: 5 $\mu$m. b) Representative trajectories of several nanoparticle tracers surrounding a PS (top) and a silica (bottom) microsphere. Scale bar: 5 $\mu$m. The arrows indicate the moving directions of the tracers. c) The displacement of nanoparticle tracers ejected away from a PS microsphere near the substrate. d) The displacement of nanoparticle tracers moving toward a silica microsphere near the substrate. The time, $t_0$, is defined as the time when tracers appeared (or disappeared) at the edge of the microsphere, that is, $r/a = 1$, where $a$ is the particle radius. The solid line is fitting with $r/a \propto C e^{-2.5}$. The error bars represent one standard deviation. The gray area represents 95% level of confidence for the fitting.
where \( a \) is the microsphere radius and \( r \) is the lateral distance from the center of the microsphere to the point where the EHD flow is evaluated. It is shown that when \( r/a \gg 1 \), the velocity \( \dot{U} \propto r^{-4} \). One can further integrate this velocity with respect to time and obtain the scaling between the radial position of a tracer nanoparticle that is convected by the flow and time: \( r/a \propto Ct^{-0.2} \). We fit the experimental data with this scaling law. From the fitting, we were able to obtain the speed of hydrodynamic flow close to the edge of PS and silica spheres, that is, the slope of the curves at \( t_0 \). They are 13.33 and 12.46 \( \mu m/s \), respectively.

### 3.2. Stern-Layer Conductivity Measurement

We have established clear evidence that PS microspheres with moderate zeta potentials can generate extensile EHD flow. Theoretically, this is only possible when the particle surface conductivity is dominated by the Stern-layer conductivity. Therefore, we aimed to measure it experimentally, incorporate it in the theoretical model, and compare the theoretical predictions with experiments. There is, however, no direct way to measure the Stern-layer conductivity. We instead used the following strategy reported in literature. We first measured the electrophoretic mobility of PS microspheres, \( \mu_{e0} \), using a commercial zeta potential analyzer. We then measured the crossover frequency of the same particles, \( \Omega_c \), using a coplanar quadrupolar electrode setup shown in Figure 1b. The crossover frequency is the frequency at which a particle’s polarizability changes its sign such as from positive to negative, whose transition is experimentally identified by observing the aggregation of particles at the center (or at the edge) of the quadrupolar electrodes due to negative (or positive) dielectrophoresis. As shown in Figure 4a, the PS microspheres demonstrated positive dielectrophoresis, and they accumulated at the edge of the electrode when the frequency of the applied electric field was relatively low (from \( \approx 100 \) Hz to \( \approx 200 \) kHz). As the frequency increased further, the PS microspheres started to aggregate in the central region of the quadrupolar electrode (Figure 4b), where the electric field was minimal. In contrast, the silica microspheres exhibited negative dielectrophoresis within the full frequency range of 100 Hz–10 MHz. No crossover frequency is found. This indicates that the Stern-layer conductivity of silica is negligibly small, which is consistent with our observation that the EHD flow surrounding it is always contractile.

Once both electrophoretic mobility and crossover frequency were obtained, we plugged them in the following equations to obtain both zeta potential \( \xi_p \) and Stern-layer conductivity \( \sigma^\text{S}_{p} \):  

\[
\frac{\mu e}{\varepsilon_m e_0 k_B T \mu_{e0}} \frac{z \sigma_p e}{k_B T} + \frac{2 Du}{z(1 + 2 Du)} \left\{ 2 \ln \left[ 1 + \exp \left( \frac{z \xi_p e}{2k_B T} \right) \right] - 2 \ln \left[ 1 + \exp \left( \frac{z \xi_p e}{2k_B T} \right) \right] \right. \\
\left. \left. + 1 + \exp \left( \frac{z \xi_p e}{2k_B T} \right) \right\} \right. \right. \\
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Based on our measurement and calculation, the Stern-layer conductivity and zeta potential of PS spheres (silica spheres) are 0.59 nS (0 nS) and −72.3 mV (−43.8 mV), respectively. The true particle zeta potential of the PS spheres becomes larger when both Stern-layer and diffusive-layer conductivities are included. This is because Stern-layer conductivity imposes a retardation effect on mobility. For example, in case of negative particle zeta potential, one can conclude that the second term in Equation (3) is always positive because the exponential term is smaller than 2ln2. However, the molecular origin of the difference in Stern-layer conductivity between PS and SiO2 microspheres is important. Unfortunately, it is difficult to probe or even speculate the reason at the molecular level. One possibility is that the silica sphere surface is porous due to the nature of hydrolysis and condensation reactions during silica particle synthesis, whereas polymeric chains are present on the PS particles. More advanced experimental tools to probe the Stern layers of micro- and nanoparticles will be needed to eventually resolve this issue.

4. Theoretical Modeling

4.1. Problem Statement and Method

To model the EHD flow surrounding PS and silica microspheres theoretically, we considered a diluted colloidal suspension sandwiched between two parallel electrodes across which an AC electric field is applied perpendicularly to the electrode. The separation between two electrodes, $2H$, is much larger than the radius of the dielectric particle $a$. As shown in Figure 5, we consider a single sphere that is located near the bottom electrode. The applied field induces mobile ions (i.e., the induced charges) accumulating within a diffusive layer near the electrode. The same field also polarizes the particle and the associated (equilibrium) double layer around it because it is charged. The induced particle dipole generates a local electric field, whose tangential component, $E_f$, acts on the induced charges near the electrode and therefore generates an electro-osmotic flow. This flow was first observed by Richetti et al.[7] and has been referred to as the EHD flow in the literature.[8,25]

In general, we consider the EHD flow of a micrometer-sized particle at the low frequency regime (i.e., $f < 10$ kHz) in an aqueous solution. Because of dissolved carbon dioxide and ion leaching from the ITO/glass substrate, the realistic estimation of the Debye length $\kappa^{-1}$ in water that is free of added salts is typically on the order of 100 nm. Therefore, it is often safe to assume that the Debye length $\kappa^{-1}$ is much smaller than the particle radius, that is, $\kappa a \gg 1$. In addition, both Peclet ($Pe = \mu u/D$, $\approx 10^{-3}$) and $\mu$ are the fluid velocity and $D$ is the ion diffusivity) and Reynolds numbers (Re $= \rho u a / \mu$, $\approx 10^{-6}$, where $\rho$ and $\mu$ are the particle density and solvent viscosity, respectively) are much less than 1. The Gauss’ and Navier–Stokes’ equations governing the bulk (outside the Debye layer of both particle and electrode) fluid can then be simplified and decoupled

\[
\nabla^2 \psi = 0
\]

\[
\nabla \cdot \mathbf{u} = 0
\]

\[
-\nabla P + \nabla^2 \mathbf{u} = 0
\]

\[

\psi = \frac{1}{\kappa} \left( 1 - i \frac{\kappa D}{\omega H} \right) e^{-i\omega t}
\]

\[
\nabla \psi \cdot \mathbf{n} = -\lambda \nabla^2 \psi
\]

\[
\]

where $\psi e^{-i\omega t}$, $P$, and $\mathbf{u}$ denote the electric potential, fluid pressure, and fluid velocity, respectively, and $\omega = 2\pi f$ is the angular frequency of the applied field.

The boundary conditions for solving the electric potential $\psi$ are the following.

On the electrode, the normal component of the electric field is assumed to be undisturbed by the presence of particle and equal to that calculated as if there is no particle.

\[
z = 0, \quad \nabla \psi \cdot \mathbf{n} = -E_0 \left( 1 - i \frac{\kappa D}{\omega H} \right) e^{-i\omega t}
\]

\[
\nabla \psi \cdot \mathbf{n} = -\lambda \nabla^2 \psi
\]

\[
\]

Figure 5. a) Schematic showing the response of a charged dielectric sphere near a bottom electrode under an AC electric field (only half period is shown). b) The bispherical coordinate system used in theoretical modeling.
where $\nabla^2 \psi = \nabla \cdot \nabla \psi$ is the surface Laplacian[26] and $\lambda$ is related to the polarization coefficient $K$ of the particle via the following relationship:

$$\lambda = \frac{1 + 2K}{2 - 2K} \quad \frac{2\pi}{2 - 2K}$$

(13)

In the literature,[9] $\lambda$ is defined as the ratio of diffusive-layer surface (complex conductivity $\sigma^d_{P_s}$) to the complex conductivity of the medium. By including the Stern-layer conductivity, it is for the z-valent symmetrical electrolyte

$$\lambda = \frac{\sigma^d_{P_s} + \sigma^s_{P_i}}{\sigma_m - i\sigma_m\eta \alpha \alpha \alpha}$$

(14)

The Stern-layer conductivity, $\sigma^s_{P_i}$, is obtained from solving Equation (3) and (4), and

$$\sigma^d_{P_s} = \frac{2\sigma_m}{\kappa} \left\{ \frac{D^+}{D^+ + D^-} \left[ \exp \left( -\frac{ZC_p^+}{2k_BT} \right) - 1 \right] + \frac{D^-}{D^+ + D^-} \left[ \exp \left( -\frac{ZC_p^-}{2k_BT} \right) - 1 \right] \right\}$$

(15)

$\sigma_m$ is the real conductivity of the medium, which is the sum of the conductivity of both cations and ions

$$\sigma_m = \sigma^d_{P_s} + \sigma_m = \frac{z^2 e^2 n_0}{k_BT} (D^+ + D^-)$$

(16)

where $n_0$ is the number concentration of the cation or anion.

Far away from the particle or the electrode, the potential corresponds to that of the applied

$$z \to \infty, \quad \psi = -E_0 z$$

(17)

With the above boundary conditions, we can solve Equation (6) in the spherical coordinate (Figure 5b) and the solution is

$$\psi = \frac{\cos \theta}{1 - \cos \theta} \left[ \frac{H(1 - 2\cos \theta)}{1 - \cos \theta} + \sin \eta_c (\cosh \eta - \cos \phi) \right]$$

$$\times \sum_{n=0}^{\infty} \left( A_n \cosh \left( \left( n + \frac{1}{2} \right) \eta \right) + B_n \cosh \left( \left( n + \frac{1}{2} \right) \eta \right) \right) P_n(\cos \phi)$$

(18)

where $P_n$ is Legendre polynomials and $\eta_c = a \cosh [(h + a) / a]$. The coefficients $A_n$ and $B_n$ are calculated by numerically solving a series of truncated lengthy linear equations.[9]

Once the electric potential $\psi$ is obtained, we can further solve the flow field surrounding the particle. The associated boundary conditions for Equation (7) and (8) are the following.

Electro-osmotic slip on the electrode right outside of the diffusive layer

$$u \cdot n = 0$$

$$u \cdot t = \frac{\epsilon \sigma \psi}{\mu} \cdot (-\nabla \psi \cdot t)$$

(19)

where $n$ and $t$ are the normal and tangential unit vectors of the electrode.

No slip on the particle surface

$$u = 0$$

(20)

Far away from the particle or the electrode

$$u = 0 \text{ and } P = 0$$

(21)

We can express the stream function $\Psi$ for this axisymmetric problem as

$$\Psi = (\cosh \eta - \cos \phi)^{-3/2} \sum_{n=0}^{\infty} W_n P_{n-1}(\cos \phi) - P_{n+1}(\cos \phi)$$

(22)

where $W_n = a_n \cosh \left( -\frac{1}{2} + n \right) \eta + c_n \cosh \left( \frac{1}{2} + n \right) \eta + b_n \sinh \left( -\frac{1}{2} + n \right) \eta + d_n \sinh \left( \frac{1}{2} + n \right) \eta$. Again, the coefficients $a_n, b_n, c_n, d_n$ are obtained numerically by applying the orthogonality.[9]

5. Results and Discussion

5.1. Comparison with Experimental Data

We plugged the measured Stern-layer conductivity and zeta potential into the theoretical model and calculated the EHD flow around a PS sphere (0.59 nS and −72.3 mV) and a silica sphere (0 nS and −81.45 mV), respectively. Figure 6a shows the cross-sectional view of the streamlines of the axisymmetric EHD flow surrounding a 2 μm PS microsphere with a moderate zeta potential in 10−5 M KCl solution, where the particle is assumed to be located at $h = 500$ nm away from the electrode. This value of separation $h$ corresponds to $5 \times 10^{-6}$, which is expected due to double-layer repulsion between the particle and substrate. As indicated by the arrows, the flow is counterclockwise and extensile, that is, being directed away from the particle, due to its high Stern-layer conductivity. Because of this, PS spheres are repelled from each other and formed nonclose-packed arrays. In contrast, silica microspheres are attracted among each other due to the clockwise and contractile EHD flow shown in Figure 6b. Given the velocity field surrounding both microspheres, we can further calculate the displacement of nanoparticle tracers near the electrode evaluated at $z = (h + a_{\text{tracer}}) / a = 0.75$ as a function of time. The theoretical prediction is overlaid on experimental measurement as shown in Figure 6c,d for both PS and silica microspheres. As can be seen, the calculated velocities, extensile or contractile, matched the flow velocities tracked by nanotracers in terms of both sign and absolute value. The excellent agreement between experiments and modeling validated our hypothesis, as the incorporation of Stern-layer conductivity can explain the extensional EHD flow surrounding particles with moderate zeta potentials. We note that the results shown in Figure 6 have no fitting parameters involved. This is particularly encouraging as it is known that predicting even the correct magnitude of the electrokinetic flow is notoriously difficult.

5.2. The Impact of Stern-Layer Conductivity and Zeta Potential

With experiment-validated theoretical modeling, we further investigated the impact of Stern-layer conductivity and particle
Zeta potential on EHD flow. Zeta potential $\zeta_p$ is commonly used to characterize the amount of surface charges on colloidal particles. If a dielectric particle is neutral ($\zeta_p = 0$) and has no Stern-layer conductivity ($\sigma_s^p$), apparently, its dipole moment will be antiparallel to the applied field in a polar solvent (such as a silica particle in water). As a result, the particle has a large but negative polarization coefficient, that is, $\text{Re}(K) \approx -1/2$. As shown by squares in Figure 7, the EHD flow will be contractile, that is, being directed toward the particle, as the tangential electric field $E_t$ points toward the particle when the induced charges near the electrode are positive. As the EHD flow varies at different separations and elevations near a sphere, we here used the velocity evaluated at $r/a = 2.5$ and $z/a = 1.5$ as an indicator of the overall strength and direction of the EHD flow. A positive (negative) velocity indicates that the flow is extensile (contractile). When the magnitude of particle zeta potential increases, the amount of polarized ions around the particle essentially increases. Therefore, the particle surface conductivity $\sigma_p^\infty$ increases, which makes the particle’s dipole less negative, but the dipole magnitude also becomes smaller. Consequently, the EHD flow velocity, although still contractile, becomes smaller.

Figure 6. EHD flow around PS and silica microspheres. The cross-sectional view of the EHD streamlines around (a) a 2 $\mu$m PS sphere ($\zeta_p = -72.3$ mV and $\sigma_s^p = 0.59$ nS) and (b) a 2 $\mu$m silica sphere ($\zeta_p = -41.5$ mV and $\sigma_s^p = 0$ nS). The applied electric field is 10 Vpp and 800 Hz. The salt (KCl) concentration is 10 $\mu$M. The separation between the microsphere and the substrate is 0.5 $\mu$m. The comparison of theoretical modeling (solid line) and experimental measurement (diamond) for the displacement of nanoparticle tracers surrounding (c) a 2 $\mu$m PS microsphere and (d) a 2 $\mu$m silica microsphere. Experimental data are the same as those shown in Figure 3.

Figure 7. The influence of zeta potential on the EHD flow around a PS microsphere in 10 $\mu$M KCl solution by incorporating the Stern-layer conductivity at $f = 800$ Hz and $E_0 = 200$ Vpp mm$^{-1}$. The velocity is evaluated at $r/a = 2.5$ and $z/a = 1.5$. 

because the electric field generated by the polarized particle becomes weaker. When the magnitude of zeta potential further increases ($|\zeta_p| > -85$ mV in Figure 7), the particle can become effectively more polarizable than the medium due to the contribution of surface conductivity of mobile ions in the diffusive layer. As a result, the EHD flow becomes extensile and positive, which is directed away from the particle. We note that this trend is qualitatively consistent with experiments performed by Woehl et al.,\cite{10} where they observed that particles suspended in strong acidic or basic solution possessed high zeta potentials ($|\zeta_p| > 110$ mV) and they were separated from each other. Instead, particles with lower zeta potentials tended to aggregate presumably due to the contractile EHD flow.

In contrast, it is rare to obtain such a high zeta potential in the pH-neutral solution. Extensile flow can still be observed such as the PS particles due to non-negligible Stern-layer conductivity. Also shown in Figure 7 is the impact of Stern-layer conductivity on EHD flow directions. Clearly, the presence of Stern-layer conductivity shifts the zeta potential dependence curve up and pushes the critical zeta potential, at which the EHD flow direction changes from contractile to extensile, toward a smaller value. One can see that an addition of 50 pS Stern-layer conductivity can shift the critical zeta potential from a high zeta potential of $-85$ mV to an experimentally achievable moderate zeta potential of $-40$ mV. A particle with even higher Stern-layer conductivity can manifest significant extensile flow around it even with low zeta potentials.

5.3. The Impact of Salt Concentration

Like many other electrokinetic phenomena,\cite{27} the salt concentration plays an influential role. As shown in Figure 8, at low salt concentrations, the EHD flow is extensile, that is, its velocity is positive if the particle’s Stern-layer conductivity is high. A higher salt concentration, in contrast, increases the medium conductivity $\sigma_m$. Consequently, the Dukhin’s number, which is the ratio of surface conductivity $\sigma_p$ to medium conductivity scaled by particle radius $a$, $Du = \sigma_p / \sigma_m a$, decreases, which can change the sign of the particle’s polarizability and the direction of the tangential electric field $E_t$. Therefore, the EHD flow becomes contractile at higher salt concentrations even if the Stern-layer conductivity is high. In addition, the EHD flow arises from the electrosomotic motion of induced charges accumulated near the electrode, whose amount increases in higher salt concentrations, as shown in the inset of Figure 8. Therefore, the magnitude of EHD flow becomes higher at high salt concentrations. For particles suspended in nonpolar solvents such as dimethyl sulfoxide (DMSO), the EHD flow will be much smaller than in DI water. This is confirmed by experiments—the propulsion speed of an asymmetric dimer in DMSO is one order of magnitude smaller than in water. We also note that the EHD velocity might be over-predicted at high salt concentrations such as 1 mm. In reality, the effective field strength might be lower due to screening by charges.$^{[14]}$

5.4. The Impact of Particle Size

As the particle size increases the magnitude of EHD flow becomes larger. As shown in Figure 9, whether the flow is extensile or contractile depends on both the particle size and Stern-layer conductivity for a constant zeta potential. This can be understood in the following paragraphs. The direction of EHD flow is essentially dictated by the Dukhin’s number $Du$. The smaller the particle is, the larger $Du$ is. Therefore, for small particles (e.g., $a < 1.5$ μm) with moderate surface conductivity, the real part of its polarization coefficient Re($K$) is positive. This explains that

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**Figure 8.** The effect of salt concentration on EHD flow surrounding a 2 μm PS microsphere with different Stern-layer conductivities. $f = 800$ Hz, $\zeta_p = -40$ mV, and $E_0 = 200$ Vpp mm$^{-1}$. The inset shows the charge density within the diffusive layer as a function of salt concentration. The velocity is evaluated at $r/a = 2.5$ and $z/a = 1.5$.

**Figure 9.** The size dependence of EHD flow around a PS microsphere with different Stern-layer conductivities. The field conditions are $f = 800$ Hz and $E_0 = 200$ Vpp mm$^{-1}$. $\zeta_p = -40$ mV. The velocity is evaluated at $r/a = 2.5$ and $z/a = 1.5$. 

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particles with 50 pS can generate extensile flow when the size is small but eventually becomes contractile as the size becomes larger. As the particle size increases, $Du$ will become smaller. The impact of particle surface conductivity becomes weaker compared with the medium conductivity, which makes the particle effectively less conducting than the medium. Therefore, the real part of the polarization coefficient becomes negative and the EHD flow turns contractile. However, the local field, $E_l$, is proportional to the volume of the colloid, which dominantly endows the particle a large magnitude of flow (Figure 9). The EHD flow velocity increases with particle size. The Stern-layer conductivity also influences the $Du$ number. When it is large (e.g., 500 pS), the critical particle radius at which the EHD flow transitions from extensile to contractile also becomes larger. At a sufficiently large radius, however, the EHD flow will still be contractile.

5.5. The Propulsion of Asymmetric EHD Motors

The enhanced understanding of EHD flow around an isotropic particle helps us understand and design colloidal motors actuated by AC electric fields. For example, by aggregating 2 μm PS and 2 μm silica microspheres via strong van der Waals attraction (i.e., in high salt concentration solutions), we can make hybrid motors of different shapes. As shown in Figure 10a, when they were dispersed in DI water, they propelled in directions that are perpendicular to the direction of the AC electric field,\[^{[6b,14]}\]

![Figure 10. Propulsion of asymmetric electrohydrodynamic motors.](image)

(a) PS–silica hybrid clusters propel with the silica lobe leading. The PS lobe appears darker than the silica lobe because of its higher refractive index. Field condition: $f = 1000$ Hz and $E_0 = 240$ Vpp mm$^{-1}$. A synthetic PS dimer propels with b) its small lobe leading in DI water but c) reverses its motion in 1 mM potassium chloride solution. Field condition: $f = 800$ Hz and $E_0 = 100$ Vpp mm$^{-1}$. Scale bars: 5 μm.

6. Conclusion

We investigated the distinct assembly behaviors of PS and silica spheres under a perpendicularly applied AC electric field. Using tracer nanoparticles, we quantified the opposite EHD flow surrounding PS and silica spheres, which underlies the separation of PS spheres and aggregation of silica spheres. We hypothesized that the Stern-layer conductivities regulate the observed opposite EHD flows and further obtained them experimentally. By incorporating the Stern-layer conductivity into the standard electrokinetetic model, we calculated the EHD flow around a dielectric spherical particle near an electrode and validated the calculation with the experimentally quantified flow around particles, which matches well. This resolves the puzzle that particles with moderate zeta potentials can generate extensile EHD flow. With the improved model, we further studied the impacts of zeta potential, Stern-layer conductivity, salt concentration, and particle size on the EHD flow systematically. We show that both the direction and magnitude of EHD flow are tuned by tailoring these parameters. High zeta potential, low salt concentration, significant Stern-layer conductivity, and small particle size tend to generate extensile EHD flow because they effectively make the particle surface conductivity larger than the medium, which leads to positive particle polarizability. The enhanced understanding on EHD flow surrounding individual particles further allows us to explain the propulsion of asymmetric clusters made of PS and silica particles.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

active matter, electric fields, electrohydrodynamics, electrokinetics, Stern layer conductivity

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