# Simultaneous Aggregation and Height Bifurcation of Colloidal Particles near Electrodes in Oscillatory Electric Fields

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**S** *Supporting Information*

**ABSTRACT:** Micrometer-scale particles suspended in NaCl solutions aggregate laterally near the electrode upon application of a low-frequency (~100 Hz) field, but the same particles suspended in NaOH solutions are instead observed to separate laterally. The underlying mechanism for the electrolyte dependence remains obscure. Recent work by Woehl et al. (PRX, 2015) revealed that, contrary to previous reports, particles suspended in NaOH solutions indeed aggregate under some conditions while simultaneously exhibiting a distinct bifurcation in average height above the electrode. Here we elaborate on this observation by demonstrating the existence of a critical frequency (~25 Hz)



below which particles in NaOH aggregate laterally and above which they separate. The results indicate that the current demarcation of electrolytes as either aggregating or separating is misleading and that the key role of the electrolyte instead is to set the magnitude of a critical frequency at which particles transition between the two behaviors.
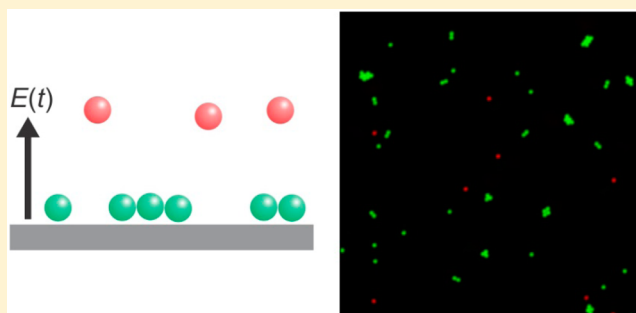
## INTRODUCTION

Micrometer-scale particles near electrodes have been widely observed to form planar aggregates in response to ac fields.[1] Early work led by Trau et al.[2,3] interpreted the particle aggregation in terms of electrohydrodynamic (EHD) fluid flow, where the presence of the particle disrupts the electric field near the electrode and creates a tangential field component, driving an EHD fluid flow directed radially inward toward the particle. Adjacent particles become mutually entrained in their respective flows, resulting in aggregation.[2,3] Ristenpart et al. further elaborated this mechanism by treating the particles as point dipoles adjacent to an ideally polarizable electrode.[4] They predicted that the magnitude of EHD flow should scale as the square of the applied ac electric field and approximately inversely with frequency, findings which have been corroborated experimentally in a variety of systems.[4−9] Although flow of some sort is believed to be the main driving force for aggregation, induced dipolar interactions also play a key role in governing the aggregation behavior, as evidenced for example by the complex morphologies generated with bidisperse,[10] confined,[11,12] or asymmetric[13,14] particles. Recent evidence has also indicated that the electrically modulated average particle height over the electrode helps govern the effective thermal motion of the particles and therefore their propensity to form randomly close-packed or crystalline aggregates.[15]

A mysterious aspect of the particle behavior, however, involves the effect of electrolyte type. Kim et al. first reported in 2002 that the same particles that aggregated in KCl or NaCl solutions would instead separate if immersed in KOH or NaOH.[16] Multiple studies since then have confirmed that the

identity of the surrounding electrolyte tremendously influences the aggregation rate of the particles.[16−20] Sides and Prieve and co-workers considered several models to explain the electrolyte dependence,[5,7,17,19,21−24] and they performed careful experiments that established a pronounced correlation between the electrolyte type and the particle height phase angle, $\theta$. Specifically, they showed that an individual particle near the electrode undergoes nanometer-scale oscillations slightly out of phase with the applied field; if $\theta < 90°$, then particles were observed to separate, while for $\theta > 90°$ they were observed to aggregate. Numerical calculations for the phase angle, however, predict separation at low frequencies and aggregation at higher frequencies,[24] behavior that has not been reported experimentally. More recently, Woehl et al. performed a broad survey of the effect of electrolyte type on the aggregation rates.[20] They found that the aggregation rate was negatively correlated with the magnitude of the electrolyte-dependent particle zeta potential, i.e., at small (large) zeta potential the particles aggregated (separated).[20] The survey appeared to strongly corroborate the idea that specific electrolytes induce either aggregation or separation.

Lateral aggregation and separation, however, are not the only behaviors observed with monodisperse suspensions. Another recent study by Woehl et al. revealed that particles underwent a bifurcation in their average height over the electrode upon application of a relatively low frequency (<100 Hz) field in

electrolytes where particles are observed to separate laterally (e.g., NaOH or HCl).[25] The fraction of particles that levitate far from the electrode was positively correlated with the applied potential and negatively correlated with frequency.[25] Woehl et al. noted that the observations pointed to a "tertiary minimum" in the electrode–particle interaction potential, and they argued that the observations were qualitatively consistent with an energy landscape predicated on a balance between EHD flow, colloidal-scale interactions, and gravity.[25] This interpretation, however, raised an important question: if a radially inward EHD flow is strong enough to push the particles up into a tertiary potential minimum, then why does the flow fail to pull the particles remaining near the electrode together into aggregates? In fact, Woehl et al. briefly reported preliminary evidence of aggregate formation in NaOH solutions, even though NaOH had been repeatedly identified previously as a separating electrolyte.[25] They did not expand on this observation, however, and it remains unclear under what conditions particles aggregate or separate while undergoing the height bifurcation.

In this letter, we elaborate on the observation of aggregation in a separating electrolyte by quantifying the aggregation dynamics of micrometer-scale particles in NaOH solutions. We establish the existence of a critical frequency, approximately 25 Hz, below which particles immediately adjacent to the electrode aggregate and above which they separate. This aggregation occurs simultaneously with the levitation of other (non-aggregating) particles to extreme distances above the electrode. The results suggest that the main role of the electrolyte type is to set the critical frequency below which aggregation occurs rather than incontrovertibly governing whether particles separate or aggregate.

## EXPERIMENTAL METHODS

The experimental methodology was similar to work described previously.[4,15,20,25] In brief, the experimental setup (Figure 1) consisted of two parallel glass slides coated with tin-doped indium oxide (ITO, 5–15 Ω sheet resistance) separated by a nonconductive poly(dimethylsiloxane) spacer 1 mm in thickness. Prior to each
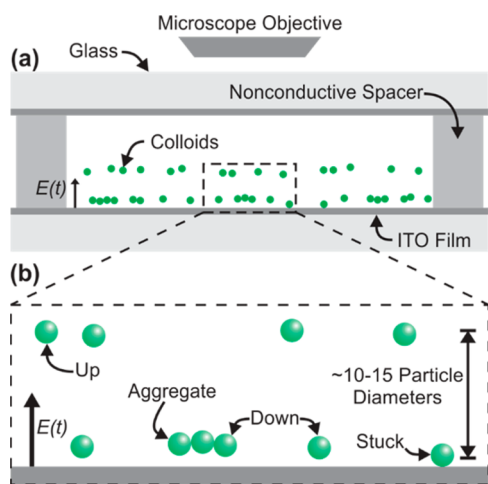


**Figure 1.** (a) Schematic of the experimental apparatus depicting particle height bifurcation after the application of an electric field (not to scale). (b) Magnification emphasizing that three possible heights occur: up, down, and stuck (i.e., irreversibly adhered to the electrode). At sufficiently low frequencies, the down particles near the electrode form aggregates.

experiment, the electrodes were washed with RBS 35 detergent, then ultrasonicated in detergent, acetone, and deionized (DI) water for 10 min each, and finally dried with filtered compressed nitrogen. Solutions of NaOH or KOH were prepared at 1 mM (conductivity, $\sigma = 254 \pm 6$ μS/cm in NaOH) using DI water (18.2 MΩ cm). Colloidal suspensions were prepared by adding 2-μm-diameter fluorescent sulfonated polystyrene (PS) particles to the NaOH solution at a volume fraction of $3 \times 10^{-4}$. Each suspension was washed three times by centrifugation and resuspension. The electrophoretic mobility measured via dynamic light scattering was −8.7 μm cm s⁻¹ V⁻¹ in NaOH (Malvern Zetasizer) with an ostensible zeta potential of −110 mV, approximated using the Helmholtz–Smoluchowski relation for small mobilities. To begin an experiment, the suspension was added to the fluid well, and particles were allowed to settle by gravity for ∼2 h to the bottom electrode. The colloidal behavior was observed with either a transmission optical microscope or a laser scanning confocal microscope (Zeiss LSM 700).

After particles settled near the electrode, a function generator applied a 4 V peak-to-peak (Vpp) voltage with frequency ranging from 5 to 150 Hz. An electrometer was used to measure the corresponding current density (cf. Supporting Information). Video recordings were started 30 s prior to the application of the electric field ($t = 0$) to establish the initial average number of particles, and the colloidal behavior was recorded for 5 to 10 min. The field was then removed, and the particles were allowed to disperse via Brownian motion for 10−15 min before repeating. All tests were performed in a randomized order to minimize possible systematic effects, yielding three trial replicates for each frequency.

## RESULTS AND DISCUSSION

Figure 2 shows representative time-lapse images of particle behavior in NaOH under different applied frequencies. Upon the application of a 4 Vpp, 50 Hz electric field (Figure 2a) the PS particles were quickly height bifurcated. Similar to the results reported by Woehl et al., particles in the upper plane moved partially out of focus while particles in the lower plane separated laterally.[25] Repeated trials showed that the likelihood for any given particle to move up was random; sometimes a given particle would levitate while other times it would remain near the electrode. After the initial height bifurcation, particles were observed to remain near their respective height indefinitely until the field was removed.

The behavior at 5 Hz, in contrast, was qualitatively different (Figure 2b). The particles quickly became height bifurcated within 60 s after the application of the electric field, where the levitating particles reached such large heights that they were no longer visible in the focal plane near the electrode. We focus here on the behavior of the particles that remained adjacent to the electrode, which strikingly did not laterally separate as observed at higher frequencies. Instead, they began to form planar aggregates on the surface of the electrode. After time periods of a few minutes, many large aggregates of four or more particles were observed. These clusters remained mobile throughout the experiment, indicating that they were not stuck to the electrode (Supporting Information Movie S1). Once the electric field was removed, the aggregates dispersed via Brownian motion. We emphasize that the particle type, surrounding electrolyte, ionic strength, and applied electric potential were identical for both trials shown in Figure 2; only the applied frequency was varied.

To quantify the aggregation behavior we used a particle-tracking methodology[4] that tracked versus time the number of unaggregated particles ($n_1$, singlets), aggregates composed of two particles ($n_2$, doublets), and higher-order aggregates (cf. Figure S1 and Movie S2). Figure 3 shows representative plots
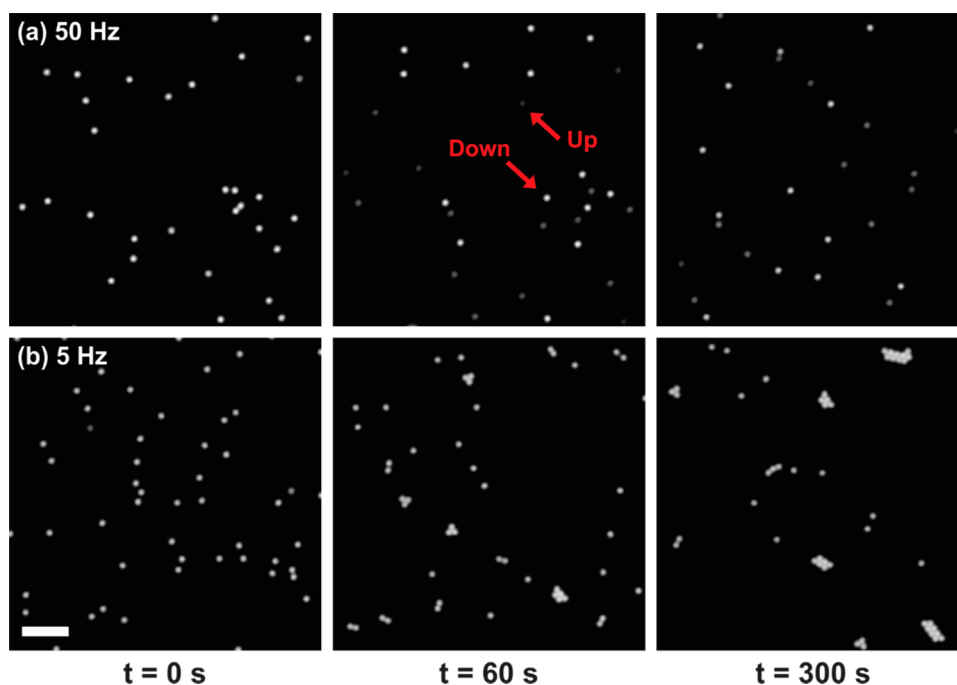
**Figure 2.** Confocal time-lapse images of 2 $\mu$m sulfonated PS particles suspended in 1 mM NaOH solution. At $t = 0$, a 4 Vpp electric field is applied (oriented out of the page). (a) At 50 Hz, the particles exhibit height bifurcation, and no aggregation is observed. (b) At 5 Hz, particles exhibit height bifurcation, but particles adjacent to the electrode aggregate quickly. By 60 s the levitated particles have moved completely out of focus. The scale bar is 10 $\mu$m.
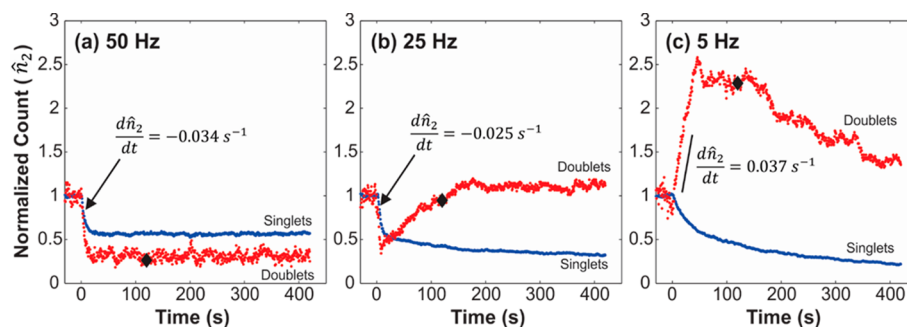


**Figure 3.** Representative examples of the number of singlets (blue) and doublets (red) versus time, normalized by the initial average number of singlets or doublets, respectively, for $t < 0$ s. Black diamonds denote the doublet concentration observed at $t = 120$ s. (a) At 50 Hz the concentrations of singlets and doublets both rapidly decrease upon application of the field and then stabilize to roughly constant values. (b) At 25 Hz the concentrations of singlets and doublets both initially decrease rapidly, but at longer times the singlet concentration gradually decreases and the doublet concentration increases. (c) At 5 Hz the singlet concentration continuously decreases while the doublet concentration initially increases rapidly. The doublet concentration then decreases at later times as the doublets combine with other particles to form triplets, quadruplets, and so forth during aggregation.

of $\hat{n}_i \equiv n_i/n_{i,o}$, where $n_{i,o}$ is the average initial concentration of aggregates of size $i$ prior to the application of the electric field, as a function of time. Note that the initial number of doublets, prior to application of the field, is not zero since Brownian motion occasionally brings particles into apparent contact; at low magnification, adjacent particles sufficiently close to one another look like they are touching. We emphasize, however, that adjacent particles could still be slightly separated vertically since the focal depth is several micrometers at the low magnifications used here. Application of the field could cause the apparent doublet to separate vertically as one levitates while the other does not; likewise, both could levitate. In either case a net decrease in $\hat{n}_2$ occurs. Typical values of $n_{1,o}$ were on the order of 1000, while $n_{2,o}$ was usually between 50 and 100.

Upon application of a 50 Hz electric field (Figure 3A), the numbers of singlets and doublets both quickly decreased by about half over the first 20 s. Both values then remained roughly constant for the duration of the experiment. The rapid decrease was primarily due to particle disappearance from the focal plane as they levitated away from the electrode. Qualitatively similar behavior was initially observed at 25 Hz (Figure 3b), where again the numbers of singlets and doublets both decreased by roughly half over the first 20 s. In contrast to the behavior at 50 Hz, however, particles slowly aggregated over a longer time scale: the doublet concentration was observed to increase gradually, eventually recovering back to its original value within a couple of minutes. During this same time period, the singlet concentration gradually decreased, as the singlets moved laterally toward one another and were

"consumed" to form doublets. Overall, the behavior was consistent with rapid height bifurcation followed by a relatively slower lateral attraction.

At the even lower frequency of 5 Hz (Figure 3c), the number of singlets again initially decreased by approximately 50% over the first 60 s and continued to decrease gradually for the duration of the experiment. No initial decrease in the concentration of doublets was observed, however: the doublet concentration immediately began rising upon application of the field, increasing by roughly 250% over the first 60 s. At even longer times the doublet concentration gradually decreased as they were consumed to form higher-order aggregates (triplets, etc.), such as those shown in Figure 2b. We emphasize that at 5 Hz a significant fraction of singlets exhibited the height bifurcation, i.e., a large fraction of the particles levitated out of the focal plane, contributing to the observed decrease in singlets with time. The main difference is that the particles left behind near the electrode aggregated so rapidly that no decrease in doublet concentration due to the height bifurcation could be registered.

To quantify the rate of aggregation, the initial slope of the time rate of change of the doublet concentration, $d\hat{n}_2/dt$, was found via linear regression over the first 30 s. Well-defined slopes could be obtained at relatively high or low frequencies (cf. Figure 3a or c), but at intermediate frequencies the rate was initially negative and then eventually positive (cf. Figure 3b). Because of this complexity, we also determined $\hat{n}_2(120)$, the absolute doublet concentration at $t = 120$ s (cf. black diamonds Figure 3). Although this time choice is arbitrary, it provides a convenient measure of whether the doublet concentration increased or decreased in a reasonable time period.

The rate of doublet aggregation (Figure 4a) and the absolute doublet count (Figure 4b) both smoothly decrease with frequency, albeit with different critical frequencies. For frequencies below $f < 20$ Hz, particles rapidly form multiparticle aggregates, while for $f > 30$ Hz particles separate and no appreciable aggregation occurs. For 20 Hz $< f <$ 30 Hz, particles near the electrode initially appear to separate but eventually form a significant number of aggregates over longer times.

To determine whether aggregation occurs in other supposedly separating electrolytes, we performed similar experiments using 1 mM KOH solutions. The results (data not shown) are extremely similar to those presented in Figures 2−4: particles separated at 50 Hz, slowly aggregated near 20 Hz, and rapidly aggregated at 5 Hz. We also tested positively charged particles in acidic electrolytes, but the particles tended to adhere irreversibly to the negatively charged ITO surface immediately upon application of the field. Nonetheless, the observation that particles aggregate in both NaOH and KOH solutions suggests that the behavior is robust.

The experimental observations presented here raise several questions. First, why has aggregation not been observed previously in these electrolytes? The short answer is that nobody appears to have previously examined such low frequencies. Most reported work in NaOH or KOH is at frequencies of 100 Hz or greater,[16−18,20,23,25] with only one previous report at 50 Hz.[19] Presumably most researchers have avoided lower frequencies because the particles tend to stick irreversibly to the electrode, especially in aggregating electrolytes such as NaCl where the particle zeta potential (and hence resistance to sticking) is lower.[20]

The second and more fundamental question is why is there a critical frequency? The observations of simultaneous aggrega-
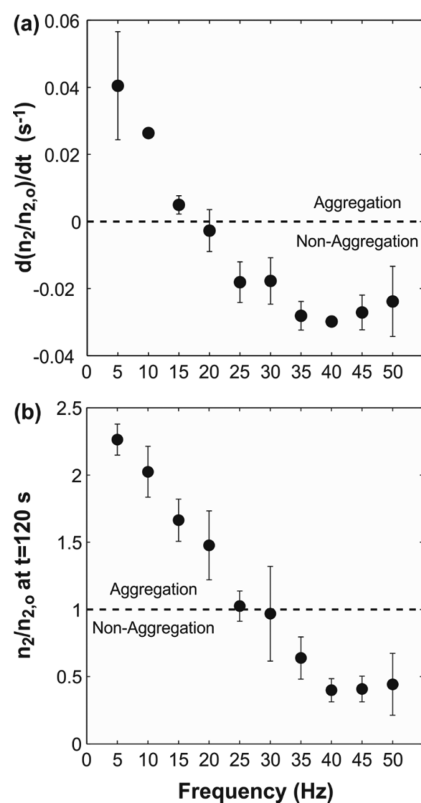


**Figure 4.** Effect of frequency on aggregation in 1 mM NaOH at 4 Vpp. (a) Initial time rate of change of the doublet concentration versus frequency. Below a critical frequency (∼20 Hz, $d\hat{n}_2/dt > 0$), particles aggregate. (b) Absolute normalized doublet concentration at $t = 120$ s versus frequency. Below a critical frequency (∼30 Hz, $\hat{n}_2 > 1$) the doublet concentration has increased compared to that at $t = 0$. Error bars are 2 standard deviations of the mean of three trial replicates.

tion and height bifurcation are qualitatively consistent with Woehl et al.'s scaling arguments for radially inward EHD fluid flow generating a vertical lift force that is balanced by gravity to form a tertiary interaction potential minimum.[25] It is still unclear, however, why below some critical frequency particle aggregation occurs. Measurements of the current density show only a very slight (∼3%) increase in electric field strength as the frequency decreases from 50 to 5 Hz, making it difficult to reconcile the behavior in terms of simply increasing the driving force (cf. Figure S3). Broadly speaking, the EHD flow magnitude is expected to scale inversely with frequency,[4] so one possibility is simply that the flow magnitude at very low frequencies is finally sufficient to overcome dipolar repulsion. Caution is necessary, however, because the scaling arguments that yield this inverse frequency dependence assume much larger frequencies, complicating quantitative comparison. Crucially, they also assume that no electrochemical reactions occur,[4,25] a condition unlikely to be satisfied at 5 Hz. Both dc-[26] and ac-generated fluid flows share the feature that the streamlines move radially inward along the electrode surface and then up around the particle, generating a vertical lift force. Although our current measurements yielded no clear evidence of asymmetries or dc offsets in the field strength (Figures S2− S5), electrochemical reactions might nonetheless help induce other types of electrically generated fluid flow such as electro-osmotic flow,[26] induced charge electro-osmosis,[7,23,27] and faradaically coupled electro-osmotic flow.[23] More detailed

modeling will be necessary to assess these and other possible driving forces for aggregation.

## SUMMARY

We demonstrated the simultaneous aggregation and height bifurcation of micrometer-scale particles in NaOH and KOH solutions, electrolytes that were previously thought only to promote particle separation in response to oscillatory fields. A key conclusion from this work is that any predictive mechanism for the effect of electrolyte type must account for the existence of a critical frequency below which aggregation occurs; theories that fail to predict this behavior[20,24] must be critically re-examined. Practically speaking, many types of particles have been observed to exhibit EHD aggregation, including not only polystyrene[1–4,10,12,15–20,23,25,28,29] and silica[10,20] but also oil droplets,[9] bacteria,[30] and colloids with more complicated shapes.[13,14] The discovery of aggregation in NaOH and KOH suggests that the phenomenon is more robust than previously thought, further expanding the range of potential systems where electric fields can be used to manipulate particle behavior near electrodes.

## ASSOCIATED CONTENT

**Ⓢ Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.lang-muir.5b02432.

> Particle-tracking methodology and current density measurements (PDF)
>
> Movie of a representative confocal *z* stack of particles exhibiting simultaneous height bifurcation and aggregation (MPG)
>
> Representative analysis of a low-magnification optical microscopy movie (AVI)

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**Notes**

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

## REFERENCES

(1) Prieve, D. C.; Sides, P. J.; Wirth, C. L. 2-D assembly of colloidal particles on a planar electrode. *Curr. Opin. Colloid Interface Sci.* **2010**, *15* (3), 160–174.

(2) Trau, M.; Saville, D. A.; Aksay, I. A. Field-induced layering of colloidal crystals. *Science* **1996**, *272* (5262), 706–709.

(3) Trau, M.; Saville, D. A.; Aksay, I. A. Assembly of colloidal crystals at electrode interfaces. *Langmuir* **1997**, *13* (24), 6375–6381.

(4) Ristenpart, W. D.; Aksay, I. A.; Saville, D. A. Assembly of colloidal aggregates by electrohydrodynamic flow: Kinetic experiments and scaling analysis. *Phys. Rev. E* **2004**, *69* (2), 021405.

(5) Sides, P. J. Electrohydrodynamic particle aggregation on an electrode driven by an alternating electric field normal to it. *Langmuir* **2001**, *17* (19), 5791–5800.

(6) Kim, J.; Guelcher, S. A.; Garoff, S.; Anderson, J. L. Two-particle dynamics on an electrode in ac electric fields. *Adv. Colloid Interface Sci.* **2002**, *96* (1–3), 131–142.

(7) Fagan, J. A.; Sides, P. J.; Prieve, D. C. Evidence of multiple electrohydrodynamic forces acting on a colloidal particle near an electrode due to an alternating current electric field. *Langmuir* **2005**, *21* (5), 1784–1794.

(8) Zhang, K. Q.; Liu, X. Y. Controlled formation of colloidal structures by an alternating electric field and its mechanisms. *J. Chem. Phys.* **2009**, *130* (18), 184901.

(9) Vigo, C. R.; Ristenpart, W. D. Aggregation and Coalescence of Oil Droplets in Water via Electrohydrodynamic Flows. *Langmuir* **2010**, *26* (13), 10703–10707.

(10) Ristenpart, W.; Aksay, I.; Saville, D. Electrically Guided Assembly of Planar Superlattices in Binary Colloidal Suspensions. *Phys. Rev. Lett.* **2003**, *90* (12), 128303.

(11) Gong, T.; Marr, D. W. M. Electrically switchable colloidal ordering in confined geometries. *Langmuir* **2001**, *17* (8), 2301–2304.

(12) Gong, T.; Wu, D. T.; Marr, D. W. M. Two-Dimensional Electrohydrodynamically Induced Colloidal Phases. *Langmuir* **2002**, *18* (26), 10064–10067.

(13) Ma, F. D.; Wang, S. J.; Wu, D. T.; Wu, N. Electric-field-induced assembly and propulsion of chiral colloidal clusters. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (20), 6307–6312.

(14) Ma, F.; Wang, S.; Smith, L.; Wu, N. Two-Dimensional Assembly of Symmetric Colloidal Dimers under Electric Fields. *Adv. Funct. Mater.* **2012**, *22* (20), 4334–4343.

(15) Dutcher, C. S.; Woehl, T. J.; Talken, N. H.; Ristenpart, W. D. Hexatic-to-Disorder Transition in Colloidal Crystals Near Electrodes: Rapid Annealing of Polycrystalline Domains. *Phys. Rev. Lett.* **2013**, *111* (12), 128302.

(16) Kim, J.; Anderson, J. L.; Garoff, S.; Sides, P. J. Effects of zeta potential and electrolyte on particle interactions on an electrode under ac polarization. *Langmuir* **2002**, *18* (14), 5387–5391.

(17) Hoggard, J. D.; Sides, P. J.; Prieve, D. C. Electrolyte-dependent pairwise particle motion near electrodes at frequencies below 1 kHz. *Langmuir* **2007**, *23* (13), 6983–6990.

(18) Hoggard, J. D.; Sides, P. J.; Prieve, D. C. Electrolyte-dependent multiparticle motion near electrodes in oscillating electric fields. *Langmuir* **2008**, *24* (7), 2977–2982.

(19) Wirth, C. L.; Rock, R. M.; Sides, P. J.; Prieve, D. C. Single and pairwise motion of particles near an ideally polarizable electrode. *Langmuir* **2011**, *27* (16), 9781–91.

(20) Woehl, T. J.; Heatley, K. L.; Dutcher, C. S.; Talken, N. H.; Ristenpart, W. D. Electrolyte-Dependent Aggregation of Colloidal Particles near Electrodes in Oscillatory Electric Fields. *Langmuir* **2014**, *30* (17), 4887–94.

(21) Fagan, J. A.; Sides, P. J.; Prieve, D. C. Calculation of ac Electric Field Effects on the Average Height of a Charged Colloid: Effects of Electrophoretic and Brownian Motions. *Langmuir* **2003**, *19* (17), 6627–6632.

(22) Fagan, J. A.; Sides, P. J.; Prieve, D. C. Vertical motion of a charged colloidal particle near an AC polarized electrode with a nonuniform potential distribution: Theory and experimental evidence. *Langmuir* **2004**, *20* (12), 4823–4834.

(23) Fagan, J. A.; Sides, P. J.; Prieve, D. C. Mechanism of rectified lateral motion of particles near electrodes in alternating electric fields below 1 kHz. *Langmuir* **2006**, *22* (24), 9846–9852.

(24) Wirth, C. L.; Sides, P. J.; Prieve, D. C. Electrolyte dependence of particle motion near an electrode during ac polarization. *Phys. Rev. E* **2013**, *87* (3), 032302.

(25) Woehl, T. J.; Chen, B. J.; Heatley, K. L.; Talken, N. H.; Bukosky, S. C.; Dutcher, C. S.; Ristenpart, W. D. Bifurcation in the Steady-State Height of Colloidal Particles near an Electrode in Oscillatory Electric Fields: Evidence for a Tertiary Potential Minimum. *Phys. Rev. X* **2015**, *5* (1), 011023.

(26) Solomentsev, Y.; Bohmer, M.; Anderson, J. L. Particle clustering and pattern formation during electrophoretic deposition: A hydro-dynamic model. *Langmuir* **1997**, *13* (23), 6058–6068.

(27) Squires, T. M.; Bazant, M. Z. Induced-charge electro-osmosis. *J. Fluid Mech.* **1999**, *509*, 217–252.

(28) Yeh, S. R.; Seul, M.; Shraiman, B. I. Assembly of ordered colloidal aggregates by electric-field-induced fluid flow. *Nature* **1997**, *386* (6620), 57–59.

(29) Bohmer, M. In situ observation of 2-dimensional clustering during electrophoretic deposition. *Langmuir* **1996**, *12* (24), 5747–5750.

(30) Brisson, V.; Tilton, R. D. Self-assembly and two-dimensional patterning of cell arrays by electrophoretic deposition. *Biotechnol. Bioeng.* **2002**, *77* (3), 290–295.