

Hexatic-to-Disorder Transition in Colloidal Crystals Near Electrodes: Rapid Annealing of Polycrystalline Domains

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(Received 17 May 2013; published 19 September 2013)

Colloids are known to form planar, hexagonal closed packed (hcp) crystals near electrodes in response to electrohydrodynamic (EHD) flow. Previous work has established that the EHD velocity increases as the applied ac frequency decreases. Here we report the existence of an order-to-disorder transition at sufficiently low frequencies, despite the increase in the attractive EHD driving force. At large frequencies (~ 500 Hz), spherical micron-scale particles form hcp crystals; as the frequency is decreased below ~ 250 Hz, however, the crystalline structure transitions to randomly closed packed (rcp). The transition is reversible and second order with respect to frequency, and independent measurements of the EHD aggregation rate confirm that the EHD driving force is indeed higher at the lower frequencies. We present evidence that the transition is instead caused by an increased particle diffusivity due to increased particle height over the electrode at lower frequencies, and we demonstrate that the hcp-rcp transition facilitates rapid annealing of polycrystalline domains.

DOI: 10.1103/PhysRevLett.111.128302

PACS numbers: 47.57.J-, 61.72.Cc

Applied electric fields cause colloids near electrodes to arrange into a wide variety of structures, including three-dimensional aggregates [1,2], hexatic crystals [2–6], random closed packed (rcp) aggregates [3–5], binary superlattices [7], wormlike structures or chains [2,3,5], and rings [2]. The close packed nature of many of these aggregates clearly indicates the existence of an attractive driving force, and the prevailing explanation is that the particles are driven together by various types of electrohydrodynamic (EHD) fluid flow (also known as induced charge electro-osmotic flow [5,6,8,9]). In this view, the particles near the electrode disrupt the electric field and corresponding free charge distribution near the electrode, inducing a tangential hydrodynamic flow that drags particles toward one another [4,7,10,11]. A key theoretical prediction is that the magnitude of the EHD flow, and hence the driving force for aggregation, should increase at lower applied frequencies [4,12]. This hypothesis has been corroborated by experimental measurements of the aggregation rate [4,13], but other observations appear to be inconsistent with the predicted effect of frequency. Liu *et al.* [14] observed an *increase* in interparticle separation as frequency decreased below approximately 250 Hz; similarly, Hoggard *et al.* [5] and Zhang and Liu [2,15] independently reported what appear to be *amorphous* aggregates, rather than crystalline aggregates, at sufficiently low frequencies (100–300 Hz). No explanation for this behavior has been proposed to date, and the nature of the forces acting on the colloids at lower frequencies remains unclear.

In this Letter, we report a counterintuitive phase transition from a hexatic closed packed (hcp) state to an entropically more favorable (disordered) closed packed

state, despite the increasing EHD driving force. The transition from hexatic-to-random closed packing is seen when decreasing frequency from roughly 500 to 100 Hz, characterized by a marked increase in interparticle spacing and decrease in orientational order. We present evidence that the transition at lower frequencies is caused by an increased particle diffusivity due to a correspondingly increased particle height over the electrode, which we propose is itself a consequence of the increased EHD flow. Finally, we exploit the order-disorder transition to rapidly anneal polycrystalline domains of particles, with important potential implications for tuning the ordering behavior of more complex colloidal systems [16–20].

Our experimental methodology is similar to that detailed elsewhere [4]. In brief, the setup consisted of parallel glass slides coated with indium tin oxide (ITO) (15Ω sheet resistance) separated by a nonconductive polydimethylsiloxane spacer (Fig. 1). Sulfate functionalized polystyrene particles with $2 \mu\text{m}$ diameter (Invitrogen, U.S.) were washed and diluted to 5×10^{-6} volume fraction in 1 mM NaCl solution. Particles were allowed to settle

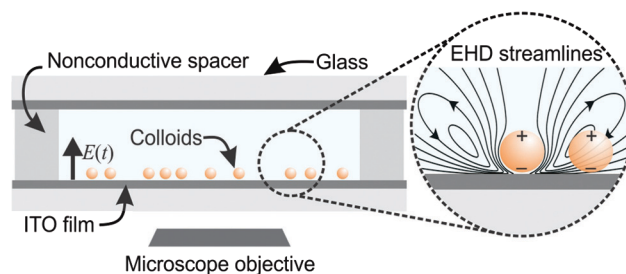


FIG. 1 (color online). Schematic of the apparatus (not to scale) and EHD flow streamlines.

near the bottom electrode by gravity, yet remained separated from the electrode due to colloidal scale forces present at the low ionic strength used here [4,21]. We induced aggregation by applying an ac potential of 5 V peak to peak at 100 Hz for 5 to 10 min. The electric field was then varied systematically between 100–4000 Hz, and the resulting aggregate morphology imaged and analyzed using standard image analysis techniques. The particles remained mobile provided the frequency was greater than ~ 50 Hz; at lower frequencies the particles tended to adhere irreversibly to the electrode.

Representative experimental results [Figs. 2(a)–2(c)] reveal three distinct regimes of behavior as a function of frequency: random closed packing, hexatic closed packing, and isotropic separation (SEP). At low frequencies [Fig. 2(a)], rcp aggregates formed with nonuniform particle spacing. The individual particles continued to exhibit Brownian motion, but the aggregates themselves remained rcp over time scales of 1 h or longer. When the frequency was instantaneously increased to 500 Hz, the particles rapidly rearranged and

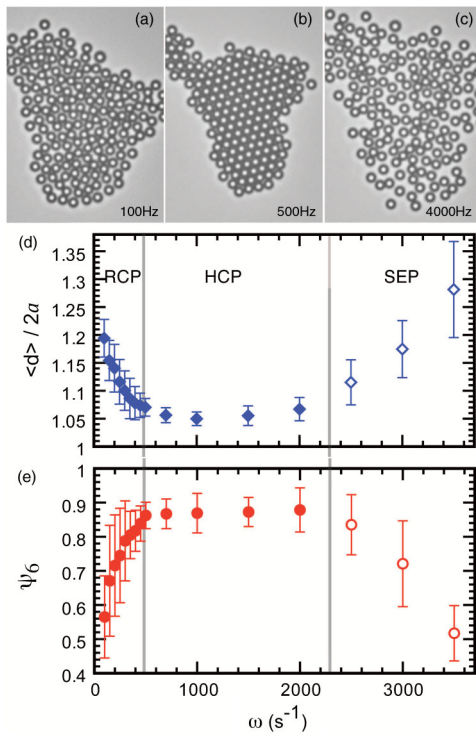


FIG. 2 (color online). The aggregation behavior of $2 \mu\text{m}$ particles versus frequency: (a) rcp at 100 Hz, (b) hcp at 500 Hz, and (c) separating at 4000 Hz. Graphs show (d) average interparticle separation and (e) orientational bond order parameter versus frequency. Vertical gray lines qualitatively denote the three distinct ordering regimes. Error bars are 1 standard deviation based on three trial replicates with at least seven unique aggregates per trial. The open symbols represent transient measurements averaged over the first 30 sec after the frequency change, and are included to illustrate the change in behavior compared to lower frequencies.

contracted within 1–2 sec to a highly ordered hcp lattice with stable uniform interparticle spacing [Fig. 2(b), cf. Movie 1 in Supplemental Material [22]]. Unlike rcp, the individual particles in hcp exhibited significantly reduced albeit visible Brownian motion. When the frequency was instantaneously increased further to 4000 Hz, the particles slowly dispersed via diffusion over the field of view, starting with the particles at the perimeter of the aggregate [Fig. 2(c), cf. Movie 1 in Supplemental Material [22]]. We emphasize that the low and high frequency behaviors were fundamentally different. At high frequencies the particles diffused away, indicating the absence of a strong attractive interaction. In contrast, at low frequencies the disordered aggregates remained close packed indefinitely, indicating the presence of long-range attractive forces.

To quantify the effect of frequency on the colloidal packing behavior, we systematically varied the frequency and measured the normalized interparticle spacing and an orientational bond order parameter [Figs. 2(d) and 2(e)]. The mean interparticle spacing $\langle d \rangle$ [Fig. 2(d)] accords with the qualitative observation that the rcp aggregates are larger, or less dense than the corresponding hcp aggregates. The most efficient packing is found in the hcp range of 500 to 2000 Hz, with $\langle d \rangle / 2a \sim 1.05$, giving a maximum two-dimensional packing fraction of 0.87 at 1000 Hz. As frequency decreased below approximately 500 Hz or increased above 2000 Hz, $\langle d \rangle / 2a$ increased monotonically (corresponding to a decreasing packing fraction). Likewise, three distinct orientational ordering regimes were observed with respect to frequency [Fig. 2(e)]. We quantified the orientational ordering using a standard orientational bond order parameter, $\Psi_6 = 1/N \sum_i [(1/N_{ij}) \sum_j \exp(i6\theta_{ij})]$, where θ_{ij} is the angle between a fixed axis and the bond separating particles i and j [23]. Between 500 and 2000 Hz $\Psi_6 \approx 1$, indicating a high degree of order, whereas Ψ_6 decreased as the frequency either decreased below 500 Hz or increased past 2000 Hz. Note that the order parameter does not exactly equal unity in hcp, presumably due to the presence of grain boundaries and occasional point defects (immobilized particles) in some of the aggregates. We reiterate that both $\langle d \rangle$ and Ψ_6 at high frequencies (> 2000 Hz) were transient since the aggregates eventually dispersed completely.

Additional experiments indicated that the hcp-rcp transition is robust. We tested for rate or hysteresis effects by linearly accelerating or decelerating through the transition at rates between ± 1 and $\pm 16 \text{ s}^{-2}$ (Fig. S1A in Ref. [22]). The value of Ψ_6 was independent of the ramp rate and varied continuously as a function of frequency, indicating a 2nd order and reversible bifurcation. Likewise, the aggregate size did not significantly alter the frequency range over which the rcp-hcp transition was observed, at least for aggregates ranging in size from 76 to 260 particles (Fig. S1B in Ref. [22]). Finally, aggregate packing experiments were also performed with $4 \mu\text{m}$ diameter polystyrene particles, with qualitatively similar results: the

packing structures at 500 or 1000 Hz with 4 μm diameter particles were significantly more ordered than those observed at 100 Hz.

The observation of particle separation at high frequencies is consistent with the EHD theory, since the flow (and hence driving force for aggregation) diminish as frequency increases ([4,12,13] and Fig. S5A in Ref. [22]). In contrast, the existence of a robust low frequency order-to-disorder transition is unexpected and raises the fundamental question: Why do the particles move apart despite an increase in the attractive driving force? One possible explanation is that the driving force does not actually increase at lower frequencies as anticipated. Indeed, our direct measurements of the current density magnitude showed that the electric field strength decreased by roughly 15% over the range 500 to 100 Hz (Fig. S5B in Ref. [22]), presumably due to screening effects associated with the concentration polarization layers near the electrodes [24]. Since the EHD flow magnitude scales as the square of the electric field strength [4,10], a natural hypothesis would be that the slightly lower electric field strength is responsible for the observed hcp-rcp transition.

Two pieces of evidence, however, conflict with this interpretation. First, we conducted experiments at constant frequency but systematically varied applied potential, and found no transition from hcp to rcp at sufficiently low field strengths. At 500 Hz, both $\langle d \rangle$ and Ψ_6 were insensitive to the applied potential above 2 V, while below 2 V the particles appear to undergo isotropic separation (Fig. S2 in Ref. [22]). In other words, decreases in field strength much larger than 15% failed to induce an hcp-rcp transition. The second piece of evidence is that qualitatively the particles aggregated much more rapidly at low frequencies, consistent with the idea of a faster EHD flow pulling them together. To quantify the speed of aggregation, we used a lower magnification and measured the rate of aggregate growth, dA/dt , where A is the total area of all aggregates within the field of view containing two or more particles. In each experiment we began with randomly dispersed particles in the absence of a field, and then at $t = 0$ the field was applied and the aggregation recorded. To good approximation A increased linearly with time, at least for the first 30–60 sec over the potentials and frequencies tested. We found that dA/dt was indeed inversely proportional to the frequency [Fig. 3(a)], strongly corroborating the existence of an increased EHD flow at lower frequencies.

If the EHD driving force is indeed higher at lower frequencies, why do the particles separate and become disordered? Insight is provided by considering an important experimental observation: the particles at low frequency appeared to exhibit much more vigorous Brownian motion, when compared to particles at higher frequencies. To quantify this behavior, we measured the particle diffusivity as a function of frequency by tracking individual particles [Fig. 3(b), inset] in very dilute

solutions (10^{-6} volume fraction) and determining the corresponding Gaussian mean squared displacement distributions versus time [22]. The variance σ of the Gaussian displacement distribution was then used to obtain the apparent diffusivity of the particle, i.e., $D = \sigma^2/2t$, where t is the time step, using standard procedures [25,26]. The experimentally measured effective diffusivities were found to be negatively correlated with the applied frequency [Fig. 3(b)].

The increased diffusivity is not due to increased temperature: simple scaling arguments suggest that heating due to the electric current in our system is negligible, and moreover the current density was observed to decrease slightly at the lower frequencies where the observed diffusivity was highest. Instead, the variation in diffusivity suggests that at low frequencies the colloidal particles reside farther from the electrode surface. Recall that the hydrodynamic resistance increases as a particle approaches a solid surface [25,27]. An unhindered particle infinitely far from a wall has a diffusivity given by the Stokes-Einstein equation, $D^\infty = k_B T / 6\pi\mu a$, so a measured

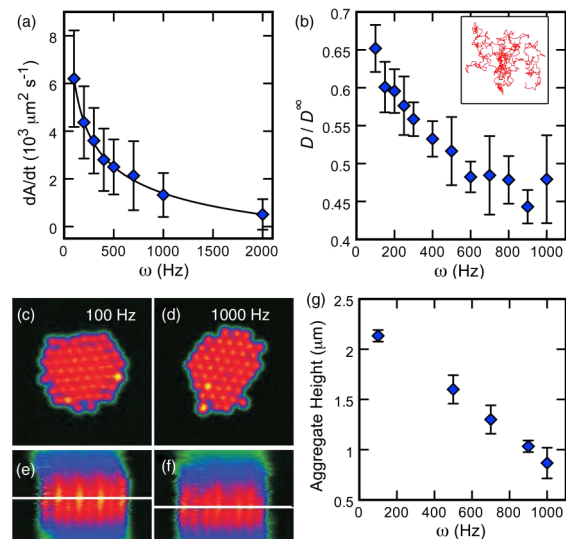


FIG. 3 (color online). (a) The rate of aggregate growth, dA/dt , versus frequency at 5 V. Solid line scales as $\omega^{-0.313}$. Error bars are 1 standard deviation over three trial replicates. (b) The normalized lateral particle diffusivity D versus applied frequency at 5 V. Each diffusivity is the mean of at least 18 isolated particles. Inset shows a representative particle trajectory over 104 sec in a $10 \times 10 \mu\text{m}$ grid at 100 Hz. (c)–(f) Representative false-colored confocal microscopy images of 2 μm fluorescent polystyrene at 1.5 V. Images include top views (c), (d) and $14 \times 23 \mu\text{m}$ cross-sectional views (e), (f) at 100 Hz (c), (e) and 1000 Hz (d), (f). The top view images were acquired during a single z scan near focus, with a scan time of 1.1 sec. The side view images are a cross section of the entire z stack acquired over ~ 4 min. The white lines in (e) and (f) denote the average vertical positions of each aggregate. (g) Electrode-to-surface aggregate height as a function of frequency. Each point is the average of 2–3 trials (cf. Fig. S4 in Ref. [22]).

thermal diffusivity smaller than D^∞ indicates greater viscous hindrance due to proximity of the surface. Previous work by Prieve and Sides and colleagues [8,21,28] used total internal reflection microscopy to probe the height of individual particles over the electrode, and although they observe a complicated dependence on the type of electrolyte [24], their measurements confirm that the average particle height can indeed vary with the applied frequency.

To directly test the hypothesis that the rcp-hcp transition is correlated with a change in height, we used a confocal microscope to measure the vertical displacement of aggregates from the electrode [Figs. 3(c)–3(g)]. At each frequency, the fluorescent intensity from a test aggregate was measured systematically as a function of vertical position (i.e., a z stack) and the resulting intensities fit to a Lorentzian distribution; the vertical position of the peak intensity corresponds to the average center of the particles within the aggregate (cf. Fig. S4 in Ref. [22]). The orthogonal projections and measured positions clearly show that the average particle height decreases by about $1 \mu\text{m}$ between 100 and 1000 Hz [Figs. 3(e), 3(d), 3(f), and 3(g)]. Taken together, the data in Fig. 3 suggest that the order-to-disorder transition at low frequencies results from an increased particle diffusivity due to increased particle height above the electrode. The increased diffusive nature of the particles at low frequencies drives the aggregates toward isotropic separation, but the strongly attractive EHD flow still holds the aggregate together albeit in a disordered state, resulting in rcp.

This interpretation begs the question: Why does the particle height change with frequency? The lateral component of the EHD fluid flow driving the aggregation is clearly highest at low frequencies [as evidenced by the rate data in Fig. 3(a)], so a likely explanation is that the EHD flow is also *pushing* the particles farther from the electrode due to the impingement of the flow on the particle (cf. qualitative streamlines in Fig. 1 and [21,29]). Since our measured particle heights at each frequency were static with respect to time, i.e., the particles resided in a potential well at some equilibrium height, clearly a vertical attractive force must balance the repulsive EHD lift force. Dipolar forces are known to strongly affect the particle interactions [1,7,30], so we hypothesize that the attractive force balancing the EHD lift force is dipolar attraction to the image dipole in the electrode. Scaling arguments based on the point dipole approximation for both the EHD lift force [4] and the induced dipole-dipole image attraction [30] yield an equilibrium height that decreases as frequency increases, qualitatively in accord with the experimental observations (Fig. S7 in Ref. [22]). These scaling arguments are based on the point dipole approximation, so more detailed calculations are necessary to obtain quantitative predictions. Nonetheless, the scaling arguments capture the main qualitative trend that the particles move away from the electrode over the frequency range where we

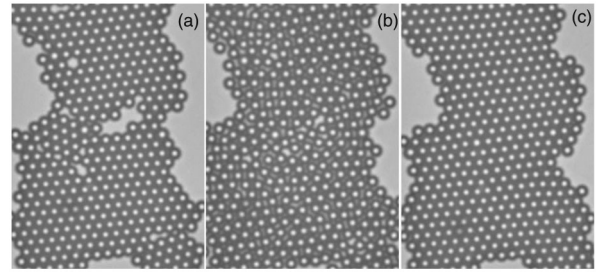


FIG. 4. Example of rapid annealing using the hcp-rcp transition. (a) 500 Hz, $t = 0$ sec, (b) 100 Hz, $t = 1$ sec, (c) 500 Hz, $t = 23$ sec, following a linear $+18$ Hz/sec increase in ω .

observe increased particle diffusivity and the corresponding hcp-rcp transition.

The existence of an order-disorder transition that maintains relatively close packing has important implications for applications that require rapid annealing of colloidal crystals near surfaces. The annealing of grain boundaries is notoriously challenging, due to the long thermal-diffusion driven wait times associated with redistribution. We demonstrate here that grain boundaries can be quickly removed by rearrangement through Brownian motion in the disordered closed packed (rcp) state observed at low frequencies (Fig. 4 and Movie 2 in Supplemental Material [22]). An initially polycrystalline domain at 500 Hz [Fig. 4(a)] transitioned to rcp by instantaneously decreasing the frequency to 100 Hz [Fig. 4(b)], and then reassembled as a single monocrystalline domain in response to a 22 sec linear sweep from 100 to 500 Hz [Fig. 4(c)]. We emphasize that the polycrystalline domains at 500 Hz were stable indefinitely (at least over time scales of ~ 1 h), but that sweeping through the hcp-rcp-hcp transitions induced annealing within 20 sec. This result confirms that redistribution and annealing of two-dimensional colloidal crystals can occur on significantly shorter time scales than expected based on thermal diffusion alone.

In summary, we demonstrated the existence of a reversible, 2nd order hcp-rcp transition for colloidal aggregates near electrodes at low applied frequencies. We explain the transition in terms of an increase in particle diffusivity due to an increased vertical height over the electrode at low frequencies. Counterintuitively, the flow responsible for pulling the particles together more strongly also pushes them farther from the electrode, increasing their effective Brownian motion and hindering crystallization. Our work sheds light on previous unexplained observations of increased interparticle separation and disordering at low frequencies [2,5,14,15]. The work also establishes a technique for rapidly annealing particles for exciting broader physical applications where monocrystalline domains near surfaces and rapid modulation of the packing behavior are desired, including investigations of two-dimensional melting and freezing, defect and grain boundary dynamics, colloidal glass transitions, and templated self-assembly of more complicated colloidal suspensions [16–20].

C. S. D. was supported by an NSF-AGS Postdoctoral Research Fellowship. We thank the CA League of Food Processors for support of this research. C. S. Dutcher and T. J. Woehl contributed equally to this work.

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