Electrically Guided Assembly of Planar Superlattices in Binary Colloidal Suspensions

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Binary colloidal suspensions are assembled into planar superlattices using ac electric fields. Either triangular or square-packed arrays form, depending on the frequency and relative particle concentrations. The frequency dependence is striking since superlattices develop at low and high frequencies but not at intermediate frequencies. We explain the low frequency behavior (<3 kHz) in terms of induced-dipole repulsion balanced by attraction resulting from electrohydrodynamic (EHD) flow. At high frequencies (20–200 kHz), EHD flow is negligible but aggregation occurs since dipole-dipole interactions become attractive.

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Monodisperse colloidal particles exhibit a wide range of behavior in electric fields near electrodes [1–9]. Application of dc or low frequency ($f < 1$ kHz) ac fields causes particles to move laterally across an electrode, yielding planar close-packed clusters [1,2]. Electrohydrodynamic (EHD) fluid flow has been invoked to explain this behavior [3–5]. In high frequency (> 1 kHz), high amplitude fields, dipole-dipole interactions produce widely spaced arrays [6,7]. At intermediate frequencies, the attractive and repulsive forces balance, as evidenced by the formation of clusters with average interparticle separations of several radii [8,9]. The ability to tune particle interactions simply by adjusting the frequency has implications for both device fabrication [10] and fundamental studies. In this Letter, we describe the behavior of suspensions with two sorts of particles with similar radii (a "binary" suspension) subjected to an ac field. It is demonstrated that the ac field produces new morphologies—"strings"of alternating particle types and triangular- and square-packed superlattices—over a range of frequencies. We explain the behavior in terms of EHD flow and induced-dipole interactions.

Our experiments utilize two optically transparent electrodes [11], separated by a 250-μm thick, Teflon© ring. The suspension is a mixture of 1.8-μm silica and 2.0-μm polystyrene particles [12], suspended in 18 MΩ/cm deionized water at a volume fraction of $\sim$0.002. After sedimentation forms a disordered particle monolayer on one electrode [Fig. 1(a)], application of a 10 kHz, 40 V/mm field (10 V peak-to-peak) induces particles to separate (laterally) into a disordered arrangement due to repulsion transverse to the applied field [Fig. 1(b)]. Lowering the frequency to 3 kHz (at constant field strength) causes particles to come together, forming planar aggregates. The aggregate morphology depends on the local (relative) particle concentrations. With a sizeable excess of polystyrene, "flowerlike" aggregates form with individual silica particles surrounded by six polystyrene particles [Fig. 1(c)]. In regions with either a 1:1 or 2:1 ratio of particles, a binary superlattice crystallizes when the frequency is lowered gradually ($\sim$0.1 kHz/sec). With a 2:1 ratio of polystyrene to silica, a triangular superlattice forms, similar to the (001) plane of an AB_2 crystal [Fig. 1(d), upper right portion of the panel]. If the concentrations of polystyrene and silica are approximately equal, then either square-packed superlattices or stripes of alternating particle types form [Fig. 1(d)]. In experiments where the high frequency step is omitted, or if the frequency is decreased "instantaneously" instead of gradually, the superlattice quality is poorer (i.e., the degree of binary periodicity is lowered).

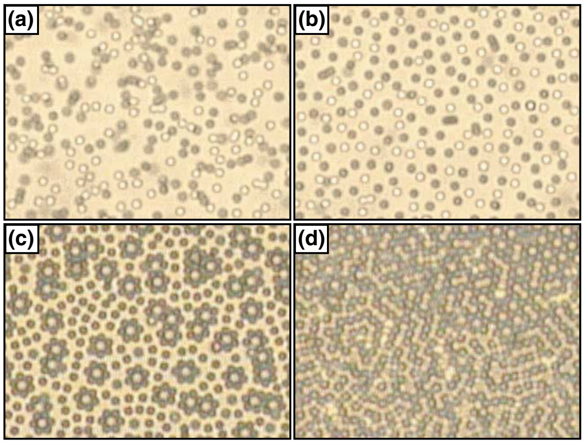

FIG. 1 (color). Optical images of planar structures formed with binary suspensions on an electrode in low frequency electric fields. Dark particles are 2.0-μm diameter polystyrene and light particles are 1.8-μm diameter silica; the field is oriented out of the page. (a) Random arrangement before application of a field. (b) Lateral separations induced with a 10 kHz, 40 V/mm field. (c) Individual silica particles typically surrounded by six polystyrene particles formed in a 3 kHz, 40 V/mm field with a local 8:1 ratio of polystyrene to silica. (d) Structures formed in a 3 kHz, 40 V/mm field with a local 2:1 ratio of polystyrene to silica. Note the region with triangular superlattices coexistent with a region of alternating lines of particles.

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The crystallization process is largely independent of the field strength above a threshold of $\sim$5 V/mm ($2 \leq f \leq 10$ kHz). Changing the field strength at constant frequency results in little or no discernible change in the lateral separation between particles, irrespective of whether they are closely aggregated (as at 2 kHz) or widely separated (as at 10 kHz). The absence of field strength dependence suggests that repulsive and attractive interaction forces scale with field strength in the same fashion. Monodisperse suspensions behave in the same way under these conditions indicating that the cause of aggregation is not intrinsically linked to a binary character. Various superlattice structures form, reproducibly, in independent experiments and various cluster morphologies are observed: ringed clusters, striped clusters, disordered clusters, and regions where the two types of particles are completely segregated. Different morphologies are often present on adjacent regions of the electrode, suggesting that factors other than the electric field and particle concentration may play a role.

Although repulsive lateral interactions keep identical particles apart at "high" frequencies (20–200 kHz), binary suspensions aggregate (Fig. 2). At a low total particle concentration ($\sim$20% area fraction), chains of alternating particle types form [Fig. 2(a)]. At higher concentrations ($\sim$80% area fraction), square or triangular superlattices form depending on the relative concentrations [Figs. 2(b) and 2(c)]. Clustering at high frequencies is sensitive to the field amplitude. At 20 V/mm, there is little sign of ordering; at 40 V/mm, particles aggregate into loose structures with some ordering; and at 60 V/mm, most of the particles arrange themselves in highly ordered binary superlattices. These observations suggest that the attractive interaction between the unlike particles is dependent on the electric-field strength between 20 and 200 kHz. If the frequency is increased from 100 kHz to 1 MHz at constant field strength, vertical columns of particles form, aligned with the field.

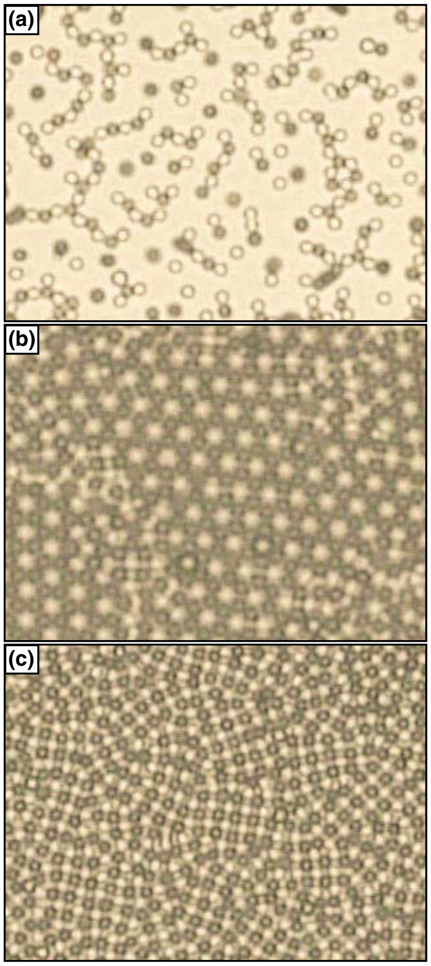

FIG. 2 (color). Optical images of planar structures formed with binary suspensions on an electrode in high frequency electric fields. The field strength is 60 V/mm at 100 kHz, oriented out of the page. Particle characteristics are the same as in Fig. 1. (a) Chains of alternating particle type with a 1:1 ratio of polystyrene to silica (20% total area coverage). (b) Triangular superlattices formed with a 2:1 ratio of polystyrene to silica (80% total area coverage). (c) Square-packed superlattices formed with a 1:1 ratio of polystyrene to silica (80% total area coverage).

Since the binary suspension aggregates at low and high frequencies but not at intermediate frequencies, several mechanisms are operative. Based on previous work with monodisperse systems, one mechanism of assembly at low frequencies is EHD fluid flow [1,3,13]. According to the EHD model, particles near the surface disrupt the free charge distribution and the electric field. This, in turn, induces flow that brings adjacent particles together. An important observation in monodisperse suspensions is that particle separation increases with frequency at lower frequencies [1,3,8,9]. This is consistent with recent theoretical modeling [4] and with the effect observed here in binary suspensions.

It is unlikely that EHD flow alone produces a superstructured arrangement. Although EHD flows are sensitive to particle size—since the particles serve to disrupt the concentration polarization layer near an electrode—they are insensitive to other particle characteristics [3,4]. As the particles used in this work are of a similar size, the small size difference appears insufficient to produce superstructure. The (repulsive) induced-dipole interaction energy between polystyrene particles, however, is about twice the silica-polystyrene or silica-silica energies and less energetically favored (see below). Given that EHD flow draws particles into close proximity, superlattices can be interpreted as structures that somehow lessen the total interaction energy by lowering the number of strongly repulsive interactions.

Since monodisperse suspensions do not aggregate for $f > 5$ kHz ($E > 10$ V/mm), it appears that EHD flow is negligible at higher frequencies. This can be understood in terms of the decrease in free charge density near the electrode in response to increasing frequency. Analysis of perfectly polarizable electrodes [14] shows that for electrodes that are widely spaced compared to the Debye length, κ^{-1}, the free charge density decays to zero as $D\kappa/fh \rightarrow \infty$. Here, $2h$ is the electrode spacing and D is the electrolyte diffusivity. For a 10^{-4} M KCl solution with $h \sim 100$ μm, the free charge density becomes quite small (compared to its zero frequency value) for $f > 10^4$ Hz. Since the EHD fluid velocity is proportional to the free charge density, the binary aggregation observed at high frequencies must arise from a different mechanism.

A relevant observation with both monodisperse and binary suspensions is that, upon application of an electric field at frequencies of 10 kHz or greater, like particles move laterally apart and, on occasion, will jump atop a neighbor. Repulsion and attraction in different directions can be understood in terms of induced dipoles, as illustrated by the point dipole interaction energy, $U_{AB} = \mathrm{Re}(\alpha_A^* \alpha_B) E_0^2 (1 - 3\cos^2\theta)/4\pi\varepsilon_s\varepsilon_0 r_{AB}^3$ [15]. Here, Re denotes the real part of the complex number, α_i is a polarizability (α_i^*—the complex conjugate), r_{AB} is the distance between particles, and θ is the angle between the electric field and the line of particle centers. Near the electrode, the interaction is repulsive if identical particles lie in the plane perpendicular to the applied field, i.e., $\theta = 90°$. In our setup, the particles are vertically unconfined (the electrode separation is 100 times larger than the particle diameters) and free to align with the field ($\theta = 0°$) by moving atop one another.

For identical particles, the sign of the interaction energy is determined solely by their relative orientation with the applied field. For unlike particles, however, attraction transverse to the applied field is possible if the real and imaginary parts of the polarizabilities have the appropriate signs, i.e., $\mathrm{Re}(\alpha_A^* \alpha_B) < 0$ [16,17]. The Clausius-Mossotti equation for a dielectric sphere in a dielectric medium [15] $\alpha_i = 4\pi\varepsilon_s\varepsilon_0 a_i^3(\varepsilon_{p,i} - \varepsilon_s)/(\varepsilon_{p,i} + 2\varepsilon_s)$ shows that the polarizability is real and attraction arises for $\varepsilon_{p,A} > \varepsilon_s > \varepsilon_{p,B}$. However, here we have dielectric particles with surface charge suspended in an electrolyte so a different line of attack is necessary.

The polarizability of a charged colloidal particle depends on, among other things, the surface charge or ζ potential, ionic strength and mobilities of the electrolyte ions, and frequency. Using the procedure outlined by Saville *et al.* [18], it can be shown that at low frequencies there is a "critical" ζ potential, $\zeta_{\mathrm{crit}} = 2(k_BT/e)\log[1 + \kappa a/(1 + 3m)]$, in a 1-1 electrolyte. Here, a is the particle radius, k_BT is the product of Boltzmann constant and absolute temperature, e is the fundamental charge unit, and m is a nondimensional ion drag coefficient [19]. For $\zeta > \zeta_{\mathrm{crit}}$ ($\zeta < \zeta_{\mathrm{crit}}$), the real part of the polarizability is positive (negative); the imaginary part is large and positive for $\zeta > \zeta_{\mathrm{crit}}$. Thus, attraction in the direction transverse to the applied electric field may obtain when one ζ potential is larger and the other smaller than the critical value. The real and imaginary parts of the polarizability of an isolated particle, calculated numerically [20], are shown as functions of frequency and zeta potential [Figs. 3(a) and 3(b)]. Note that the polarizability is a nonmonotonic function of frequency, the real component peaks at $\sim$100 kHz, and that for frequencies between $\sim 10^3$ and 10^5 Hz the polarizabilities have the appropriate signs. For 2-μm diameter particles in 10^{-4} M KCl, ζ_{crit} is -90 mV. The polystyrene and silica particles used in this

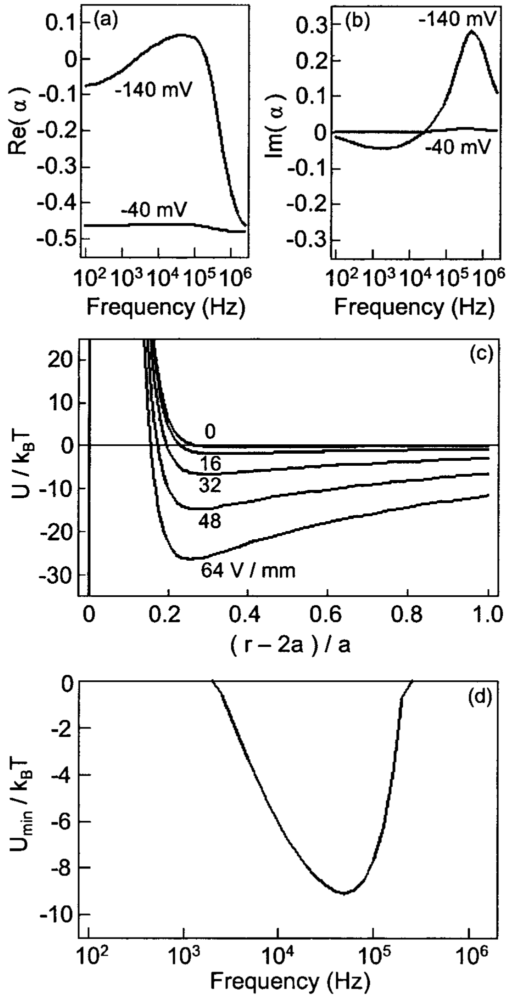

FIG. 3. Polarizability and interaction energies for 2-μm particles with zeta potentials of -40 mV and -140 mV in 0.1 mM KCl. (a) Real part of the polarizability of an isolated particle as a function of frequency and zeta potential. (b) Imaginary part of the polarizability. (c) The modified DLVO particle interaction energy, including a dipolar interaction term, as a function of separation for different field strengths at 100 kHz. (d) The depth of the secondary minimum at 40 V/mm as a function of frequency (over the frequency range where such minima exist). Outside the attractive window, the interaction is repulsive.

work have surface potentials of -40 and -140 mV so dipolar attraction is consistent with our model.

To estimate the interaction energy, the DLVO theory [21] was modified by adding a dipole-dipole attraction. Since the particles are dissimilar, we used the Hogg-Healy-Fuerstenau formulation for electrostatic interaction between particles with unequal zeta potentials [22], with additional terms from a power series expansion for larger potentials [23]. Attraction due to dispersion forces was modeled with an "effective" Hamaker constant of $2.5\ k_BT$. The model shows [Fig. 3(c)] that there is a secondary minimum in the attraction at surface-to-surface separations of ~ 0.25 radii with a depth proportional to the field strength. Since the particles are in a "secondary minimum," they should disperse readily once the electric field is removed, as observed experimentally.

As noted earlier, the polarizability and hence the depth of the secondary minimum are frequency dependent [Fig. 3(d)]. The depth of the secondary minimum is largest around 10^5 Hz in this scenario and levels off to zero below 10^3 Hz and above 10^6 Hz. The maximum in interaction energy at 10^5 Hz is consistent with the behavior observed experimentally. That the transverse interaction energy is purely repulsive at frequencies greater than 10^6 Hz explains why aggregation is not observed above this frequency. However, the model indicates a transverse attraction between 10^3 and 10^4 Hz, while repulsion is observed. One possible explanation for this discrepancy is that the model omits the effect of EHD flow on the electrokinetic processes that determine the magnitude of the polarizability at low frequencies. A more complete model would take account of proximity of the electrode and its effects on EHD flow.

In summary, we have demonstrated that electric fields can be used to modulate the interaction energies of particles with different polarizabilities and developed a theoretical framework for the interaction forces over a wide range of frequencies. At certain frequencies and relative particle concentrations, a diverse assortment of planar superstructures is obtained. The electric-field approach presented here might also be extended to multicomponent colloidal suspensions. Techniques for guiding the long-range organization of particles, such as those based on physically imposed particle confinement [24] or UV light directed particle motion [13], could be used in conjunction with our technique to improve long-range order.

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