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One- and two-dimensional assembly of colloidal ellipsoids in ac electric fields

John P. Singh, Pushkar P. Lele, Florian Nettesheim,* Norman J. Wagner, and Eric M. Furst†
Department of Chemical Engineering and Center for Molecular and Engineering Thermodynamics, University of Delaware, Newark, Delaware 19716, USA

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We investigate the assembly of colloidal ellipsoids in ac electric fields. Polystyrene latex ellipsoids with aspect ratios 3.0, 4.3, and 7.6 orient with the applied field and, at sufficient field strengths, interact to form particle chains at an angle with respect to the field. The characteristic chain angle decreases with increasing aspect ratio. The angled chains combine laterally to form an open centered rectangular two-dimensional structures belonging to the *c*2*mm* plane group. This chaining and assembly behavior is explained based on calculations of the particle pair interactions explicitly accounting for the electric field and shape of the ellipsoids.

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The solution phase assembly of colloidal particles using external fields is a powerful means for achieving structured and ordered phases, with potential applications in photonics [1,2], biosensors [3,4], electronic devices [5,6], and displays [7,8]. Suspensions of spherical colloidal particles exhibit rapid self-assembly in response to the application of an external ac electric field [2]. This disorder-to-order transition is driven by the interactions between particles, which polarize due to the contrast between their dielectric properties and that of the suspending medium [9]. The induced dipole-dipole interactions first lead to the formation of particle chains oriented in the field direction. These dipolar chains subsequently laterally combine to form hexagonal two-dimensional (2D) particle arrays.

The effect of particle shape on the disorder-to-order transition in electric fields remains unexplored, despite the fact that shape plays an important role in many applications, including the control of polarization modes of propagated light in photonic crystals [10,11]. Nonetheless, recent work recognizes that anisotropy in shape or properties is a key to forming complex higher-order structures from dispersions via self-assembly [12–14]. Excluded volume interactions alone lead to the expression of a rich equilibrium phase behavior in colloidal suspensions of anisotropic particles [15–18]. At dilute concentrations, where excluded volume effects are negligible, the shape dependence of the depletion interaction [19,20] and capillary forces [21,22] provide control over the interactions between particles and, ultimately, the self-assembled structures that form.

In this Rapid Communication, we report experiments investigating the assembly of ellipsoidal colloidal particles in ac electric fields. Similar to spherical particles, ellipsoids orient and form particle chains in the field direction. Surprisingly, however, chains of ellipsoids form at a distinct angle with respect to the applied field. Subsequent lateral coalescence of the angled chains leads to open particle arrays, in contrast to the hexagonal-close-packed arrays obtained for spheres. Similar structures are observed for three different aspect ratios of the particles. We explain these observations using a simple model based on the polarization interactions between pairs of particles as the underlying mechanism of the assembly process. We find that the most stable configuration for two interacting ellipsoidal particles is to align at an angle with respect to the applied field. Before discussing these results in detail, we first briefly detail our materials and methods.

Anisotropic polystyrene particles are fabricated using the methods of Keville *et al.* [23] and Ho *et al.* [24]. Monodisperse spherical polystyrene latex particles with a diameter of 3 μm are dispersed in a supersaturated solution of poly(vinyl alcohol) (PVA, Fluka 40-88, degree of hydrolysis 86.7–88.7, $M_w = 2.05 \times 10^5$, degree of polymerization $\sim$4200) in water, which is then cast and dried, resulting in a thin film. The film is heated above the glass transition temperature of polystyrene ($T > T_g \approx 105\ ^\circ$C) in a silicone oil bath and stretched uniaxially. After rapidly cooling the film, the PVA matrix is dissolved in a 7:3 water-isopropanol solution. The recovered anisotropic particles are redispersed in water and 2.5 mM sodium dodecyl sulfate (SDS). Three aspect ratios are investigated here, $\alpha = b/a = 3.0$, 4.3, and 7.6, where a and b are the particle polar and equatorial radii, respectively.

A *coplanar* electrode geometry is used to generate the electric field [Fig. 1(a)]. The electrodes are fabricated on a clean glass slide (25×75 mm, Fischer Scientic) by first depositing a 10 nm chromium layer followed by 100 nm of gold using an electron-beam evaporator (Thermionics, VE series). A similar electrode geometry was used earlier to study the assembly and interactions of spherical particles [2,25,26]. The gap between the electrodes is 2 mm. The glass slide and electrodes are cleaned before each use using a freshly prepared cleaning solution (Nochromix, Godax Laboratories) and a plasma cleaner (Harrick Plasma, PDC-32G). Using an adhesive spacer and a coverslip, a chamber is built over the electrodes with a height of approximately 100 μm. A particle solution with a volume fraction of 10^{-3} is injected into the chamber using capillary action and the ends are sealed using a UV curing epoxy (NOA 81, Norland). We take care to avoid introducing air bubbles into the chamber. The ac electric field is generated using a function generator (Agilent technologies, 33220A) amplified 50$\times$ (Tegam, 2340). A

*Present address: du Pont de Nemours Company, Experimental Station, Wilmington, Delaware, USA.
†Corresponding author; furst@udel.edu

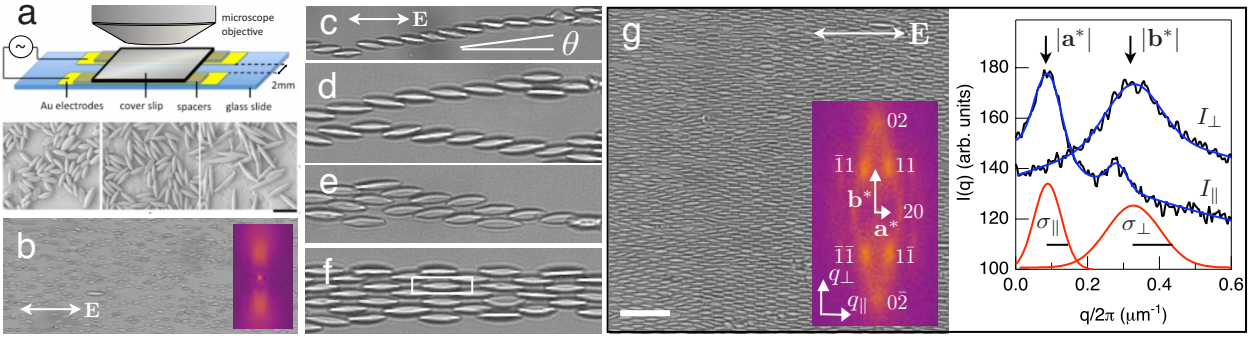

FIG. 1. (Color online) (a) A schematic of the experimental setup and scanning electron microscopy (SEM) images of colloidal ellipsoids with aspect ratios $\alpha=3.0$, 4.3, and 7.6. The scalebar is 10 μm. (b) Particles ($\alpha=3.0$) orienting in the electric field for $E=99$ V/cm and $\omega=10$ kHz. The Fourier transform power spectrum is shown in the inset. [(c) and (d)] At higher field strengths ($E\geq 180$ V/cm), chains form with a characteristic angle with respect to the field, θ. Chain angles are observed for both $+\theta$ and $-\theta$. (e) Two chains combine laterally. (f) Further growth leads to arrays with a centered rectangular unit cell, shown by the white box. (g) At higher concentrations, long-range order occurs. The scale bar is 25 μm. The inset shows the image power spectrum with the lattice vectors $\mathbf{a}^*$ and $\mathbf{b}^*$. To the right is the magnitude of the power spectrum for line segments through the (11) peak parallel and perpendicular to the field. Smooth lines (blue) show the total fits to $I_\parallel$ and $I_\perp$. The lower red Gaussian curves show the anisotropic width of the peak with the corresponding standard deviations $\sigma_\parallel$ and $\sigma_\perp$.

1 μF capacitor is used in series to eliminate any residual dc component. The range of frequencies ω examined in our work varies between 1 and 10 kHz and the rms value of the applied field strength E ranges from 0 to 400 V/cm.

At the beginning of each experiment, the ellipsoidal particles are randomly oriented. After applying the electric field, the particles orient with their major axes aligned in the field direction [Fig. 1(b)], which reduces the energy between the induced polarization of the particles and the external field [9]. The inset of Fig. 1(b) shows the power spectrum of the image Fourier transform. The anisotropic "lobed" pattern indicates particle orientation with the field, but long-range order is not evident. As the field strength increases, the induced polarization of the particles leads to interparticle interactions and subsequent assembly into chains in the field direction. At frequencies $\omega>1$ kHz, the orientation and assembly is field strength dependent. Chaining is observed at approximately $E>100$ V/cm, similar to the order-disorder transition of polystyrene latex spheres [2,25]. This transition is expected to occur when the maximum polarization-induced attraction between particles overcomes the thermal energy k_BT.

As noted above, the first unexpected effect of the ellipsoidal particle shape is the angle θ that the dipolar chains form with respect to the applied field, as shown in Figs. 1(c) and 1(d). The chains orient equally between the positive and negative angles with respect to the field direction. Above approximately $E=180$ V/cm these angled chains subsequently combine laterally, as shown in Fig. 1(d), again analogous to the fashion in which dipolar chains of spheres form particle arrays [2]. Further growth occurs as additional chains join the structure, leading to ordered two-dimensional arrays [Fig. 1(e)]. Each particle in the array has four nearest neighbors, in contrast to the hexagonal-close-packed lattice reported previously for spherical particles [2]. Similar structures are observed for all three aspect ratios of ellipsoids.

In order to investigate the structure of ellipsoidal particle arrays further, we increased the suspension concentration by tilting the sample cell for 20 min and allowing the particle chains to drift together by gravitational sedimentation. The resulting structure is shown in Fig. 1(g), along with the corresponding Fourier transform power spectrum (inset). In the power spectrum, distinct peaks indicating long-range order are now apparent. The structure is a centered rectangular unit cell belonging to the *c*2*mm* plane group, reflecting the vertical and horizontal mirror planes. The lattice vectors are aligned with the field direction $\mathbf{a}^*$ and orthogonal to the field $\mathbf{b}^*$; their magnitudes are $|\mathbf{a}^*|=0.56\pm0.01$ μm^{-1} and $|\mathbf{b}^*|=2.06\pm0.02$ μm^{-1}.

An estimate of the average crystalline domain size L is determined from the standard deviation of the (11) peak magnitude σ, $L=2\pi/\sigma$ [27]. The magnitude of the power spectrum is taken parallel $I_\parallel$ and perpendicular $I_\perp$ to the field along the line segments $q_\perp=|\mathbf{b}^*|$ and $q_\parallel=|\mathbf{a}^*|$, respectively, and averaged over the four symmetric quadrants. As shown in Fig. 1(g), both $I_\parallel$ and $I_\perp$ are modeled by the sum of three Gaussian curves (solid lines) yielding the location and width of the (11) peak. The peak width is clearly anisotropic, indicating different domain sizes parallel and perpendicular to the field. The standard deviations are $\sigma_\parallel=0.054\pm0.002$ μm^{-1} and $\sigma_\perp=0.105\pm0.002$ μm^{-1}, corresponding to domain sizes of $L_\parallel\approx16$ μm and $L_\perp\approx8.1$ μm, or about 1.7 unit-cell lengths and 3.1 unit-cell widths.

The results shown above demonstrate the significant effects particle shape has on field-directed self-assembly of colloids, leading specifically here to unusual chaining angles and open arrays. We quantify the distribution of chain angles that three or more particles subtend with the applied field for the three particle aspect ratios and find average angles between $\theta=10°$ and 15° (Fig. 2). The chains of particles with the smallest aspect ratio ($\alpha=3.0$) exhibit the largest angles, $\theta=16\pm5°$, while for the largest aspect ratio ($\alpha=7.6$), $\theta=11\pm3.5°$. The width of the distribution also decreases with increasing α.

Why do ellipsoidal particles form angled chains in electric fields when spherical particles do not? As a first approximation, we consider the energy of interaction between two point dipoles each centered within the volume of an ellipsoid. The interaction energy between aligned dipoles $\mathbf{P}_1$ and $\mathbf{P}_2$ with centers of mass separated by the vector $\mathbf{r}$ is

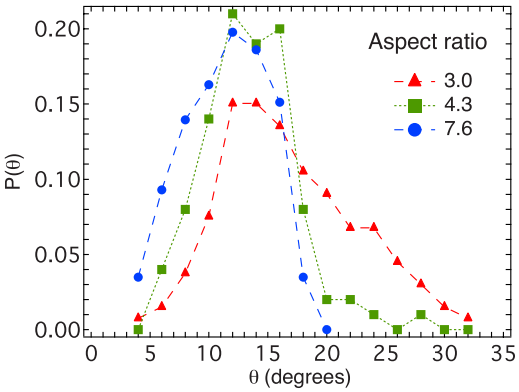

FIG. 2. (Color online) Distribution of chain angles that three or more particles subtend with the applied field for three particle aspect ratios.

$$U_{dd} = \frac{\mathbf{P}_1 \cdot \mathbf{P}_2}{r^3} - 3\frac{(\mathbf{P}_1 \cdot \mathbf{r})(\mathbf{P}_2 \cdot \mathbf{r})}{r^5}. \quad (1)$$

The minimum energy (maximum attraction) occurs when the dipoles are aligned in the field direction ($\theta=0$) and increases with the angle, becoming repulsive at $\theta \geq 57°$. When we account for the ellipsoid shape, the radial interaction energy as a function of angle with respect to the field θ is attractive, but unlike spheres, the energy minimum energy occurs at angles $\theta > 0$, in agreement with our experiments. The angles of the minimum energy are $\theta=36°$, 38°, and 39° for aspect ratios $\alpha=3.0$, 4.3, and 7.6, respectively. Although this calculation provides the important insight that the chaining angle arises for ellipsoidal particles due to the competition between the θ and $\mathbf{r}$ dependence of the dipolar interaction, the calculated angles are considerably larger than the experimental values, and the angle of the interaction minimum *increases* with increasing aspect ratio, which is the opposite trend observed in the experiments.

To make further progress, we consider the electric field around an ellipsoid with its major axis oriented with an external field. The external applied potential is ϕ_0, and the

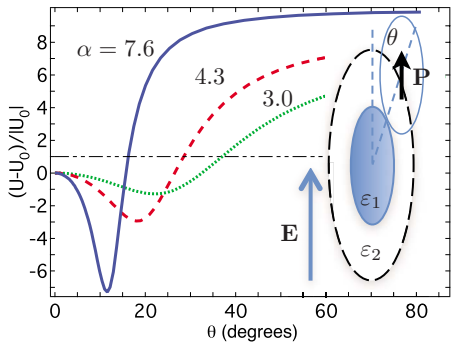

FIG. 3. (Color online) Calculated energy of a point dipole with ellipsoidal shape in the vicinity of an ellipsoidal particle. A schematic of the model is shown in the inset. The two particles maintain a point contact as the angle between them increases. The scaled interaction energy exhibits a minimum at nonzero angle with respect to the field. The dashed line denotes $U=0$.

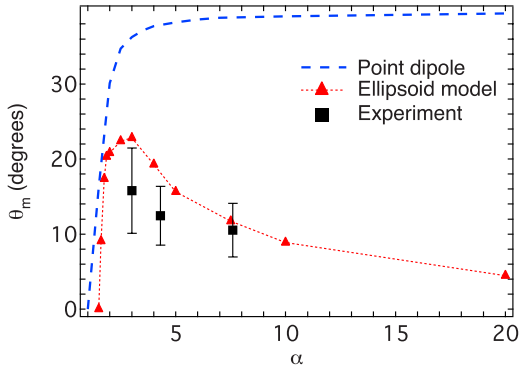

FIG. 4. (Color online) The angle of the interaction energy minimum at contact for point dipoles centered in two ellipsoids and the electrostatic model compared to the experiments for colloidal ellipsoids (triangles).

resulting potential is governed by the Laplacian, $\nabla^2\phi=0$. This is solved using ellipsoidal coordinates (ξ, η, ζ) to obtain the field due to the presence of an ellipsoidal particle using continuous potential conditions and the displacement field on the surface of the ellipsoid as boundary conditions. The potential outside the particle is [28,29]

$$\phi^+ = \frac{\phi_0(abc/2)(\epsilon_1-\epsilon_2)/\epsilon_2 \int_\xi^\infty 1/((s+a^2)R_s)ds}{1+(abc/2)(\epsilon_2-\epsilon_1)/\epsilon_2 \int_0^\infty 1/((s+a^2)R_s)ds}, \quad (2)$$

where $R_s=((s+a^2)(s+b^2)(s+c^2))^{1/2}$, ϵ_1 and ϵ_2 are the dielectric constant of the medium and particle, respectively, a is the particle polar radius, and b, c are the equatorial radii. For the prolate spheroids considered in this work ($b=c$),

$$\int_0^\infty \frac{ds}{(s+a^2)R_s} = \frac{1}{a^3e^3}\left[\ln\left(\frac{1+e}{1-e}\right) - 2e\right], \quad (3)$$

where the eccentricity is $e=\sqrt{1-b^2/a^2}$. The resulting electric field is given as $\mathbf{E}=-\nabla\phi^+$.

Next, we calculate the energy of a point dipole $\mathbf{P}$ oriented in the external field direction around the first particle, $U=\mathbf{P}\cdot\mathbf{E}$, again taking into account the ellipsoidal shape of the particles. The dielectric constants for the particle and the media in the calculation are $\epsilon_1=2.5$ and $\epsilon_2=80$, respectively. Figure 3 shows the energy as a function of the angle. The minimum energy occurs at $\theta \approx 22°$ for $\alpha=3$, while $\alpha=7.6$ exhibits a minima at $\theta \approx 12°$. Figure 4 shows the energy minimum as a function of aspect ratio. Notably, the angle of the energy minimum is nonmonotonic with respect to aspect ratio; the minimum occurs at higher angles as α increases from 1.5 to approximately 3, and then decreases to approximately 4.5° for $\alpha=20$. For rodlike particles, θ is expected to be close to zero. Particles with aspect ratio less than 1.5 exhibit minima at $\theta=0°$, and thus, slightly deformed particles should form chains which are aligned with the field, similar to spheres. While the use of a point dipole and ellipsoidal excluded volume for the second particle in our model is an approximation to the full solution of two interacting

ellipsoids, the calculated chaining angles, based on the minimum interaction energy, agree with the angles observed experimentally.

In conclusion, it has been shown in this work that the one- and two-dimensional assembly of colloidal ellipsoids in ac electric fields is remarkably different than spherical particles. Unlike spherical particles, ellipsoids form dipolar chains at an angle with the applied field. This angle persists in the assembled structure leading to open two-dimensional arrays. A model accounting for the electric field around a polarized ellipsoid quantitatively explains these experimental observations. Other important effects play roles in the field-driven self-assembly of high aspect ratio particles that are otherwise absent for suspensions of spheres. For instance, when the concentration exceeds the number density $\rho \gg 1/a^3$ before applying the field, hindered rotation causes the kinetic arrest of the suspension into a jammed state, thereby frustrating the order-disorder transition. In preliminary studies, we find that the ability to rapidly switch the induced colloidal interactions on and off can be used to overcome such jamming, leading to new approaches for nonequilibrium assembly and structural annealing. Annealing may also help increase the crystalline domain size, since this appears to be limited by defects formed during the collision between oppositely angled chains. In all, the unique structures formed by anisotropic colloidal particles in electric fields will likely serve as building blocks for new photonic, sensor, and electronic device technologies.

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