

NANO MICRO
small

Supporting Information

for *Small*, DOI: 10.1002/smll. 201102265

Liquid Crystal Order in Colloidal Suspensions of Spheroidal Particles by Direct Current Electric Field Assembly

*Aayush A. Shah , Heekyoung Kang , Kevin L. Kohlstedt , Kyung Hyun Ahn , Sharon C. Glotzer , Charles W. Monroe , and Michael J. Solomon **

Supporting Information

1. 3D Spherical Close Packed Colloidal Crystals

To assess the function of the electric field device described in the main text, we formed colloidal crystals of spheres, and compared the results with previous reports that used different particle and solvent systems.^[1,2] For an applied voltage of 0.66 V, a suspension of 1.4 μm poly(dimethylsiloxane) stabilized poly(methyl methacrylate) spheres^[3] in cyclohexylbromide and decalin (68:32 wt%) formed a dense multilayer colloidal crystal. High-quality positional ordering is apparent from CLSM images of the colloidal structure in a plane parallel to the electrode surface (Figure S-1a; the plane depicted is the first colloid layer above the electrode) and in a perpendicular plane (Figure S-1b; this image shows multilayer ordering at least up to $\sim 40 \mu\text{m}$ from the electrode surface). These close packed colloidal crystals formed rapidly ($t < 1 \text{ hr}$) and persisted while the constant voltage was applied. When the applied voltage was removed, the ordered array melted and the colloidal particles diffused from the electrode until an apparently homogeneous concentration between the electrode gap was achieved. Although small regions of the self-assembly are shown in Figure S-1 (and the figures of the main text), confocal imaging at multiple points in the specimen showed that the crystal structure of the electrodeposited colloids was uniform across the full 19.6 mm^2 cross sectioned area of the gap.

2. Experimental and Theoretical Particle Mobility Measurements in the presence of a DC Electric Field

Our hypothesis is that the electrophoretic mobility of the particles in the DC electric field causes the suspension to densify at the electrode. To evaluate this claim, we tracked the electric-field induced displacement of dilute suspensions of charged spheres in our device as a function of time, and compared to the predicted mobility based on a simultaneous measurement of the current. We used a 0.5-vol% spherical PS particle solution suspended in DMSO. The diameter of the spheres was 1.10 μm and the measured zeta potential ζ was -41 ± 11 mV. This solution was introduced in our device, which was connected to a potentiostat and placed on a confocal microscope stage. We applied an external voltage of 2.75 V, while simultaneously acquiring a time series of images at the rate of 1.4 fps in a plane parallel to the direction of the electric field (perpendicular to the electrode). The particles moved to the oppositely charged electrode, and the current was simultaneously recorded by the potentiostat.

We experimentally calculated the particle velocity due to the applied voltage by using particle-tracking algorithms based on the methods of Crocker and Grier.^[4] Particles suspended in DMSO without an applied electric field were confirmed to exhibit Brownian motion. In contrast, when the electric field was applied, the particles experienced motion due to electrophoretic force as well as random Brownian motion. The mean displacement in the direction of the field was calculated for every 5 frames (2.6 s), and then converted to an instantaneous mean velocity, to yield the instantaneous velocity over the duration of the experiment. The experimental mobility showed fluctuations due to random Brownian motion. From the measured current we computed the electric field to which the particles were

subjected using Equation (2) in the main text. We then calculated the particle velocity U for the particles, which have a thin Debye layer, using Smoluchowski's mobility equation (Equation (3) in the main text). As discussed in the main text, the experimental and theoretical electrophoretic velocities agreed well over the full duration of the experiment; the average variability was 11% as in Figure S-2. Thus, electrophoretic deposition was the dominant mechanism of motion due to the external electric field.

3. Force and Electrophoretic Mobility in the Smoluchowski limit

We calculate the electrophoretic mobility of a particle in the thin Debye layer limit ($\kappa D \rightarrow \infty$). Here, κ is the Debye length and D is the minor radial dimension of the spheroid. We begin by assuming the applied field \mathbf{E} in the capacitor is small compared to the field due to the particle double layer. The forces acting on the particle are the retarding drag of the particle, and the electrostatic force coupled with the hydrodynamic interactions of the ions. Thus, the force balance is:^[5]

$$\mathbf{F}_e = \mathbf{F}_d = -\left[\int_{V_f} \epsilon \epsilon_0 \nabla^2 \phi \frac{\partial \phi}{\partial x} dV \right] \mathbf{E} + \left[\int_{V_f} \epsilon \epsilon_0 \mathbf{u}_r \nabla^2 \phi \frac{\partial \phi}{\partial x} dV \right] \mathbf{E} = \mu \mathbf{A}_r \cdot \mathbf{U}, \quad (\text{S1})$$

where \mathbf{A}_r is the resistance matrix for the particle.^[5,6] The resistance matrix incorporates information about the shape of the particle. In Eqn. (S-1) ϕ , φ are the potentials induced by the ambient field and double layer around the spheroid, respectively, μ is the solvent viscosity and \mathbf{u}_r represents the disturbance flow field. Here, we do not include the effect of hydrodynamic interactions of the rods with the wall, and thus characterization of the electric field strength by measurement of the

mobility should be performed far from the cell boundary. To solve for the mobility U , it is required to solve two boundary value problems in f and φ with the disturbance velocity field \mathbf{u}_r .^[6,7] The result is

$$4\pi\mu\mathbf{A}_r \cdot \mathbf{U} = 4\pi\epsilon\epsilon_0\varphi_o\mathbf{A}_r \cdot \mathbf{E} . \quad (\text{S-2})$$

We note that when $\kappa R \rightarrow \infty$, the resistance matrix cancels out on both sides. With the boundary condition of constant surface potential $\varphi_o \rightarrow \zeta$, which gives rise to the familiar form of the electrophoretic mobility (Eqn. (4) of the main text)

$$U_s = \frac{\epsilon\epsilon_0\zeta}{\mu} E , \quad (\text{S-3})$$

where ζ is the zeta potential of the spheroid.

The component of the force acting on the charged particle acting in the direction of the electric field is given by

$$F_e = \epsilon\epsilon_0 E \zeta \langle A_r \rangle , \quad (\text{S-4})$$

with the averaged resistance tensor given as $\langle A_r \rangle$ (averaged over the two axis of translation).

4. Force and Electrophoretic Mobility of a prolate spheroid with a small Debye length

We calculate here the mobility of the prolate spheroid assuming a thin, but not negligible Debye layer. Equation (S-4) gives the magnitude of the electrophoretic force F_e acting on a prolate spheroid with a thin Debye layer. The average translational resistance matrix $\langle A_r \rangle$ for a prolate spheroid, averaged over the two axis of translation, is given by,

$$\begin{aligned}
\langle A_r \rangle &= \frac{64\pi}{3(4\chi + L^2\alpha_1)} + \frac{128\pi}{3(4\chi + D^2\alpha_2)}, \\
\alpha_1 &= \frac{4}{L^2\nu^2} \left(\chi - \frac{4}{L} \right), \\
\alpha_2 &= \frac{2}{L\nu^2} \left(\frac{4}{D^2} - \frac{\chi}{L} \right), \\
\chi &= \frac{4}{L\nu} \ln \left[\frac{L}{D} (1 + \nu) \right], \\
\nu &= \sqrt{1 - \frac{D^2}{L^2}}.
\end{aligned} \tag{S-5}$$

Here, L is the major axis length of the spheroid and D is the minor axis length and the geometric parameters α_1 , α_2 , χ , and ν are given in Eqn. (S-5).

To include effects of our finite Debye length, we use the asymptotic expansion by O'Brien and Ward^[8] in the limit of thin Debye lengths ($\kappa D \gg 1$) to calculate the mobility of a prolate ellipsoid. In this expansion, the electrophoretic mobility is written in terms of β and the deviation with respect to the Smoluchowski limit decays with $1/\kappa D$.

$$\beta \sim \frac{e^{\bar{z}/2}}{\kappa D}, \tag{S-6}$$

with $\bar{z} = ez\zeta/kT$. Here, e is the electronic charge, z is the charge number, k is the Boltzmann constant and T is the temperature. For our experimental conditions, $\beta \approx 0.13$

For $\beta \ll 1$, the mobility is

$$U = \frac{e\zeta}{\mu} E - \frac{\varepsilon\varepsilon_0 kT}{3e\mu} \left(\bar{z} - \frac{2}{z} \ln 2 \right) [f^{\parallel}(\beta) + 2f^{\perp}(\beta)] E, \quad (\text{S-7})$$

where $f^{\parallel}(\beta)$ and $f^{\perp}(\beta)$ are the geometric factors for the aligned and transverse cases, respectively. We note that when $\kappa D \rightarrow \infty$, $f^{\parallel}(0) = f^{\perp}(0) = 0$. Finally, if we scale U by Eqn. (S-3), we can write a scaled dimensionless mobility U/U_s that approaches unity at the Smoluchowski limit.

For our assembly conditions the scaled mobility is $U/U_s = 0.95 \pm 0.11$. Thus, we can conclude that our spheroids have sufficiently low surface potential and thin Debye layer such that the shape of the ellipsoid does not have a significant effect on the mobility and the force in comparison to the Smoluchowski limit. We note however that the mobility is strongly dependent on the surface potential of the spheroid to the extent that relatively small changes in charge number can have significant effects upon the ion retardation forces. For our system, we are safely within the Smoluchowski limit and calculations of the spheroidal Peclet numbers and forces are calculated in that limit.

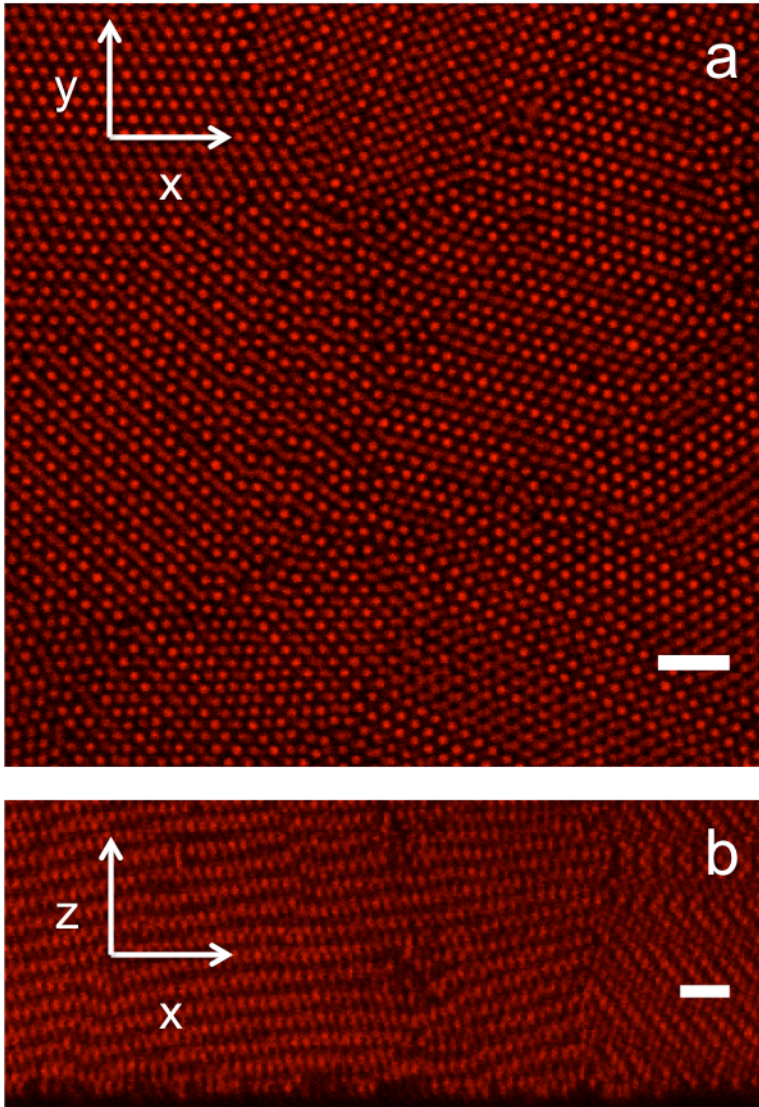


Figure S-1: Spherical PMMA particles dispersed in a mixture of CHB and decalin form colloidal crystals on application of a constant voltage of 0.66 V/mm. Scale bars are 5 μm . (a) Image of the self-assembled structure in a plane parallel to the electrode surface. (b) Image of the colloids in a plane perpendicular to the electrode surface. The electrode surface is at the bottom of the image.

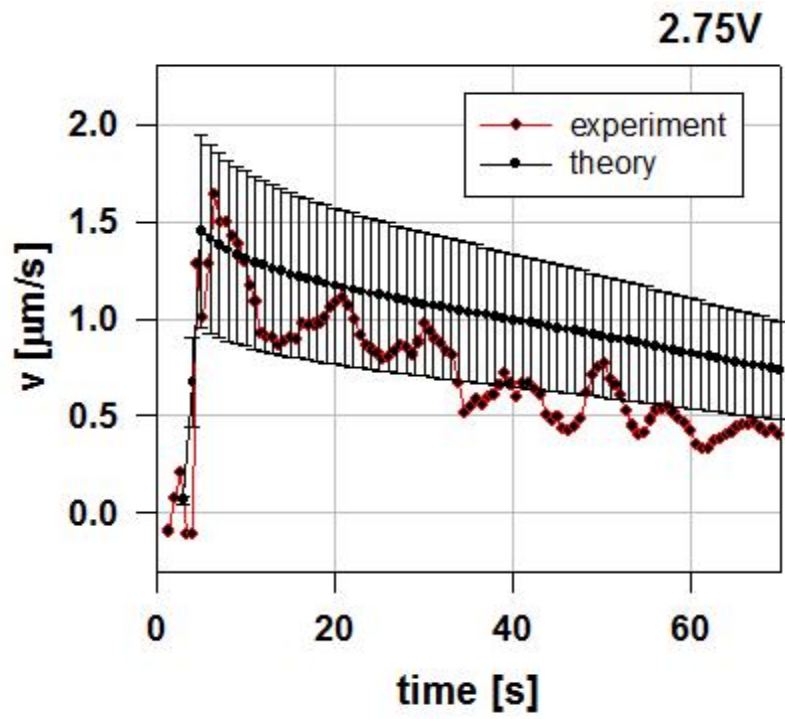


Figure S-2: Comparison of the mobility calculated theoretically and experimentally.

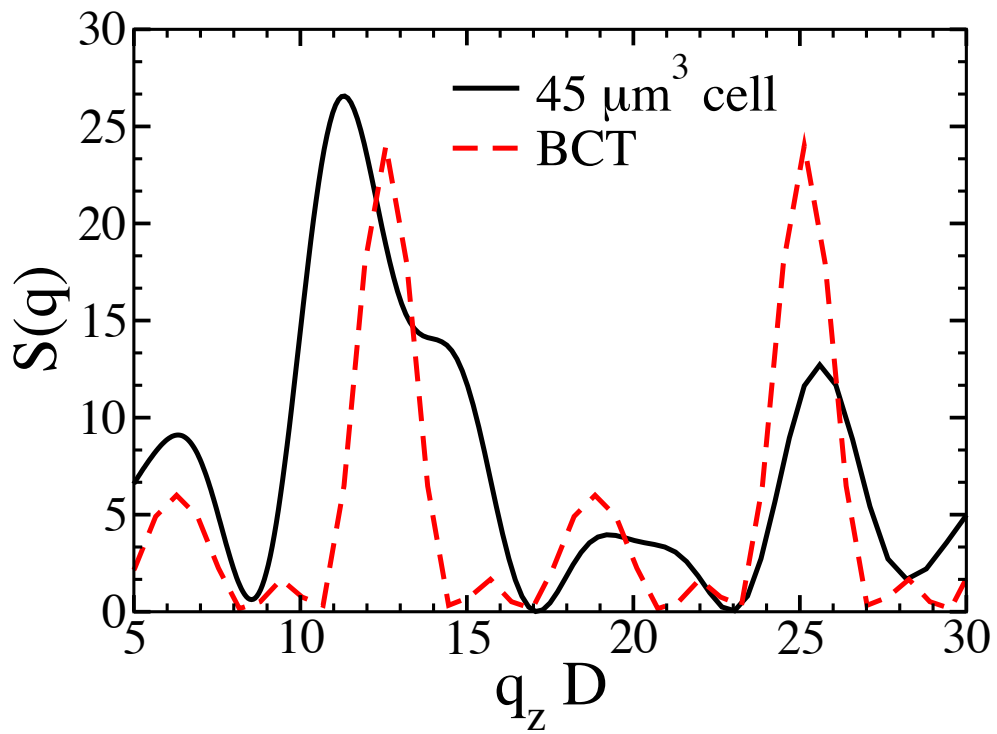


Figure S-3: Structure factor calculation for a $45 \mu\text{m}^3$ subsection of the assembled spheroids.

References:

- 1 A. L. Rogach, N. A. Kotov, D. S. Koktysh, J. W. Ostrander, G. A. Ragoisha, *Chemistry of Materials* 2000, **12**, 2721.
- 2 K. S. Napolskii *et al.*, *Langmuir* 2010, **26**, 2346.
- 3 A. Mohraz, M. J. Solomon, *Langmuir* 2005, **21**, 5298.
- 4 J. C. Crocker, D. G. Grier, *Journal of Colloid and Interface Science* 1996, **179**, 298.
- 5 M. Teubner, *The Journal of Chemical Physics* 1982, **76**, 5564.
- 6 B. J. Yoon, S. Kim, *Journal of Colloid and Interface Science* 1989, **128**, 275.
- 7 S. S. Dukhin, V. N. Shilov, *Advanced Colloid Interface Science* 1980, **13**, 153.
- 8 R. W. O'Brien, D. N. Ward, *Journal of Colloid and Interface Science* 1988, **121**, 402.