

Supplementary material:

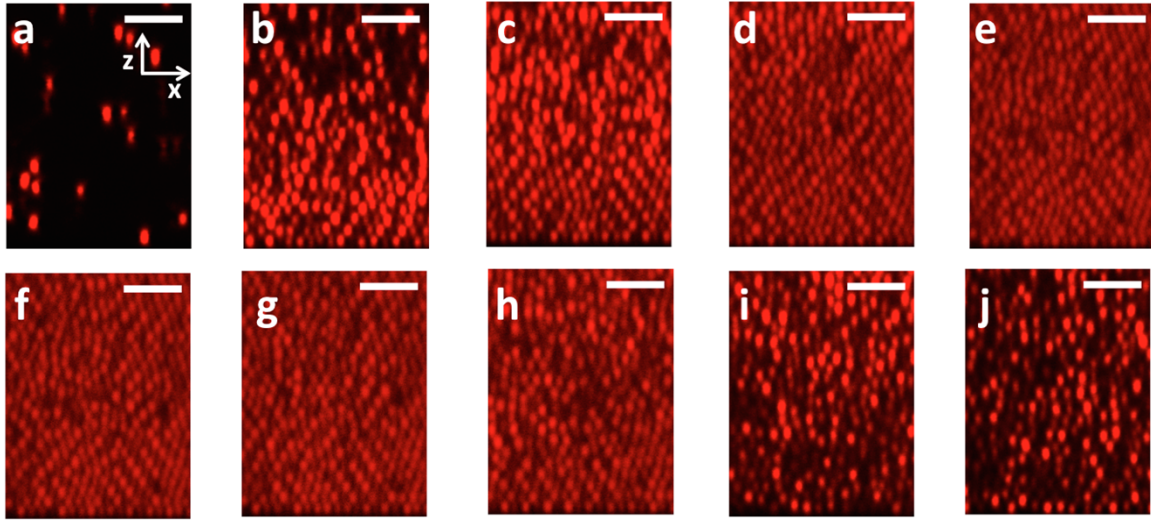
Kinetics of colloidal deposition, assembly, and crystallization in steady electric fields

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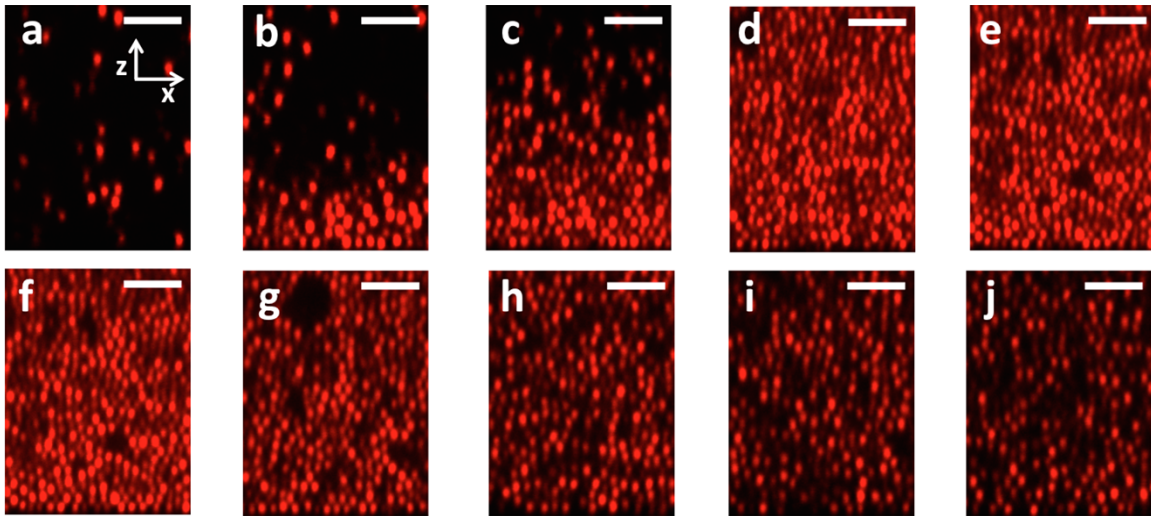
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Movie S1. *Electrophoretic colloidal deposition, crystallization and relaxation at $Pe = 0.25$.*

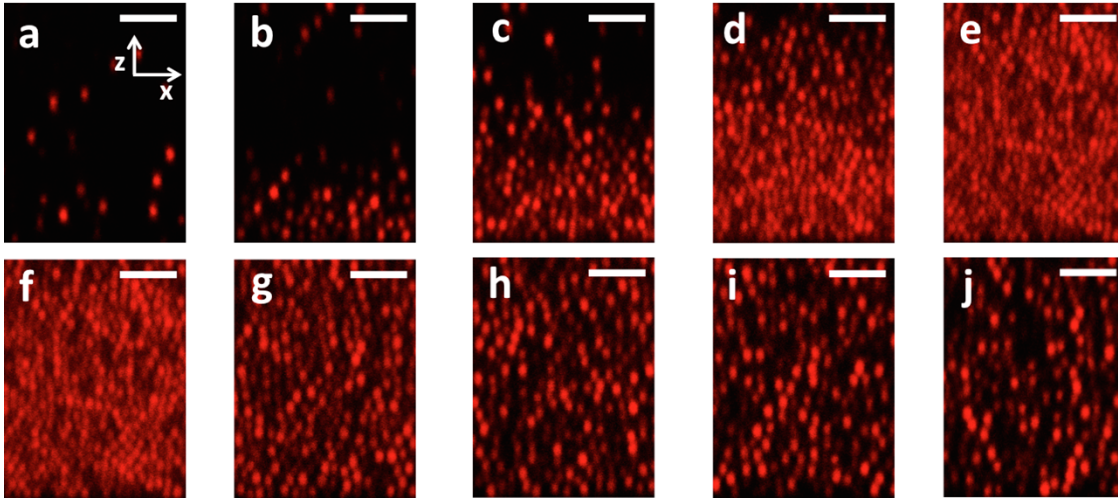
PHSA stabilized PMMA colloids, prepared at 2% initial volume fraction with 1 mM TBAC in a mixture of CHB and decalin, are subjected to a steady DC electric field ($i = 0.51 \text{ nA/mm}^2$, $Pe = 0.25$) and imaged with confocal microscopy in a 2D axial plane ($49.50 \times 15.93 \text{ }\mu\text{m}^2$) at a rate of one frame every three seconds. The colloids electrophoretically migrate toward and deposit at an ITO-coated electrode surface. After approximately 40 minutes of deposition, crystallinity propagates one-dimensionally through the deposit at a uniform rate of 198 nm/min. After 180 minutes of deposition, the DC field is switched off, and osmotic pressure-driven relaxation is imaged for 90 minutes. The movie is time lapsed to 200 frames per second. Scale bar is 5 μm .



SI Figure 1. CLSM images of DC electric field-assisted colloidal assembly at $Pe = 0.14$ (a-e) and subsequent relaxation of this structure upon removal of the field (f-j). a) just prior to application of the steady field; b) 30 minutes after application; c) 1 hour; d) 2 hours; e) 3 hours. f) relaxation at the moment of field removal; g) 5 minutes after removal of field; h) 15 minutes; i) 30 minutes; j) 90 minutes. Scale bar is $5 \mu\text{m}$.



SI Figure 2. CLSM images of DC electric field-assisted colloidal assembly at $Pe = 0.80$ (a-e) and subsequent relaxation of this structure upon removal of the field (f-j). a) just prior to application of the steady field; b) 30 minutes after application; c) 1 hour; d) 2 hours; e) 3 hours. f) relaxation at the moment of field removal; g) 5 minutes after removal of field; h) 15 minutes; i) 30 minutes; j) 90 minutes. Scale bar is $5 \mu\text{m}$.



SI Figure 3. CLSM images of DC electric field-assisted colloidal assembly at $Pe = 1.07$ (a-e) and subsequent relaxation of this structure upon removal of the field (f-j). a) just prior to application of the steady field; b) 30 minutes after application; c) 1 hour; d) 2 hours; e) 3 hours. f) relaxation at the moment of field removal; g) 5 minutes after removal of field; h) 15 minutes; i) 30 minutes; j) 90 minutes. Scale bar is $5 \mu\text{m}$.

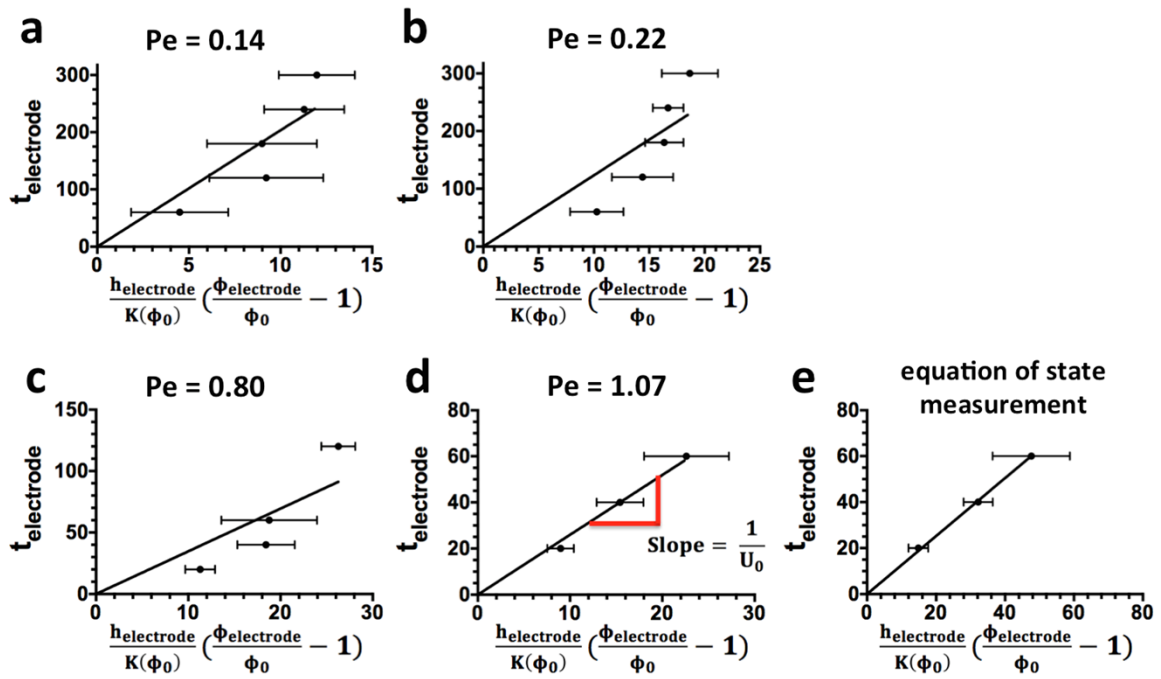
Supplementary Note 1. Electrostatic and electric field characterization of the particle-solvent systems

Colloidal sedimentation theory was adapted to deposition in steady electric fields to infer the electrophoretic velocity of dilute colloids (U_0) at each Pe condition studied, as well as for the characterization of the electric field force for the characterization of the equation of state of the charged colloids. As described by Russel et al. ¹ and as applied by Kim et al., ² mass conservation connects the time rate of change in colloidal volume during sedimentation to a flux in particle density. Under dilute conditions, the relationship is:

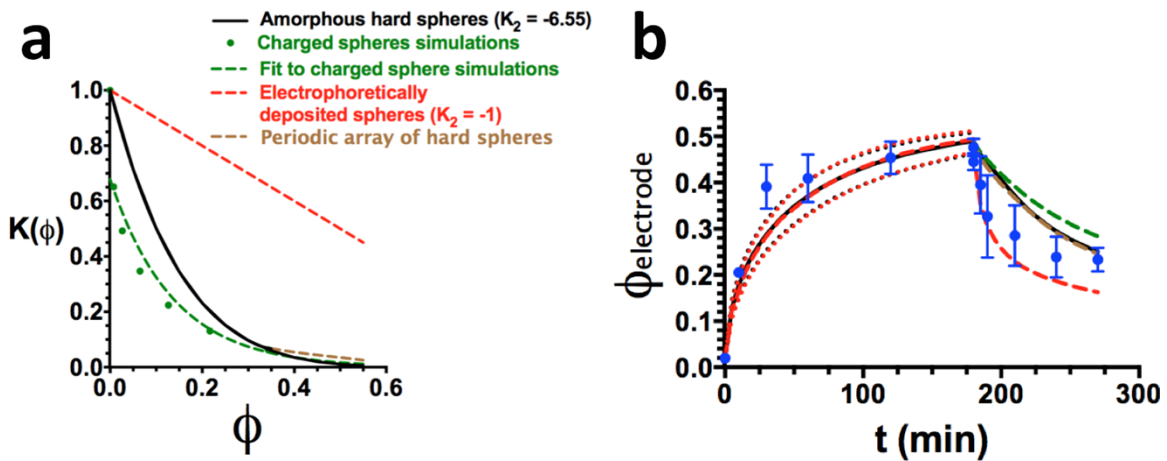
$$\frac{h_{electrode}}{t_{electrode}} = U_0 \frac{\phi_0 K(\phi_0)}{\phi_{electrode} - \phi_0} \quad \text{eqn. S1}$$

Here, $t_{electrode}$ is the time required to achieve a given volume fraction ($\phi_{electrode}$) of height $h_{electrode}$, and ϕ_0 is the initial volume fraction of the colloids. Here we take $h_{electrode}$ to be four colloidal layers, consistent with the resolution used elsewhere in the paper. $K(\phi)$ is given in the main text

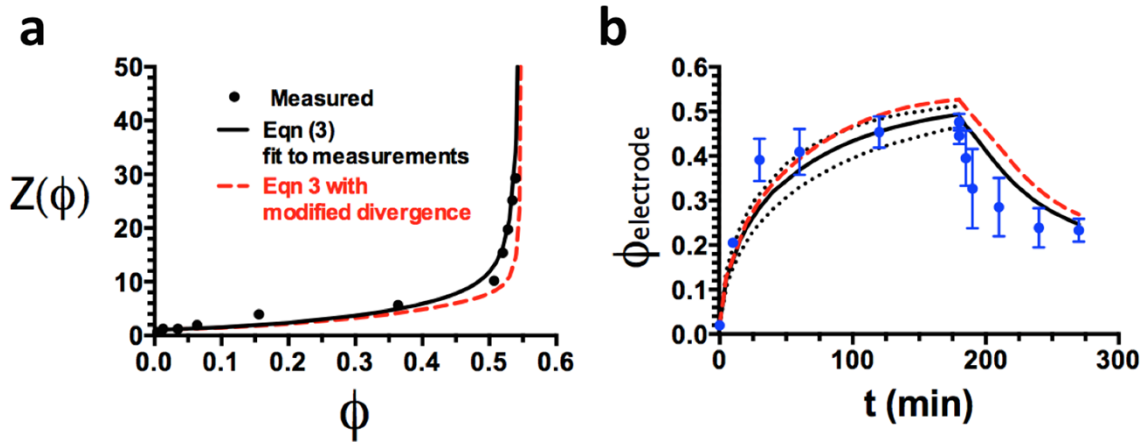
of the paper. From eqn. (S1), plotting $t_{electrode}$ versus $\frac{h_{electrode}}{K(\phi_0)} \left(\frac{\phi_{electrode}}{\phi_0} - 1 \right)$ yields a proportional relationship, the inverse of which is the free particle electrophoretic velocity (U_0). This characterization was carried out at early times ($t_{electrode} \leq 0.15t_{SS}$) at each condition. Initial volume fractions were 0.02 at all Pe conditions and 0.01 for the equation of state characterization. Linear regression of the data to eqn. S1 is shown in Supplementary Figure 4. U_0 values are reported in Table 1.



SI Figure 4. Analysis of early time deposition results to determine U_0 at a) $Pe = 0.14$, b) $Pe = 0.22$, c) $Pe = 0.80$, d) $Pe = 1.07$, and e) the equation of state characterization.



SI Figure 5. Comparison of mobility functions available for modeling, as parameterized by Table 1. a) $K(\phi)$ for hard spheres in the absence of an electric field (black, solid curve, $K(\phi) = (1-\phi)^{-K_2}$, $K_2 = -6.55$), for electrophoretically deposited spheres (red, dashed curve, $K(\phi) = (1-\phi)^{-K_2}$, $K_2 = -1$), for spheres in a periodic array (brown, dashed curve) as per the function reported in Sangani and Acrivos,³ and charged spheres in the high charging limit (green data points) as reported in Gilleland et al.,⁴ and an empirical fit to these simulation points (green, dashed curve). b) Figure 5b ($\phi_{\text{electrode}}(t)$, $Pe = 0.22$) reports eq. (1) deposition predictions for various mobility functions appropriate to this Pe . Note that deposition predictions are relatively insensitive to the mobility formulation; however, the fast initial decay of volume fraction in the relaxation portion of the experiment is well modeled by $K_2 = -1$. Predictions for $K(\phi)$ for crystalline and for charged spheres differ only to small degree from those for amorphous hard spheres.



SI Figure 6. Sensitivity of model results to changes in $Z(\phi)$. a) Comparison of experimentally derived $Z(\phi)$ with an alternative functional form with a steeper divergence (dashed curve) so as to better approximate the crystalline branch of a phase transition. b) Predictions of eqn (1) for $\phi_{\text{electrode}}(t)$ for deposition and relaxation at $Pe = 0.22$ with the two compressibility models reported in (a). The different divergence behavior has modest effect on the predictions, particularly for the late stage of the deposition. The model parameter in eqn (3) for the alternative $Z(\phi)$ is $a_1 = 4 - 1.4/\phi_p$, where $\phi_p = 0.55$.

SI References

- 1 W.B. Russel, D.A. Saville, and W.R. Schowalter, *Colloidal Dispersions (Cambridge Monographs on Mechanics)* (Reprint ed, 1992).
- 2 Y. Kim, A. A. Shah and M. J. Solomon, *Nature Communications*, 2014, **5**, 3676.
- 3 A. S. Sangani and A. Acrivos, *International Journal of Multiphase Flow*, 1982, **8**, 343-360.
- 4 W. T. Gilleland, S. Torquato and W. B. Russel, *Journal of Fluid Mechanics*, 2011, **667**, 403-425.