Electronic Supplementary Material (ESI) for Lab on a Chip

Multiple Electrokinetic Actuators for Feedback Control of Colloidal Crystal Size

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Supplemental Information

Movies

200_target.avi (3MB): 200 particle crystal assembled using EPEO vs. NDEP.

150_target.avi (2.5MB): 150 particle crystal assembled using EPEO vs. NDEP.

100_target.avi (2.5MB): 100 particle crystal assembled using EPEO vs. NDEP.

50_target.avi (2MB): 50 particle crystal assembled using EPEO vs. NDEP.

Electric Field

The electrodes in a quadrupole device (modeled as four point poles) have an analytical electric potential given by,[1]

$$V(x,y) = \frac{V_o}{2}\ln\left[\frac{x^4 + y^4 + 2\left(x^2 - y^2 + x^2y^2\right) + 1}{x^4 + y^4 + 2\left(y^2 - x^2 + x^2y^2\right) + 1}\right] \tag{1}$$

$$\boldsymbol{E} = -\nabla V(x,y) \tag{2}$$

where x and y are non-dimensional coordinates normalized by half the electrode gap (with the origin at the quadrupole center), V is the electric potential, V_o is the magnitude of the applied voltage, $\boldsymbol{E}$ is the electric field vector, and $E_{mag} = |\mathbf{E}|$ is the magnitude of the local electric field.

Dielectrophoresis

At high frequencies, induced dipoles on particles interact with the nonuniform electric field (Eq (1)). The in-plane spatial variation of this scalar potential energy $u^{dep}(x,y)$ and the associated time-averaged DEP force $\boldsymbol{F}^{dep}$ due to an inhomogeneous electric field $\boldsymbol{E}$ is given by,[2, 3]

$$\begin{aligned} u^{dep}(x,y) &= -2kT\lambda f_{cm}^{-1}\left|\boldsymbol{E}^*\right|^2 \\ \boldsymbol{F}^{dep} &= -\nabla u^{dep}(x,y) \end{aligned} \tag{3}$$

where k is Boltzmann's constant, T is absolute temperature, $\boldsymbol{E}^* = \boldsymbol{E}/E_0$ is the local normalized electric field, $E_0 = 0.5V_{pp}/d_g$ is the normalization constant with d_g being separation between cross

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electrode pairs and V_{pp} is the applied AC field's peak-to-peak voltage. The ratio λ of the relative polarization and Brownian energies[4] is given as $\lambda = \pi\varepsilon_m a^3(f_{cm}E_0)/kT$ where a is the radius of the colloidal particle. The Clausius-Mosotti factor, f_{CM}, determines whether the particle moves towards the field minima or maxima[3] and is given by,[3]

$$f_{cm} = \mathrm{Re}\left[\left(\tilde{\varepsilon}_p - \tilde{\varepsilon}_m\right)/\left(\tilde{\varepsilon}_p + 2\tilde{\varepsilon}_m\right)\right] \tag{4}$$

where $\tilde{\varepsilon}_m$ and $\tilde{\varepsilon}_p$ are complex particle and medium permitivities of the form, $\tilde{\varepsilon}=\varepsilon\text{-i}\sigma/\omega$, where σ is conductivity, and ω is angular frequency. Particle conductivity is given as $\sigma_p=2K_n/a$, where K_n is surface conductance.[5] When $f_{cm} < 0$ ($f_{cm} > 0$) the particle is less (more) polarizable than the medium and is transported to the field minimum (maximum).

Electrophoresis and Electroosmosis

A potential difference applied at electrode surface causes ions with electrostatic double layers to move and drag fluid, a transport mechanism referred to as electroosmosis. Simultaneously, charged colloids undergo electrophoresis when they become attracted to electrodes of opposite polarity.[6] The superposition of electrophoresis and electroosmosis is linearly proportional to the local electric field,[7]

$$\boldsymbol{V}_{EPEO} = \frac{\varepsilon_m\left(\zeta_p - \zeta_w\right)}{4\pi\mu}\boldsymbol{E} \tag{5}$$

$$\boldsymbol{F}_{EPEO} = 6\pi\mu a\boldsymbol{V}_{EPEO} \tag{6}$$

where μ is the medium viscosity and the zeta potential, ζ, where the subscripts denote particle (p) and wall (w). The force, $\boldsymbol{F}_{EPEO}$, is the net electroosmotic flow scaled by the Stokes drag coefficient.

Size Dependent Crystallinity Order Parameter

To compute the size dependence of $\langle C_6\rangle$ for 2D hexagonal close packed particles with a hexagon morphology, the total number of particles, N, based on the number of shells, S, (see Fig S1A) is given by,[8]

$$N = 3S\left(S+1\right)+1 \tag{7}$$

which can be inverted to obtain the number of shells based on the number of particles as,

$$S = -\left(1/2\right) + \left[\left(1/3\right)\left(N-1\right)+\left(1/4\right)\right]^{1/2} \tag{8}$$

The number of interior, vertex, and edge (non vertex) particles can be found from Eq (7) as,

$$\begin{aligned} N_{\text{interior}} &= 3S\left(S-1\right)+1 \\ N_{\text{edge}} &= 6S-6 \\ N_{\text{vertex}} &= 6 \end{aligned} \tag{9}$$

which allows $\langle C_6\rangle$ to be computed using individual particle C_6 values shown in Fig S1A as,

$$\left\langle C_6\right\rangle_{HEX} = N^{-1}\left[6N_{\text{interior}} + 4N_{\text{edge}} + 3N_{\text{vertex}}\right] = N^{-1}6\left(3S^2+S\right) \tag{10}$$

Although the above equations are intended for an integer number of shells, Eq (8) can be substituted for S on the right hand side of Eq (10) to compute $\langle C_6 \rangle$ as a continuous function of N.

To compute the size dependence of $\langle C_6 \rangle$ for 2D hexagonal close packed particles with a square morphology, N, can be related to the number of particles on one side of the square, S_P, (see Fig S1B) as,[9]

$$N = S_P\left(S_P + 1\right) \tag{11}$$

which can be inverted as,

$$S_P = -\left(1/2\right) + \left[N + \left(1/4\right)\right]^{1/2} \tag{12}$$

The following formulas capture the number of particles having different individual C_6 values as,

$$\begin{aligned} N_6 &= \left(S_P - 2\right)\left(S_P - 1\right) \\ N_5 &= S_P - 1 \\ N_4 &= 2\left(S_P - 2\right) \\ N_3 &= S_P + 1 \\ N_2 &= 2 \end{aligned} \tag{13}$$

where the number of interior, N_{I}, and edge, N_{E}, particles can be found from Eq (13) as,

$$\begin{aligned} N_{\mathrm{I}} &= \left(S_P - 2\right)\left(S_p - 1\right) \\ N_{\mathrm{E}} &= 4S_P - 2 \end{aligned} \tag{14}$$

Eq (13) also allows $\langle C_6 \rangle$ to be computed using individual particle C_6 values shown in Fig S1B as,

$$\left\langle C_6 \right\rangle_{SQ} = N^{-1} \sum_{x=2}^{6} x N_x = N^{-1}\left(6S_P^2 - 2S_P - 2\right) \tag{15}$$

which can be computed as a continuous function of N by substituting Eq (12) for S_P on the right hand side of Eq (15).

Size Dependent Radius of Gyration

To compute the radius of gyration, R_g, for 2D hexagonal close packed particles within regular polygon morphologies, it is useful to consider the area, A_{HCP}, occupied by N hexagonal close packed disks with area fraction, $\phi_{HCP}=6^{-1}\pi 3^{0.5}$, as,

$$A_{HCP} = \pi a^2 N \phi_{HCP}^{-1} = 6 \cdot 3^{-0.5} a^2 N \tag{16}$$

which can be equated to the area of a square, $A_{SQ}=L_{SQ}^2$, to determine the length of each side vs. N as,

$$L_{SQ} = 6^{0.5} 3^{-0.25} a N^{0.5} \tag{17}$$

which can then be used in the expression for R_g for a square as,

$$R_{g,SQ} = 2^{0.5}12^{-0.5}L_{SQ} = 3^{-0.25}aN^{0.5} \tag{18}$$

Similarly, A_{HCP} in Eq (16) can be equated to the area of a hexagon, $A_{\mathrm{HEX}}=(3/2)3^{0.5}L_{\mathrm{HEX}}^{2}$, to determine the length of each side vs. N as,

$$L_{HEX} = 2\cdot 3^{-0.5}aN^{0.5} \tag{19}$$

which can then be used in the expression for R_{G} for a hexagon as,

$$R_{g,HEX} = 2^{-1}5^{0.5}3^{-0.5}L_{HEX} = 5^{0.5}3^{-1}aN^{0.5} \tag{20}$$

Figure Captions

Figure S1. Hexagonally closed packed array of particles confined to (A) hexagon and (B) square morphologies with colors indicating the number of hexagonal close packed neighbors as $C_6 = 6$, blue; $C_6 = 5$, black; $C_6 = 4$, green; $C_6 = 3$, red; $C_6 = 2$, yellow.

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Figure S1