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,\textsuperscript{1}

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

\begin{equation}
E = -\nabla V(x, y)
\end{equation}

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, \(E\) is the electric field vector, and \(E_{mag} = |E|\) 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 \(F^{dep}\) due to an inhomogeneous electric field \(E\) is given by,\textsuperscript{2,3}

\begin{equation}
u^{dep}(x, y) = -2kT \hat{a} f_{cm}^{-1} |E^*|^2
\end{equation}

\begin{equation}
F^{dep} = -\nabla u^{dep}(x, y)
\end{equation}

where \(k\) is Boltzmann’s constant, \(T\) is absolute temperature, \(E^* = E/E_0\) 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 \( \lambda \) 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,

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

where \( \tilde{\varepsilon}_m \) and \( \tilde{\varepsilon}_p \) are complex particle and medium permitivities of the form, \( \tilde{\varepsilon} = \varepsilon - i\sigma/\omega \), where \( \sigma \) is conductivity, and \( \omega \) 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,\(^7\)

\[
V_{EPEO} = \frac{\varepsilon_m (\zeta_p - \zeta_w)}{4\pi \mu} E
\]

\[
F_{EPEO} = 6\pi \mu a V_{EPEO}
\]

where \( \mu \) is the medium viscosity and the zeta potential, \( \zeta \), where the subscripts denote particle (p) and wall (w). The force, \( F_{EPEO} \), 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,\(^8\)

\[
N = 3S(S + 1) + 1
\]

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

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

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

\[
N_{\text{interior}} = 3S(S - 1) + 1
\]

\[
N_{\text{edge}} = 6S - 6
\]

\[
N_{\text{vertex}} = 6
\]

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

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

\[
N = S_p (S_p + 1)
\]

which can be inverted as,

\[
S_p = -(1/2) + \left[N + (1/4)\right]^{1/2}
\]

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

\[
\begin{align*}
N_6 &= (S_p - 2)(S_p - 1) \\
N_5 &= S_p - 1 \\
N_4 &= 2(S_p - 2) \\
N_3 &= S_p + 1 \\
N_2 &= 2 
\end{align*}
\]

where the number of interior, \( N_I \), and edge, \( N_E \), particles can be found from Eq (13) as,

\[
\begin{align*}
N_I &= (S_p - 2)(S_p - 1) \\
N_E &= 4S_p - 2
\end{align*}
\]

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

\[
\langle C_6 \rangle_{SQ} = N^{-1} \sum_{x=2}^{6} xN_x = N^{-1} \left(6S_p^2 - 2S_p - 2\right)
\]

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,

\[
A_{HCP} = \pi a^2 N \phi_{HCP}^1 = 6 \cdot 3^{-0.5} a^2 N
\]

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,

\[
L_{SQ} = 6^{0.5} 3^{-0.25} a N^{0.5}
\]

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

$$L_{\text{HEX}} = 2 \cdot 3^{-0.5} a N^{0.5}$$

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

$$R_{g,\text{HEX}} = 2^{-1}5^{0.5}3^{-0.5} L_{\text{HEX}} = 5^{0.5} 3^{-1} a N^{0.5}$$

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.

References

Figure S1