Dielectrophoretic On-chip Manipulation and Assembly of Nanoparticles, Microparticles and Droplets

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On-chip colloidal engineering

**Microelectronics**

- Electrical (photonic) signals
- Electrical (photonic) signals

**Microfluidics**

- Electrical signals or pressure
- Liquid manipulation, reactions and analysis

**Nanogen**

- ?

- Electrical signals
- Synthesis of micro- and nanostructured materials

**IBM**

- ?
Dielectrophoretic force acting on particles in planar electrode gap

\[ \vec{F}_{\text{DEP}} = 2\pi \varepsilon_1 \text{Re} \{ K(w) \} R^3 \nabla E_{\text{rms}}^2 \]

The Clausius – Mossotti function \( K \) may have complex frequency behavior

\[
\text{Re} \{ K \} = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} + \frac{3(\varepsilon_1 \sigma_2 - \varepsilon_2 \sigma_1)}{\tau_{MW}(\sigma_2 + 2\sigma_1)^2 \left(1 + w^2 \tau_{MW}^2\right)}
\]

\[
\tau_{MW} = \frac{\varepsilon_2 + \varepsilon_1}{\sigma_2 + 2\sigma_1}
\]

Maxwell-Wagner charge relaxation time

- Positive dielectrophoresis: \( K > 0 \). Particles are attracted to electric field intensity maxima.
- Negative dielectrophoresis: \( K < 0 \). Particles are repelled.
Phenomenology of $F_{\text{DEP}}$

\[
\vec{F}_{\text{DEP}} = 2\pi \varepsilon_0 \varepsilon_1 K R^3 \nabla E^2 \\
K = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}
\]

- $F_{\text{DEP}}$ depends upon the magnitude and sign of the Clausius – Mossotti function:
  - **Positive dielectrophoresis:** $K > 0$ (or $\varepsilon_2 > \varepsilon_1$). Particles are attracted to electric field intensity maxima.
  - **Negative dielectrophoresis:** $K < 0$ (or $\varepsilon_2 < \varepsilon_1$). Particles are attracted to electric field intensity minima and repelled from maxima.

- $F_{\text{DEP}}$ is proportional to particle volume.
- $F_{\text{DEP}}$ is proportional to the dielectric permittivity of the medium, $\varepsilon_2$.
- The DEP force vector is directed along the electric field gradient, which, in general, is not parallel to the electric field vector.
Advantages of using alternating (AC) field

- Avoid electrophoresis and electroosmosis
- Avoid electrolysis
- Works with any particles
- Use the frequency dependence of $F_{DEP}$

A couple of important electrode geometries ($K > 0$)
Example: Dielectrophoretic behavior of latex microspheres

Low dielectric permittivity $\varepsilon_2$
Increased conductivity $\sigma_2$ (counterion atmosphere)

\[
\text{Re} |K| \rightarrow \begin{cases} 
\frac{\sigma_2 - \sigma_1}{\sigma_2 + 2\sigma_1} > 0 & \text{for } w \tau_{MW} \ll 1 \\
\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} < 0 & \text{for } w \tau_{MW} >> 1 
\end{cases}
\]

- DC conduction governs low-frequency DEP attraction
- Dielectric polarization governs high-frequency DEP repulsion

Second field-induced force: Particle chaining

Interactions between induced dipoles along the direction of the field

\[ F_{\text{chain}} \text{ (max)} = -C \pi \varepsilon R^2 K^2 E^2 \]
\[ 3 < C < 10^3 \]

- \( F_{\text{chain}} \) is always attractive.
- Proportional to \( K^2 \)
- Weaker dependence on particle size than the direct dielectrophoretic force.
Summary:
Electrophoretic + Dielectrophoretic interactions on chip

\[ E_0 \]
\[ \nabla E_0 \]
\[ F_{\text{chain}} \]
\[ F_{\text{EP}} \]
\[ F_{\text{DEP}} \]

DC/AC field
Overview – objects for on-chip manipulation

- **Nanoparticles**: 5 - 10 nm
- **Microspheres**: 500 - 1000 nm
- **Live cells**: 5 - 10 µm
- **Droplets (from particle suspensions)**: 500 - 1000 µm
Dielectrophoretic assembly of microwires from gold nanoparticles

Suspension of nanoparticles 10-25 nm

High concentration along the field gradient

Depleted area behind the wire

Planar electrode

Speed of growth \( \leq 50 \, \text{µm/s} \)

Experimental image

Theoretical gradient strength

500 µm
Dielectrophoretic assembly of conductive microwires from metallic nanoparticles in suspension

High magnification, 8X speed

Microwire structure by SEM

Bulk

Surface
Quantification of microwire growth rate

- Assembly rate is not a function of field intensity $E$
- Diffusion controlled process
- Bulk growth faster due to larger diffusion volume
Modeling and simulation of microwire assembly

Finite element electrostatic calculations using conformal triangles mesh (TriComp package)
Simulation of the kinetics of microwire assembly

Bulk wires

Simulation

Experimental image – bulk wires

Realistically reproduces the dynamics and features observed in real wire growth

Simulation of the kinetics of assembly

Surface wires

Simulation proves the role of low-\(\varepsilon\) substrate and initial conditions
Control of wire branching and position

Straight unbranched wire through the bulk
(high viscosity)

Parallel arrays on surface
(high frequency, low intensity)
Predicting wire assembly in the presence of conductive object in the liquid

Growing wires would spontaneously complete the circuit through the object.
Summary – Microwire assembly

We have learned to control
- Wire type – bulk or surface
- Assembly pattern – single straight or massively parallel
- Growth direction & interfacing

We can simulate and predict
- The kinetic assembly process
- The growth pattern and direction

Ready for nanotech applications
- Bioelectronic interfacing
- Chemical and biological sensors
- Structures with anisotropic thermal and electrical properties

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- Droplets (from particle suspensions): $500 - 1000 \text{ µm}$
Photonic crystals via microsphere assembly ...

... can be made exactly the way we want them, but slow and expensively

... have been made quickly, but without long range orientation
Overview of geometries used in electrical field driven assembly

Holgado et al., 1999, Rogach et al., 2000, etc.

S. Fraden, A. Blaaderen, 2001

Trau, Saville and Aksay, 1995, Gong and Marr, 2001, etc.

DC Voltage

Metal

Oil

Solid

ITO Glass

Glass

Presented here
Dielectrophoretic assembly of electrically tunable photonic crystals

Experiment schematics

Latex or silica
500 - 1000 nm
Dynamics of the DEP controlled crystallization:
Laser diffraction
Stages of the 2D crystallization: Microscopy and diffraction

- Single domain cm-scale crystals with specific orientation
- Switchable 2D phase transitions

Quantitative measurements via the 2D crystal diffraction pattern

von Laue equation for 2D point scatterers

\[ h = \frac{n \lambda_c}{\sin \theta} \]

Corrected for the refractive index of the composite media

\[ \lambda_c = \frac{\lambda_o}{(\phi n_p^2 + (1-\phi)n_w^2)^{1/2}} \]

\[ \sin \theta = \frac{n_{\text{cell}}}{n_{\text{air}}} \sin \theta_{\text{meas}} \]

Corrected for refraction on exiting the cell
Effect of electrolyte concentration on distance between particle surfaces

- Precise simple measurements of interactions in particle ensembles
Controlling the crystallization: Effect of field and frequency

Scaling approximation

\[
- \frac{F_{\text{chain}}^T}{C \pi \varepsilon_1 K(\omega)^2} = \text{const} = r_i^2 E_{i,\text{chain}}^2
\]

Data for particles of three sizes: 0.7, 1 and 1.4 \( \mu \)m

- Crystallization threshold not a strong function of particle size
Controlling the crystallization – effect of glycerol

Assembly of 2D crystals is prevented above 25 % glycerol

![Graph showing the effect of glycerol on 2D crystals, 1D Chains, and Disordered systems.]

- Separations, study of colloidal self-organization fundamentals

DEP assembly of cell chains for biosensors

5 μm yeast cells

DEP chaining of 0.1% yeast cell solution in 10 μM PBS

50-60 V
200 Hz
Cell-particle dipole interactions as a function of voltage and frequency
Summary – 1D and 2D arrays by dielectrophoresis

- Rapid and simple assembly technique
- Extremely large crystals with specific orientation without microfabricated templates
- Model for combination of chaining and dielectrophoresis supported by direct observation and diffraction
- Can measure electrostatic interactions in particle ensembles
- Electrically tunable photonic devices demonstrated
- Can be applied to making cell-nanoparticle biocomposites
Dielectrophoretic on-chip manipulation of suspended droplets

... can we manipulate droplets and why?
Conventional microfluidics with channels

Permanently rigged “pipes”, specific design for pre-defined operations

More like Factory-on-a-chip than Lab-on-a-chip
Handling dispersions and biological objects a problem
Previous work on moving droplets by electric fields

The channels are gone, but the walls are still there

Contact angle hysteresis, surface fouling, precipitation or aggregation forbidden, transport of cells, particles and biomolecules problematic


Dielectrophoretic chips with suspended microdroplets: **Basic principle**

Liquid – liquid chip system without walls or channels
Calculated field intensities for the two equilibrium droplet positions.

Droplet-chip geometry to scale.
Finite element electrostatic calculations using conformal triangles mesh (TriComp package).
Fluid chip function 1:
Dielectrophoretic transport of multiple droplets in series
Dielectrophoretic manipulation: 
Droplet speed and field intensity

\[ \vec{F}_{\text{hydr}} \approx 6\pi \mu RV = \vec{F}_{\text{DEP}} = 2\pi \varepsilon_1 \text{Re} |K(w)| R^3 \nabla E^2 \]
**Suspended drop transport: Energy dissipation**

- No energy dissipation is detected by current monitoring or drop observations
- Estimate for the energy required to move a 500 nL water droplet 1 cm at 2 mm/s:

<table>
<thead>
<tr>
<th>Assumptions and approximations</th>
<th>Droplet moved in fluorinated oil</th>
<th>Hemispherical droplet dragged on solid surface</th>
<th>Viscous flow in microfluidic channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>type of estimation</td>
<td>Overestimate</td>
<td>Underestimate</td>
<td>Underestimate</td>
</tr>
<tr>
<td>Energy required / J</td>
<td>≤ $9.4\times10^{-10}$</td>
<td>≥ $1.6\times10^{-7}$</td>
<td>≥ $1.4\times10^{-4}$</td>
</tr>
<tr>
<td>Energy ratio</td>
<td>1</td>
<td>170</td>
<td>150000</td>
</tr>
</tbody>
</table>

*Extremely low energy needed for suspended droplet transport*
Fluid chip function:
Mixing of two droplets at electrode track junctions

gold nanoparticles →
sulfate latex →
Fluid chip function:
Complex precipitated shells

$\text{Ca}_3(\text{PO}_4)_2$
precip. shell $\rightarrow$

Unique possibilities for materials synthesis and encapsulation
Fluid chip function:
Mixing of two droplets of aqueous suspension and encapsulation inside oil droplet

sulfate latex →
gold nanoparticles →
dodecane →
"Outside-in" templating:
Advanced structured particles templated by surface tension

The droplets float suspended on the surface of perfluorinated hydrocarbon oil.

Droplet shape depends on Bond number

\[ \beta = \frac{\Delta \rho g b^2}{\gamma_{12}} \]

For \( \beta \geq 1 \) the droplets flatten.
Droplet assembly
Examples of the advanced structured obtained

\[ \beta \rightarrow 0 \]
Spherical

\[ \beta > 0 \]
Thoroidal “doughnuts”
Metal coated doughnuts
Half-magnetic

Dielectrophoretic chips with microdroplets: Internal particle separations

Thermal gradients due to evaporation lead to Marangoni effect and thermophoretic particle separation on top.
Fluid chip parallelization:
Simultaneous materials synthesis in multiple on chip droplet “microreactors”

Massive parallelization possible
Encapsulation inside oil droplet: Polymerized shells

Photopolymerized particles with hexanediol diacrylate (HDDA)

Encapsulated suspension droplets

Polymer laced with gold nanoparticles

All products can be encapsulated
Summary: Liquid-Liquid Microfluidics

- Microfluidics without any walls or channels
- Simple, inexpensive, flexible, great experimentation tool
- Fundamental effects yet to be explained: droplet charging and internal polarization
- Technological potential for
  - Parallelization
  - Single cell/biomolecule transport
  - Materials synthesis by particle assembly or precipitation
  - Precipitation and agglutination microassays

On-chip field driven assembly

- Efficient and controllable
- Works with particles on any size
- Engineered microfabrication
- Allows interfacing colloid structures with electric microcircuits

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http://crystal.che.ncsu.edu
http://www.che.ncsu.edu/velevgroup/