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

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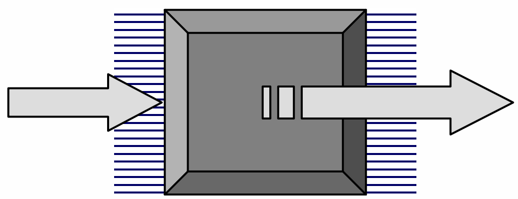
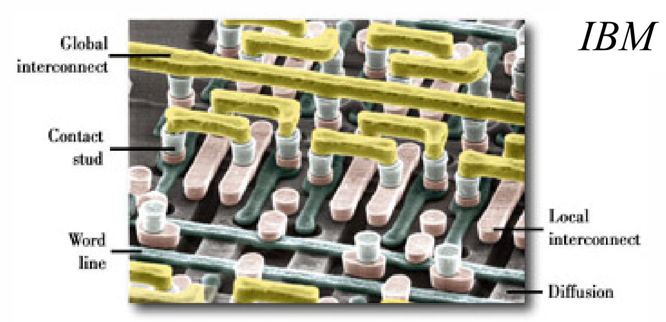
On-chip colloidal engineering

Microelectronics

Electrical
(photonic)
signals



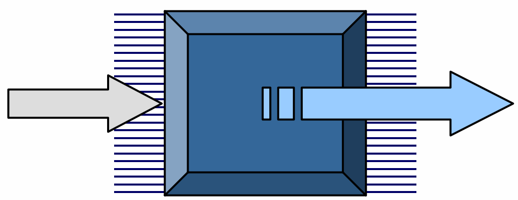
Electrical
(photonic)
signals



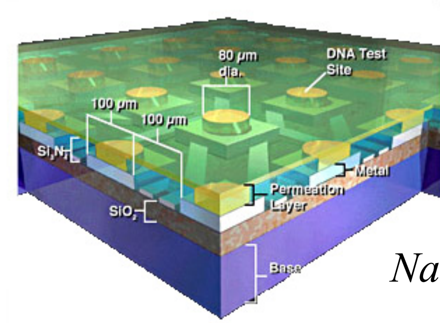
IBM

Microfluidics

Electrical
signals or
pressure



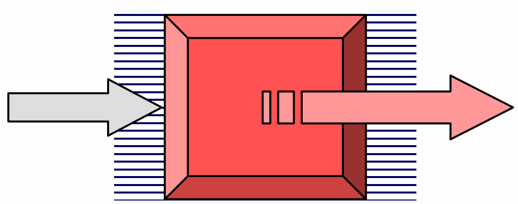
Liquid manipulation,
reactions and analysis



Nanogen

?

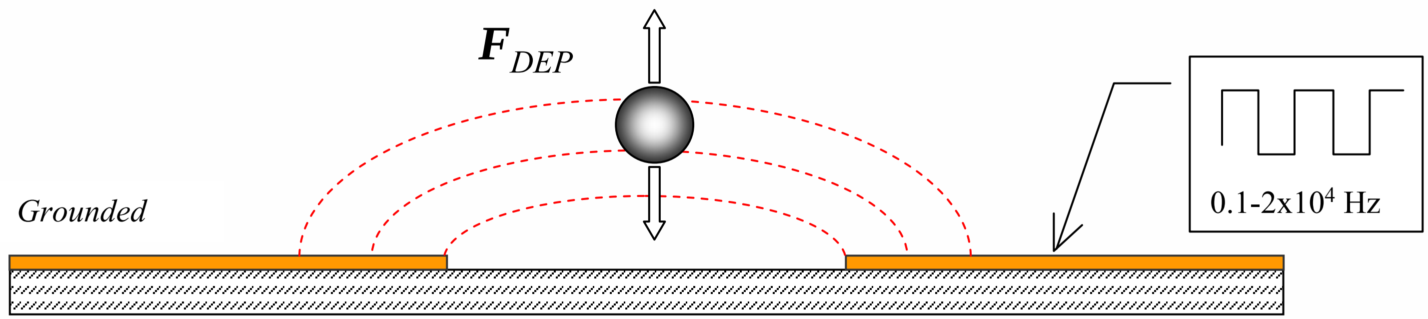
Electrical
signals



**Synthesis of micro- and
nanostructured materials**

?

Dielectrophoretic force acting on particles in planar electrode gap



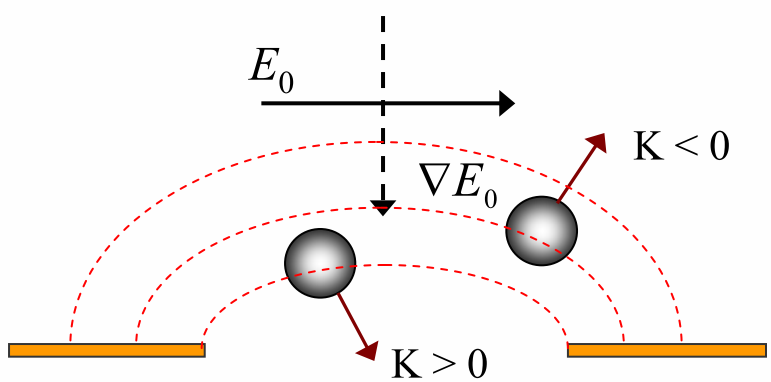
$$\vec{F}_{DEP} = 2\pi\,\varepsilon_1\,\mathrm{Re}\left|\underline{K}(w)\right|\,R^3\,\nabla E_{rms}^2$$

The Clausius – Mossotti function *K* may have complex frequency behavior

$$\mathrm{Re}\left|\underline{K}\right| = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} + \frac{3\left(\varepsilon_1\,\sigma_2 - \varepsilon_2\,\sigma_1\right)}{\tau_{MW}\left(\sigma_2 + 2\sigma_1\right)^2\left(1 + w^2\,\tau_{MW}^2\right)}$$

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

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_{DEP}

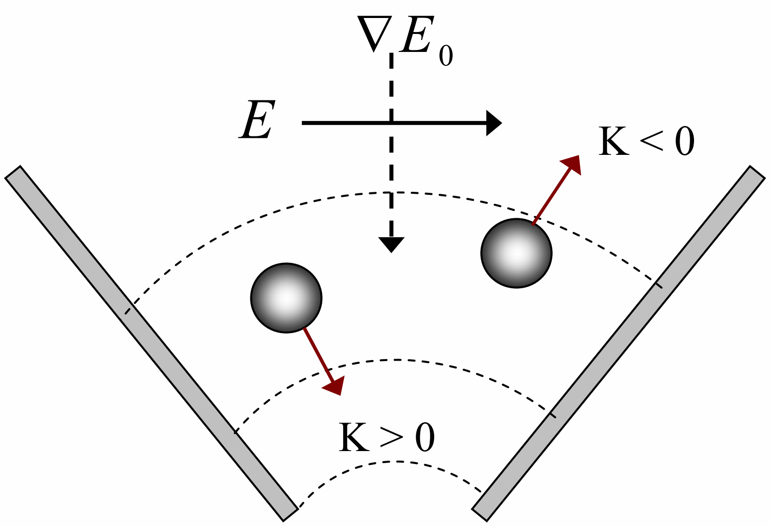
$$\vec{F}_{DEP} = 2\pi\,\varepsilon_0\,\varepsilon_1\,K\,R^3\,\nabla E^2$$

$$K = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}$$ Clausius-Mossotti function

- ♦ F_{DEP} depends upon the magnitude and sign of the Clausius – Mossotti function:

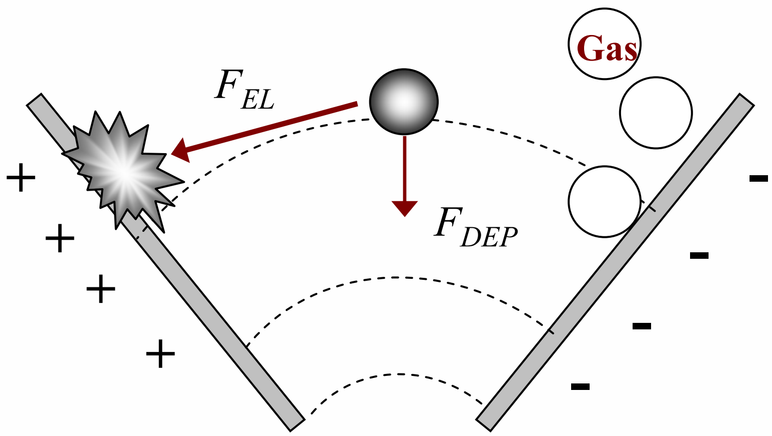
➢ Positive dielectrophoresis: $K > 0$ (or $\varepsilon_2 > \varepsilon_1$). Particles are attracted to electric field intensity maxima.

➢ Negative dielectrophoresis: $K < 0$ (or $\varepsilon_2 < \varepsilon_1$). Particles are attracted to electric field intensity minima and repelled from maxima.



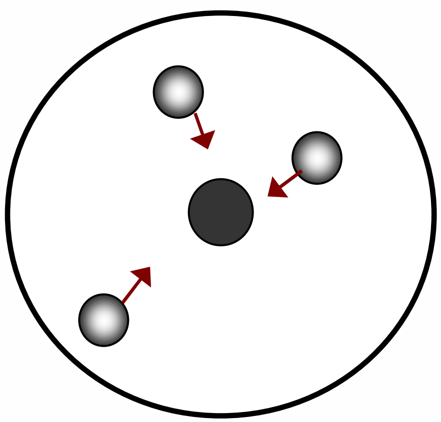
- ♦ F_{DEP} is proportional to particle volume.
- ♦ F_{DEP} is proportional to the dielectric permittivity of the medium, ε_2.
- ♦ The DEP force vector is directed along the electric field gradient, which, in general, is not parallel to the electric field vector

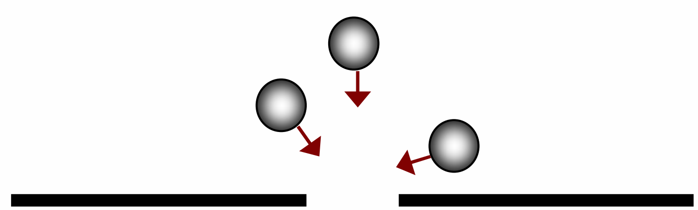
Advantages of using alternating (AC) field



- ♣ 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)

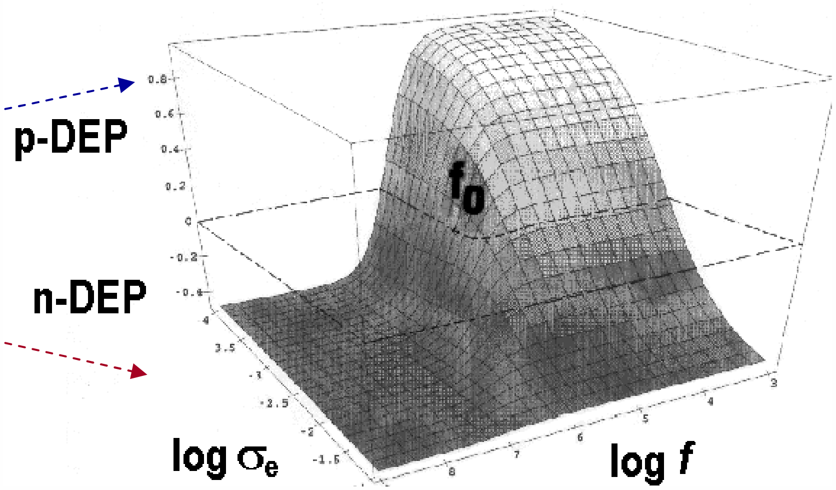




Example:
Dielectrophoretic behavior of latex microspheres

Low dielectric permittivity ε_2
Increased conductivity σ_2 (counterion atmosphere)

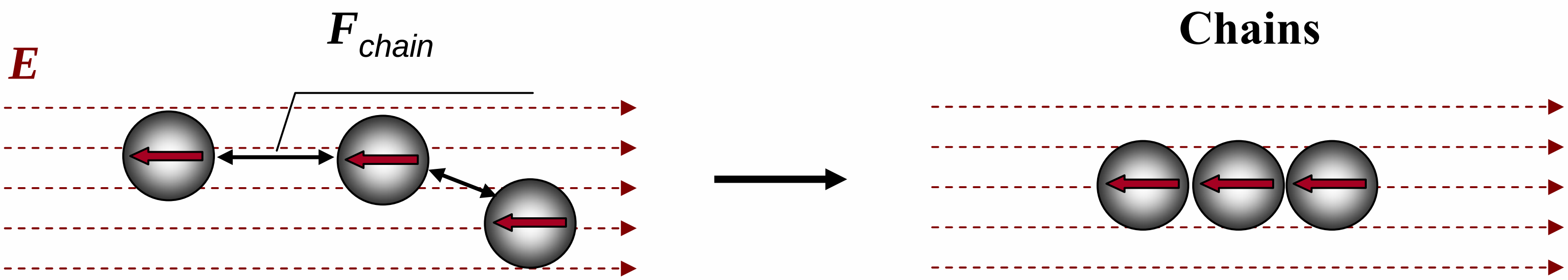
$$\mathrm{Re}\left|\underline{K}\right| \rightarrow \begin{cases} \dfrac{\sigma_2 - \sigma_1}{\sigma_2 + 2\sigma_1} > 0 \quad \textit{for } w\,\tau_{MW} << 1 \\[2ex] \dfrac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} < 0 \quad \textit{for } w\,\tau_{MW} >> 1 \end{cases}$$



T. Müller et al., *J. Phys. D: Appl. Phys.* **29**, 340 (1996).

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

Second field-induced force: Particle chaining

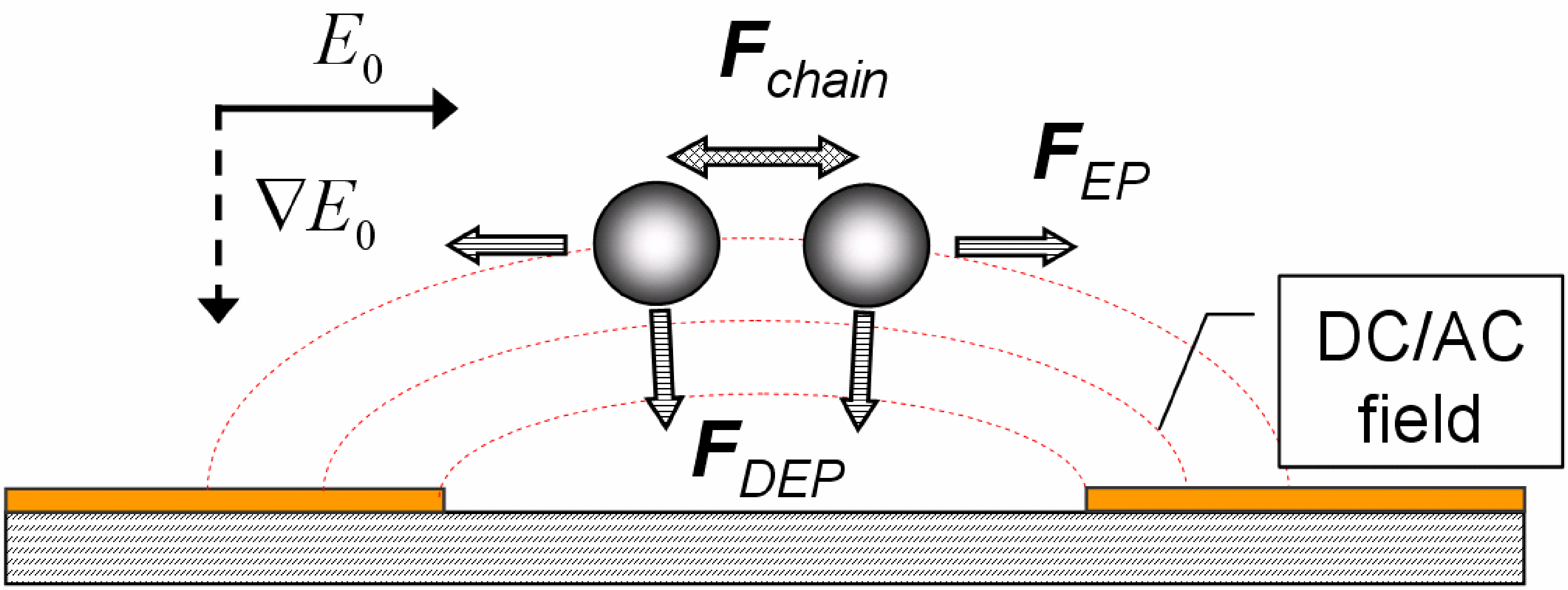


Interactions between induced dipoles along the direction of the field

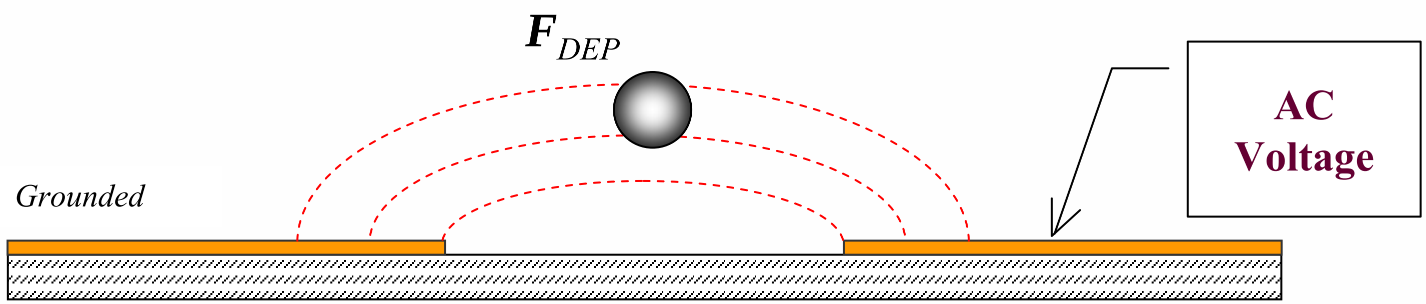
$$F_{chain}(\max) = -C\,\pi\,\varepsilon\,R^2\,K^2\,E^2$$
$$3 < C < 10^3$$

- F_{chain} is always attractive.
- Proportional to K^2
- Weaker dependence on particle size than the direct dielectrophoretic force.

Summary:
Electrophoretic + Dielectrophoretic interactions on chip



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

Experimental image

Speed of growth
≤ 50 μm/s

Suspension of
nanoparticles
10-25 nm

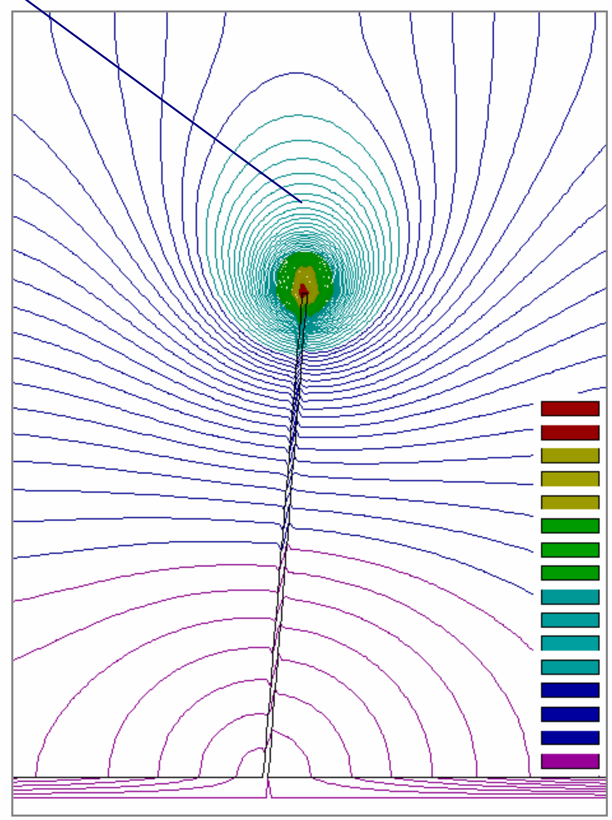
Depleted
area behind
the wire

Planar
electrode

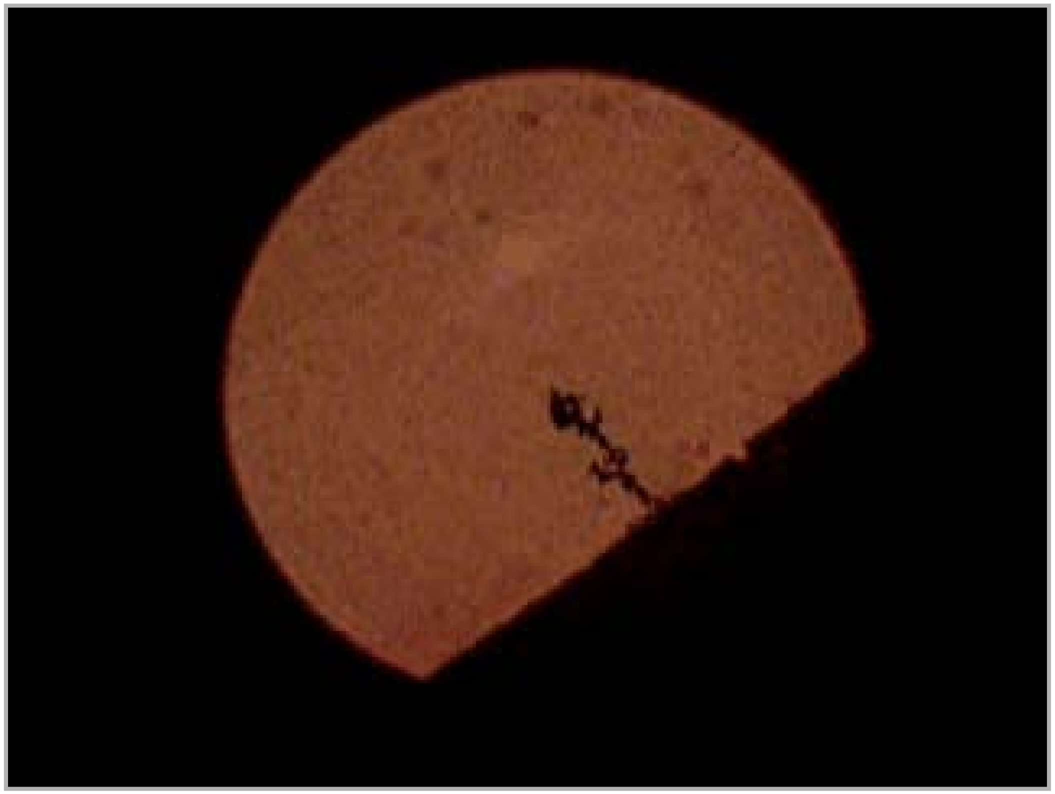
500 μm

Theoretical gradient strength

High concentration along the field gradient



Dielectrophoretic assembly of conductive microwires from metallic nanoparticles in suspension

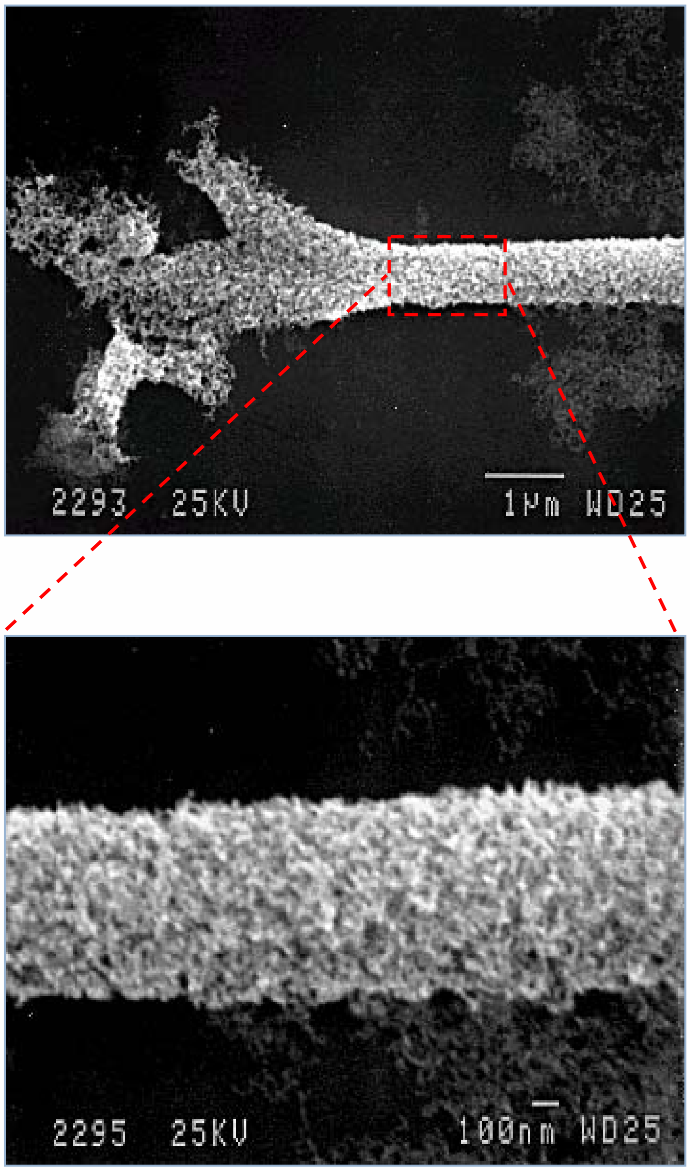


High magnification, 8X speed

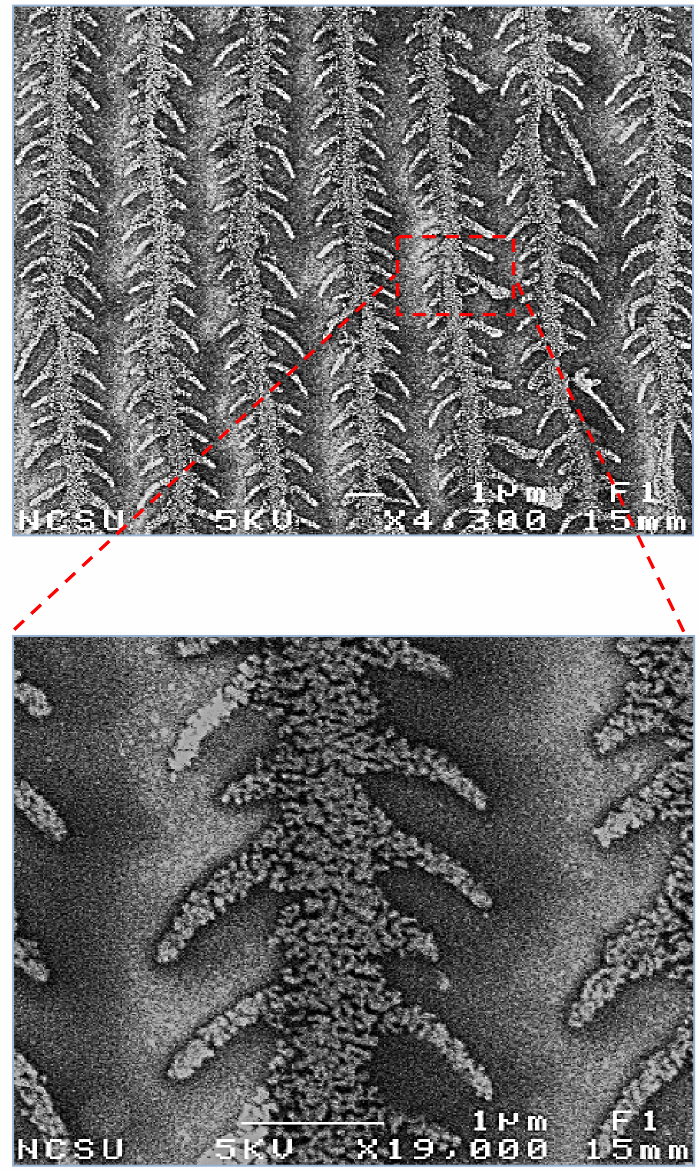
Hermanson, Lumsdon, Kaler and Velev, *Science*, <u>294</u>, 1082 (2001).

Microwire structure by SEM

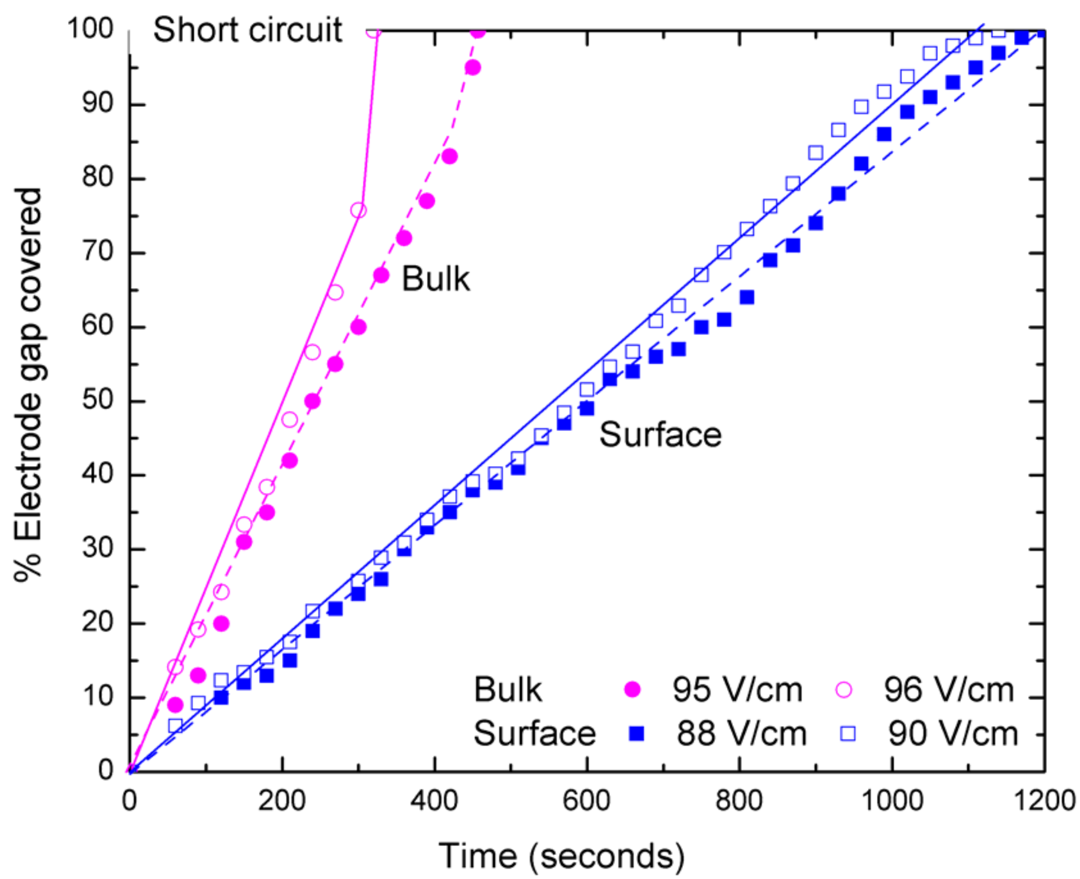
Bulk



Surface



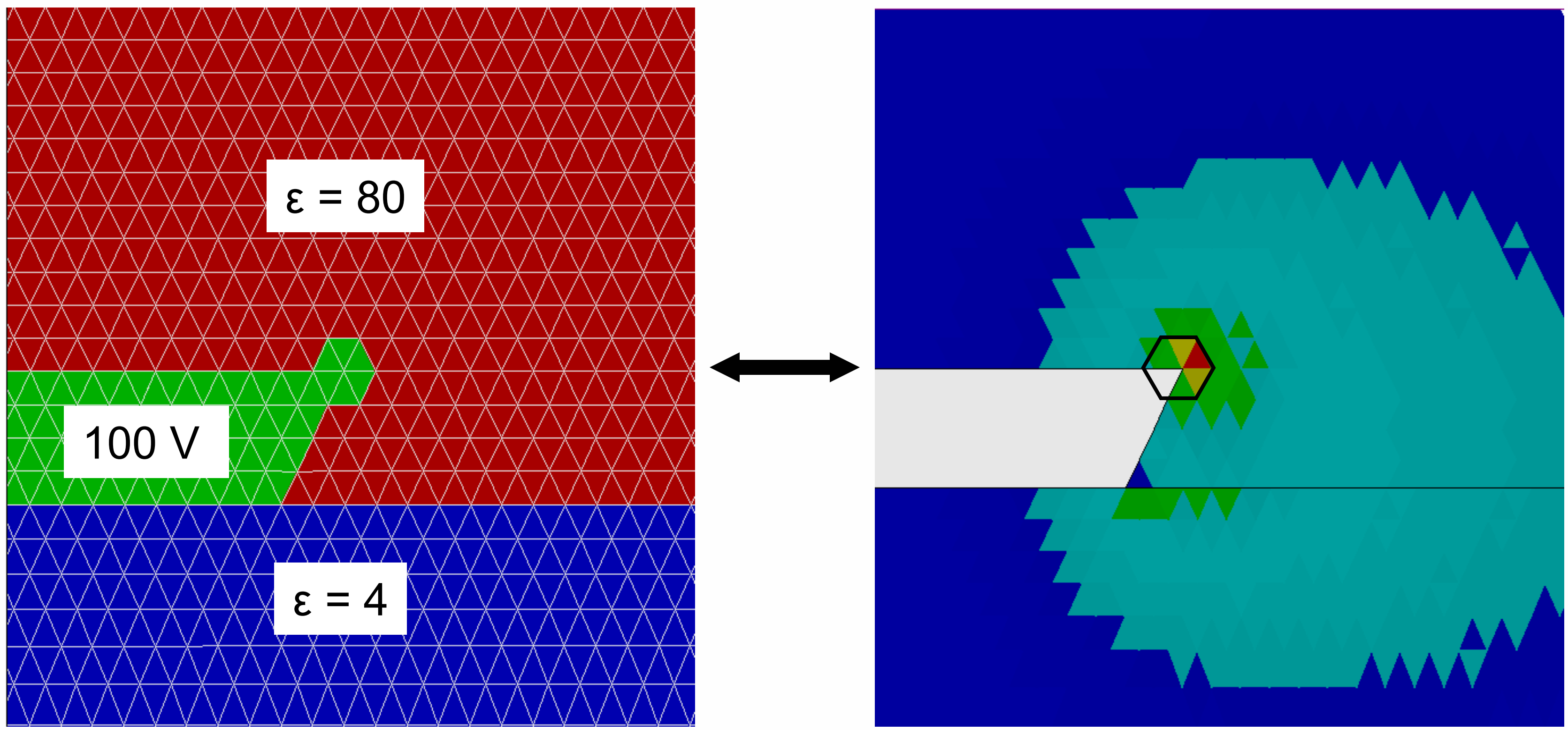
Quantification of microwire growth rate



- Assembly rate is not a function of field intensity *E*
- Diffusion controlled process
- Bulk growth faster due to larger diffusion volume

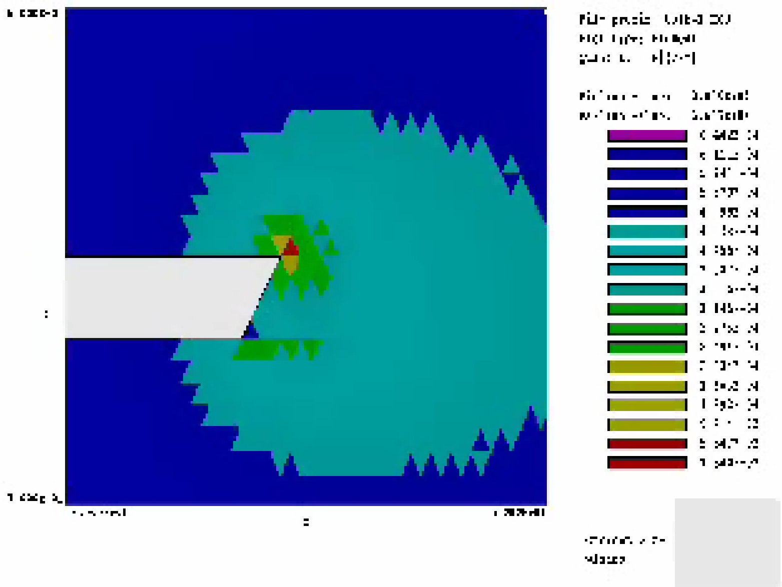
Modeling and simulation of microwire assembly

Finite element electrostatic calculations using conformal triangles mesh (TriComp package)

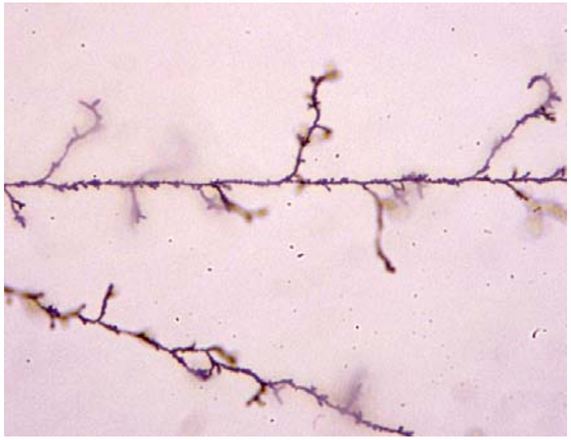


Simulation of the kinetics of microwire assembly

Bulk wires



Simulation



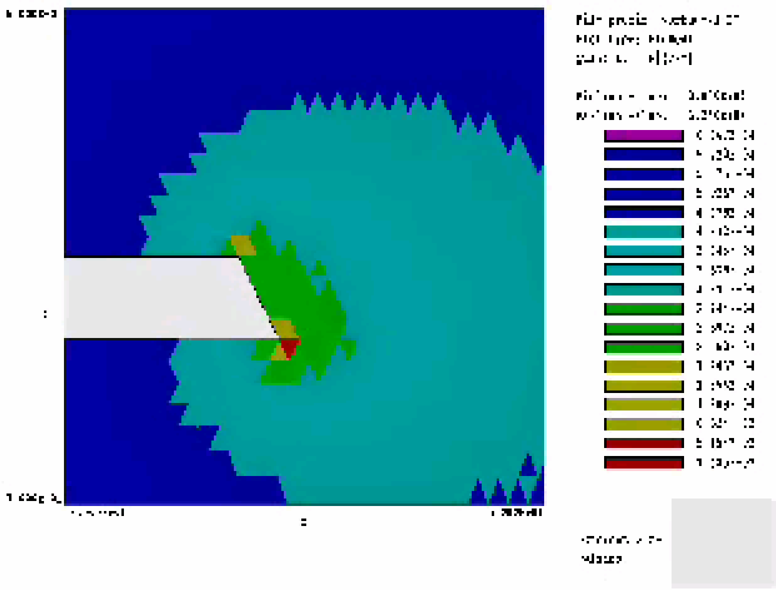
Experimental image – bulk wires

Realistically reproduces the dynamics and features observed in real wire growth

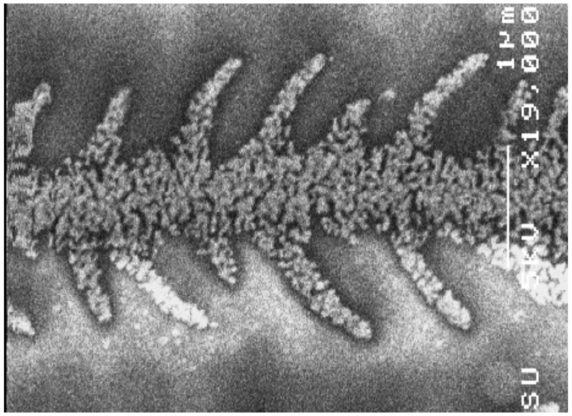
Bhatt and Velev, *Langmuir*, 20, 467 (2004)

Simulation of the kinetics of assembly

Surface wires



Simulation



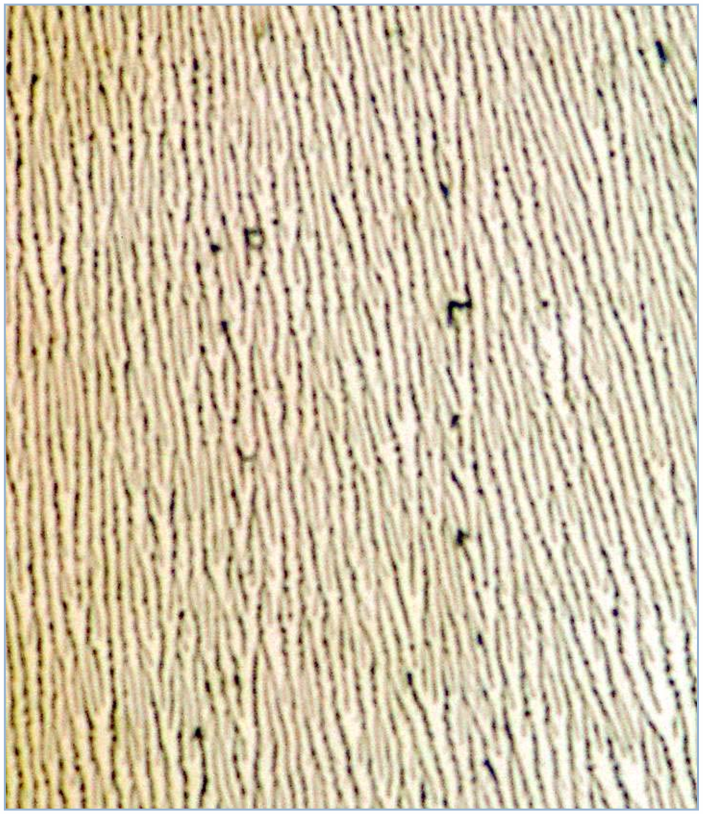
Experimental image – surface wires

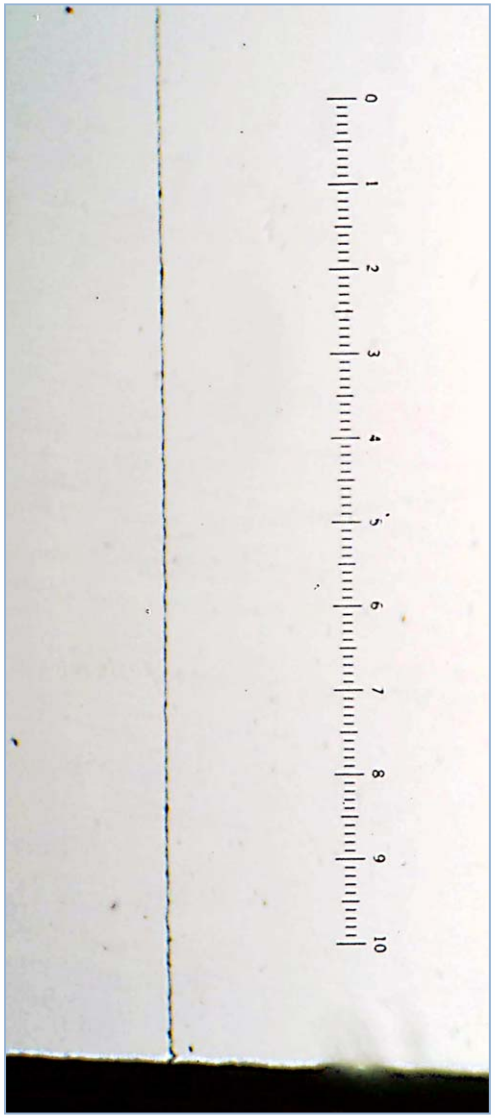
Simulation proves the role of low-ε substrate and initial conditions

Control of wire branching and position

Straight unbranched wire through the bulk
(high viscosity)

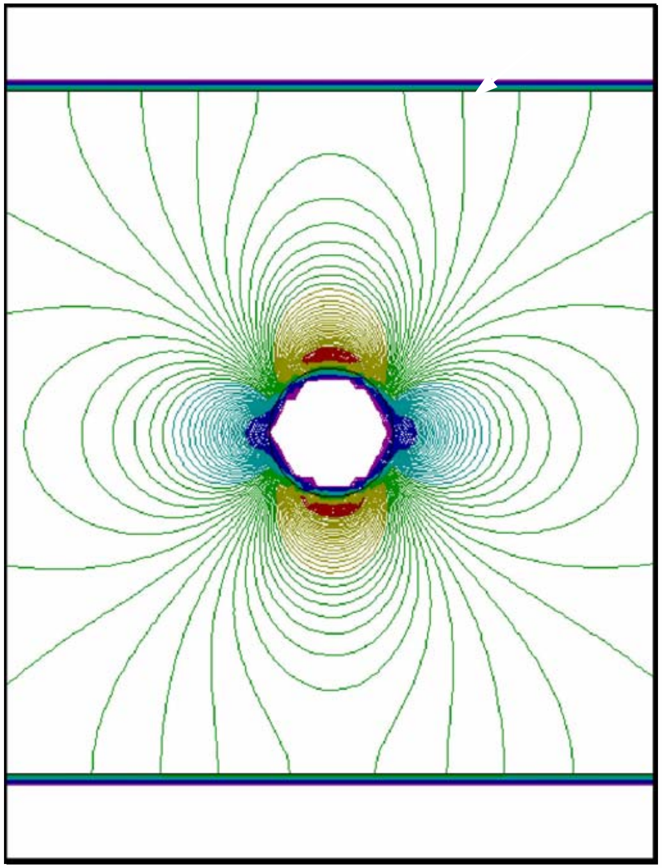
Parallel arrays on surface
(high frequency, low intensity)

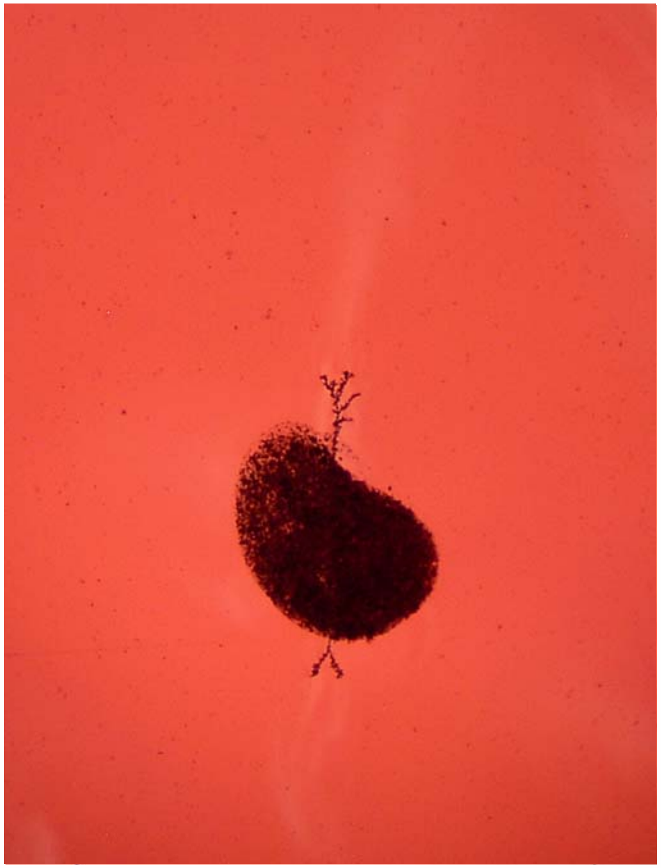




Predicting wire assembly in the presence of conductive object in the liquid

Model





Experiment

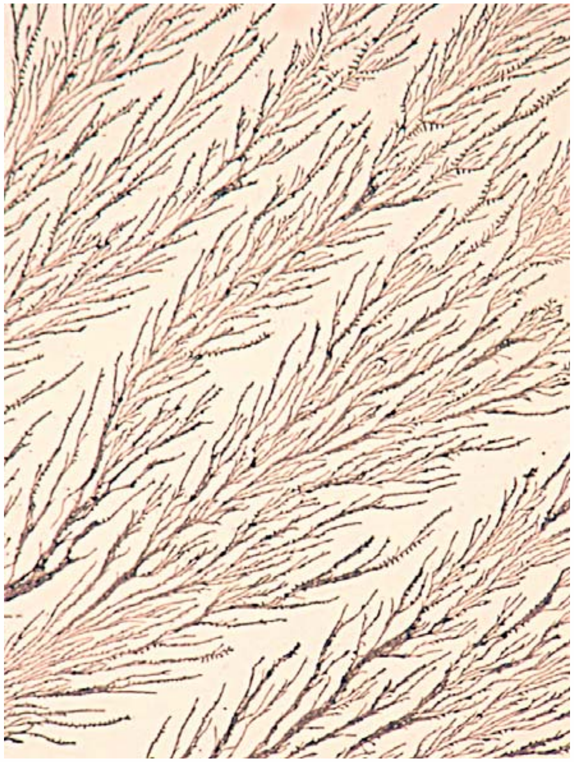
Growing wires should spontaneously complete the circuit through the object

Wire assembly should begin at the object even though it is not connected

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

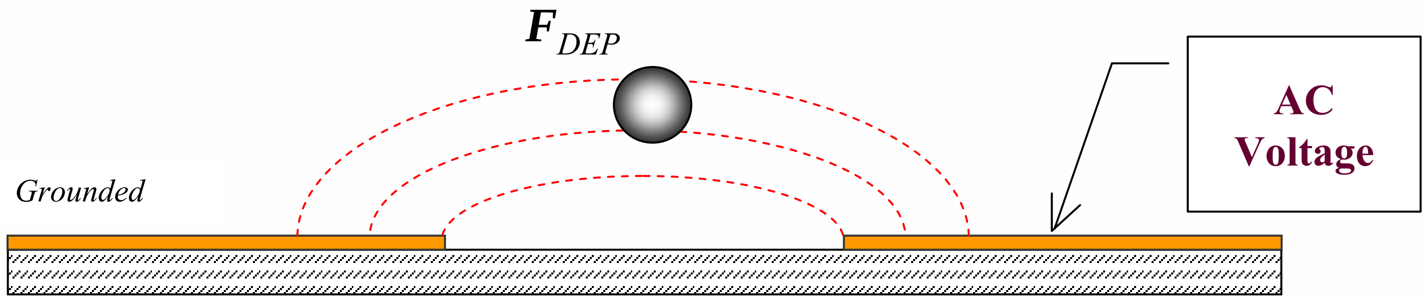
- The kinetic assembly process
- The growth pattern and direction

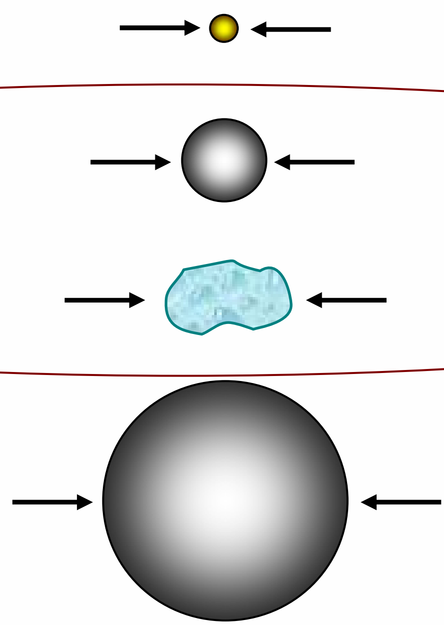
Ready for nanotech applications

- Bioelectronic interfacing
- Chemical and biological sensors
- Structures with anisotropic thermal and electrical properties

Bhatt and Velev, *Langmuir*, 20, 467 (2004)

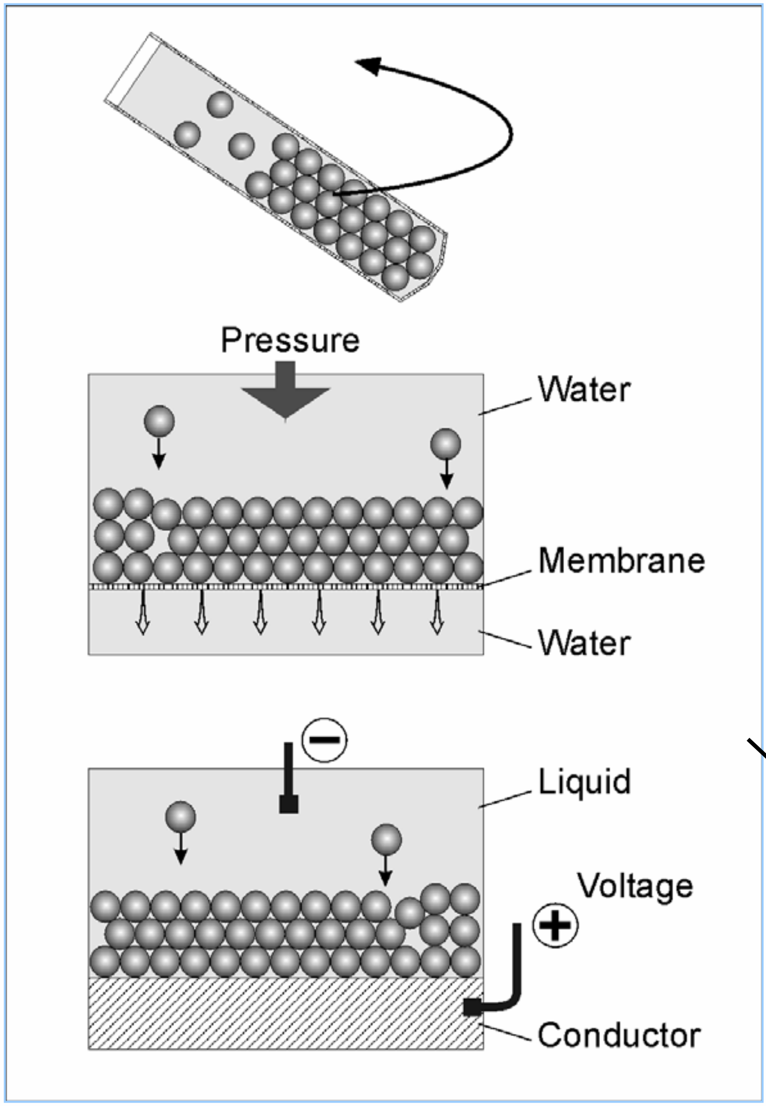
Overview – objects for on-chip manipulation

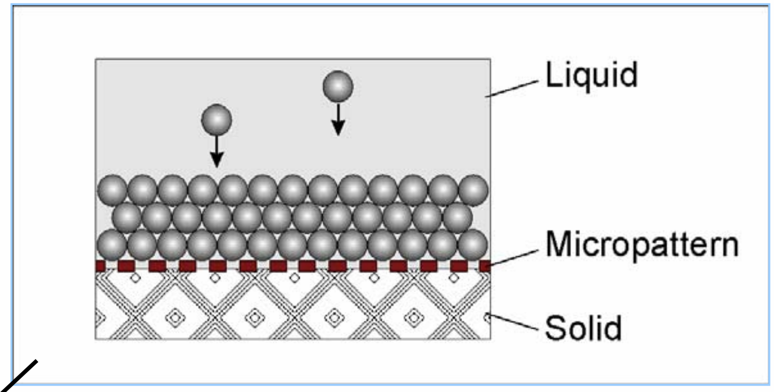




Nanoparticles	**5 - 10 nm**
Microspheres	**500 - 1000 nm**
Live cells	**5 - 10 µm**
Droplets (from particle suspensions)	**500 - 1000 µm**

Photonic crystals via microsphere assembly …



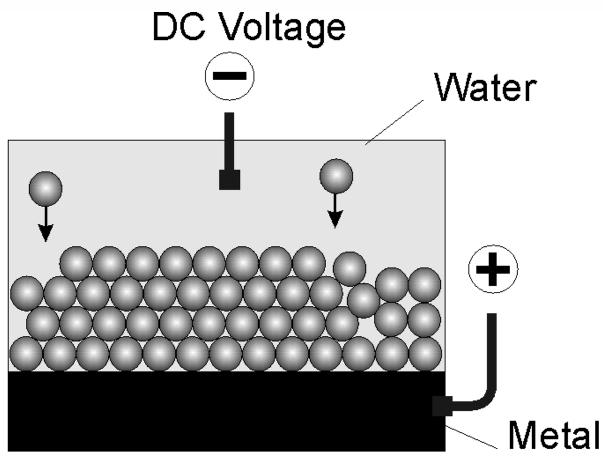


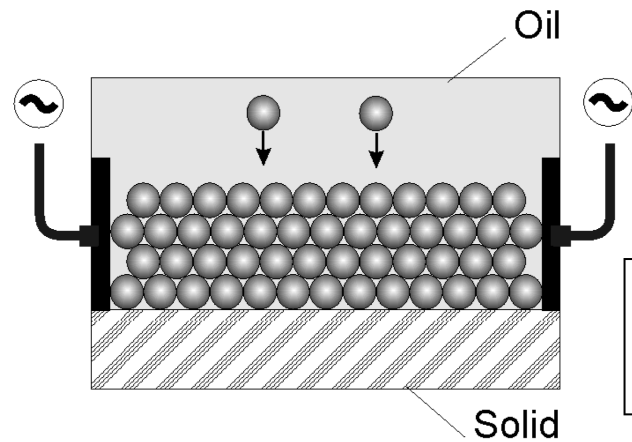
… can be made exactly the way we want them, but slow and expensively

… have been made quickly, but without long range orientation

Overview of geometries used in electrical field driven assembly

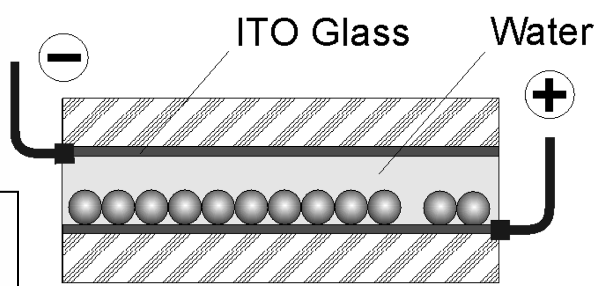
Holgado et al., 1999, Rogach et al., 2000, etc.

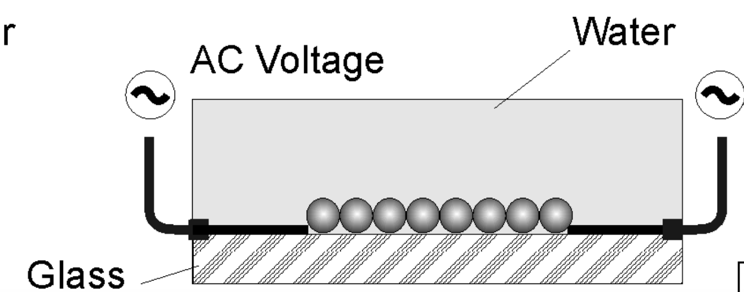




S. Fraden, A. Blaaderen, 2001

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



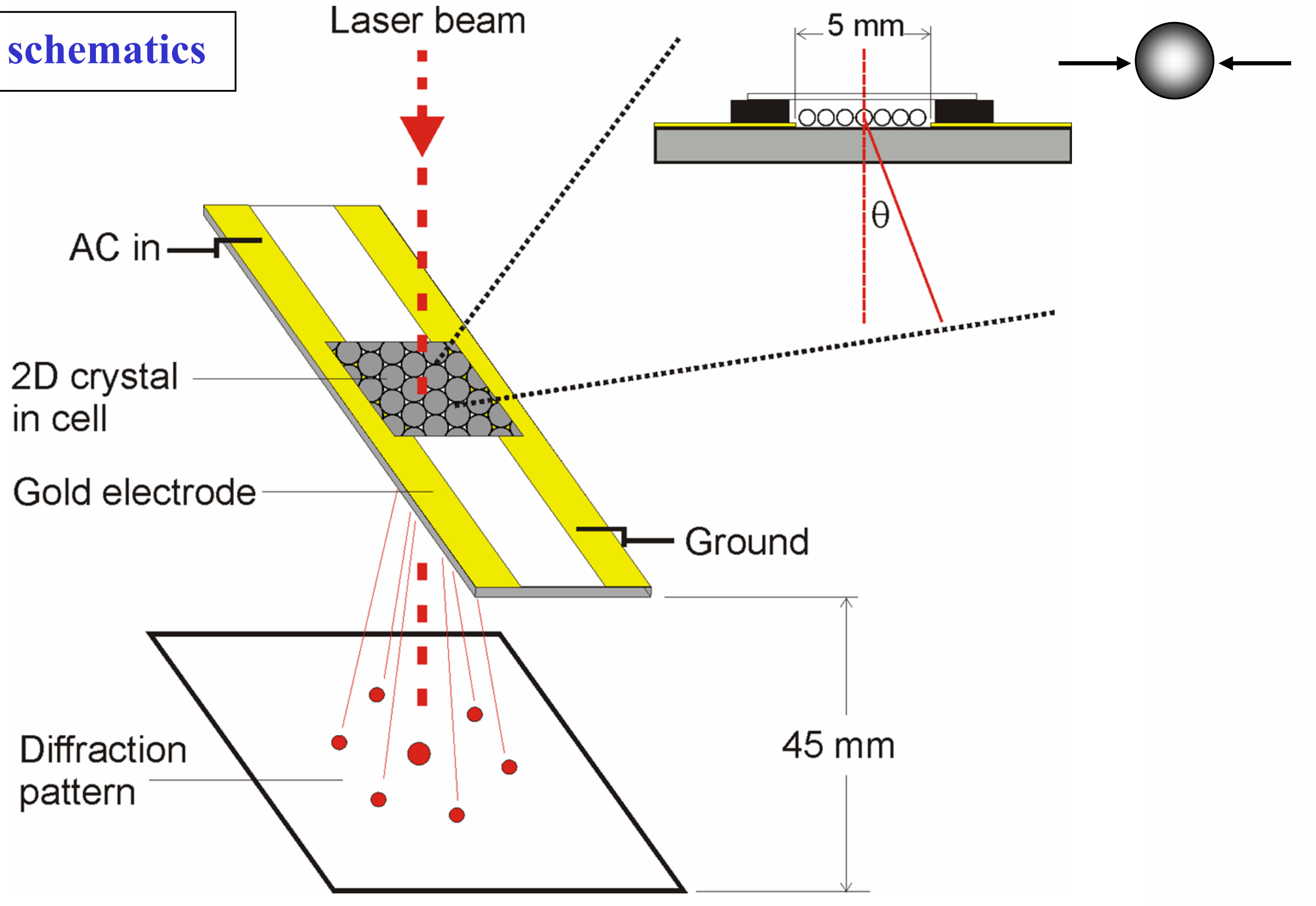


Presented here

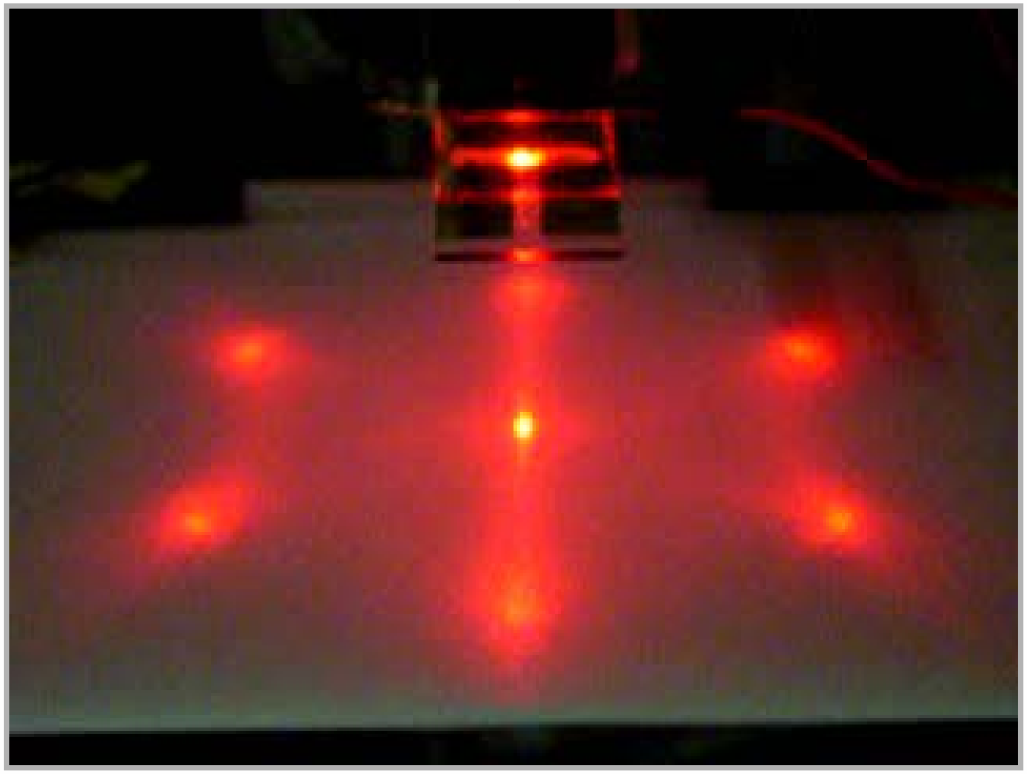
Dielectrophoretic assembly of electrically tunable photonic crystals

Latex or silica
500 - 1000 nm

Experiment schematics

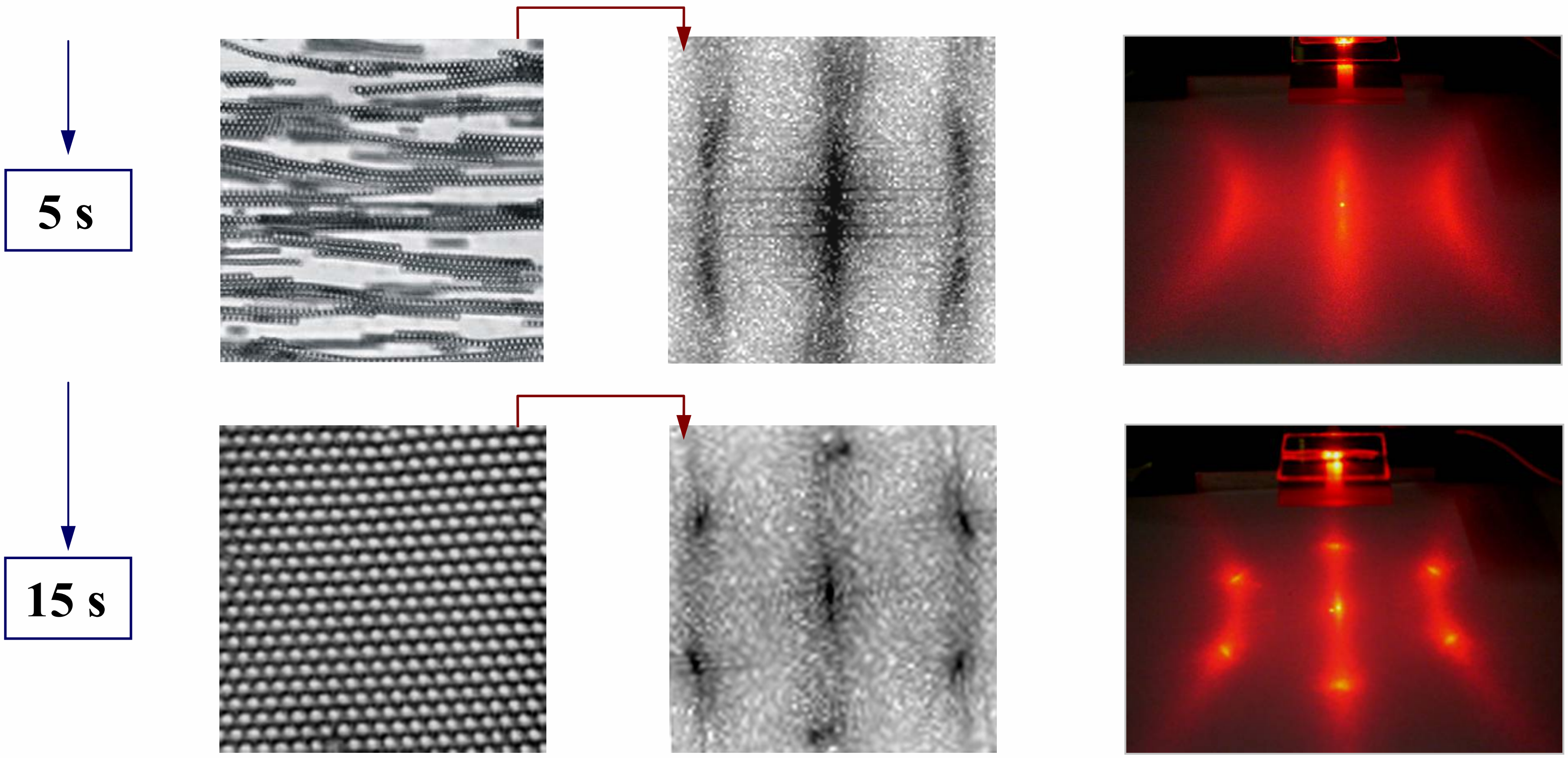


Dynamics of the DEP controlled crystallization:
Laser diffraction



Stages of the 2D crystallization: Microscopy and diffraction

Optical micrograph　　Fourier transform　　Diffraction pattern

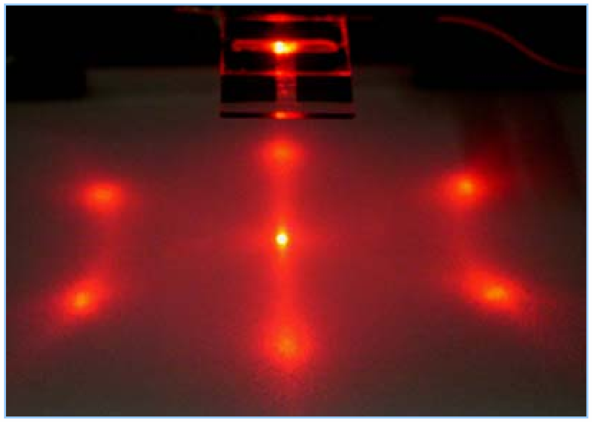


- Single domain cm-scale crystals with specific orientation
- Switchable 2D phase transitions

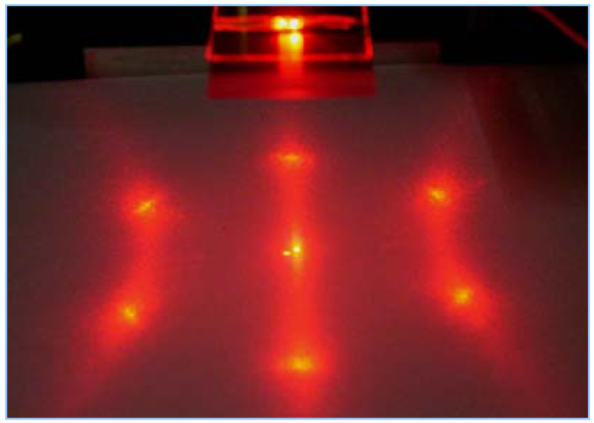
Lumsdon et al., *Appl. Phys. Lett.*, 82, 949 (2003).

Quantitative measurements via the 2D crystal diffraction pattern

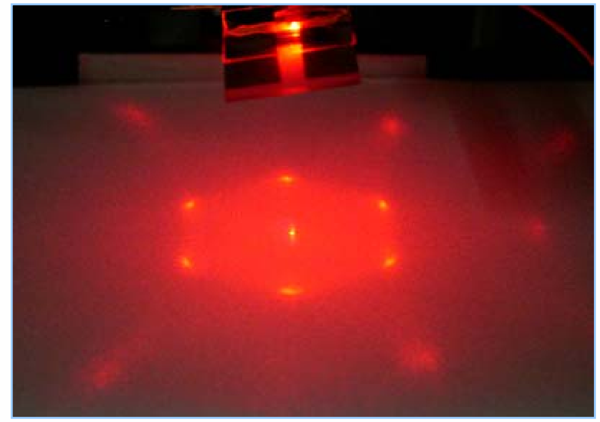
0.7 µm diameter latex



1.0 µm diameter latex



1.4 µm diameter latex



von Laue equation for
2D point scatterers

$$h = \frac{n\,\lambda_c}{\sin\theta}$$

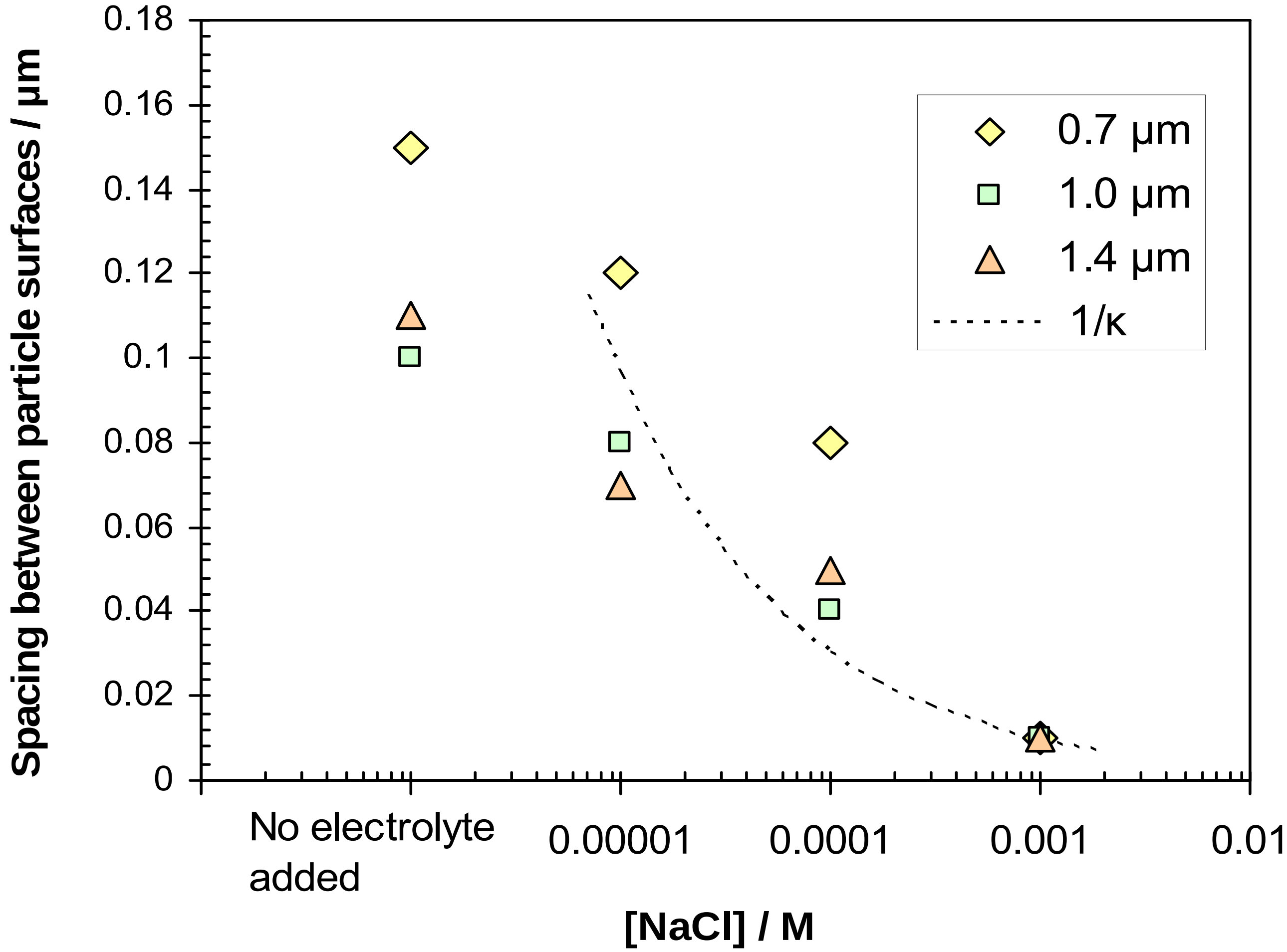
Corrected for the refractive index of the composite media

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

Corrected for refraction on exiting the cell

$$\sin\theta = \frac{n_{cell}}{n_{air}} \sin\theta_{meas}$$

Effect of electrolyte concentration on distance between particle surfaces

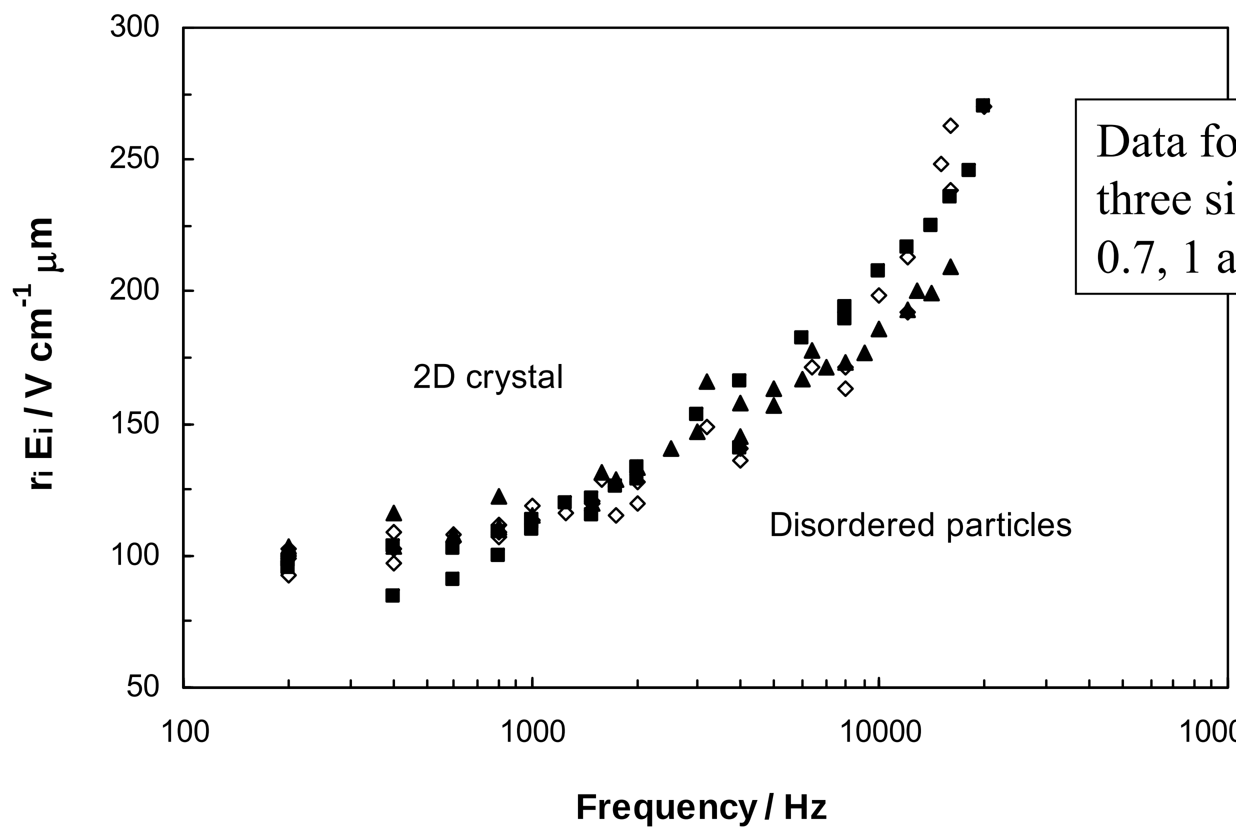


- Precise simple measurements of interactions in particle ensembles

Controlling the crystallization: Effect of field and frequency

Scaling approximation

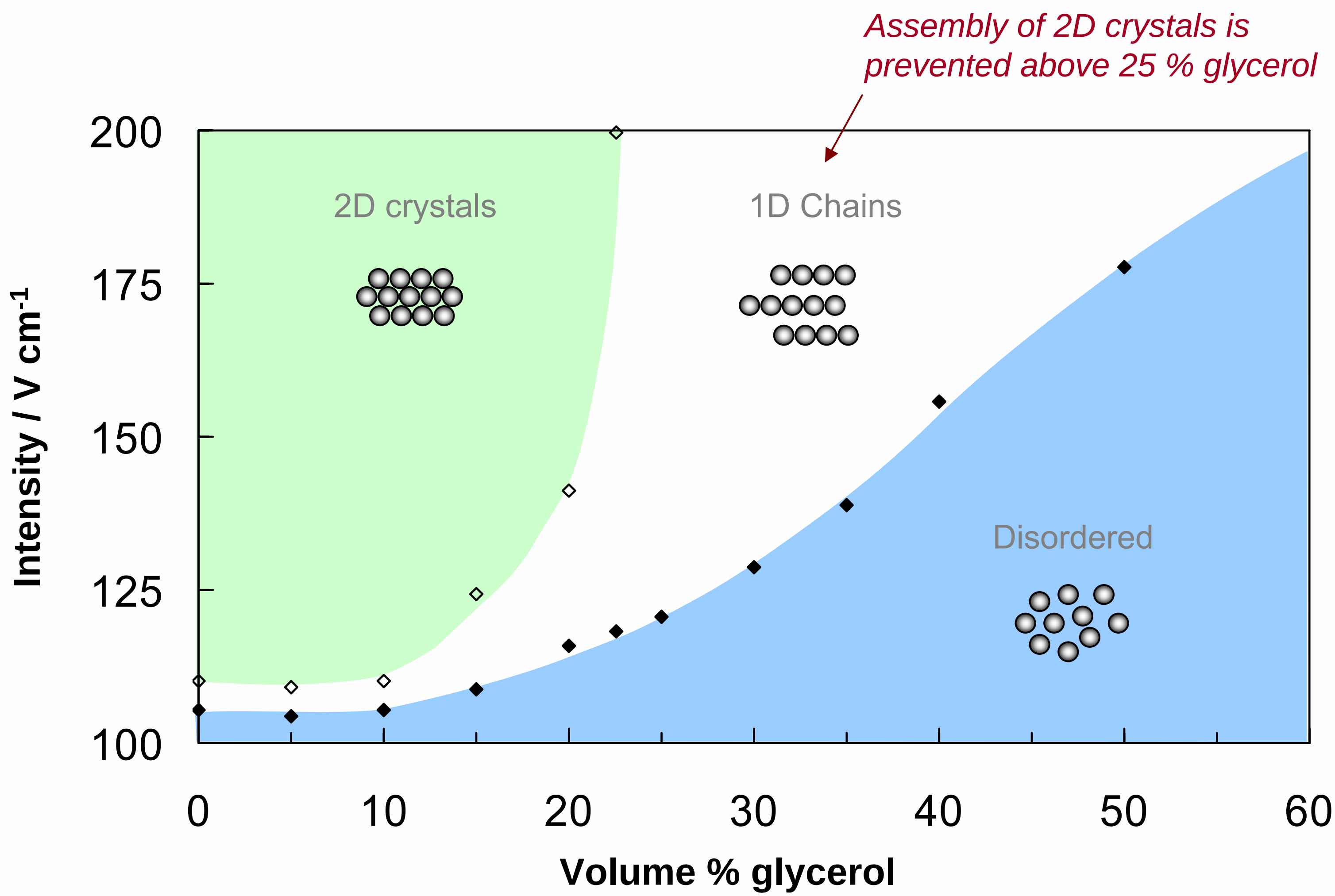
$$\frac{-F^{T}_{chain}}{C\,\pi\,\varepsilon_1\,K(\omega)^2} = const = r_i^2 E_{i,chain}^2$$



Data for particles of three sizes: 0.7, 1 and 1.4 μm

- Crystallization threshold not a strong function of particle size

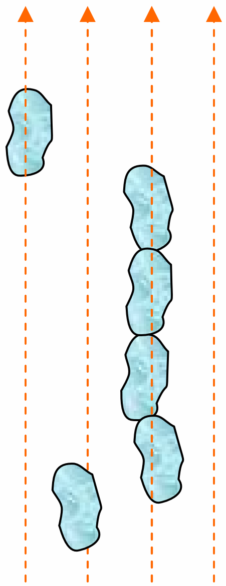
Controlling the crystallization – effect of glycerol



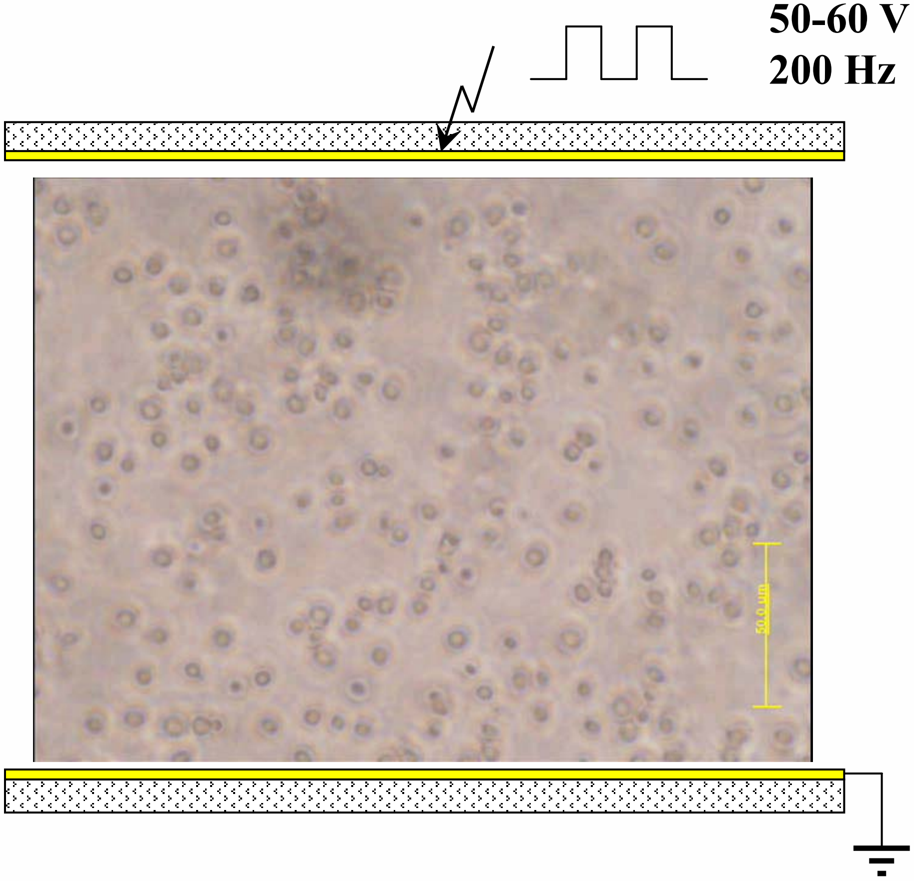
- Separations, study of colloidal self-organization fundamentals

Lumsdon, Kaler and Velev, *Langmuir*, 20, 2108 (2004).

DEP assembly of cell chains for biosensors

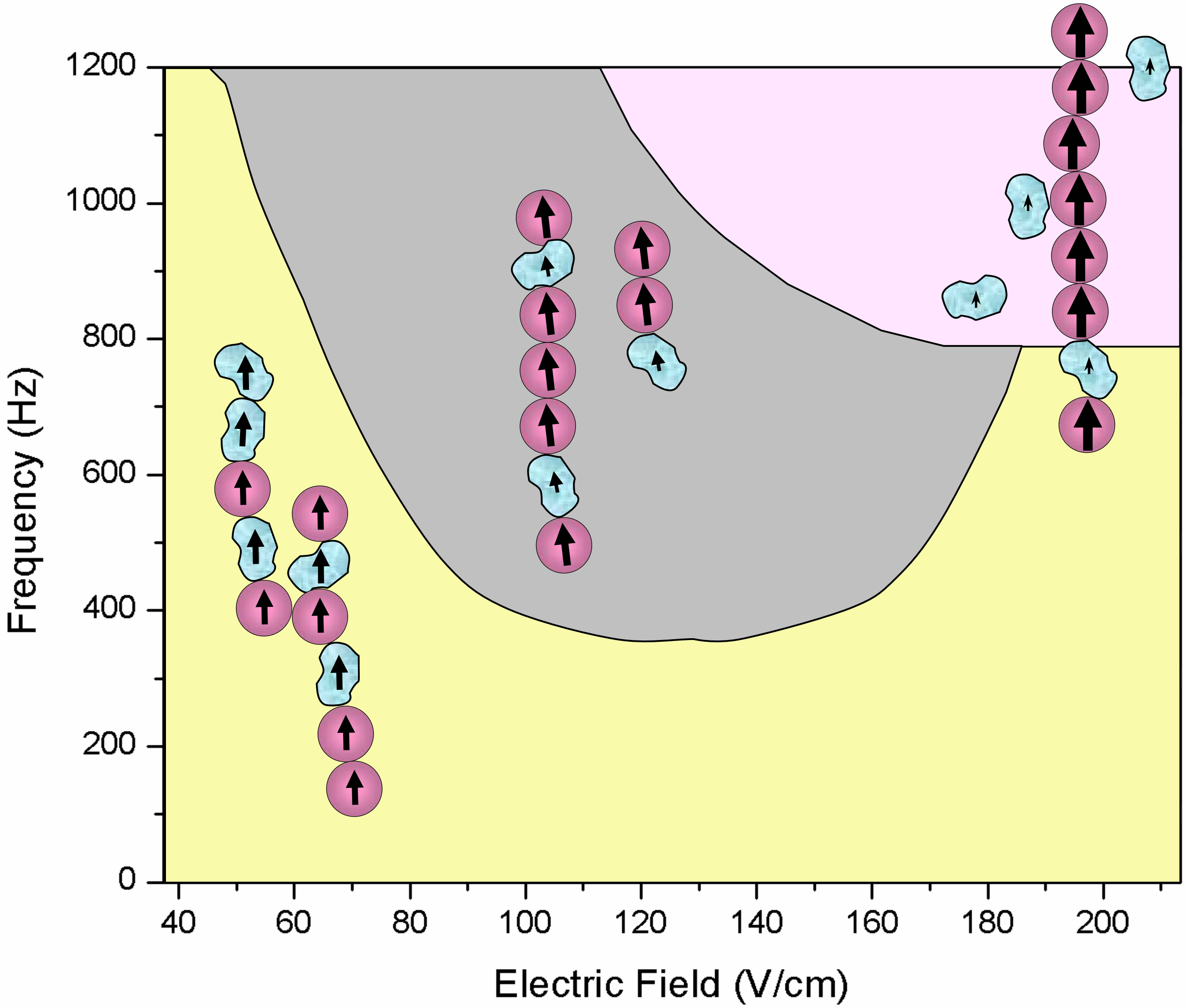


5 μm yeast cells



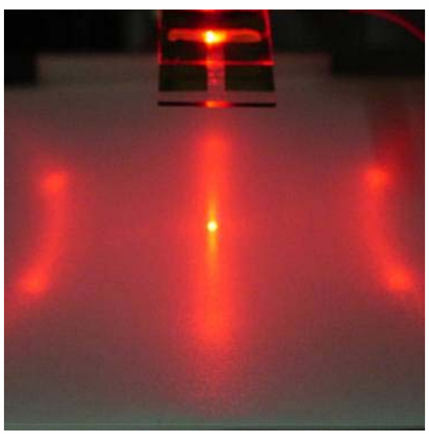
DEP chaining of 0.1 % yeast cell solution in 10 μM PBS

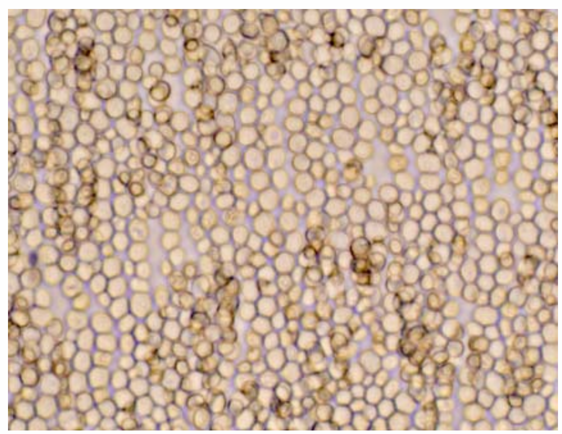
Cell-particle dipole interactions as a function of voltage and frequency



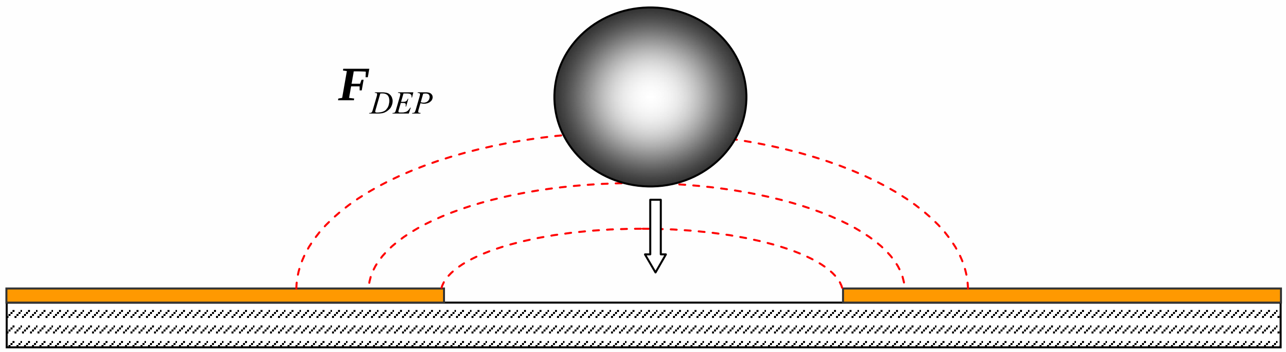
Summary – 1D and 2D arrays by dielectrophoresis

- 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



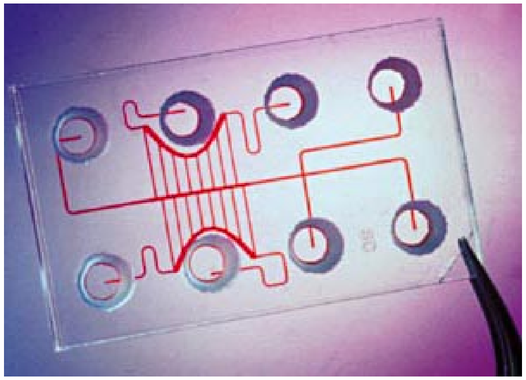


Dielectrophoretic on-chip manipulation of suspended droplets

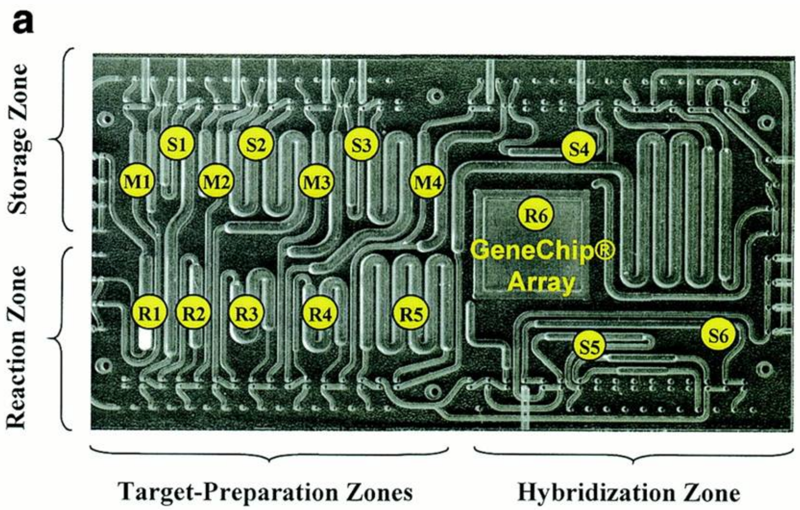


… can we manipulate droplets and why?

Conventional microfluidics with channels



Caliper Technologies



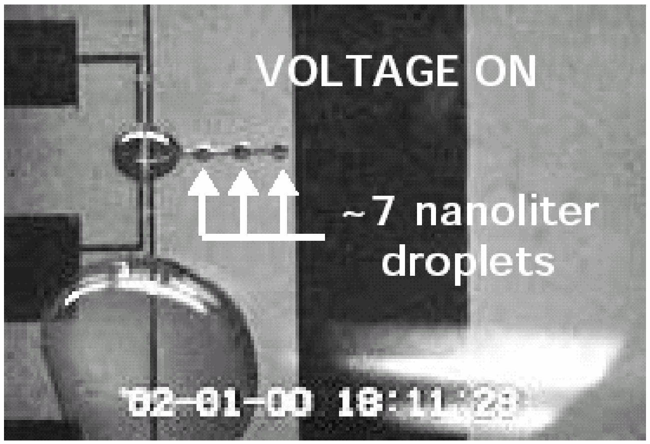
Anderson et al., *Nucleic. Acids Res.* **28**:60

Permanently rigged "pipes", specific design for pre-defined operations

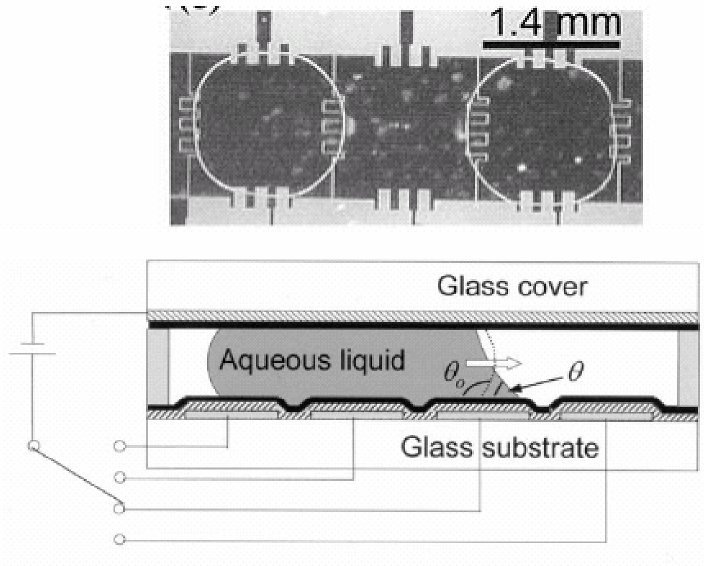
↓

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



Jones et al. *J. Appl. Phys.* **89**:1441 (2001).
Jones, *J. Electrostat.* **51**:290-299 (2001).



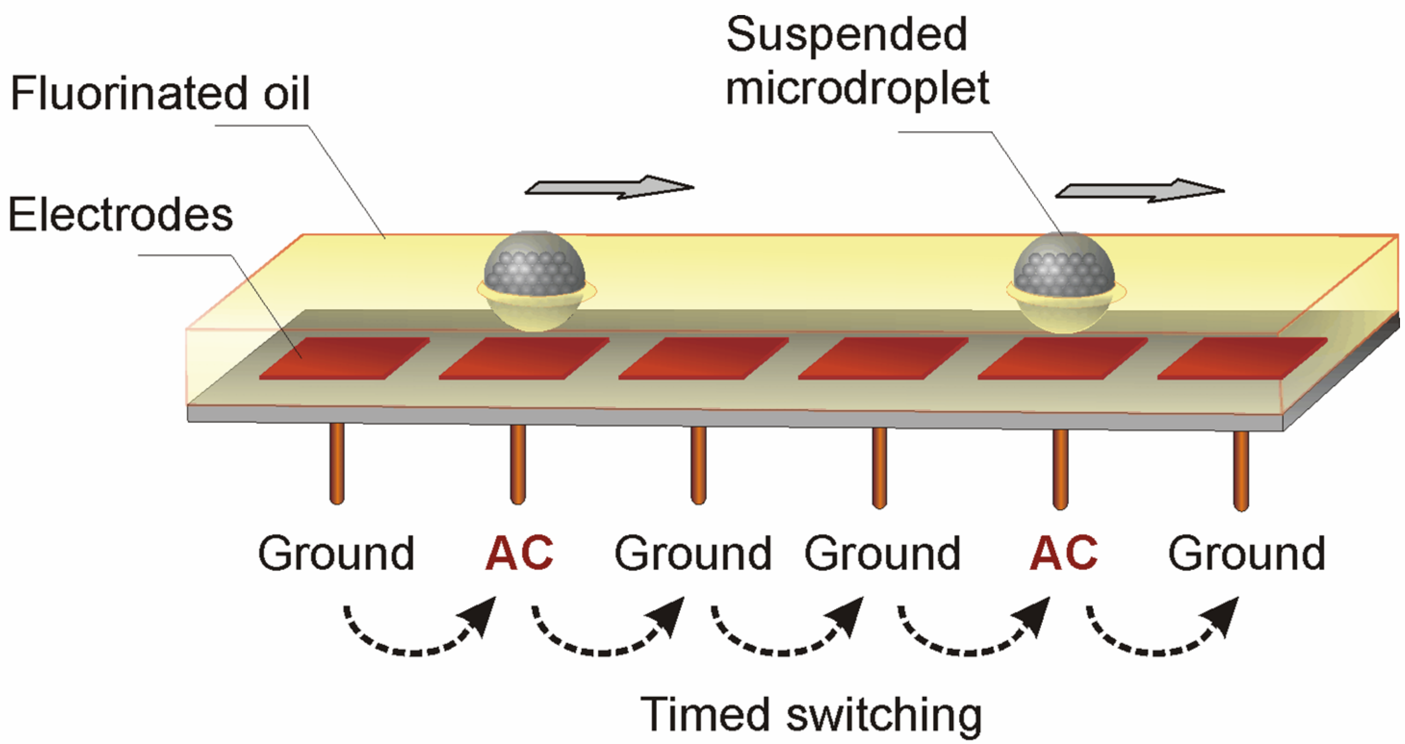
Pollack et al. *Appl. Phys. Lett.* **77**:1725 (2000).
Cho et al. *J. Microelectrom. S.* **12**:70-80 (2003).

The channels are gone, but the walls are still there

↓

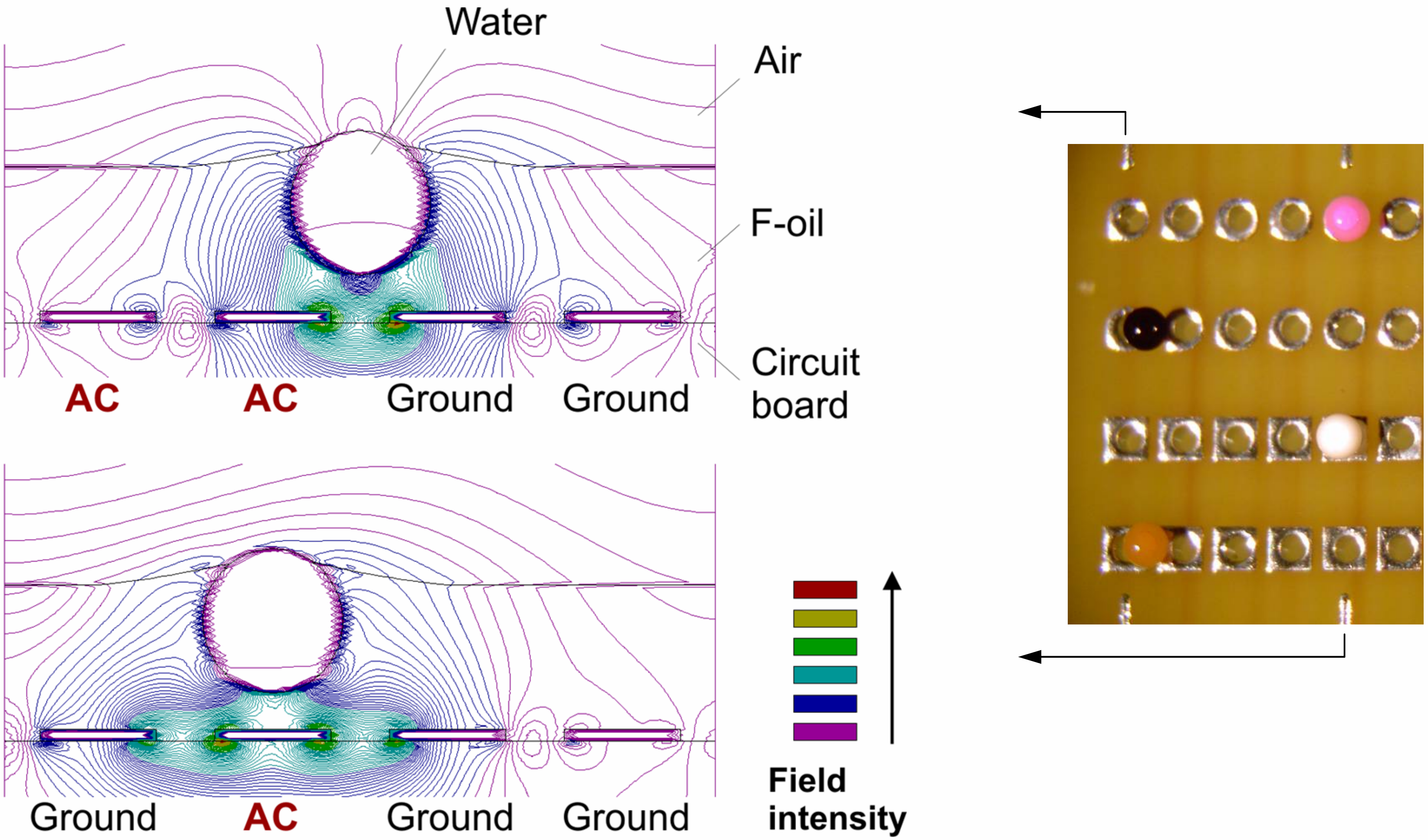
Contact angle hysteresis, surface fouling, precipitation or aggregation forbidden, transport of cells, particles and biomolecules problematic

Dielectrophoretic chips with suspended microdroplets: Basic principle



Liquid – liquid chip system without walls or channels

Calculated field intensities for the two equilibrium droplet positions

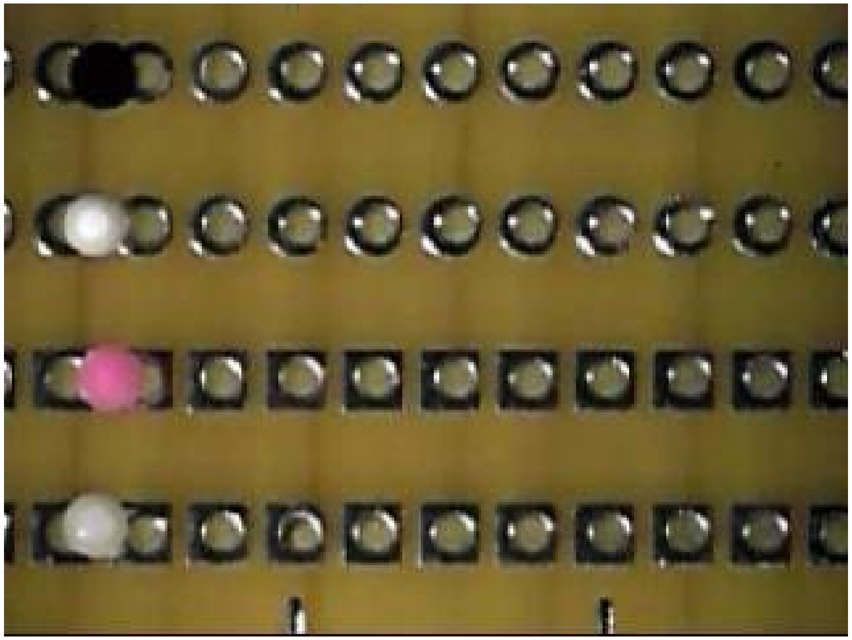


Droplet-chip geometry to scale.

Finite element electrostatic calculations using conformal triangles mesh (TriComp package).

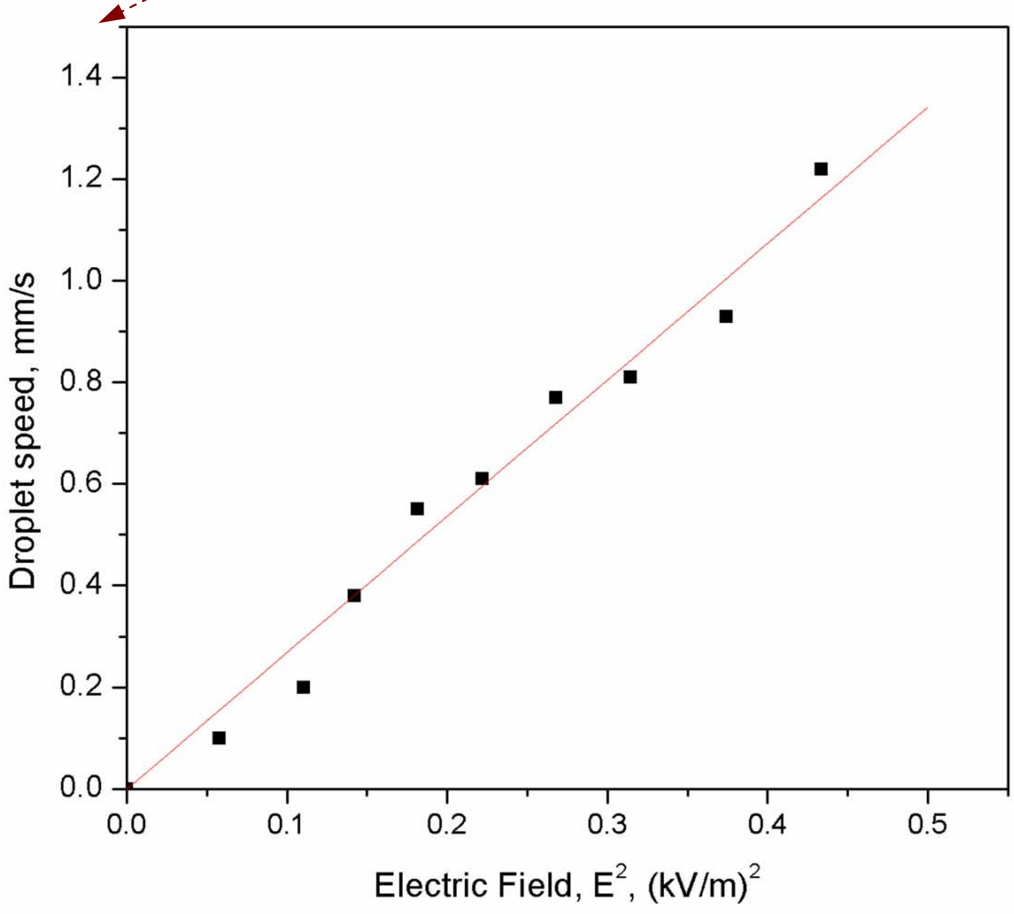
Fluid chip function 1:

Dielectrophoretic transport of multiple droplets in series



Dielectrophoretic manipulation: Droplet speed and field intensity

$$\vec{F}_{hydr} \approx 6\pi\mu R V = \vec{F}_{DEP} = 2\pi\varepsilon_1 \mathrm{Re}\left|\underline{K}(w)\right| R^3 \nabla E^2$$



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:

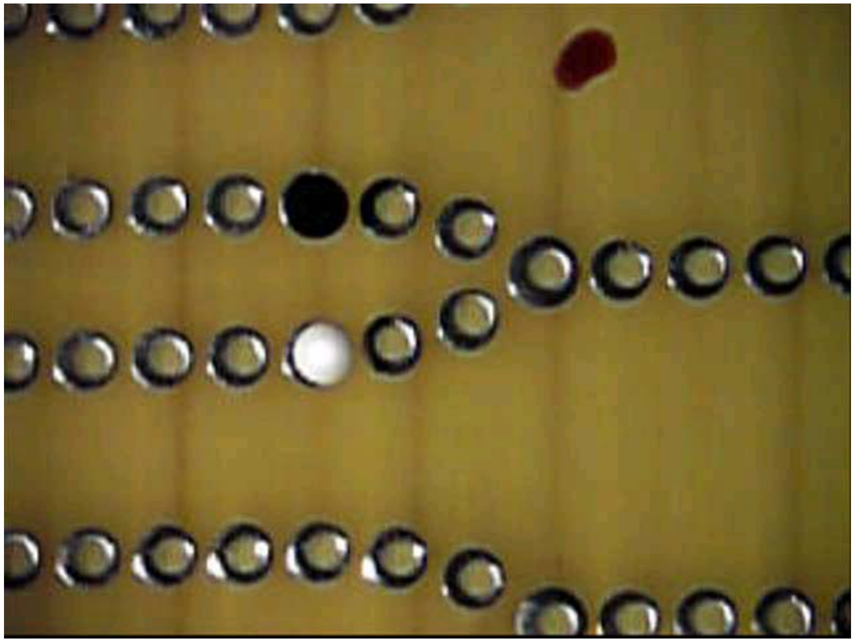
	Droplet moved in fluorinated oil	Hemispherical droplet dragged on solid surface	Viscous flow in microfluidic channel
Assumptions and approximations	• Stokes sphere in bulk liquid	• $\theta_{Advancing}$ = 90 deg • $\theta_{Receding}$ = 80 deg • No viscous dissipation	• Circular channel of diameter 20 µm • Poiseuille flow
Type of estimation	Overestimate	Underestimate	Underestimate
Energy required / J	**$\leq 9.4\times10^{-10}$**	**$\geq 1.6\times10^{-7}$**	**$\geq 1.4\times10^{-4}$**
Energy ratio	**1**	**170**	**150000**

Extremely low energy needed for suspended droplet transport

Fluid chip function:
Mixing of two droplets at electrode track junctions

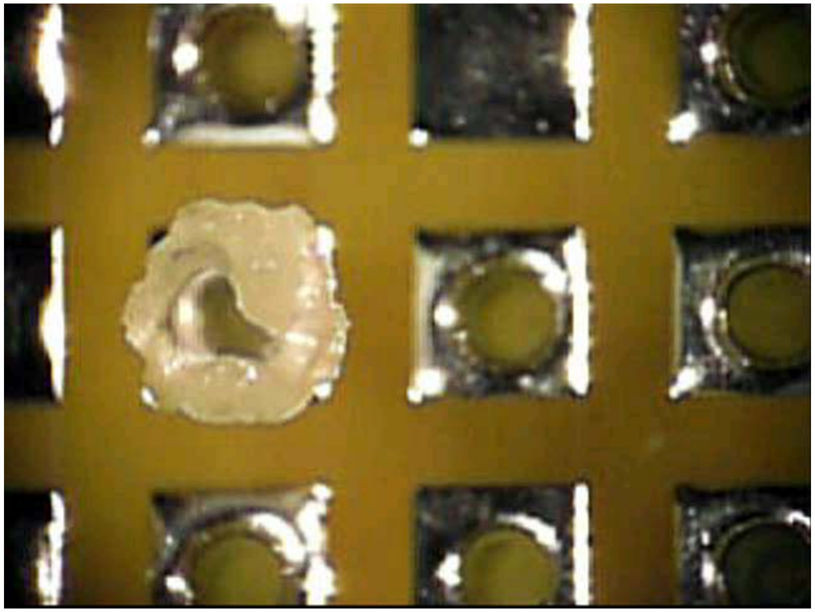
gold nanoparticles →

sulfate latex →



Fluid chip function:
Complex precipitated shells

$Ca_3(PO_4)_2$
precip. shell →



Unique possibilities for materials synthesis and encapsulation

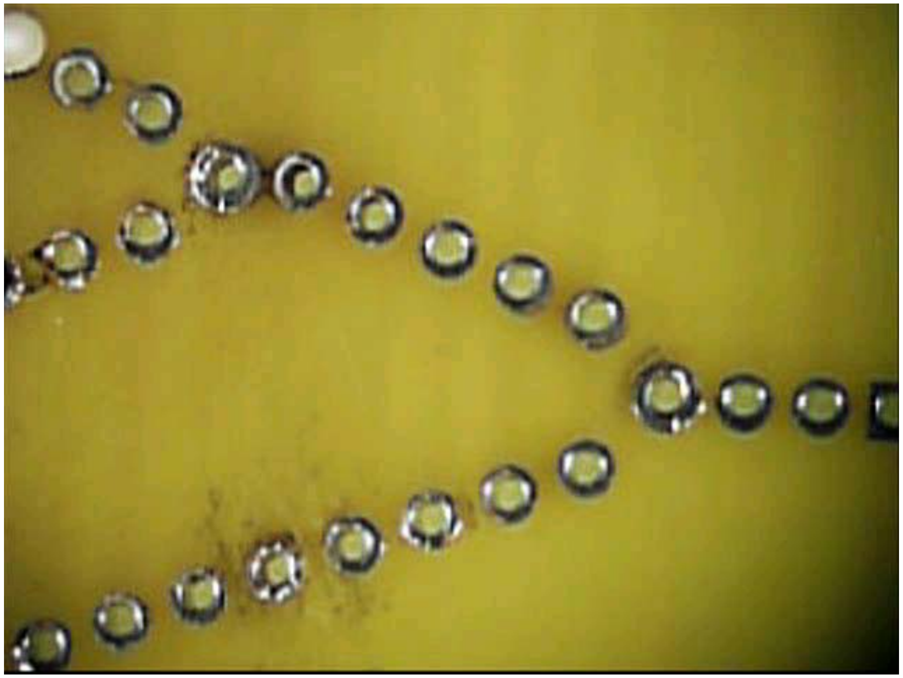
Fluid chip function:

Mixing of two droplets of aqueous suspension and encapsulation inside oil droplet

sulfate latex →

gold nanoparticles →

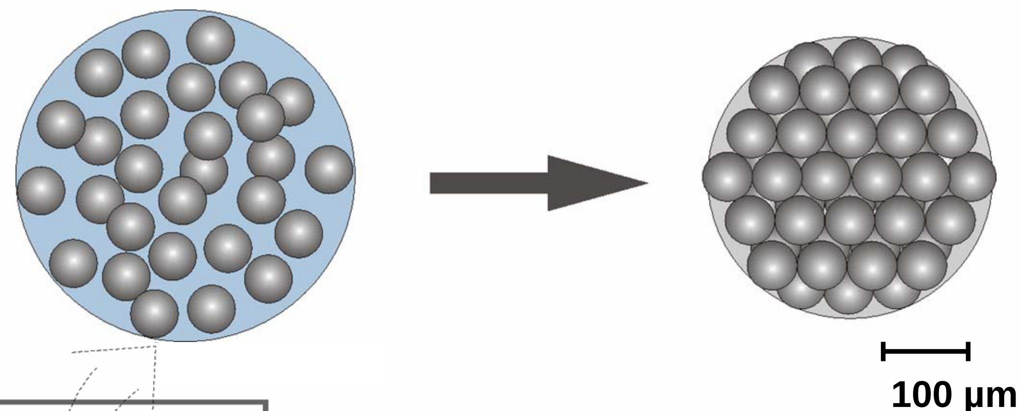
dodecane →

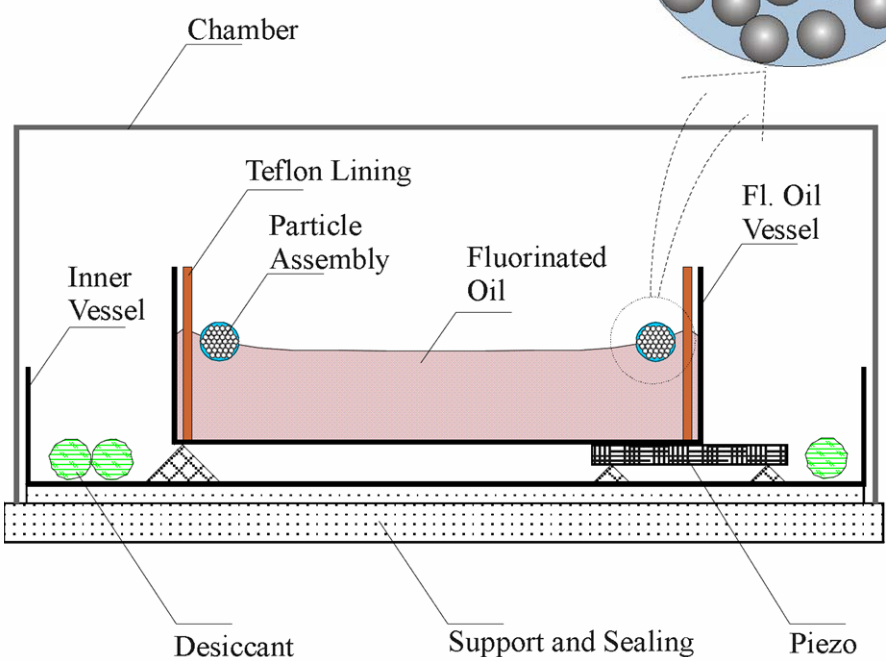


"Outside-in" templating:

Advanced structured particles templated by surface tension

The droplets float suspended on the surface of perfluorinated hydrocarbon oil





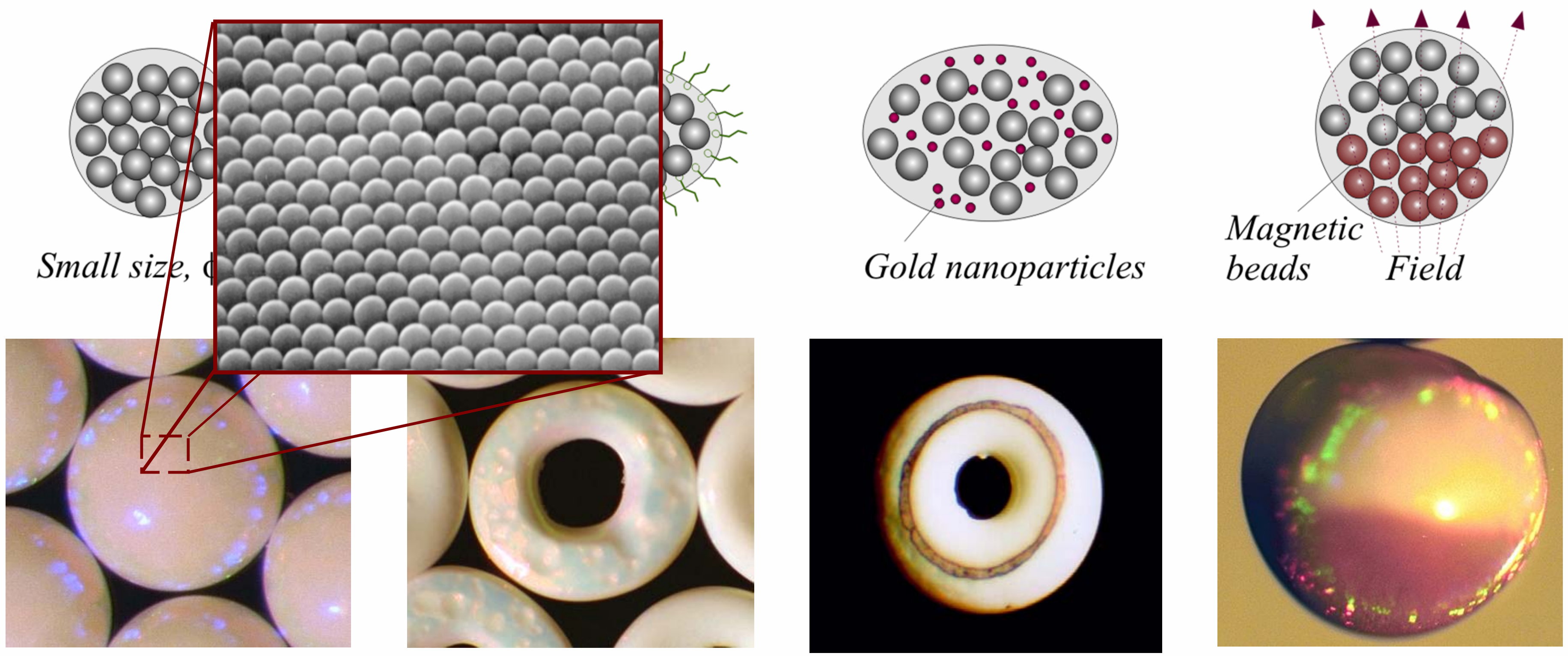
Droplet shape depends on Bond number

$$\beta = \frac{\Delta\rho\, g\, b^2}{\gamma_{12}}$$

For $\beta \geq 1$ the droplets flatten

Droplet assembly

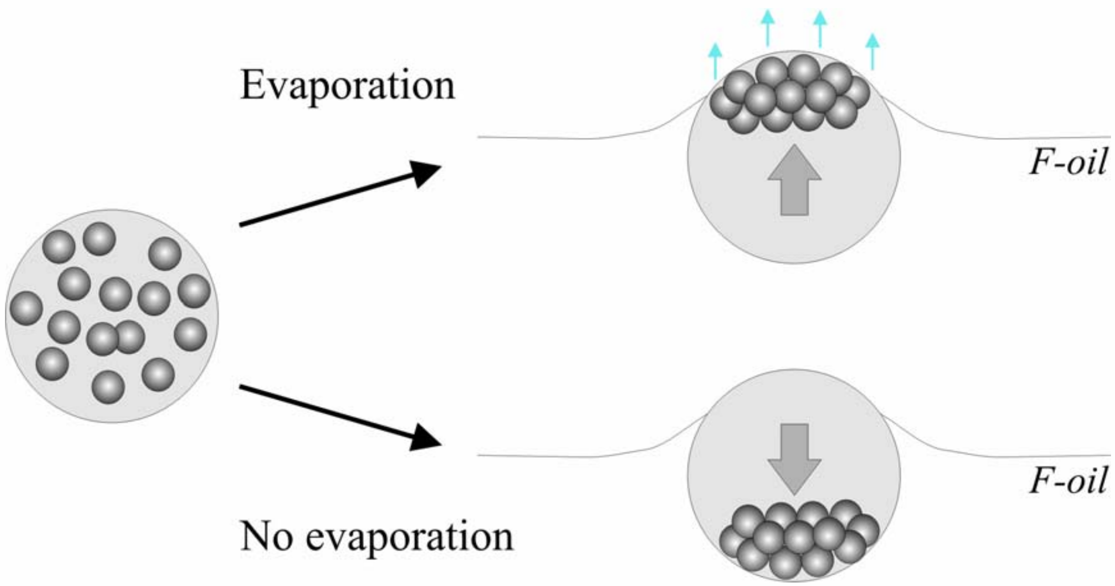
Examples of the advanced structured obtained



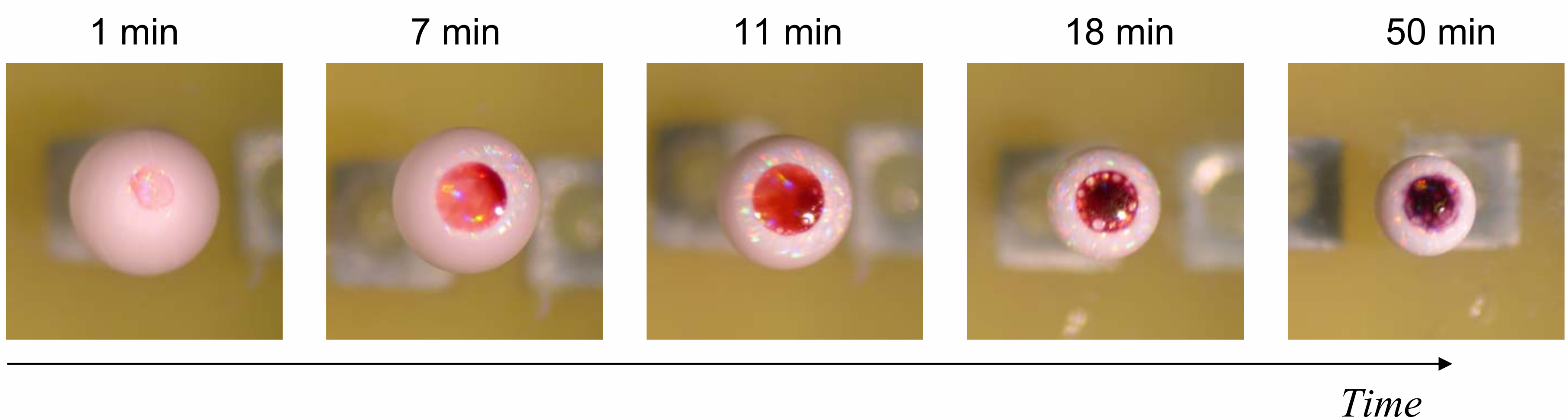
$\beta \to 0$	$\beta > 0$		
Spherical	Thoroidal "doughnuts"	Metal coated doughnuts	Half-magnetic

Velev, Lenhoff and Kaler, *Science*, 287, 2240 (2000).

Dielectrophoretic chips with microdroplets:
Internal particle separations

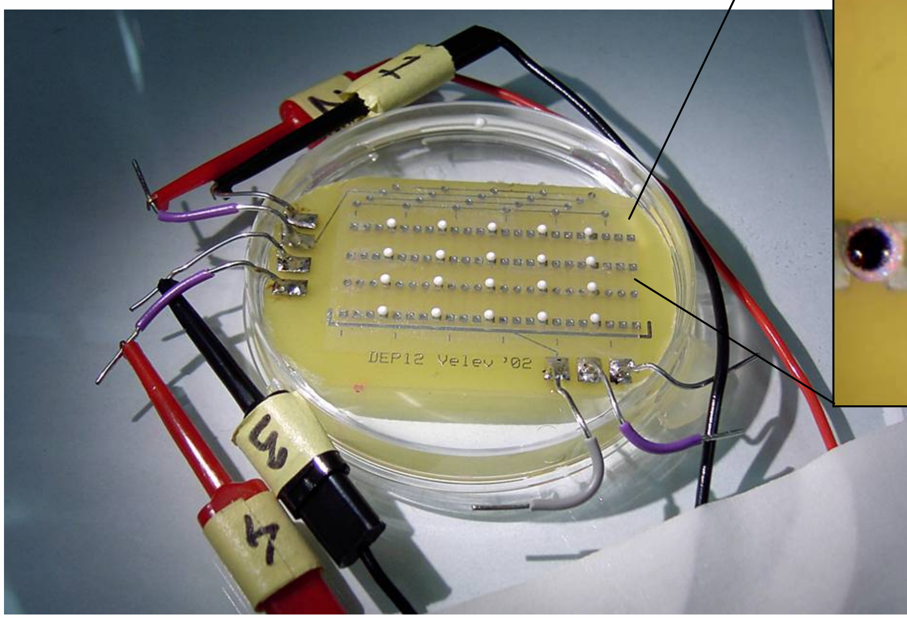


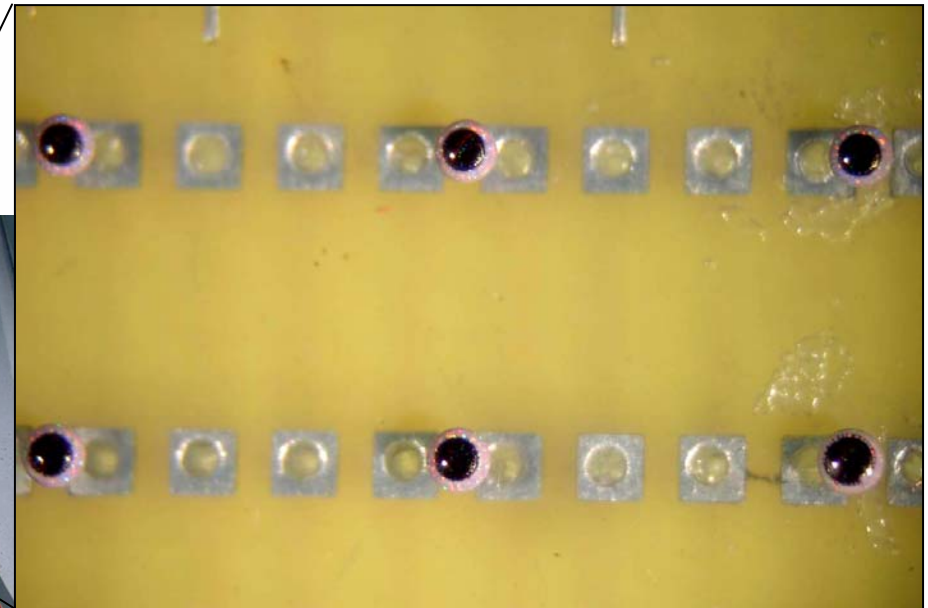
Thermal gradients due to evaporation lead to Marangoni effect and thermophoretic particle separation on top



Fluid chip parallelization:

Simultaneous materials synthesis in multiple on chip droplet "microreactors"



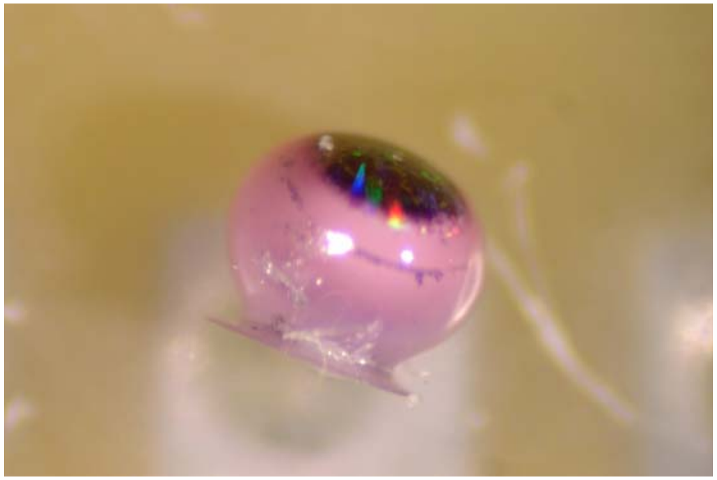


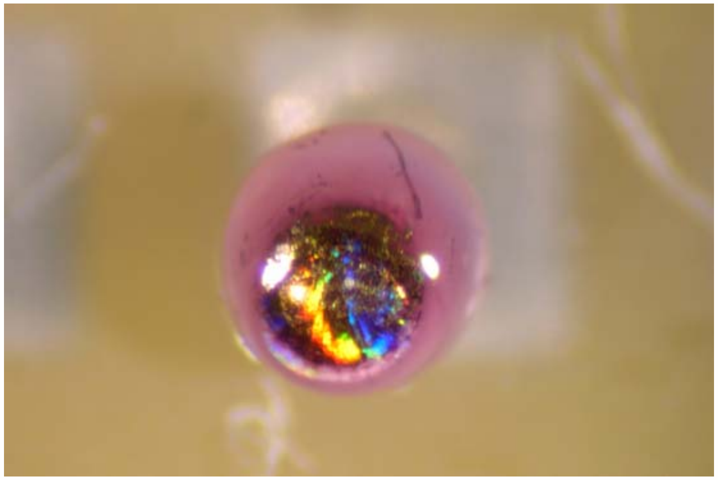
Advanced particle assembly in droplets

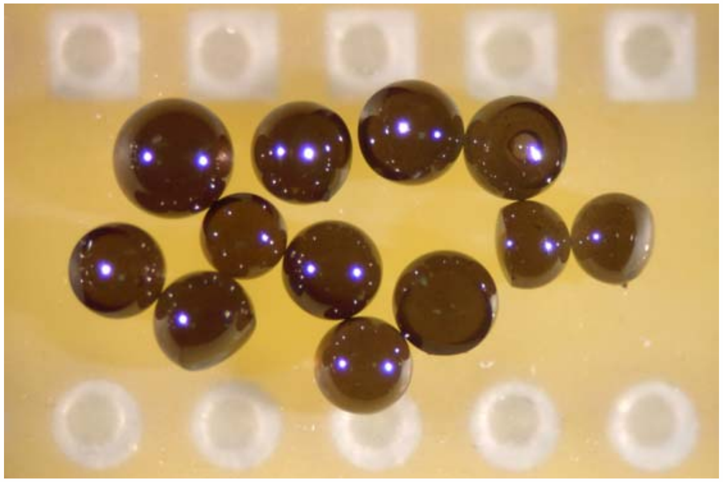
Massive parallelization possible

Encapsulation inside oil droplet: Polymerized shells

Photopolymerized particles with hexanediol diacrylate (HDDA)







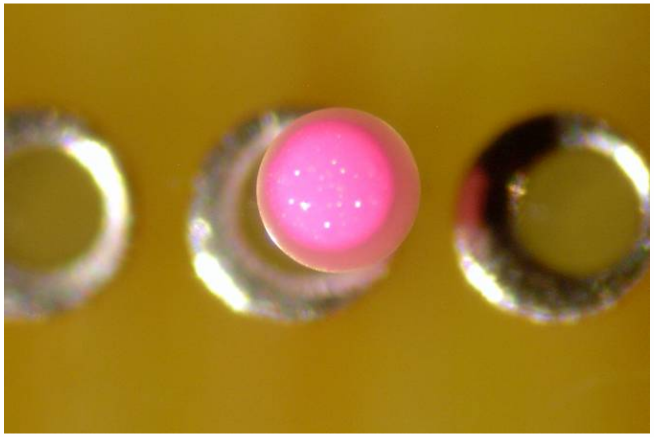
Encapsulated suspension droplets

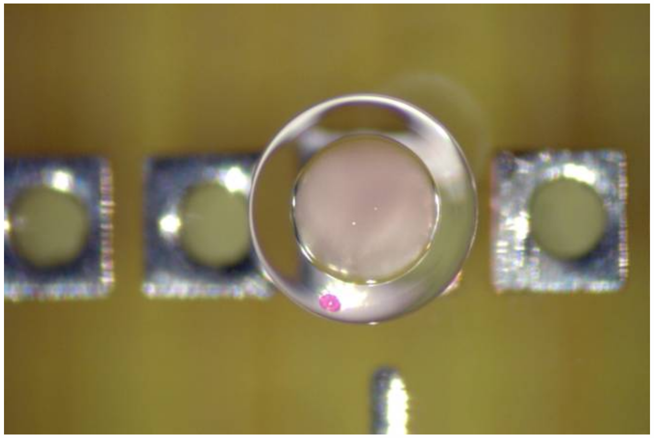
Polymer laced with gold nanoparticles

All products can be encapsulated

Summary: Liquid-Liquid Microfluidics

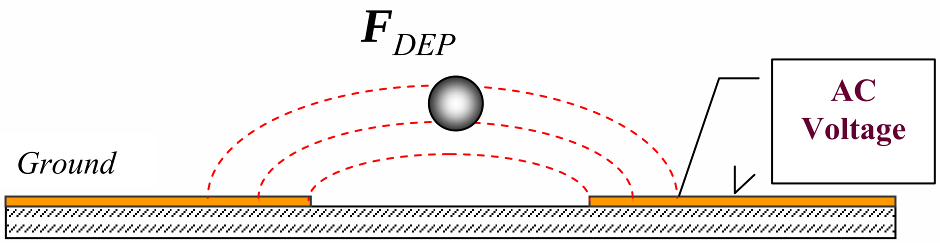
- Microfluidics without any walls or channels
- Simple, inexpensive, flexible, great experimentation tool
- Fundamental effects yet to be explained: droplet charging and internal polarization
- Technological potential for
  - Parallelization
  - Single cell/biomolecule transport
  - Materials synthesis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





Velev, Prevo and Bhatt, *Nature*, 426, 515 (2003)

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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ARO STIR

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http://crystal.che.ncsu.edu

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