Directed Assembly by Energy Stored in Soft Matter

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Soft Matter Self-Assembly
29 June - 7 July 2015
International School of Physics
"Enrico Fermi"
Villa Monastero

PENN

Motivation

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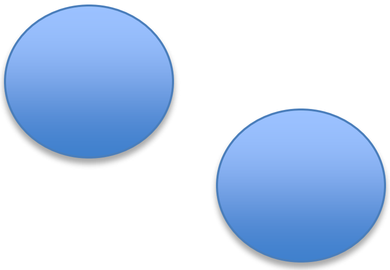
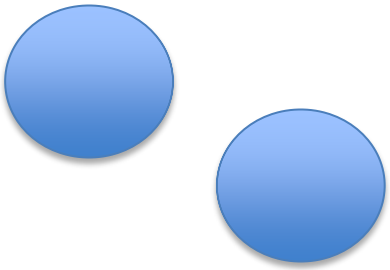
Energy of interaction:

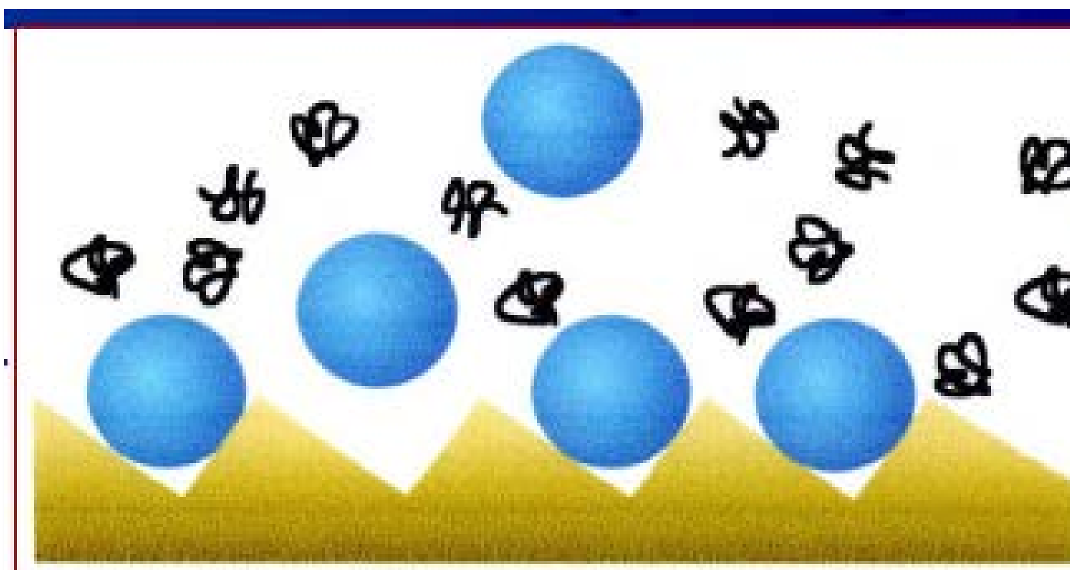
Aroms: Lennard Jone potential;
Born repulsion--thermal

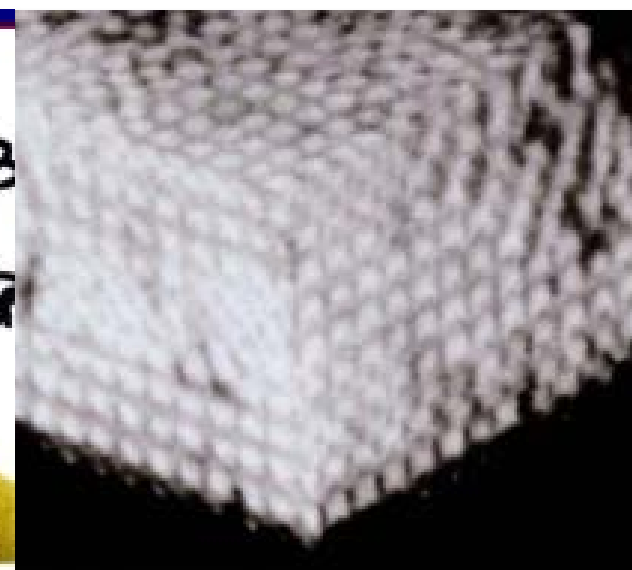


Energy of interaction:

Colloids: eg: electrostatics, van der Waals, excluded volume -thermal



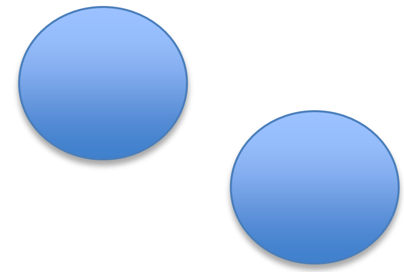




Small particles can serve as model “atoms” or “molecules”

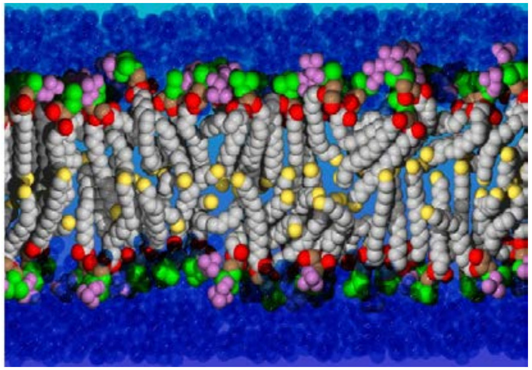
Energy of interaction:

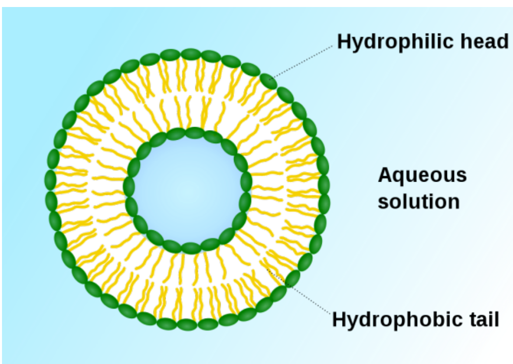
Colloids: eg: electrostatics, van der Waals, excluded volume - thermal

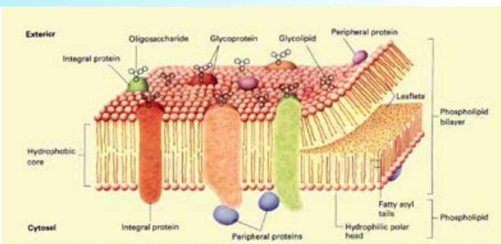


Bigger, non-Brownian particles can serve as model “atoms” or “molecules” in zero temperature limit to let us learn about their interactions

Self Assembly







▲ **Figure 13-1** A phospholipid bilayer constitutes the basic structure of biological membranes. The hydrophobic fatty acyl tails of the phospholipids form the middle of the bilayer; the polar, hydrophilic heads of the phospholipids line both surfaces. Integral proteins have one or more regions embedded in the lipid bilayer. Peripheral proteins are primarily associated with the membrane by specific protein-protein interactions. Oligosaccharides bind mainly to membrane proteins; however, some bind to lipids, forming glycolipids.

Directed Assembly

Typically: Apply an external (electro-magnetic) field to drive particles into some structure

Usually $\gg k_B T$

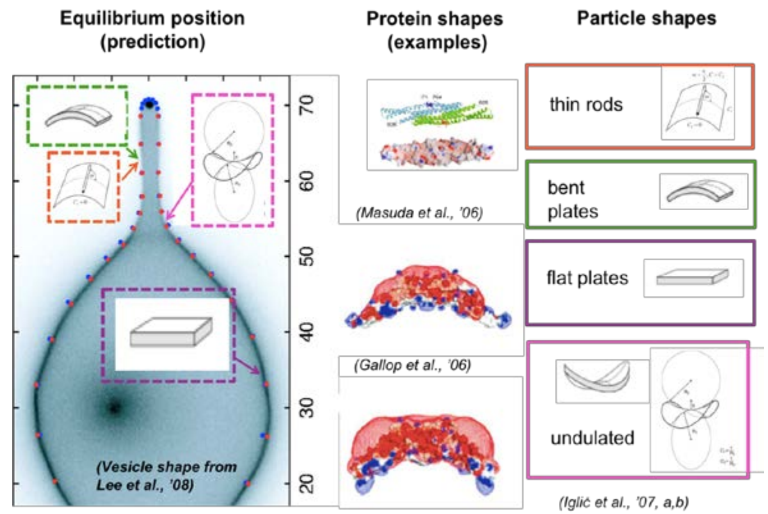
Directed Assembly by Energy Stored in Soft Matter

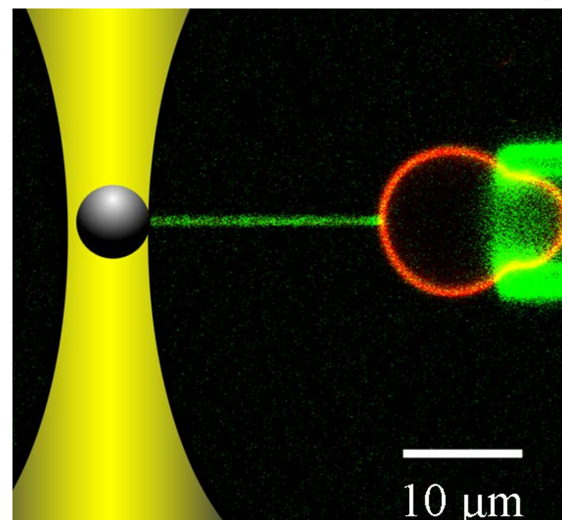
Particles distort soft matter

Distortions store energy

This energy can direct particles
 to assemble

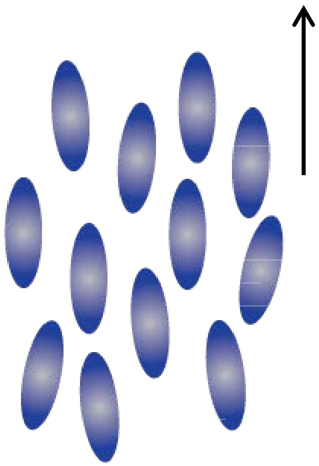
e.g. curvature generating
 and sensing proteins





Baumgart lab

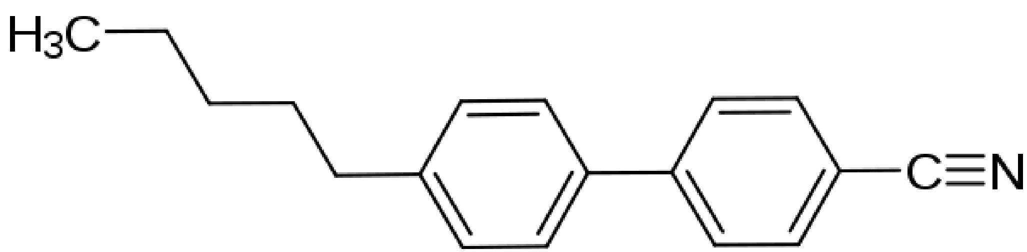
Example: 5CB: Nematic Thermotropic Liquid Crystal

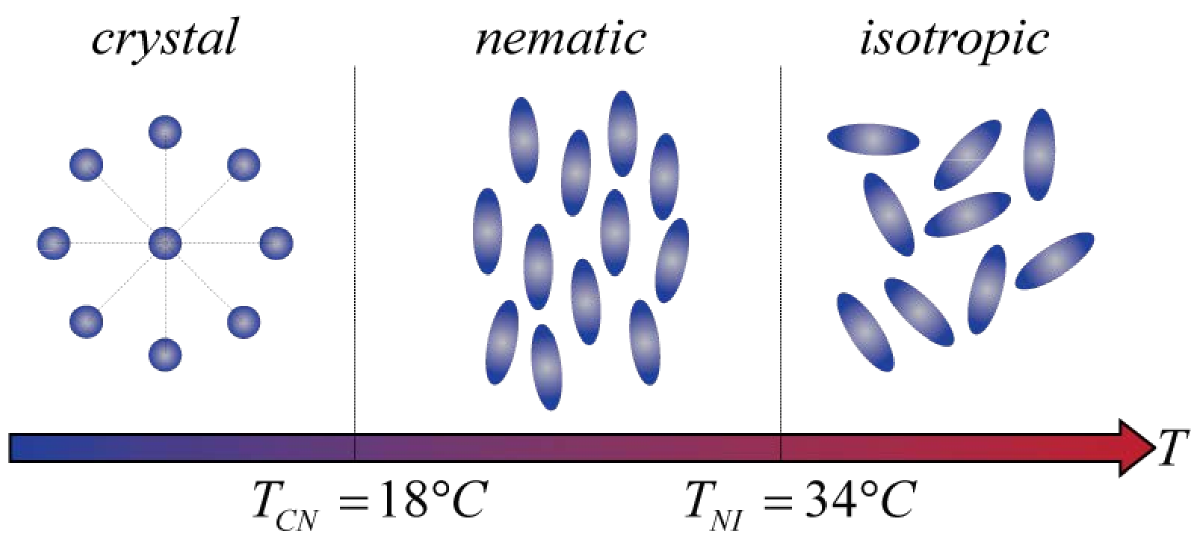


$\vec{n} = director$

nematic

4-Cyano-4'-pentylbiphenyl (5CB)



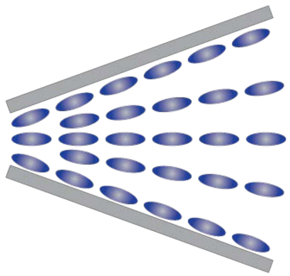


Elastic Distortions & Defects

Fundamental Elastic Distortions

splay

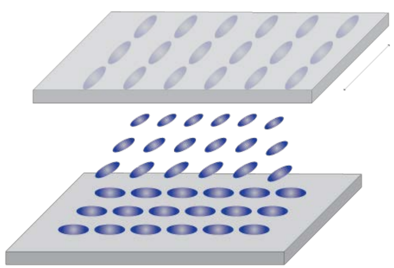
div $\mathbf{n} \neq 0$



$$E_{splay} = \frac{1}{2} K_1 \left[\nabla \cdot \mathbf{n} \right]^2$$

twist

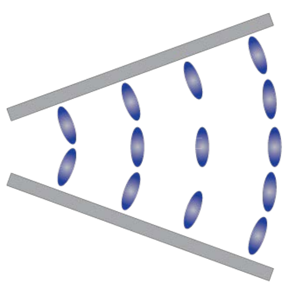
curl $\mathbf{n} \perp \mathbf{n}$



$$E_{twist} = \frac{1}{2} K_2 \left[\mathbf{n} \cdot \left(\nabla \times \mathbf{n} \right) \right]^2$$

bend

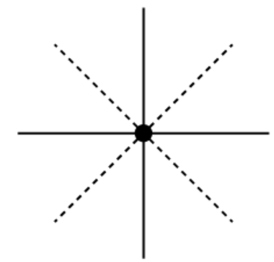
curl $\mathbf{n} \parallel \mathbf{n}$



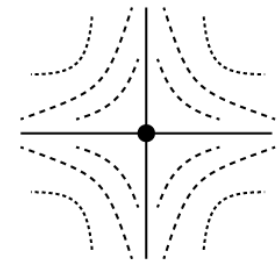
$$E_{bend} = \frac{1}{2} K_3 \left[\mathbf{n} \times \left(\nabla \times \mathbf{n} \right) \right]^2$$

$$\boxed{F_v = E_{splay} + E_{twist} + E_{bend}}$$

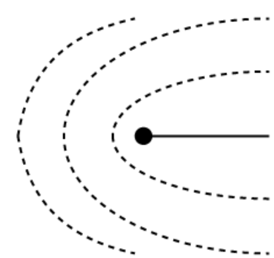
Topological Defects



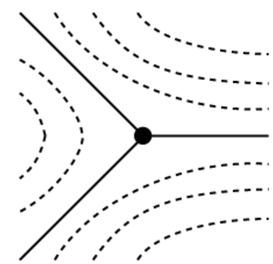
$s = 1$



$s = -1$



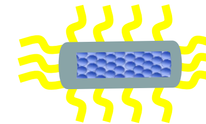
$s = \frac{1}{2}$



$s = -\frac{1}{2}$

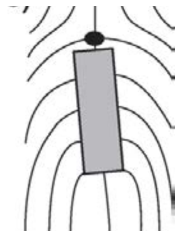
$$\boxed{s = \frac{\theta}{2\pi}}$$

Elastic Distortions & Defects: rods



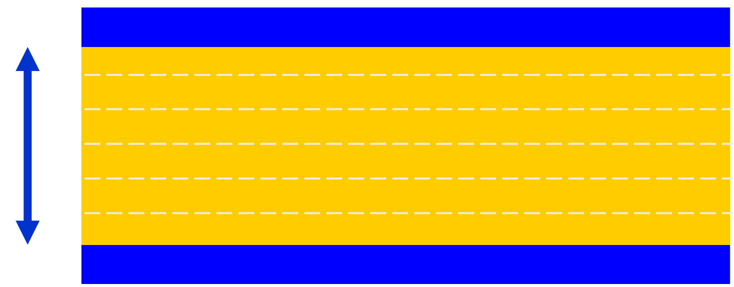
Microrod -induced defect structure in LC: DIPOLE*

DP small h; QP large h; DP chaining
U.Tkalec et al., Soft Matter, 2008

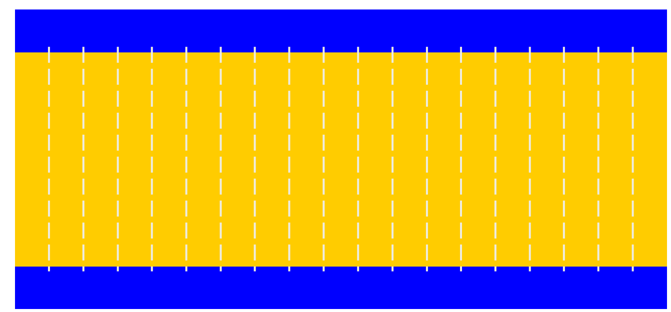


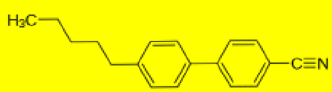
Planar anchoring of nematic LC

h=25μm



Homeotropic anchoring





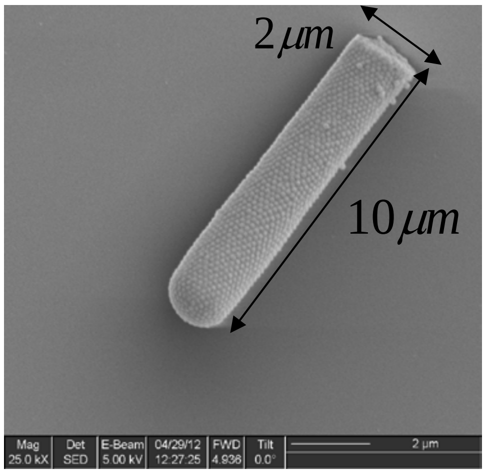
Nematic LC
Analogy to electrostatics

$$F_{\text{har}} = \tfrac{1}{2} K \sum_{\mu = x,y} \int d^3 r (\nabla n_\mu)^2$$

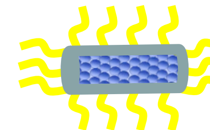
$$\nabla^2 n_\mu = 0$$

$$n_\mu = \frac{A^\mu}{r} + \frac{\mathbf{p}^\mu \cdot \mathbf{r}}{r^3} + \frac{c^\mu_{ij} r_i r_j}{r^5} + \cdots$$

Elastic Distortions & Defects: rods

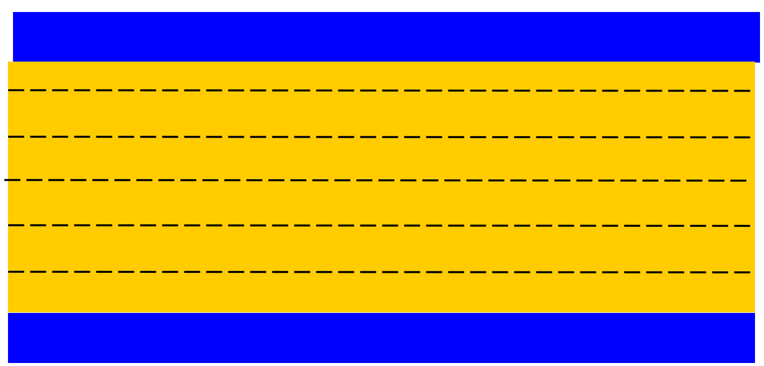


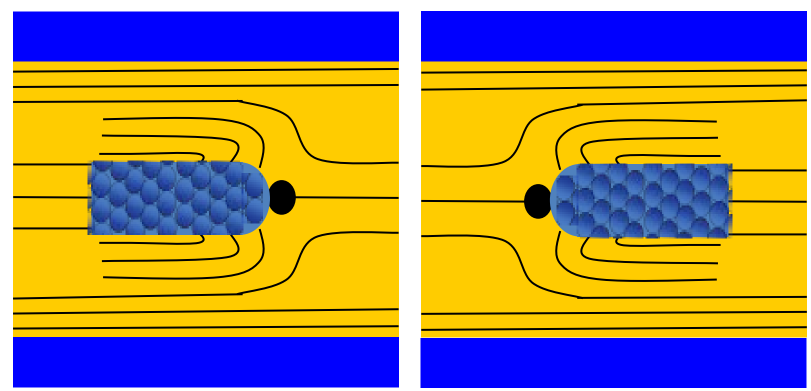
- Contain silica nps
- treated with DMOAP to impose homeotropic anchoring of NLC at their surfaces



Dipolar deformation:
Point defect at curved end

Planar anchoring





Dipoles

- in x-y plane
- parallel or antiparallel alignment

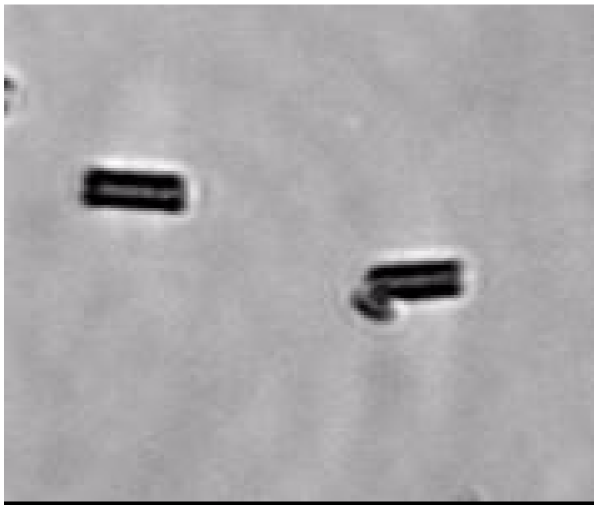
Elastic Distortions & Defects: rods

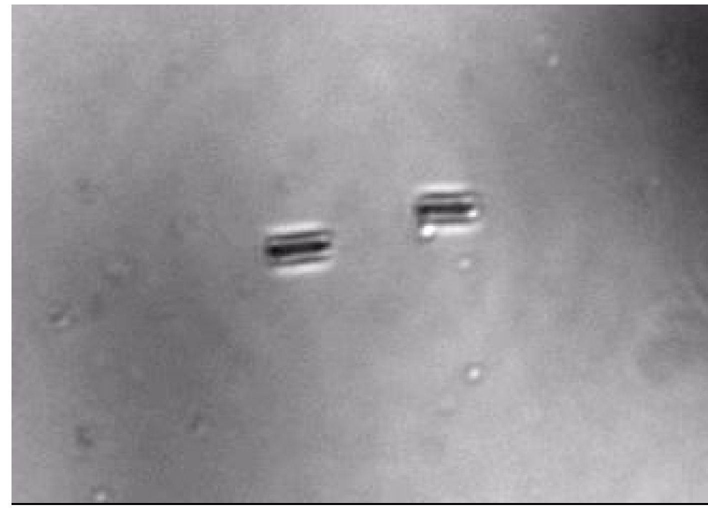
$\Delta E \sim 300\text{-}1200kT$

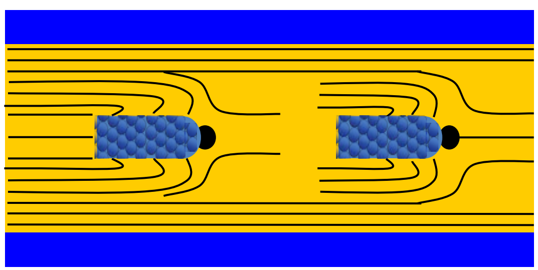
Parallel dipoles: chain

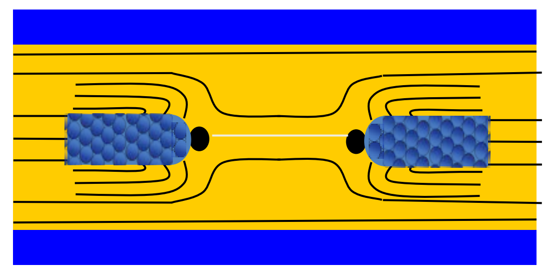
Anti-parallel dipoles: side-to-side

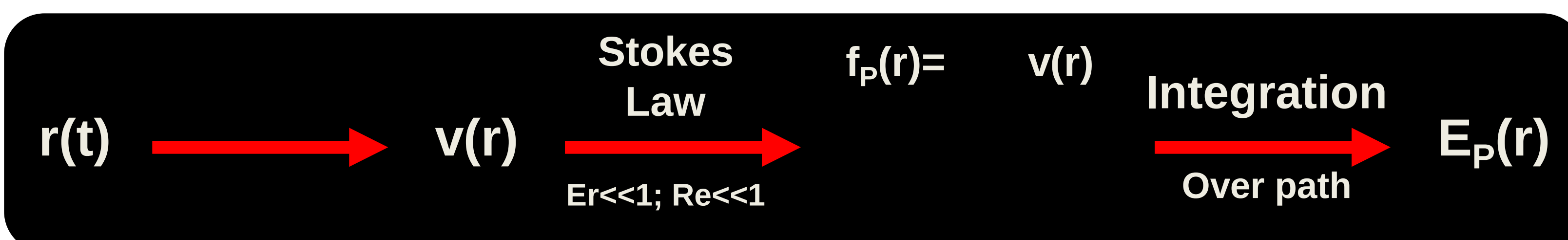
110s



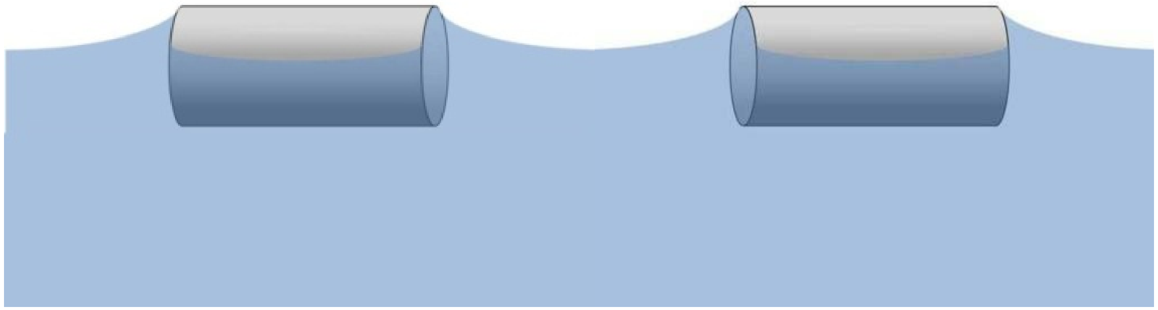




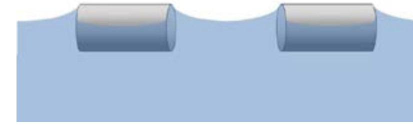




Capillary interactions between particles trapped at fluid interfaces



Cylindrical particles on planar interfaces

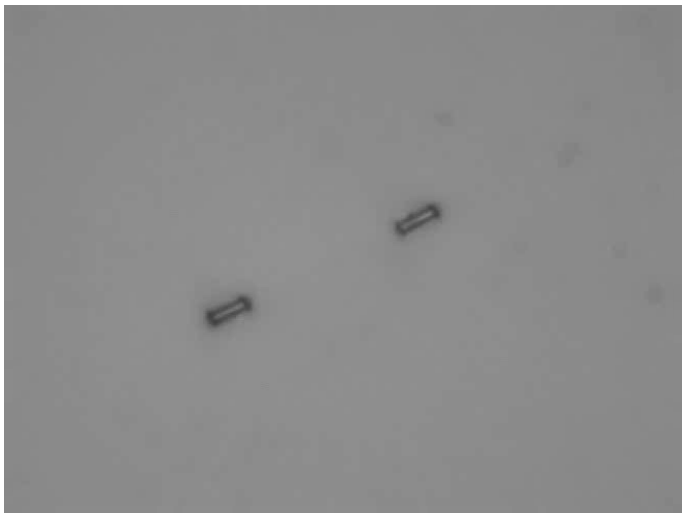


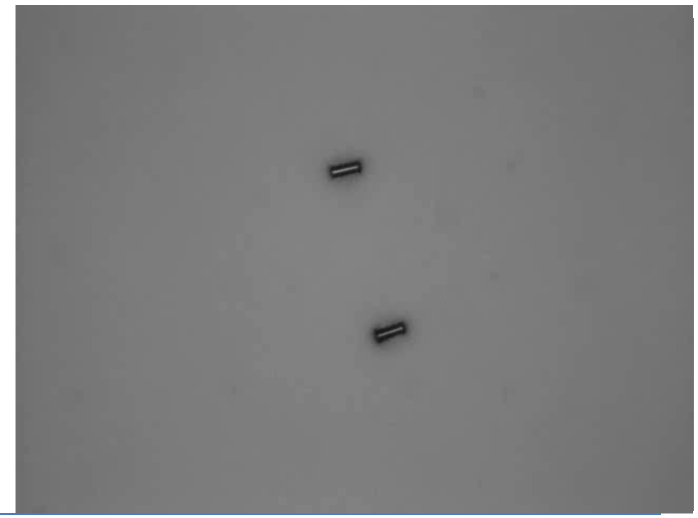
$\Delta E \sim 10^7$ kT

$50\,\mu m$

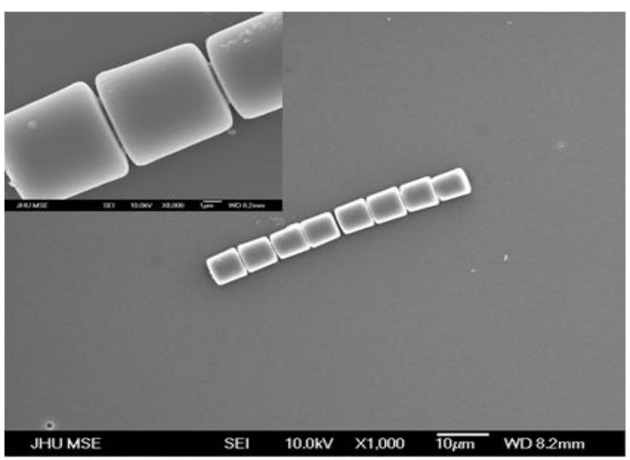
$r_{12init} \sim 180\,\mu m$

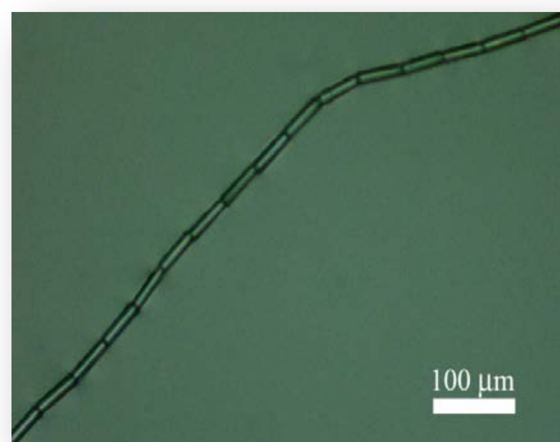
L/2R ~ 2.5





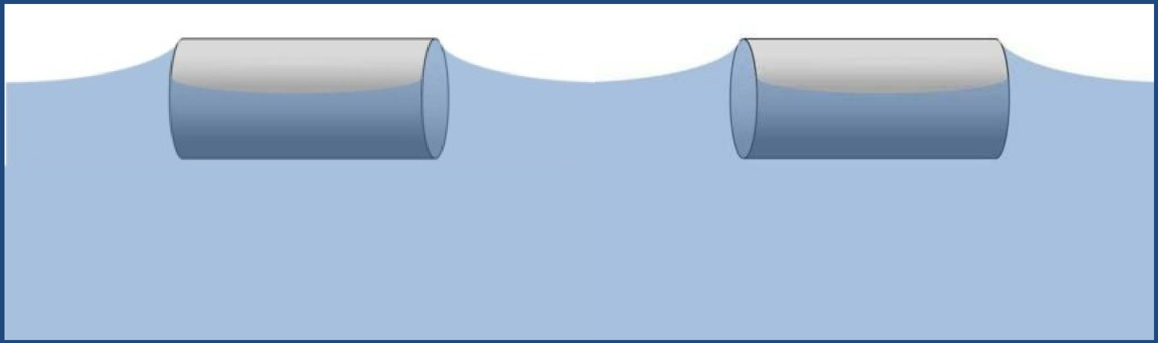
L/2R ~ 1.2





Lewandowski et al, *Langmuir 2010*

Preamble



Length scales

Capillary length= $\sqrt{\dfrac{\gamma}{\Delta\rho g}}$

Particle radius= a

Geometric length of container= L

Radius of curvature of the interface = c^{-1}

Concept:

Surface tension
Wetting energies
Pinning sites

Assume:

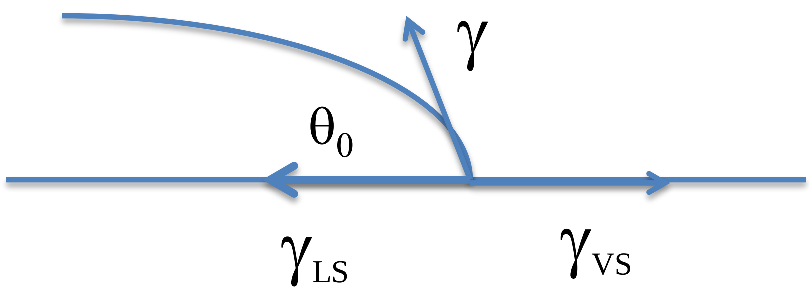
$$\begin{cases} Bo = \dfrac{\Delta\rho g a^2}{\gamma} \ll 1 \\ ac \ll 1; \quad \varepsilon = \left|\nabla h\right| \ll 1 \end{cases}$$

Boundary conditions at the three phase contact line

Equilibrium:

Young's equation

$$\gamma_{LS} - \gamma_{VS} + \gamma \cos\theta_0 = 0$$



Contact line pinning

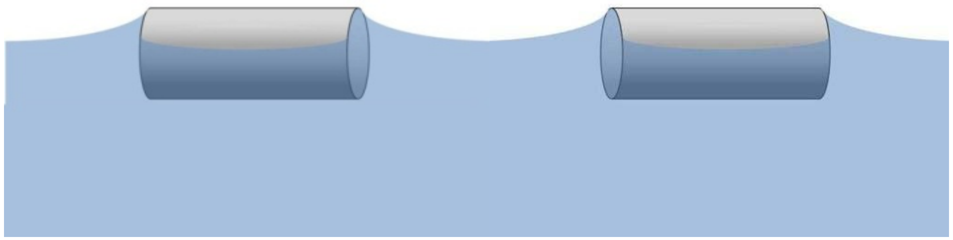
Contact lines becomes trapped at
Rough sites
Patchy wetting (See Blake)

- D. Stamou, C. Duschl and D. Johannsmann, Phys. Rev. E, 2000, 62, 5263.
- D. M. Kaz, R. McGorty, M. Mani, M. P. Brenner and V. N. Manoharan, Nat. Mater, 2012, 11, 138.
- S. Razavi, I. Kretzschmar, J. Koplik and C. E. Colosqui, J. Chem. Phys., 2014, 140, 014904.

Equations governing the shape of isotropic fluid interfaces

Young Laplace Equation

$$2H\gamma = \Delta P$$

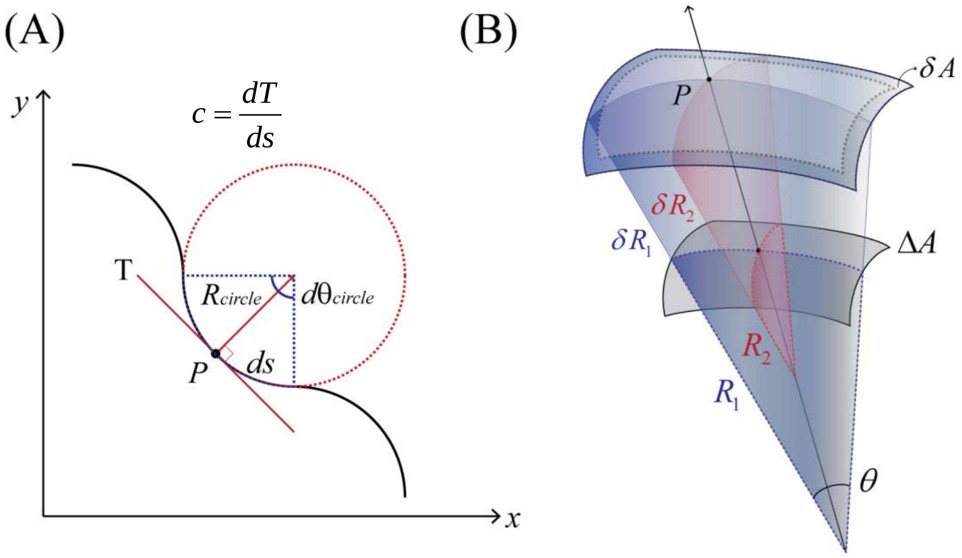


If $\Delta P = 0$, and assuming small slopes:

$$\nabla^2 h = 0$$

Principle radii of curvature

$R_1;R_2$



$c_1=1/R_1$; $c_2=1/R_2$

Curvature

Decompose into isotropic and traceless (deviatoric) parts:

$$\nabla\nabla h_0^I(\boldsymbol{X}) = \frac{1}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} = H_0$$

BOWL

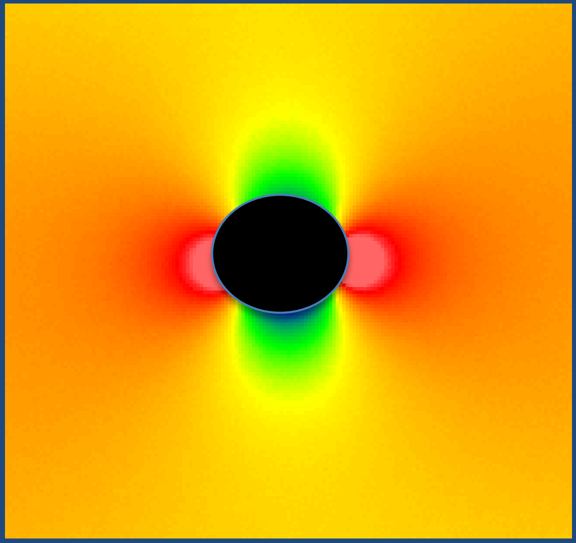
$$\nabla\nabla h_0^D(\boldsymbol{X}) = \frac{1}{2}\left(\frac{1}{R_1}-\frac{1}{R_2}\right)\begin{bmatrix}\cos\varphi & \sin\varphi\\ \sin\varphi & -\cos\varphi\end{bmatrix} = \frac{1}{2}\Delta c_0 \cos 2\varphi$$

SADDLE

$$h_{host} = \frac{\Delta c}{4} r^2 \cos 2\phi + \frac{H_0}{2} r^2$$

Particles trapped at planar interfaces:

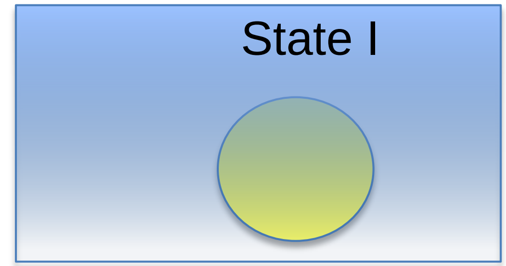
1. equilibrium contact lines
2. pinned contact lines



Particle at equilibrium at a planar interface

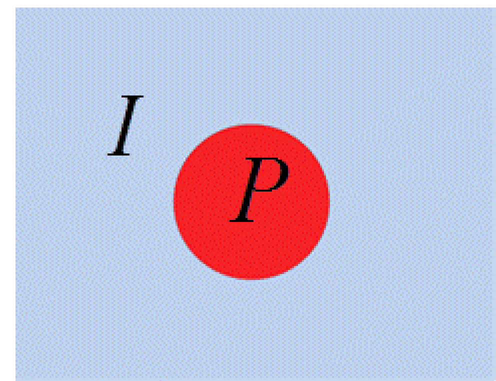
$$\Delta E_{planar}$$

$$E_1 = \gamma_{LS} 4\pi a^2 + \gamma \iint_{I+P} dxdy$$

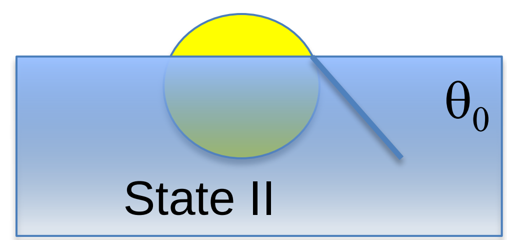


$$dA_{LV} = dxdy;$$

$$\text{integration domain} = I + P$$

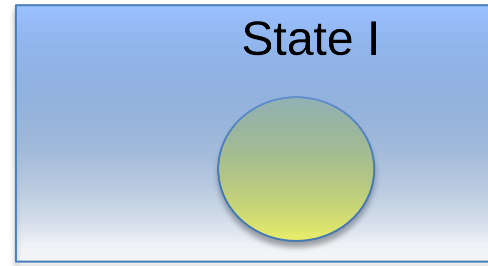


$$E_{II} = \gamma_{LS} A_{LSII} + \gamma_{VS} A_{VSII} + \gamma \iint_{I} dxdy$$

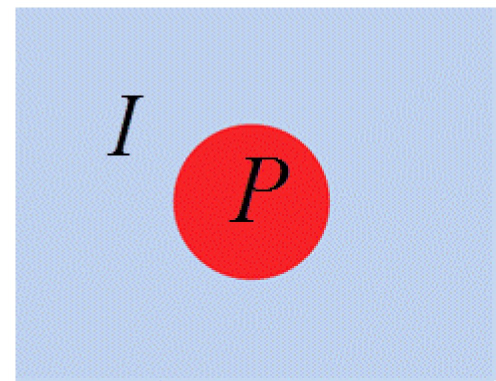


Particle at equilibrium at a planar interface

$$\Delta E_{planar}$$



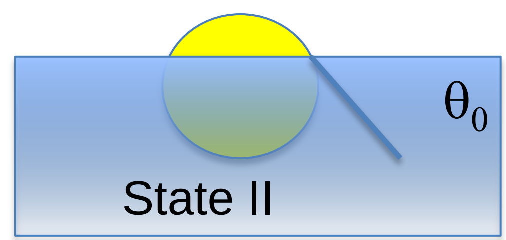
$$\Delta E = E_{II} - E_{I} = (\gamma_{VS} - \gamma_{LS})\Delta A_{VS} + \gamma_{LV}\Delta A_{LV}$$



$$-\Delta A_{LS} = \Delta A_{VS} = 2\pi a^2 (1 - \cos\theta_0)$$

$$\Delta A_{LV} = -\iint_P dxdy = -\pi a^2 \sin^2\theta_0$$

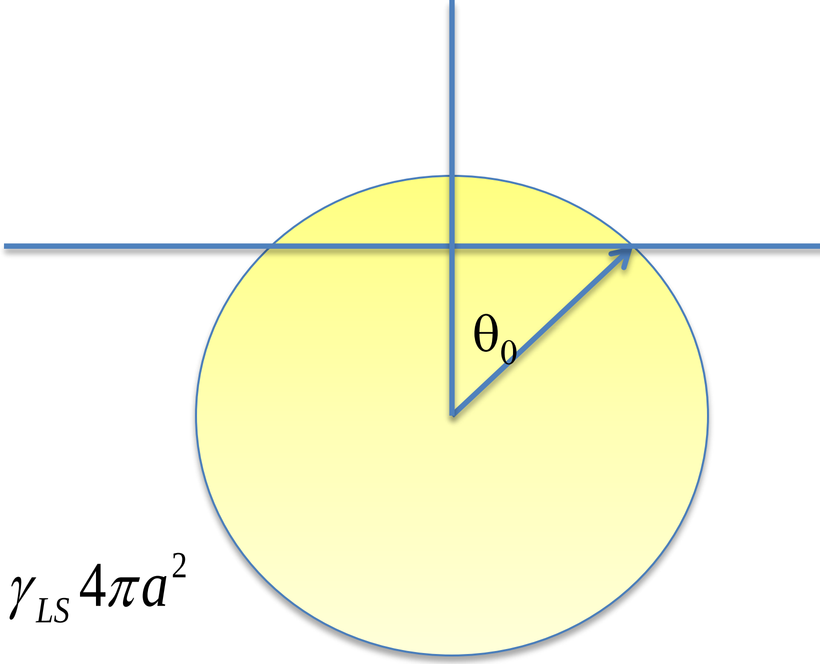
$$\Delta E_{planar} = E_{II} - E_{I} = -\gamma_{LV}\pi a^2 (1 - |\cos\theta_0|)^2$$



Pieranski's trapping energy

P. Pieranski, Phys. Rev. Lett., 1980, 45, 569.

Details



$$E_{planar} = E_2 - E_1 = \gamma_{LS} A_{LSII} + \gamma_{VS} A_{VSII} - \gamma \iint_P dxdy - \gamma_{LS} 4\pi a^2$$

$$A_{LSII} = 4\pi a^2 - 2\pi a^2 (1 - \cos\theta_0)$$

$$A_{VSII} = 2\pi a^2 (1 - \cos\theta_0)$$

$$= 2\pi a^2 (\gamma_{VS} - \gamma_{LS}) + 2\pi a^2 \cos\theta_0 (\gamma_{LS} - \gamma_{VS}) - \gamma\pi a^2 \sin^2\theta_0$$

$$= \gamma\pi a^2 (2\cos\theta_0 - 2\cos^2\theta_0 - \sin^2\theta_0)$$

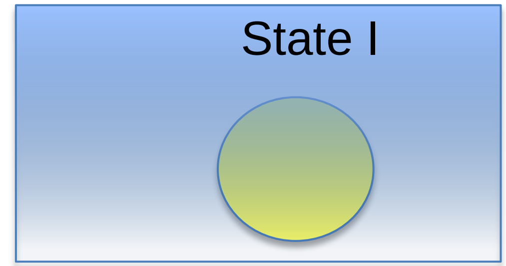
$$= -\gamma\pi a^2 [\cos^2\theta_0 - 2\cos\theta_0 + 1]$$

$$= -\gamma\pi a^2 (1 - \cos\theta_0)^2$$

Comment on absolute value

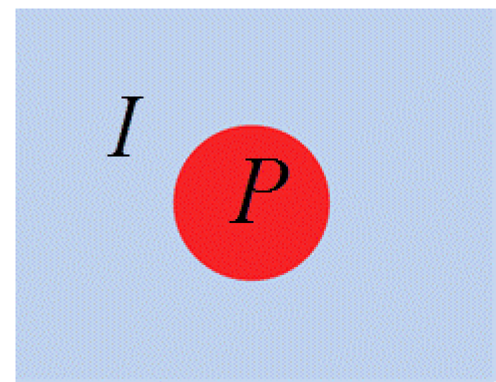
Particle at equilibrium at a planar interface

$$\Delta E_{planar}$$



$$\Delta E_{planar} = E_{II} - E_{I} = -\gamma_{LV}\pi a^2 (1 - |\cos\theta_0|)^2$$

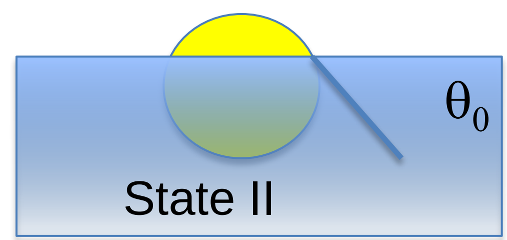
Pieranski's trapping energy



Particle: make a "hole" in the interface.

Reduces the energy of the system.

Reduction modulated by the equilibrium contact angle.



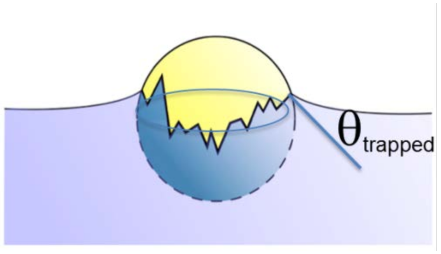
Surface tension: typically 10-20k_BT/nm^2

Microparticles: 10^6 -10^7 k_BT of trapping energy

What if the contact line is pinned?

Particle disturbs the interface:

$\nabla^2 h = 0;\quad$ multipole expansion



$$h(r,\phi) = a_0 + b_0 \ln r + \sum_{m=1}^{\infty} (a_m r^m + b_m r^{-m}) \cos m\phi + (c_m r^m + d_m r^{-m}) \sin m\phi$$

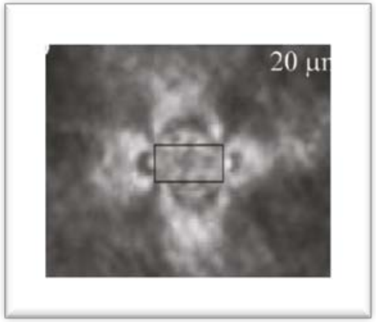
Monopole and dipole are zero in absent of external force and torque

$$h = h_{qp} \frac{a^2}{r^2} \cos 2\phi + \text{faster decaying terms}$$

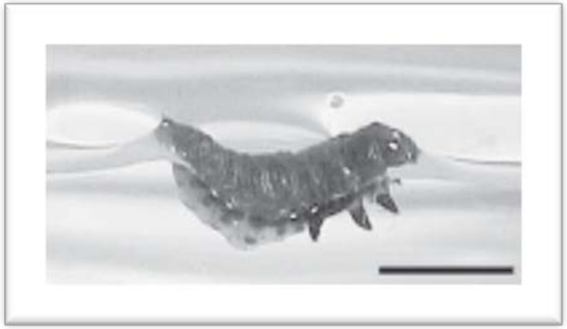
Particle shape, boundary condition makes deformation: Examples of quadrupolar deformation fields

Poppy seed ~1mm
Hinsch '82

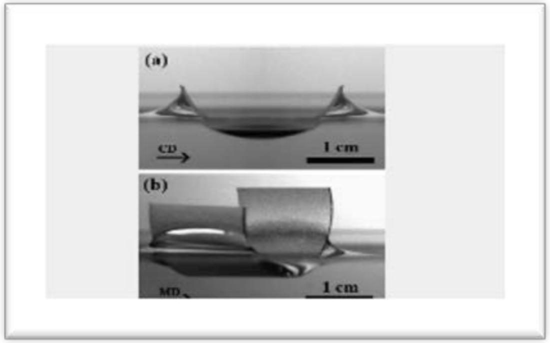
Ellipse '05-'06
Loudet



Cylinder '08-'10
Lewandowski



Water lily leaf beetle 2mm Hu '05

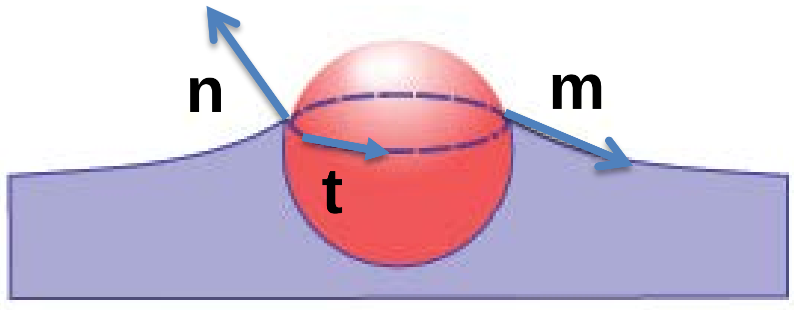


Paper strip '11 Douezan

Undulated contact line owing to particle shape

Monopole deformation is zero absent external force

$$h = b_0 \ln r$$



$$\mathbf{t} = -1\mathbf{e}_\phi$$

$$\mathbf{n} = \mathbf{e}_r - \frac{b_0}{a}\mathbf{e}_z$$

$$m_k = -(e_{21k}e_{n1} + e_{23k}e_{n3})$$

$$\mathbf{m} = \mathbf{e}_r + \frac{b_0}{a}\mathbf{e}_z$$

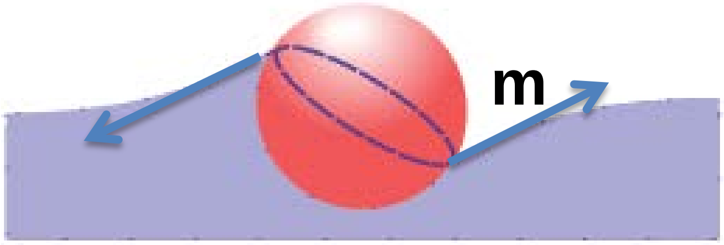
$$\mathbf{F} = \gamma \oint_C \mathbf{m} ds$$

$$\mathbf{m} = \mathbf{e}_r + \frac{b_0}{a}\mathbf{e}_z$$

$$F_z = \gamma \frac{b_0}{a}(2\pi a) = 2\pi\gamma b_0$$

Dipolar deformaiton is zero absent external torque

$$h = b_1 \frac{a}{r} \cos\phi$$



$$\mathbf{m} = \mathbf{e}_r - \frac{b_1}{a}\cos\phi\,\mathbf{e}_z$$

$$\mathbf{e}_R = \mathbf{e}_r + \frac{b_1}{a}\cos\phi\,\mathbf{e}_z$$

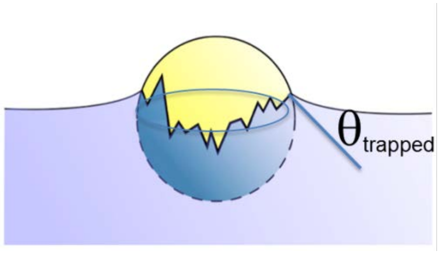
$$(\mathbf{e}_R x \mathbf{m})_k = e_{13k}(-\frac{b_1}{a}\cos\phi) + e_{31k}\frac{b_1}{a}\cos\phi$$

$$(\mathbf{e}_R x \mathbf{m}) = 2\frac{b_1}{a}\cos\phi\,\mathbf{e}_\phi$$

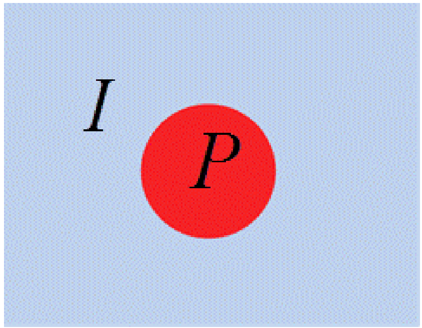
$$\mathbf{T} = \gamma \oint_C \mathbf{e}_R x \mathbf{m} ds = 2a\gamma b_1 \mathbf{e}_{\mathrm{y}}$$

What if the contact line is pinned?

Particle disturbs the interface:



$$h = h_{qp}\frac{a^2}{r^2}\cos 2\phi + \text{faster decaying terms}$$



$$dA_{LV} \approx \left[1 + \frac{\nabla h \bullet \nabla h}{2}\right] dxdy$$

$$E_{II} = \gamma_{LS} A_{LS\,II} + \gamma_{VS} A_{VSII} + \gamma \iint_I dA_{LV} - \gamma \iint_P dA_{LV}$$

Owing to symmetries, disturbance does not alter LS or VS contributions

$$\Delta E = E_{II} - E_1 = \Delta E_{Pieranski} + E_{dist;hqp} = -\gamma_{LV}\pi a^2 (1 - |\cos\theta_{trapped}|)^2 + \gamma\pi h_{hqp}{}^2$$

Details

$$E_{dist,hqp} = \gamma_{LV} \iint_I \frac{\nabla h_{hqp} \bullet \nabla h_{hqp}}{2} dxdy$$

$$\nabla h_{qp} = \frac{\partial h_{qp}}{\partial r}\mathbf{e_r} + \frac{1}{r}\frac{\partial h_{qp}}{\partial \theta}\mathbf{e_\theta}$$

$$\frac{\partial h_{qp}}{\partial r} = -2h_{qp}\frac{a^2}{r^3}(\cos 2\theta)$$

$$\frac{1}{r}\frac{\partial h_{qp}}{\partial \theta} = 2h_{qp}\frac{a^2}{r^3}(-\sin 2\theta)$$

$$\left(\frac{\partial h_{qp}}{\partial r}\right)^2 = \left(-2h_{qp}\frac{a^2}{r^3}\right)^2 (\cos^2 2\theta)$$

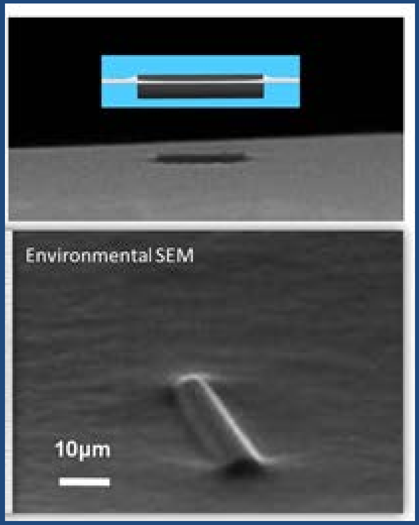
$$\left(\frac{1}{r}\frac{\partial h_{qp}}{\partial \theta}\right)^2 = \left(2h_{qp}\frac{a^2}{r^3}\right)^2 (\sin^2 2\theta)$$

$$\left(\frac{\partial h_{qp}}{\partial r}\right)^2 + \left(\frac{1}{r}\frac{\partial h_{qp}}{\partial \theta}\right)^2 = \left(2h_{qp}\frac{{r_p}^2}{r^3}\right)^2$$

$$2A_{\text{self particle}} = \left(2h_{qp}\right)^2 \int_a^\infty \left(\frac{a^4}{r^6}\right) r\,dr\,d\theta$$

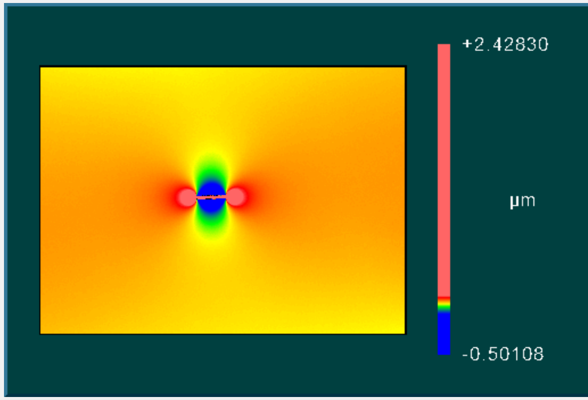
$$A_{\text{self particle}} = 4{h_{qp}}^2 \pi a^4 \int_a^\infty r^{-5} dr = \pi {h_{qp}}^2$$

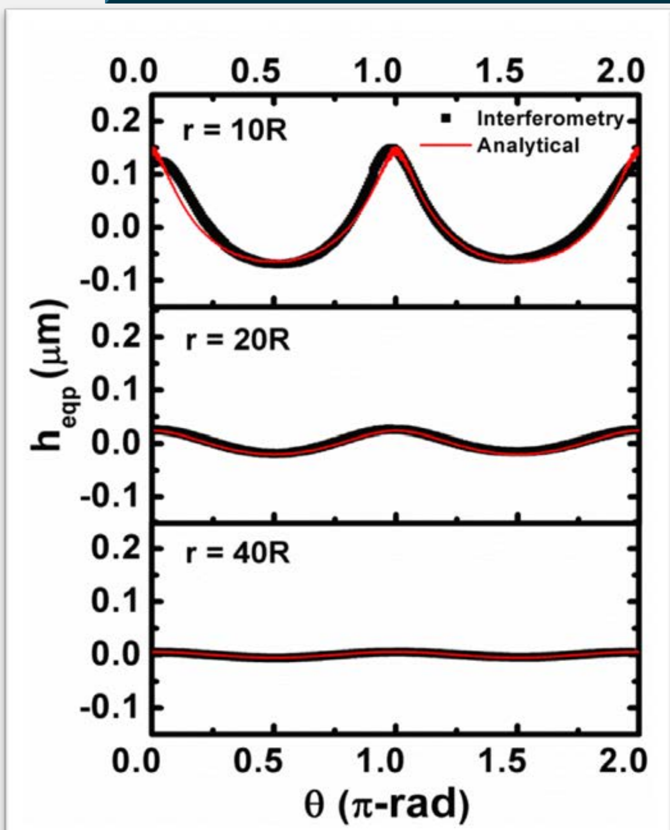
Trapping of particles on interfaces: non-spherical shapes

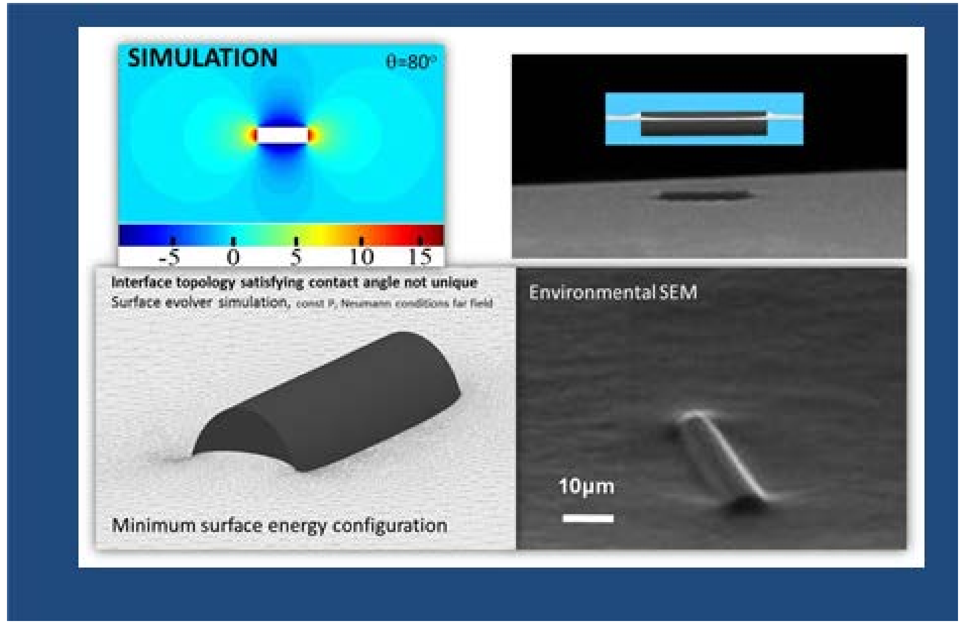


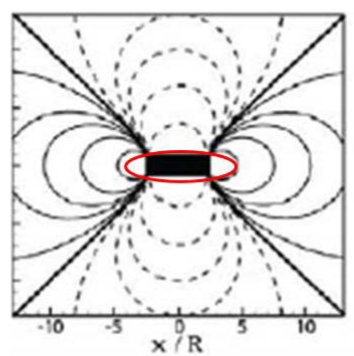
Shape of interface around isolated cylinder

Λ=6; R=10um

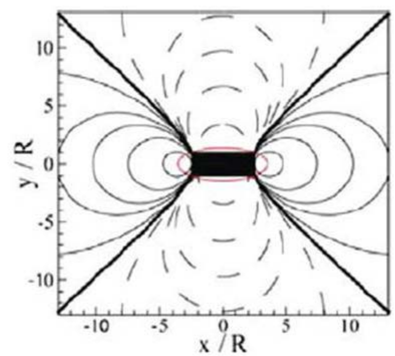




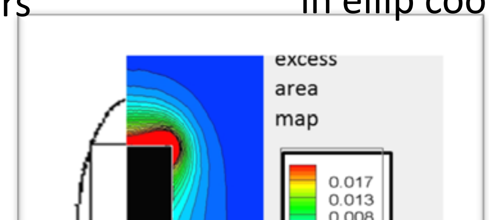




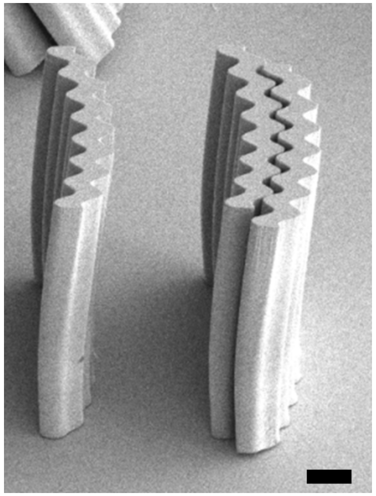
Isoheight contours



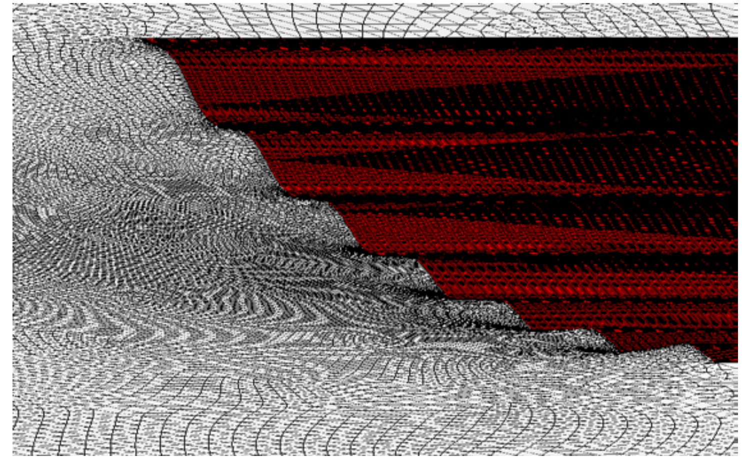
Quadrupole in ellip coord

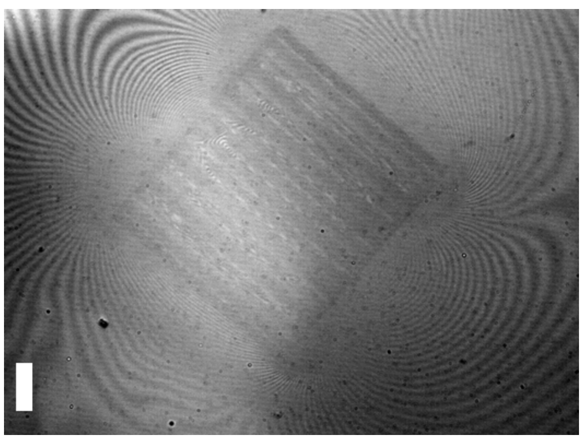


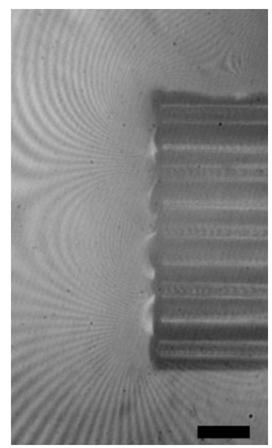
Model roughness

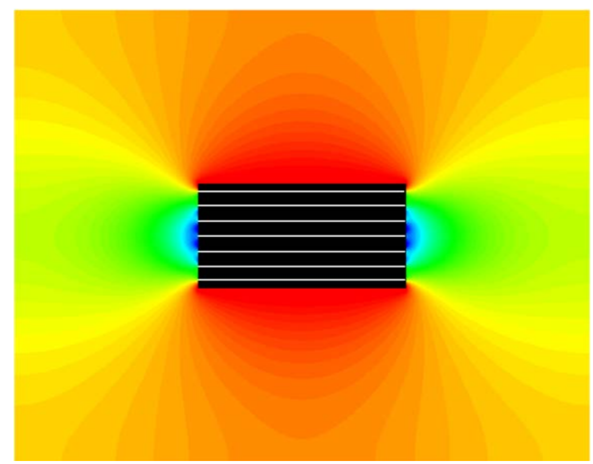


Scale bar 50 microns









Summary for particles on planar surfaces

Particles become trapped at planar fluid interfaces.

Perfectly smooth spheres at equilibrium are trapped and do not perturb the interface.

Particles with pinned contact lines, patchy wetting or non-spherical shapes distort the interface around them.

Distortions due to various particle features observed at different distances from the particle.

All: quadrupolar distortions in the far field.

Moderate to near field, features like particle elongation become apparent.

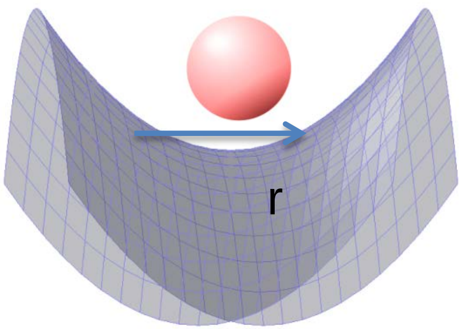
Closer still, waviness, roughness and sharp edges play a role.

Trapping of particles on interfaces: curved interfaces

What if an interface is curved?

$$a\Delta c \ll 1$$

Focus: saddle-shaped surfaces



$$h_{host} = \frac{1}{2}(c_1 x^2 + c_2 y^2) = \frac{\Delta c}{4} r^2 \cos 2\phi$$

$$\Delta c = c_1 - c_2 = \frac{1}{R_1} - \frac{1}{R_2}$$

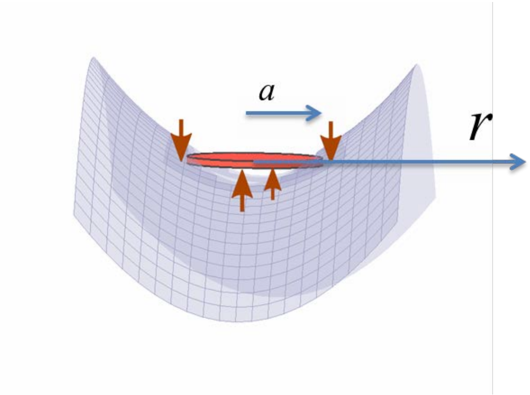
$$\Delta E = E_{II} - E_1 = \gamma_{LS} \iint_{\Delta A_{LS}} dA_{LS} + \gamma_{VS} \iint_{\Delta A_{VS}} dA_{VS} + \gamma_{LV} \iint_{\Delta A_{LV}} dA_{LV}$$

Because of symmetries, the SL and SV areas do not change from planar case

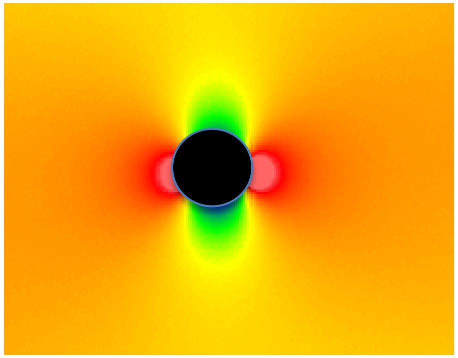
$$\Delta A_{LV} = \Delta A_{LV;\,\mathrm{planar}} + \Delta A_{LV;\,\Delta c}$$

Two cases: pinned contact line; equilibrium contact lines (see arxiv, Sharifi-Mood, Liu, KJS)

Pinned contact line: shape of interface with particle



$$\begin{cases} a\Delta c \ll 1 \\ |\nabla h| \ll 1 \end{cases} \qquad h_{host} = \frac{\Delta c}{4} r^2 \cos 2\phi$$



$$\nabla^2 h = 0$$

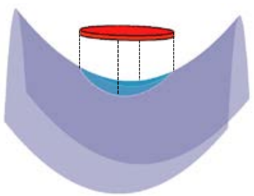
$$h(r = a) = h_{qp} \cos 2\phi$$

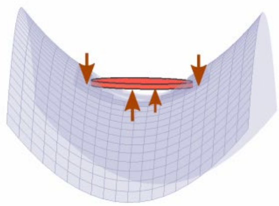
$$h(r \to \infty) = h_{host}$$

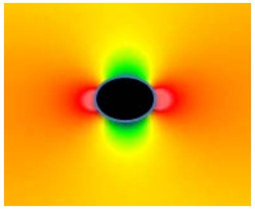
$$h = \frac{\Delta c a^2}{4} \frac{r^2}{a^2} \cos 2\phi + \left(\frac{-a^2 \Delta c}{4} + h_{qp}\right) \frac{a^2}{r^2} \cos 2\phi$$

$$h = h_{host} + \eta_{ind} + \eta_{qp}$$

ΔA_{LV}: Pinned contact line







$$\nabla\eta = \nabla\eta_{hqp} + \nabla\eta_{\Delta c}$$

$$\Delta A_{LV} = \Delta A_{LV,planar} - \iint_P \left(\frac{\nabla h_{host} \bullet \nabla h_{host}}{2}\right) dxdy + \iint_I \left(\frac{\nabla\eta \bullet \nabla\eta}{2}\right) dxdy + \iint_I \left(\nabla\eta \bullet \nabla h_{host}\right) dxdy$$

the increased area of hole under the particle=the increased area of interface from η_{ind}

$$\iint_P \left(\frac{\nabla h_{host} \bullet \nabla h_{host}}{2}\right) dxdy = \iint_I \left(\frac{\nabla\eta_{ind} \bullet \nabla\eta_{ind}}{2}\right) dxdy$$

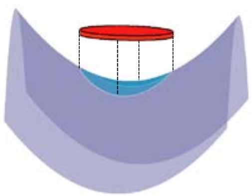
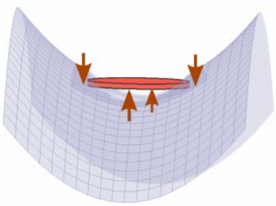
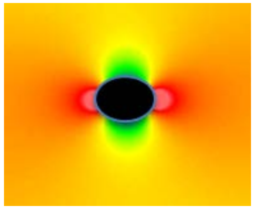
$$\gamma \iint_I \left(\frac{\nabla\eta_{hqp} \bullet \nabla\eta_{hqp}}{2}\right) dxdy = E_{dist,hqp,planar} = \pi h_{qp}{}^2$$

$$\iint_I \left(\nabla\eta_{hqp} \bullet \nabla\eta_{ind}\right) dxdy = -\frac{\pi}{2}\Delta c a^2 h_{qp}$$

$$\iint_I \left(\nabla\eta_{hqp} \bullet \nabla h_{host}\right) dxdy = 0; \quad \iint_I \left(\nabla\eta_{hqp} \bullet \nabla h_{host}\right) dxdy = 0^{**}$$

**typically reported as $-\frac{\pi a^4 \Delta c^2}{8}$ owing to in appropriate neglect of outer contour.

$\Delta E(\Delta c)$: Pinned contact line

$$\Delta E = \Delta E_{planar} - \gamma \pi a^2 \frac{h_{qp} \Delta c}{2}$$

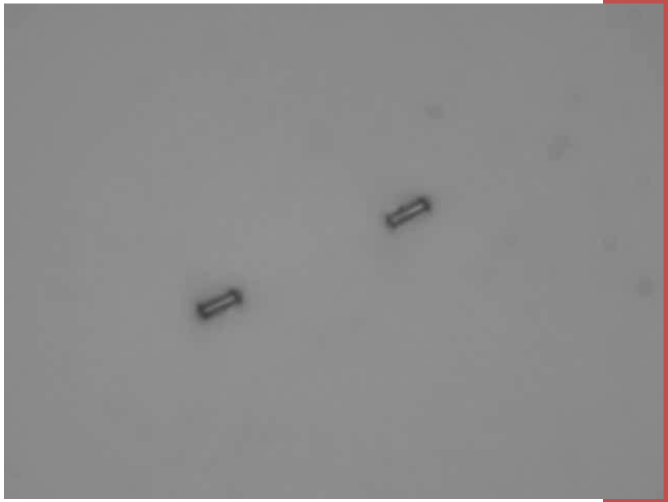
Lewandowski et al (KJS) 2008
Lu, Sharifi-Mood, Liu, (KJS) 2015

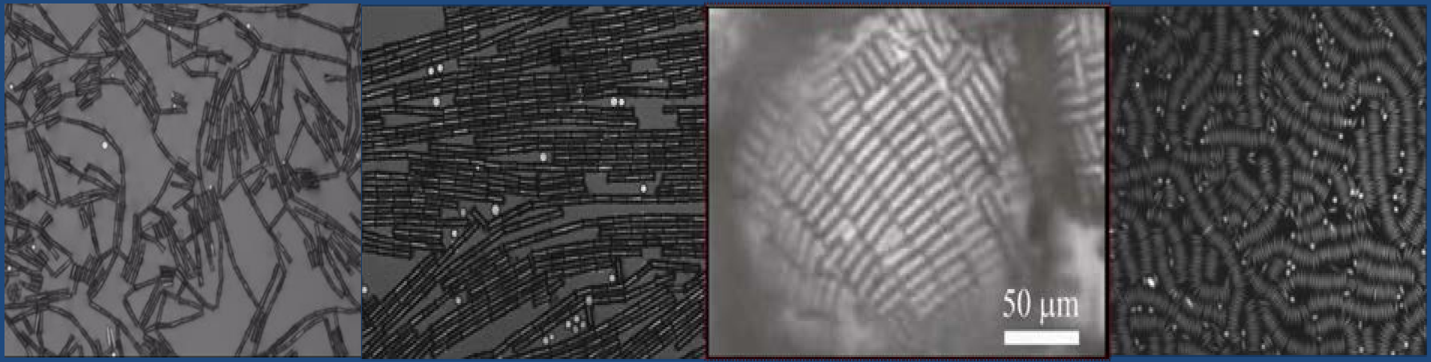
Including Mean Curvature

- See notes

Pair Interactions:

Pinned contact lines



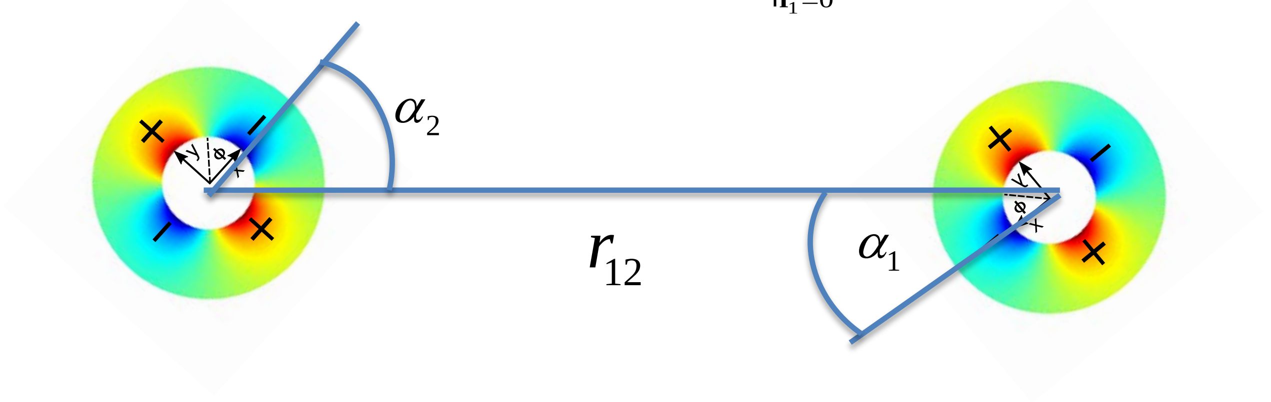


Pair interaction

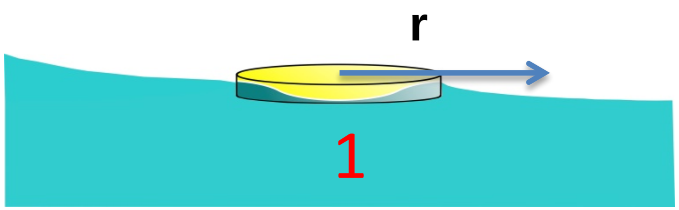
Stamou et al. PRE 2000

$$h_2 = \frac{h_{qp2} a^2}{r_2^2} \cos(2\phi_2 + \alpha_2)$$

$$h_2 = h_2\big|_{\mathbf{r}_1=0} + \mathbf{r} \cdot \nabla h_2\big|_{\mathbf{r}_1=0} + \mathbf{r} \cdot \frac{\nabla\nabla h_2}{2} \cdot \mathbf{r}\Big|_{\mathbf{r}_1=0} + \ldots$$



Pair interaction: Method of reflections



Particle 1 experiences far field boundary condition created by particle 2

$$h_2 = h_2\big|_{\mathbf{r}_1=0} + \mathbf{r}\cdot\nabla h_2\big|_{\mathbf{r}_1=0} + \mathbf{r}\cdot\frac{\nabla\nabla h_2}{2}\cdot\mathbf{r}\Big|_{\mathbf{r}_1=0} + \ldots$$

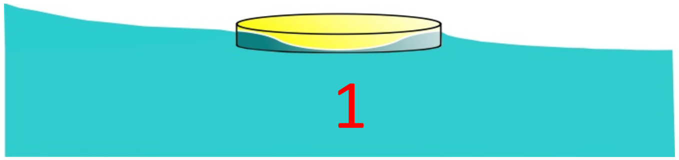
Particle 1 sits in a host interface defined by particle 2

Particle 1

- COM changes position: PV WORK
- rotates into plane of disturbance eliminating dipole
- Sees far field curvature

Stamou et al PRE 2000

Solving for shape of interface around particle 1



$$\nabla^2 h_1 = 0$$
$$h_1(r=a) = h_{qp_1}\cos 2(\phi - \alpha_1),$$

$$h_1(r_1 \to \infty) = \frac{3h_{qp_2}a^2}{r_{12}^4} r^2 \cos 2(\phi + \alpha_2)$$

$$h_1 = \frac{3h_{qp_2}a^2}{r_{12}^4} r^2 \cos 2(\phi + \alpha_2) + \eta_1$$

$$\eta_1 = -\frac{3h_{qp_2}a^2}{r_{12}^4}\frac{a^4}{r^2}\cos 2(\phi + \alpha_2) + h_{qp_1}\frac{a^2}{r^2}\cos 2(\phi - \alpha_1)$$

$$\eta_1 = \eta_{ind} + \eta_{qp}$$

$$\eta = \left(\frac{-a^2\Delta c}{4} + h_{qp}\right)\frac{a^2}{r^2}\cos 2\phi$$

$$\Delta c \text{ from particle } 2 = \frac{12h_{qp_2}a^2}{r_{12}^4}\cos 2(\phi + \alpha_2)$$

treatment differs from literature

Pair interaction

Here- we respect bc at particle and in far field

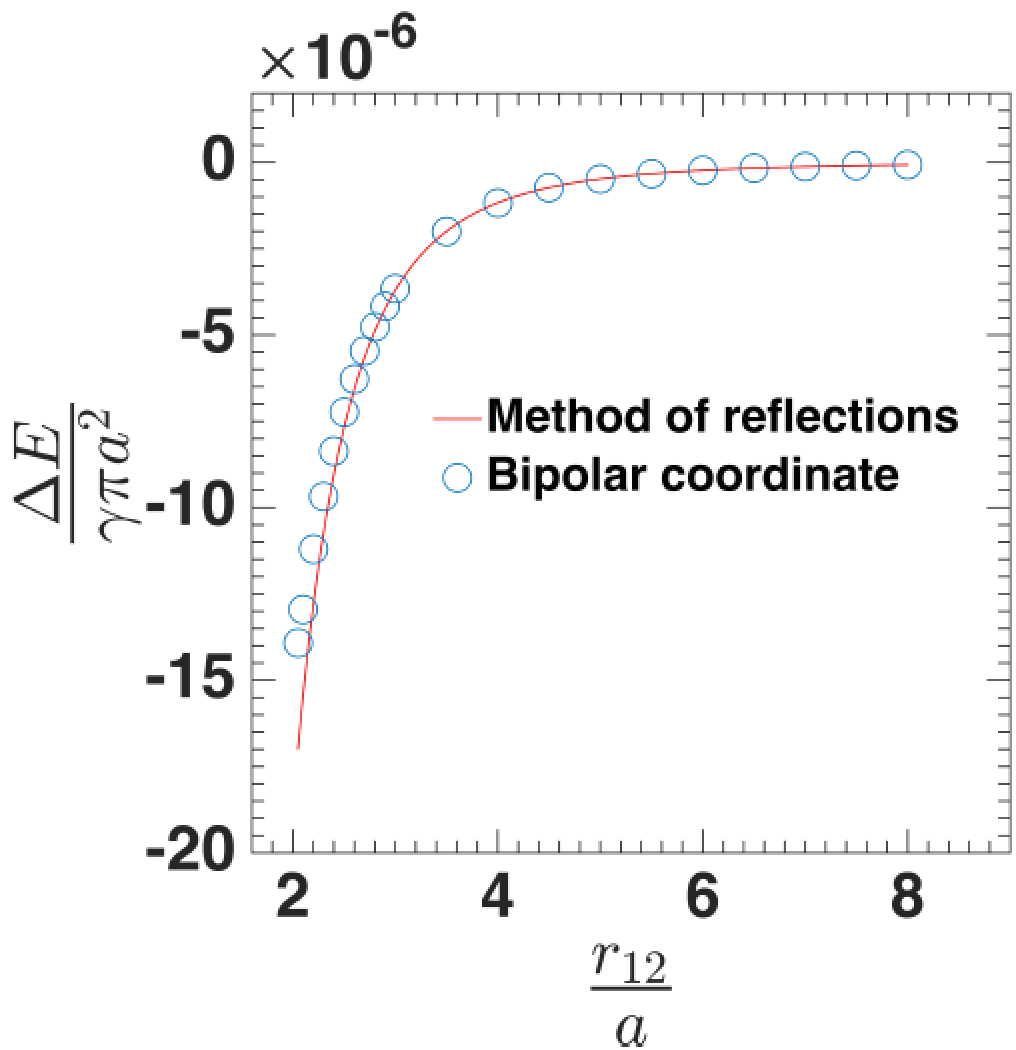
$$\Delta E = -\gamma\pi a^2 \frac{h_{paticle}(a)\Delta c}{2}$$

$$\Delta E = -\gamma\pi a^2 \frac{12 h_{qp_2} h_{qp_1} a^2}{r_{12}{}^4} \cos 2(\alpha_1 + \alpha_2)$$

Particles attract owing to spatially dependent curvature made by neighbor

Mirror symmetric orientations- local torque in the plane of the interface

Pair interaction: comparison



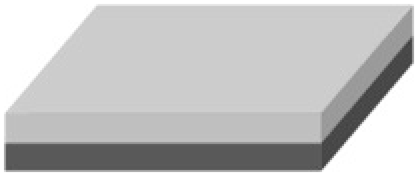
First reflected mode does excellent job of capturing interaction even close to contact.

This is because the induced quadrupole decays very rapidly close to the particle.

Here compared to bipolar solution for interacting quadrupoles.

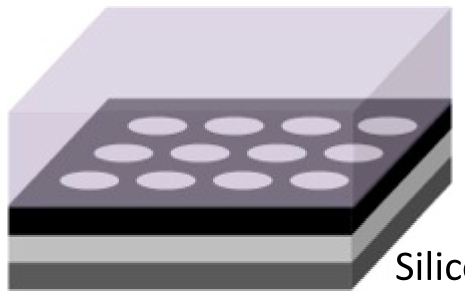
(Dipole interaction subtracted)

Fabrication of SU-8 particles by lithography



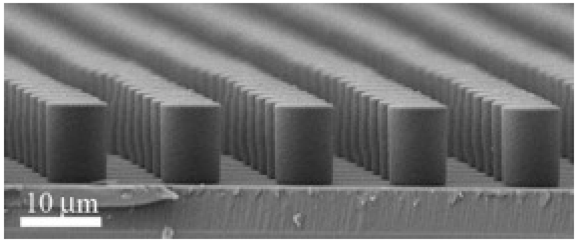
SU-8 negative photoresist
Silicon Wafer

Expose resist through mask



UV light
Mask
SU-8 photoresist
Silicon Wafer

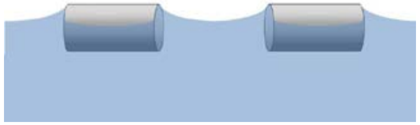
Develop photoresist



SU-8 Particles
Silicon Wafer

Sonicate in ethanol to free particles

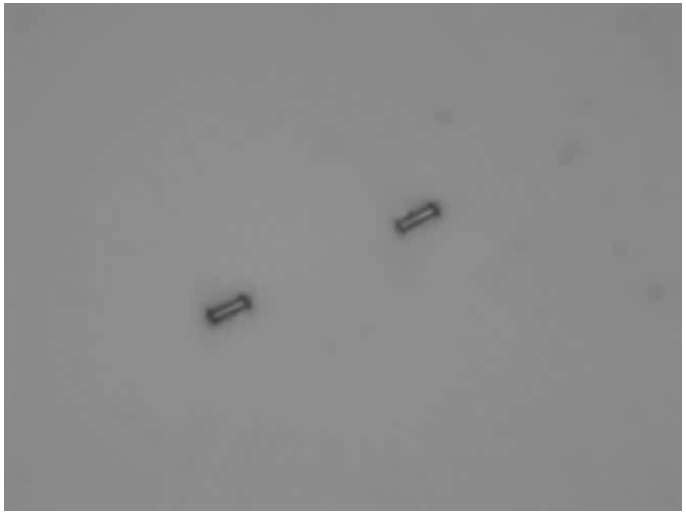
Cylindrical particles on planar interfaces

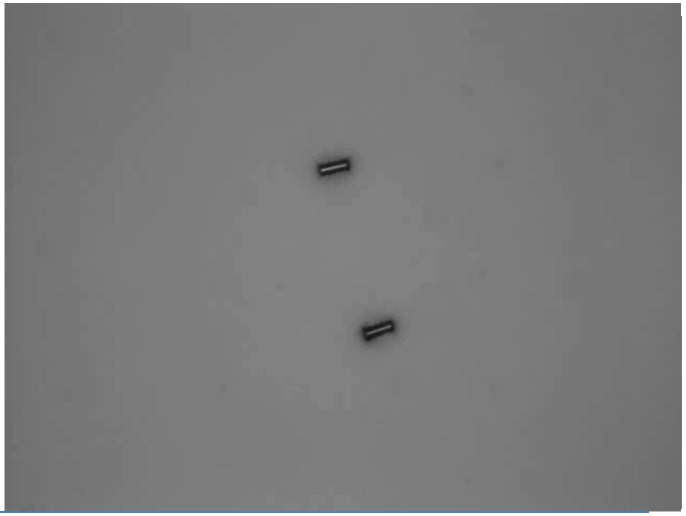


$r_{12init} \sim 180\mu m$

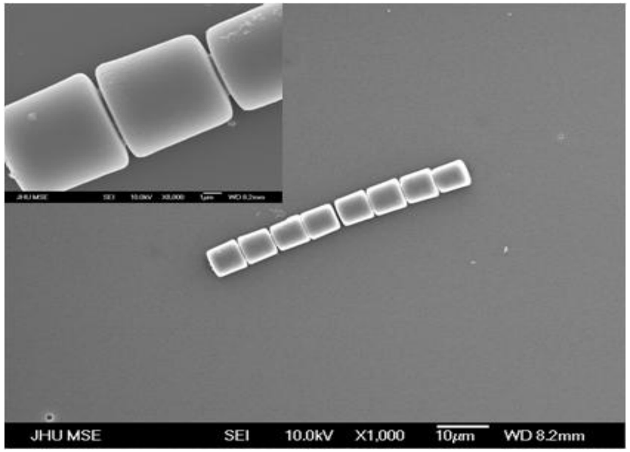
$50\mu m$

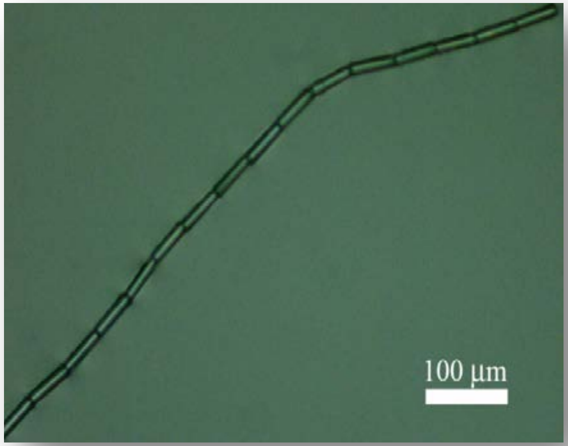
L/2R ~ 2.5





L/2R ~ 1.2



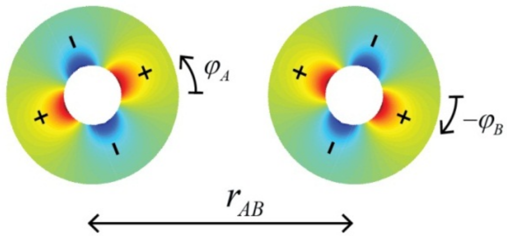


Lewandowski et al, *Langmuir 2010*

Surface area decreases when deformations overlap

Far field interactions

$$A_{LV} \approx \int_S 1 + \frac{\nabla h \cdot \nabla h}{2}\, dS \sim A_{plane} + A_{excess}$$



<u>Interaction Energy</u>

$$E_{12} = \gamma A_{12} = -12\gamma\pi h_{qp}^2 \cos 2(\varphi_A + \varphi_B)\left[\frac{a}{r_{12}}\right]^4$$

Superposition approx. *
Stamou, *PRE* **62**, 2000

Here- method of reflections

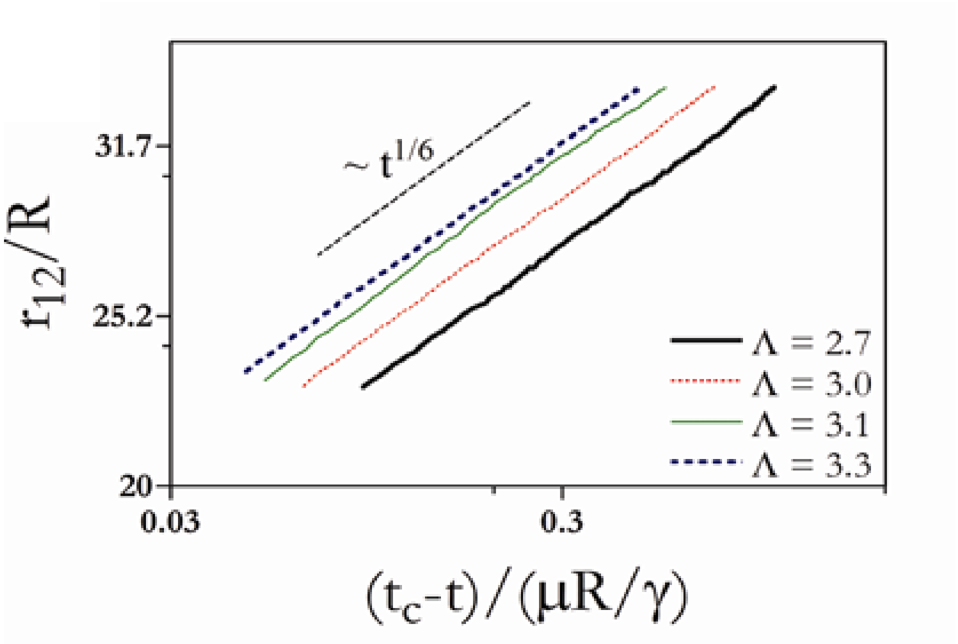
<u>Force of Attraction</u>

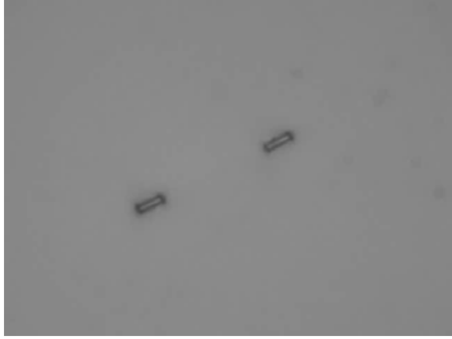
$$F_{12} = -\gamma \frac{dA_{excess}}{dr_{12}} = 48\gamma\pi a\left[\frac{h_{qp}^2}{a^2}\right]\cos 2(\varphi_1 + \varphi_2)\left[\frac{a}{r_{12}}\right]^5$$

$\varphi_1 = -\varphi_2$
$F_{12} \sim r_{AB}{}^{-5}$

Excess area drives interactions
but no preferred orientation

Far field: Quadrupolar Attraction: power law





$$r_{12} = C\left(t - t_c\right)^{\alpha}$$

$$\alpha = \frac{1}{6}$$

$$F_{12} = -F_{drag} = -C_d 6\pi R_{cyl}\mu \frac{dr_{12}}{dt}$$

$$r_{12}^{-5} \sim \frac{dr_{12}}{dt}$$

$$dt \sim r_{12}^{5} dr_{12}$$

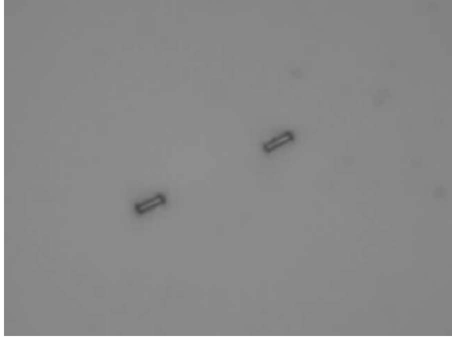
$$\left.\begin{aligned} r_{12} &= C\left(t - t_c\right)^{\alpha} \\ \Delta E(r_{12}) &\propto r^{\left(2 - 1/\alpha\right)} \end{aligned}\right\}$$

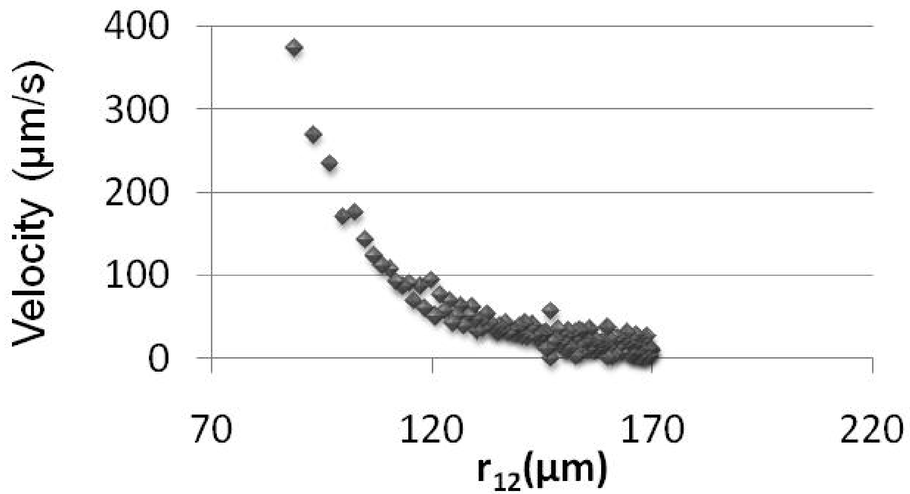
$$\left(2 - 1/\alpha\right) = -4$$

$$\alpha = \frac{1}{6}$$

ELLIPSOIDS: C. Loudet et al, *PRL*, 018301, 2005

Extract magnitude of far field interaction energy





$(\Lambda = 3.1 \pm 0.1,\ R = 5.0\ \mu\text{m}, r_1 = 16R \text{ and } r_2 = 36R)$.

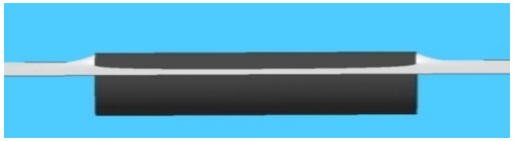
Viscous dissipation

$$\Delta E^{Drag} = -6\pi\mu R C_D \int_{r_f}^{r_i} \boldsymbol{v}(\boldsymbol{r}')\boldsymbol{dr}' = -2.16 \pm 0.65x10^5 kT$$

$$0.6\Delta E^{Drag} = -2.24 \pm 0.67\ x\ 10^5 kT$$

C_D>1.73 for Λ=3

Youngren and Acrivos



Cylinder~ 60% immersed

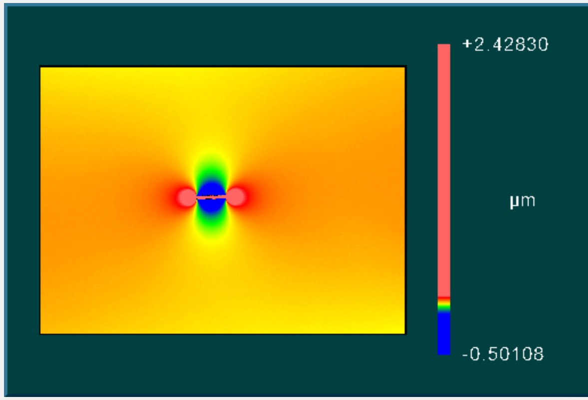
Capillary interaction energy

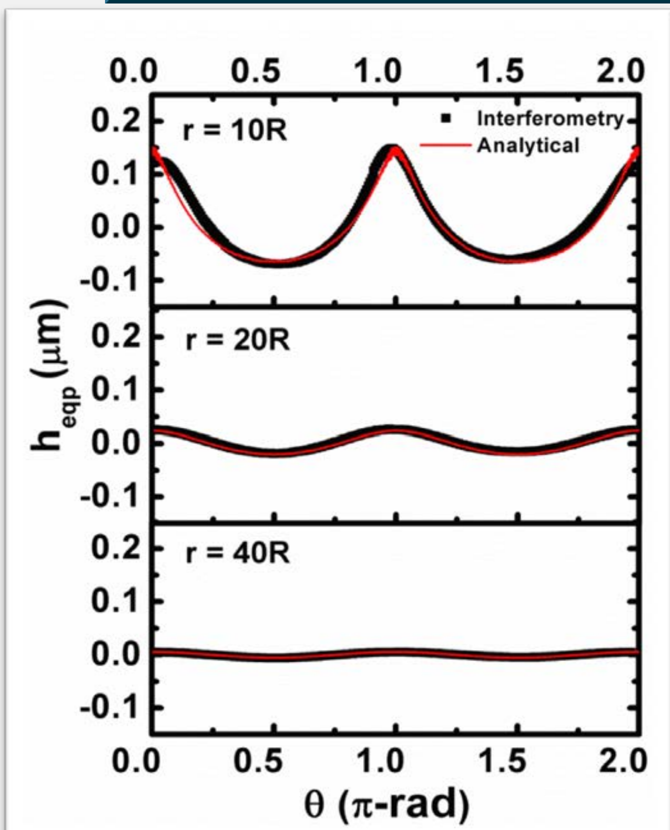
$$\Delta E \cong -12\pi\gamma H_p^2 \left(1 - \frac{(L/D-1)^2}{(L/D+1)^2}\right) R^4 \left(\frac{1}{r_{12,f}^4} - \frac{1}{r_{12,i}^4}\right) = -0.985\text{x}10^5 kT$$

predicted

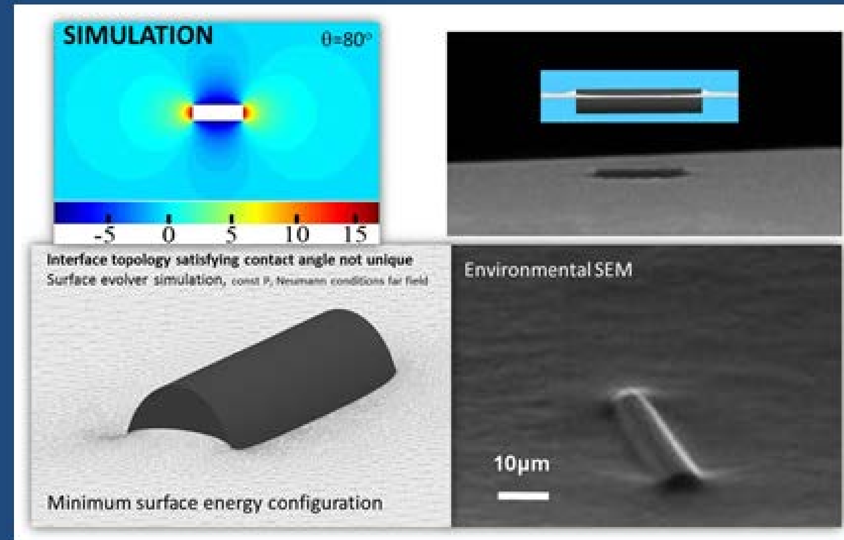
Asymptotic exp

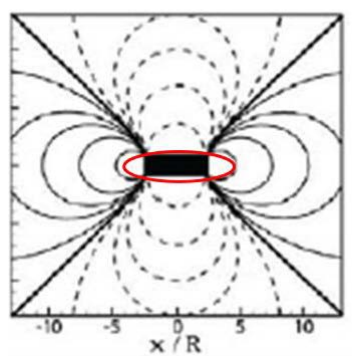
Λ=6; R=10um



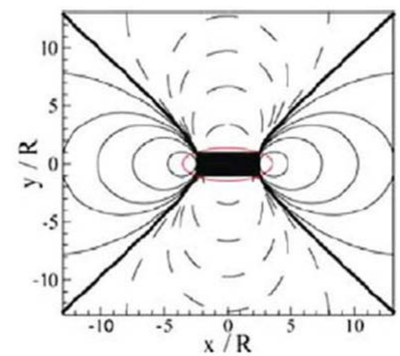


Shape of interface around isolated cylinder

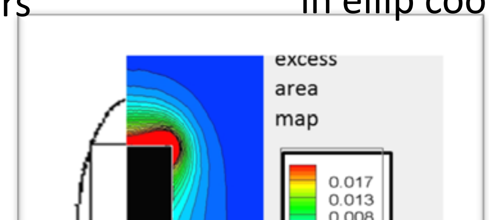




Isoheight contours

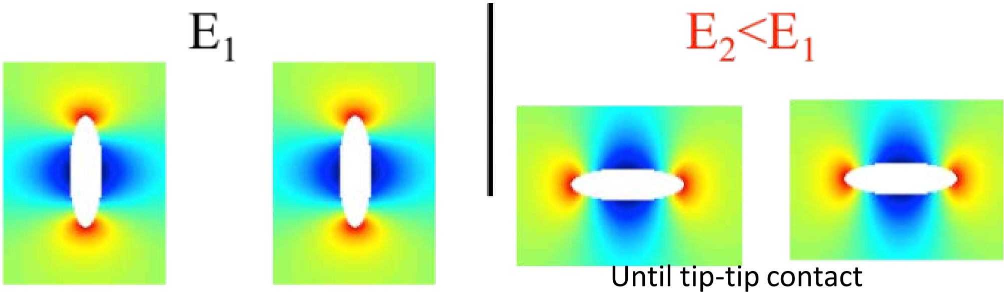


Quadrupole in ellip coord



Quadrupoles in Elliptical Coordinates
Near field Torque

Langmuir 2010



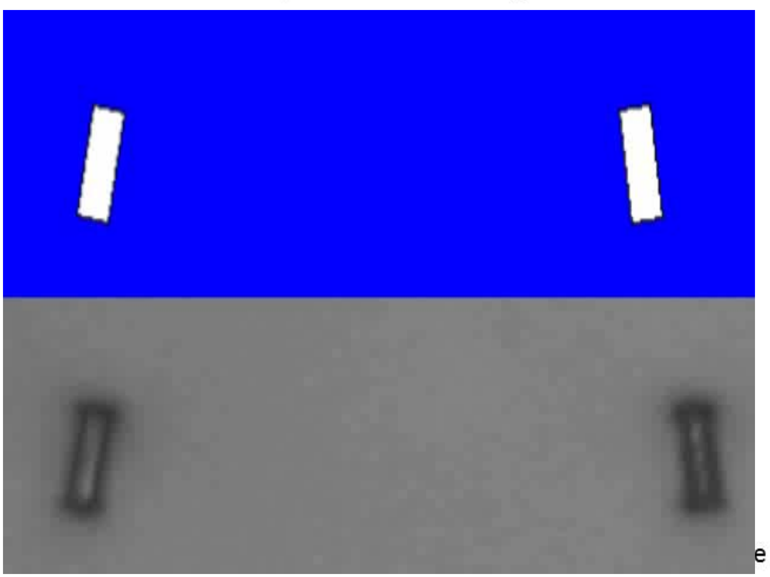
Until tip-tip contact

$$T_{orque} \sim \frac{\Delta E}{\Delta \theta} \sim 1/r_{12}^{\;6}$$

Rotation: very local; decays steeply

Botto et al. Soft Matter 2012
Botto et al- Review, SM 2012

Analysis and experiment



e (slowed down X4)

Euler Scheme

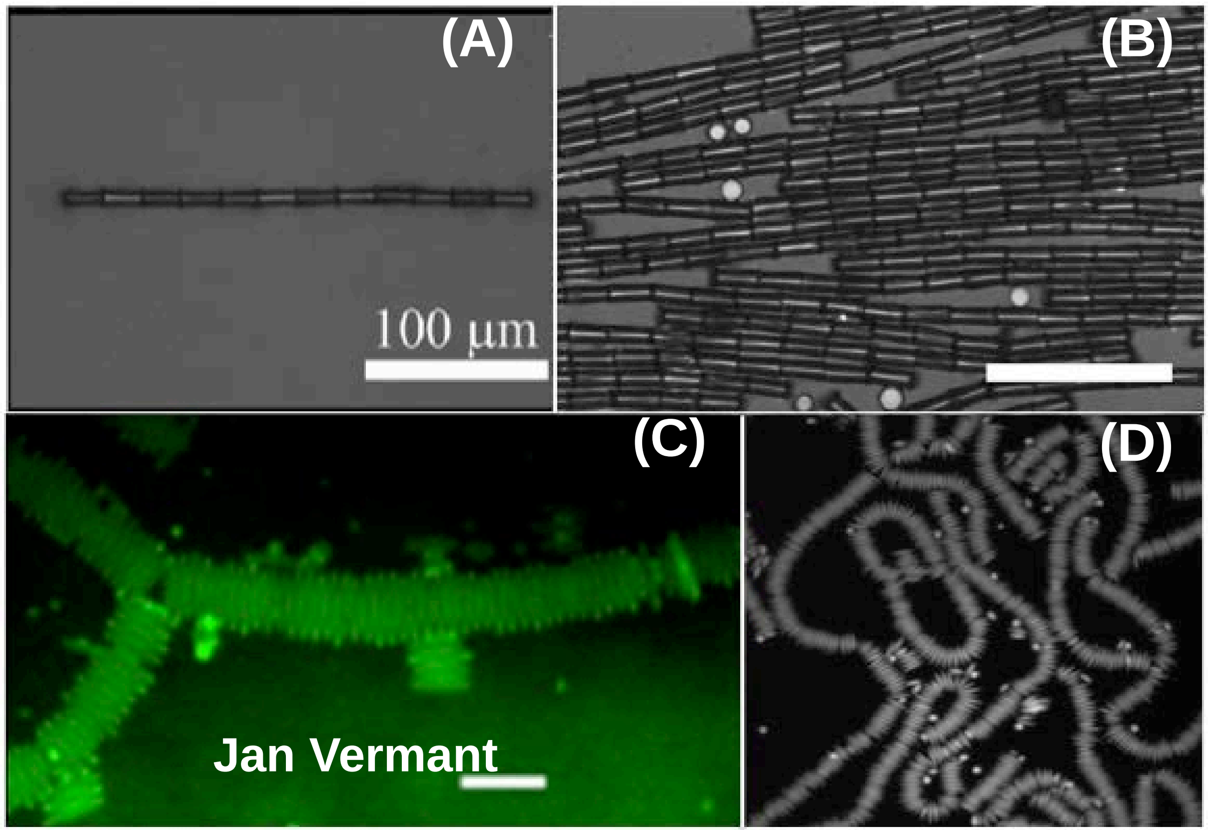
Trajectory computed as:

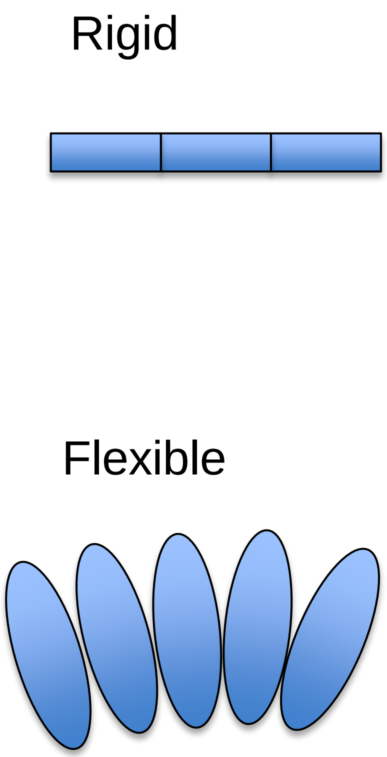
$$x^{n+1} = x^n + \frac{\Delta t}{6\pi\mu R f_T}\left(\frac{\partial E}{\partial x}\right)^n \qquad \theta^{n+1} = \theta^n + \frac{\Delta t}{8\pi\mu R^3 f_R}\left(\frac{\partial E}{\partial \theta}\right)^n$$

(used experimentally measured drag coeffs f_t & f_r)

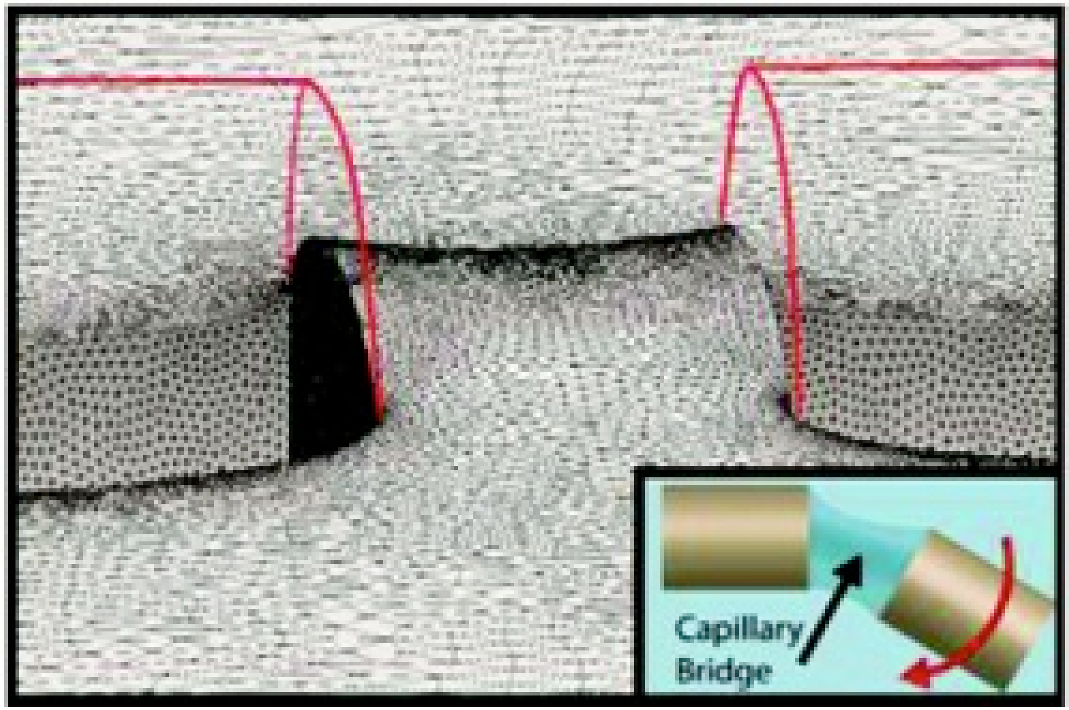
Lewandowski et al Langmuir 2010

Capillary assembly strongly dependent on shape

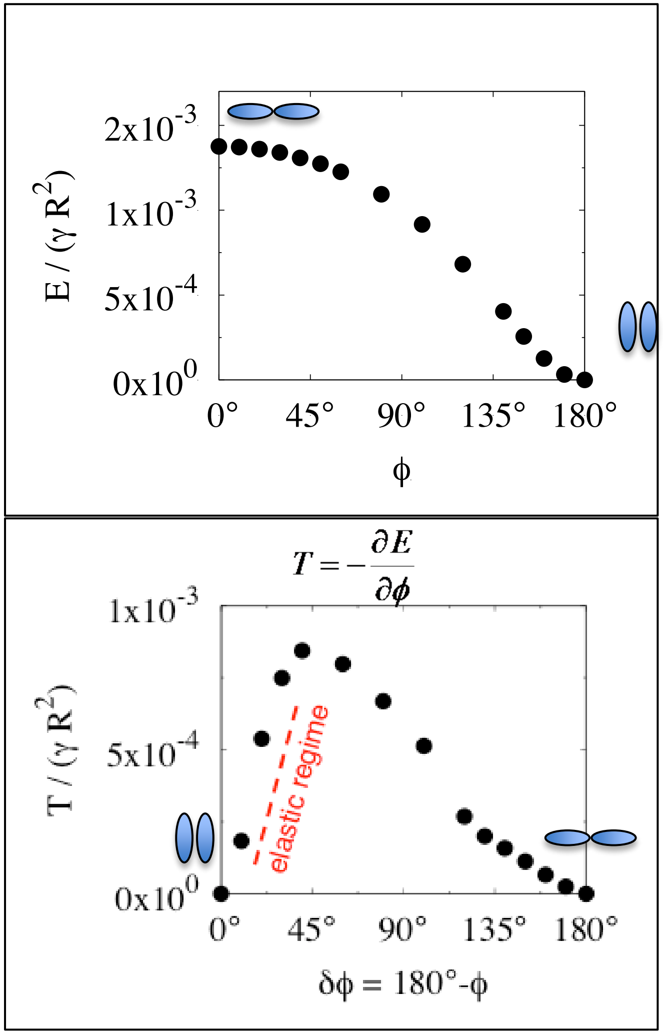


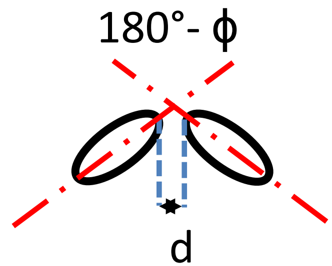


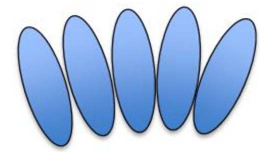
(A) Lewandowski *et al*, Langmuir 2010. (B) Botto, Yao *et al*, Soft Matter 2012.
(C) Zhang *et al*, JACS, 2011. (D) Courtesy of Jan Vermant. Scale bar = 100 μm.

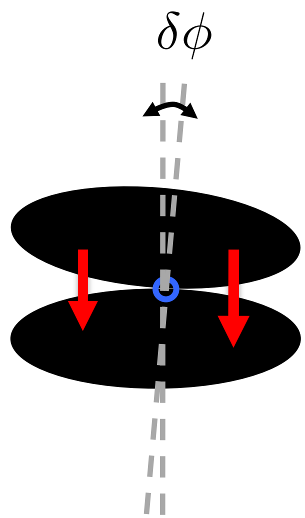

Capillary
Bridge

Capillary energy landscape for ellipsoids

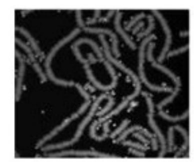








‘Rolling’



elastic element

T=κC

Flexural rigidity:

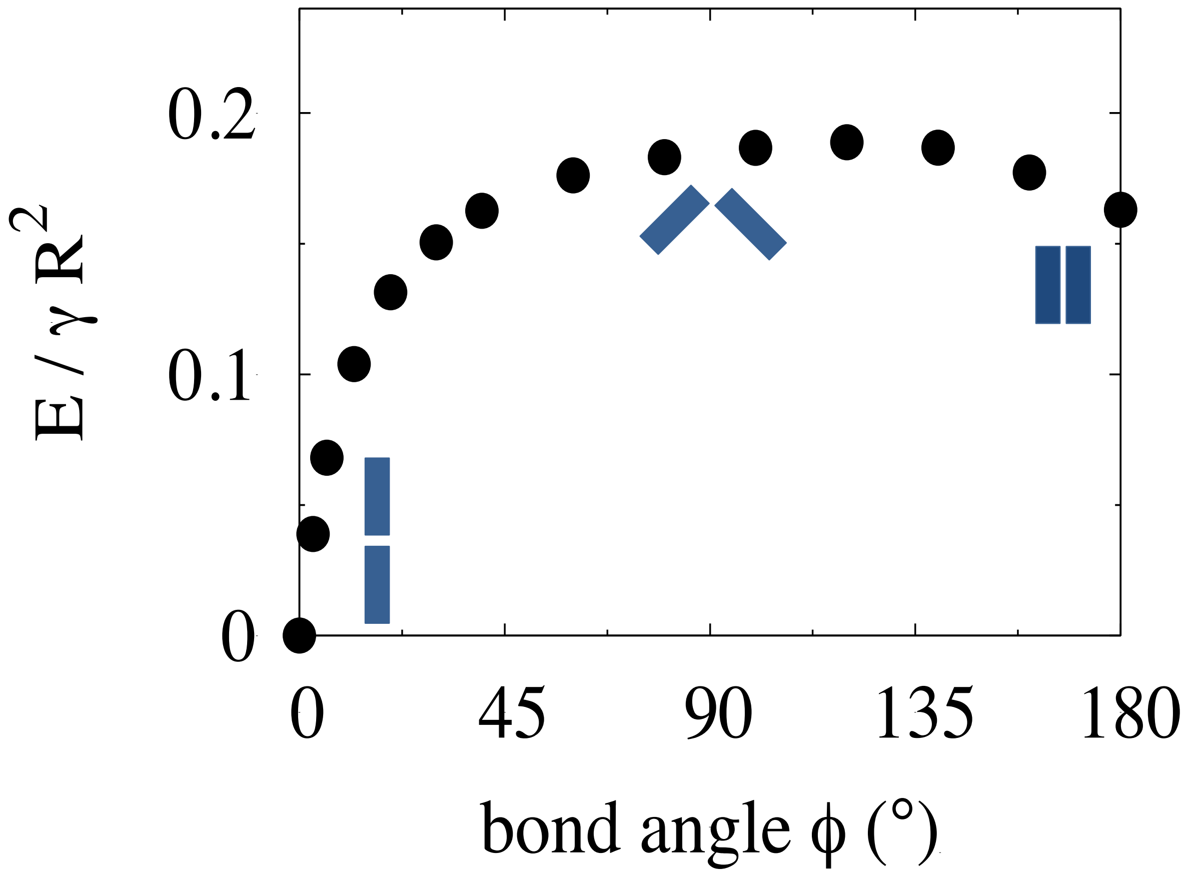
$$\kappa = (2R)^{-1}\frac{\partial T}{\partial \phi}(0)$$

$$\kappa \sim 2RG = 0.003\gamma R^3$$

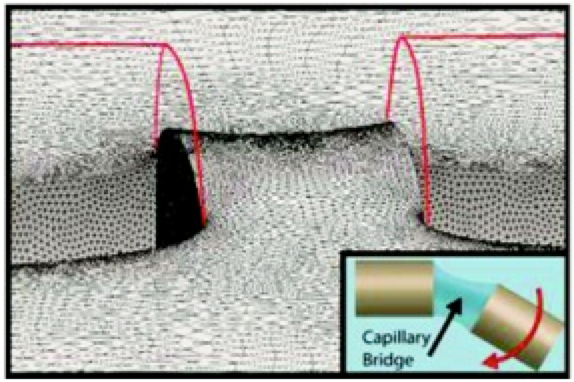
Modest torque to bend the chain
$T \sim 10^3$ kT

Capillary energy landscape for cylinders

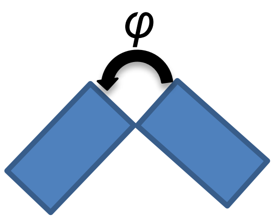
E ~ 10^7 kT



Capillary Bridge

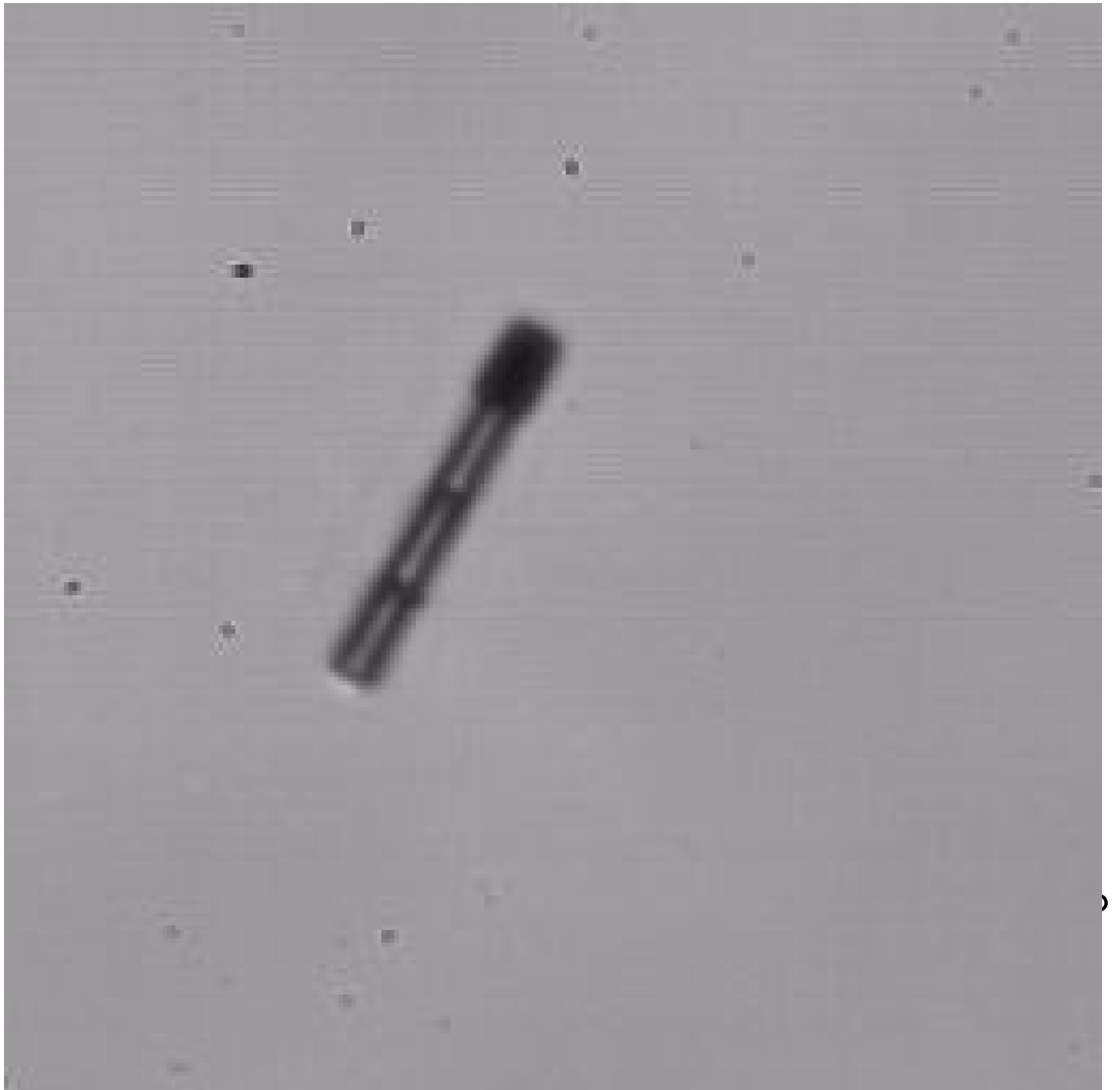


HINGING MOTION
steric constraint

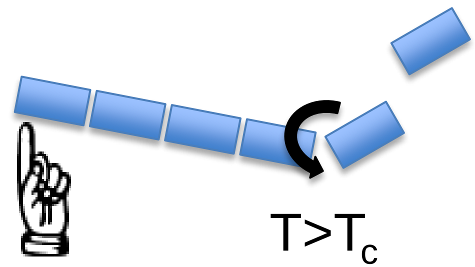


Energy barrier for different assembly configurations

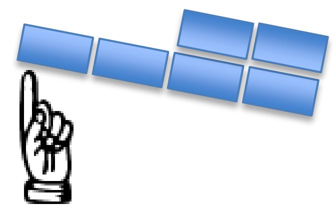
Yield Torque: chain of cylinders



Constant torque experiment

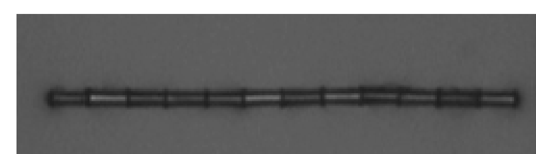


critical bending moment should break chain



cylinder should snap to side-to-side

Chain stiff below a yield torque, $T_C \sim 10^7$ kT

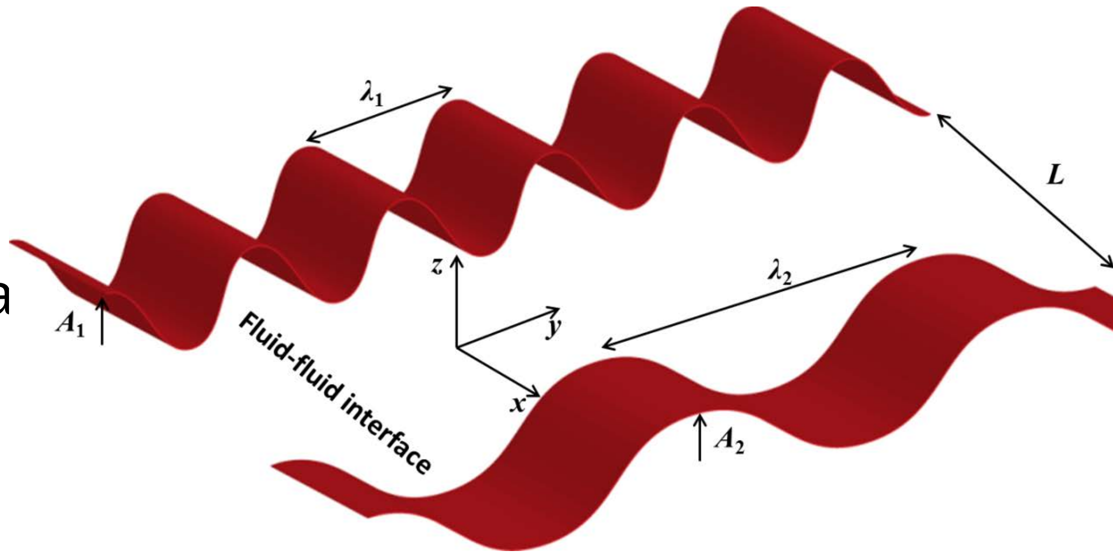


Can we impart repulsion to counter this attraction?

- Lucassen

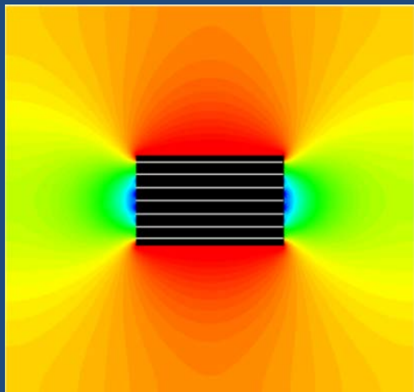
Colloids and Surfaces 65, 1992

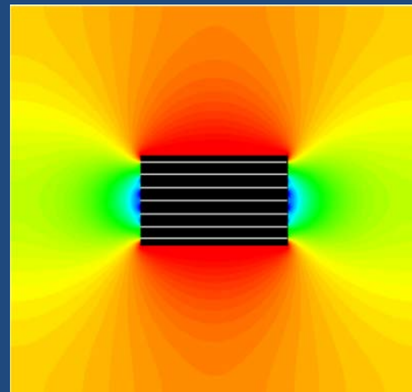
  - Interaction between sinusoidal contact lines
  - liquid-vapor surface area minimized, attractive interactions if same
    - Frequency
    - Amplitude
    - In phase
  - Else- repulsive



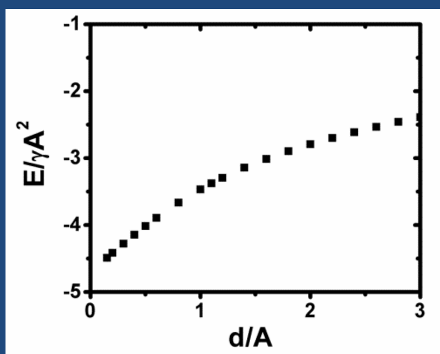
Model roughness

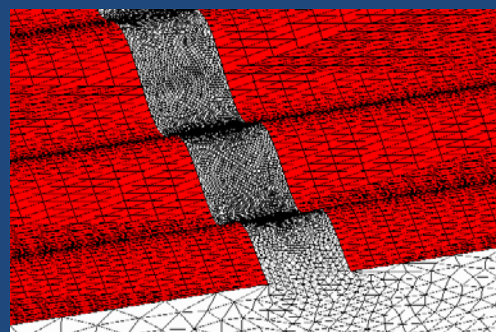
Attraction in far field, interacting undulations in near field





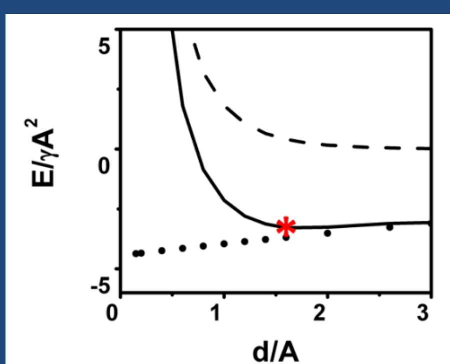
Far from contact: interact like capillary quadrupoles

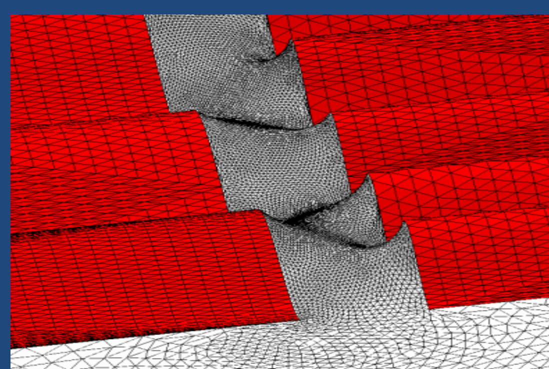




Particles with matching wavelengths: Enhanced attraction

Area decreases steeply as particles approach

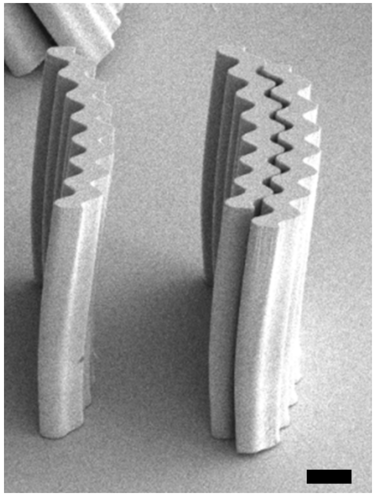




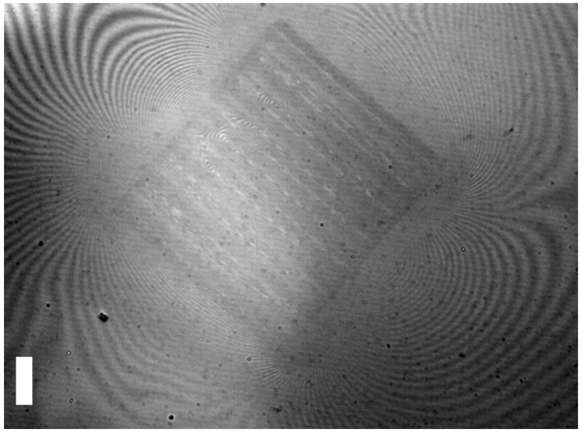
Particles with differing wavelengths: **NEAR FIELD REPULSION**

Area increases steeply as particles approach

Microparticles with corrugated edges

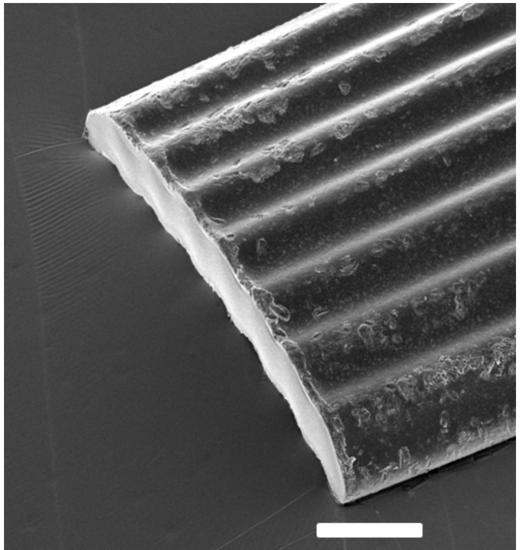


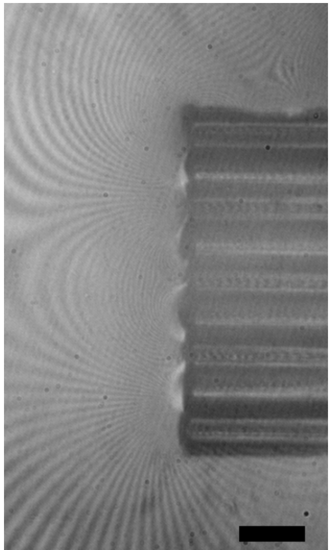
Lithography; SU-8
θ~80°



At air-water interface:
quadrupole apparent

Scale bar = 50 μm

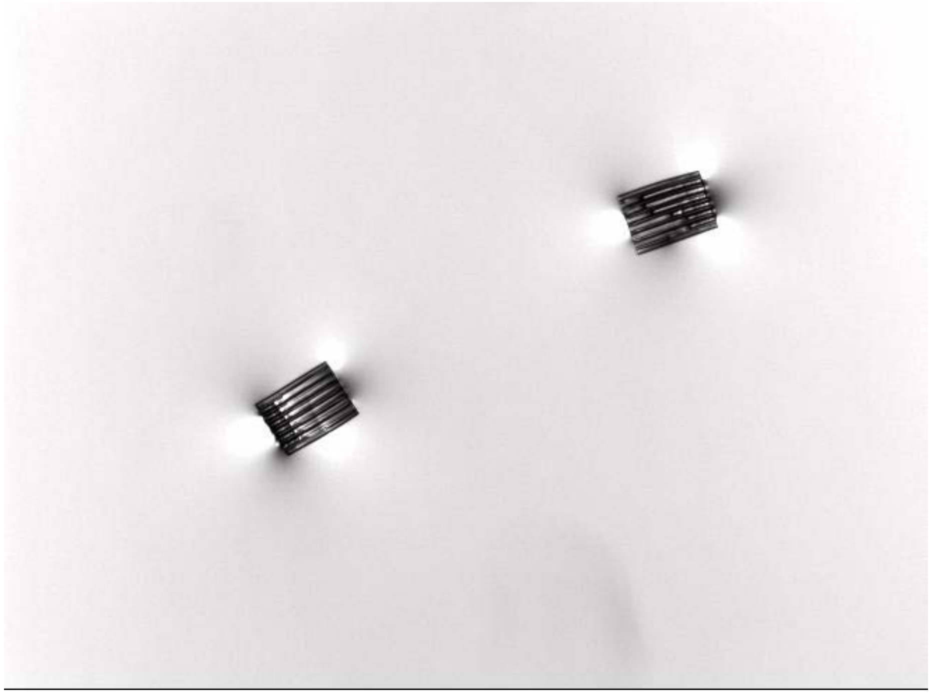




Distortion of interface near particle:

Near field sinusoidal undulations

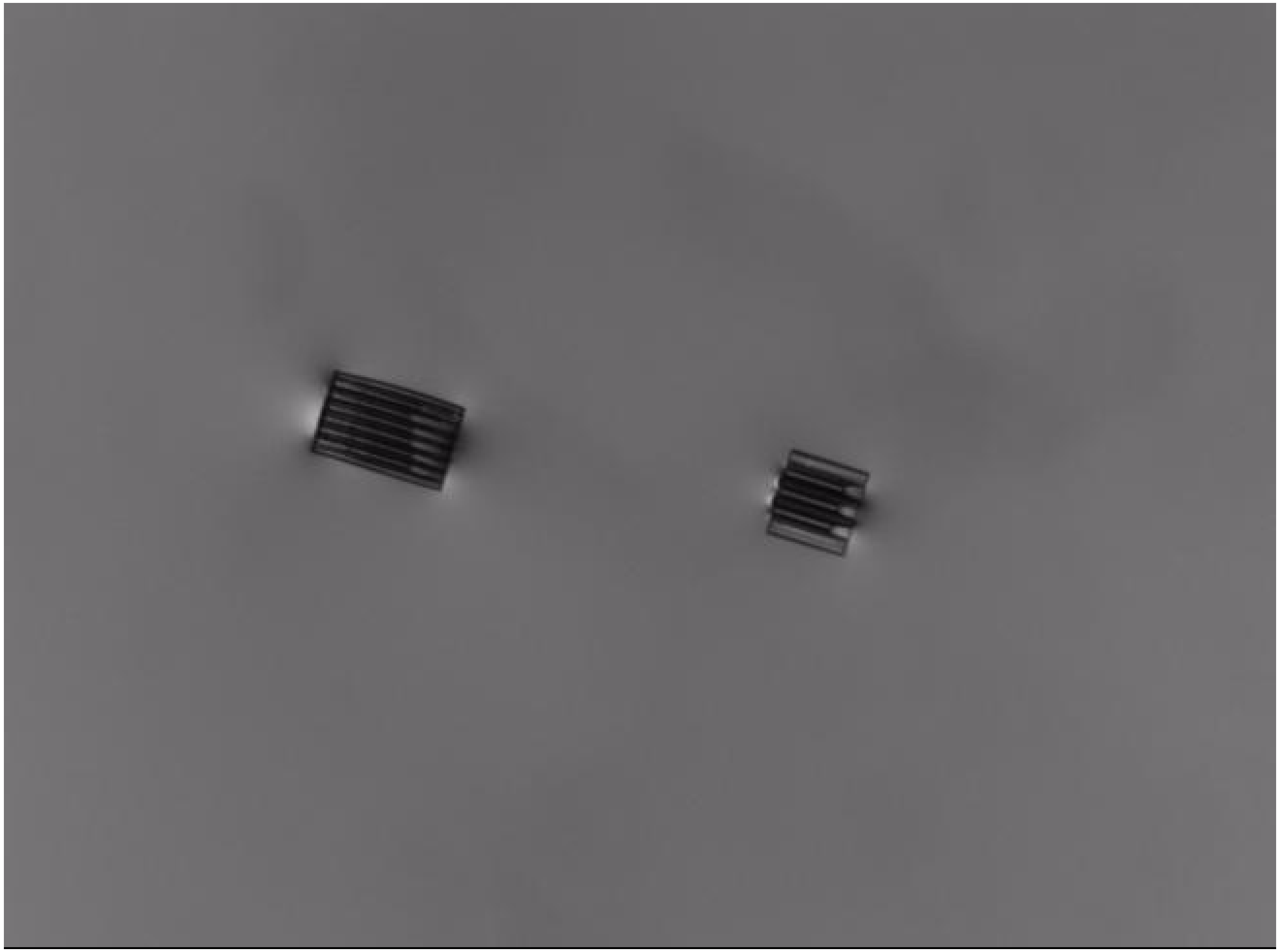
Microparticles with corrugated edges: Matching particles



Microparticles with corrugated edges with differing wavelengths

air-water interface

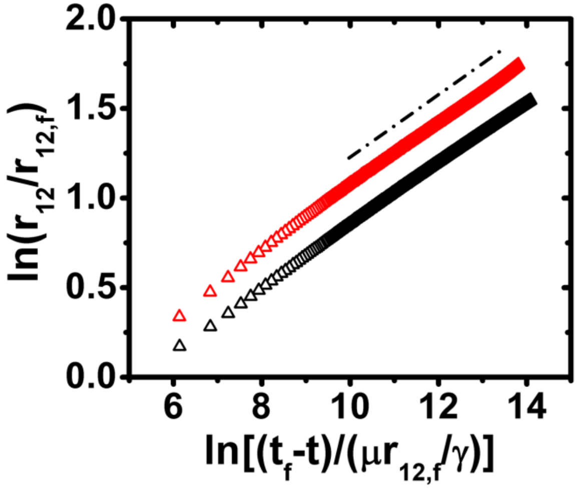
W=270um
L=360um
λ=36um

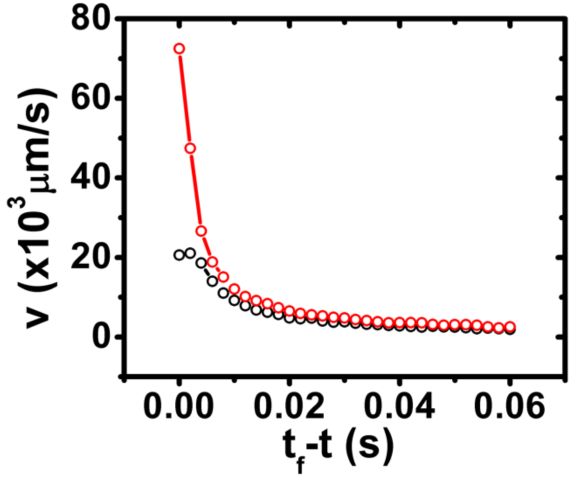


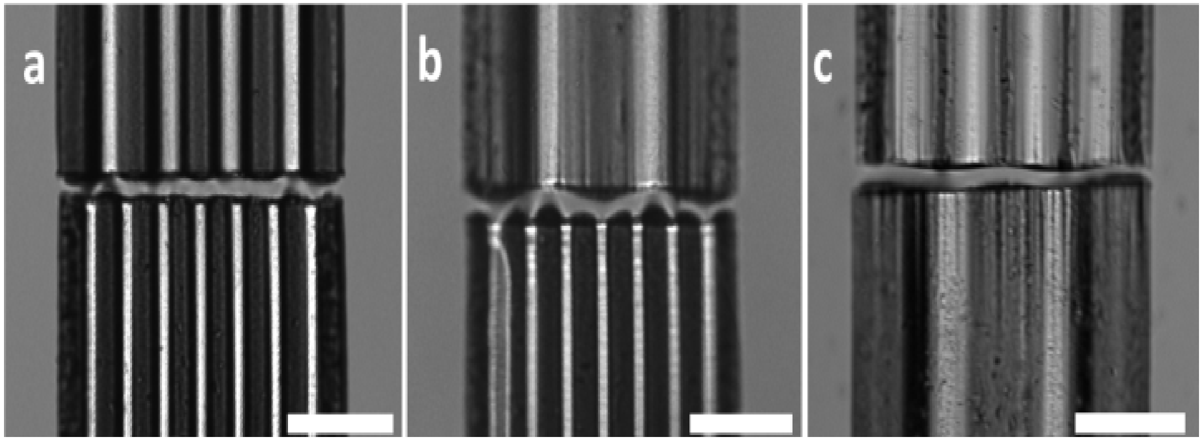
W=270um
L=235 um
λ=36um

Near field capillary repulsion

Microparticles differing wavelengths assemble to finite separation distance







Scale bar
100 micron

Summary for particles pair interactions on planar surfaces

Particles become trapped at planar fluid interfaces.

Particles with pinned contact lines, patchy wetting or non-spherical shapes distort the interface around them.

Distortions due to various particle features observed at different distances from the particle.

All: quadrupolar distortions in the far field. These drive mirror symmetric arrangements and attraction

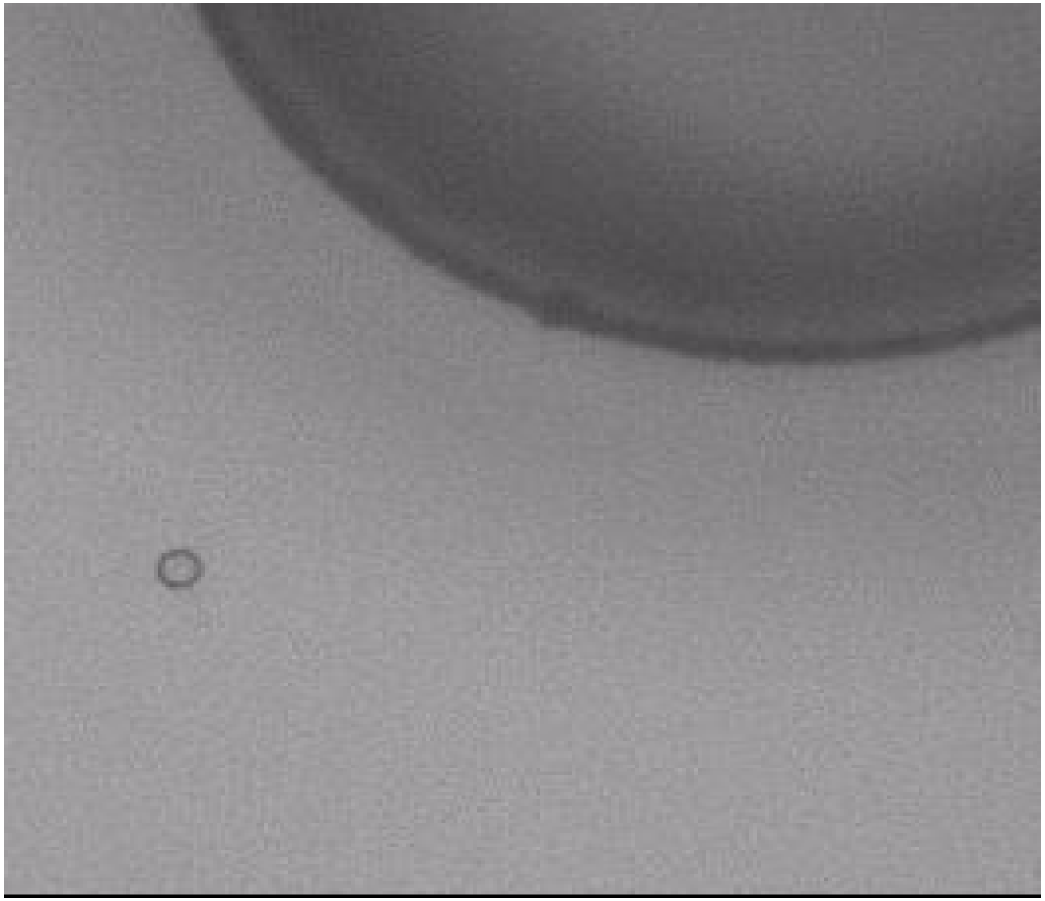
Moderate to near field, features like particle elongation become apparent. This drives preferred orientations to minor axis.

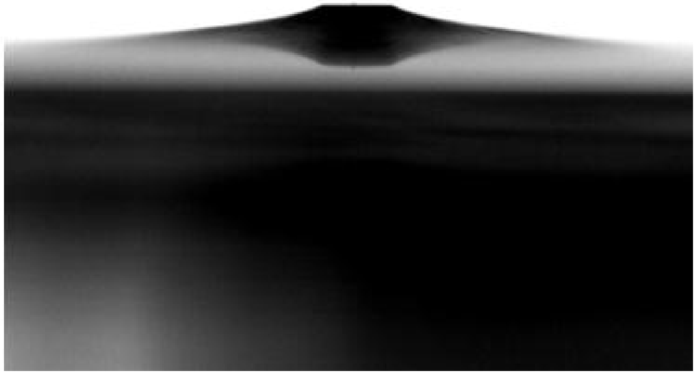
Closer still, waviness, roughness and sharp edges play a roles. Waviness can give near field repulsion. Corners, sharp edges, can cement very strong bonds and preferred oreintations.

Curvature driven motion

Planar disk

$$\Delta E = -\int F_{drag} ds = -C_D 6\pi\eta a \int v ds$$



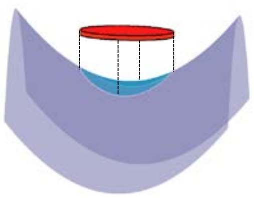


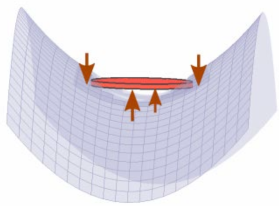
Lamb's drag coeff
(μav=0.002Pa s)

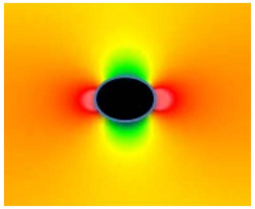
Real time
Disk: 5 micron radius; Post: 125 micron radius

$\Delta E(\Delta c)$: Pinned contact line

$$\nabla h_{dist} = \nabla h_{hqp} + \nabla h_{dist,\Delta c}$$







$$\Delta E = \Delta E_{planar} - \gamma \pi a^2 \frac{h_{qp} \Delta c}{2}$$

Δc(position)

$$h_p = 30 - 35 nm$$

$$a = 5 \mu m$$

$$\theta_0 = 90^0$$

$$\gamma = 46 \frac{mN}{m}$$

$$\Delta c = 5 \times 10^{-3}$$

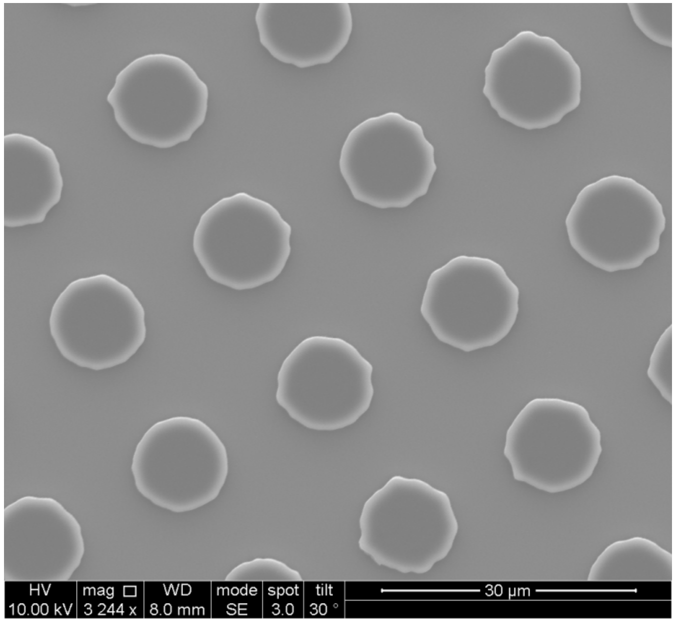
$$F_L = -\frac{\Delta E}{2a} = -4.8 \times 10^{-13} N$$

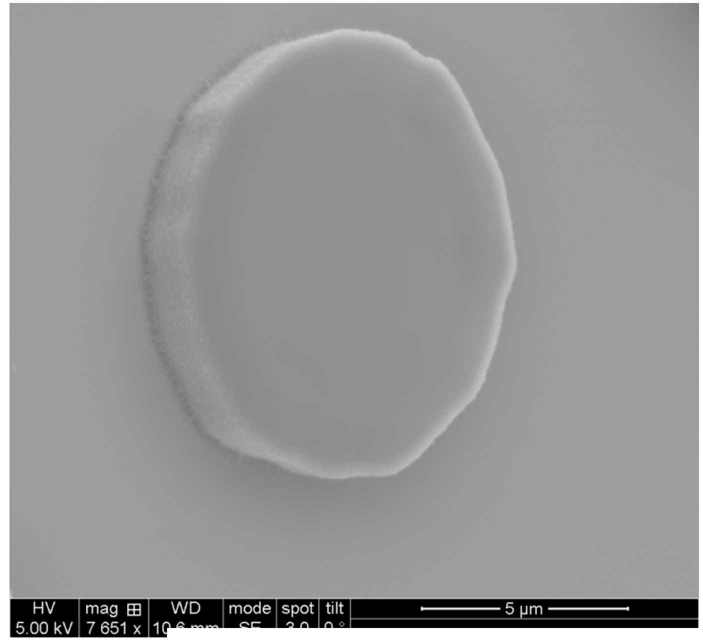
$$\Delta c = 10^{-2}$$

$$F_L = -\frac{\Delta E}{2a} = -1.4 \times 10^{-12} N$$

Lewandowski et al. (KJS) 2008
Cavallaro et al (KJS) PNAS 2011
Lu et al (KJS) JCIS 2015
Sharifi-Mood et al (KJS) arxiv (2015)

Planar disks

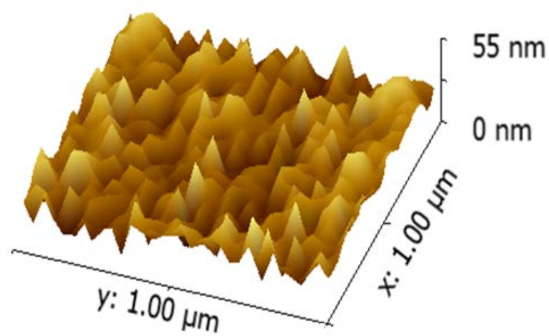




$$disk:\ a=5\mu m$$

$$\delta a = 225 \pm 55\ nm$$

$$\zeta = \frac{\delta a}{a} = 0.045 \pm 0.011$$



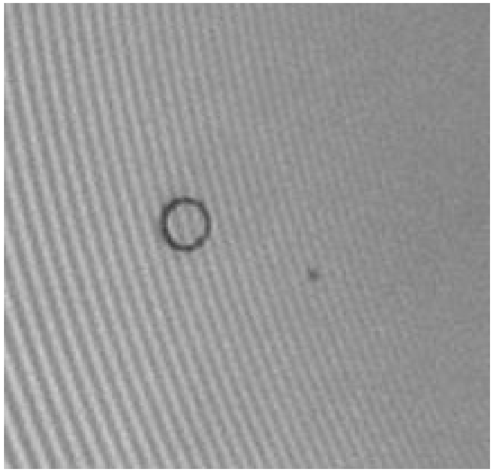
AFM

Roughness:

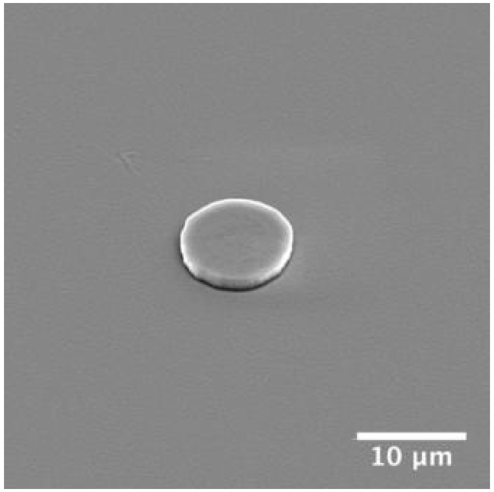
RMS

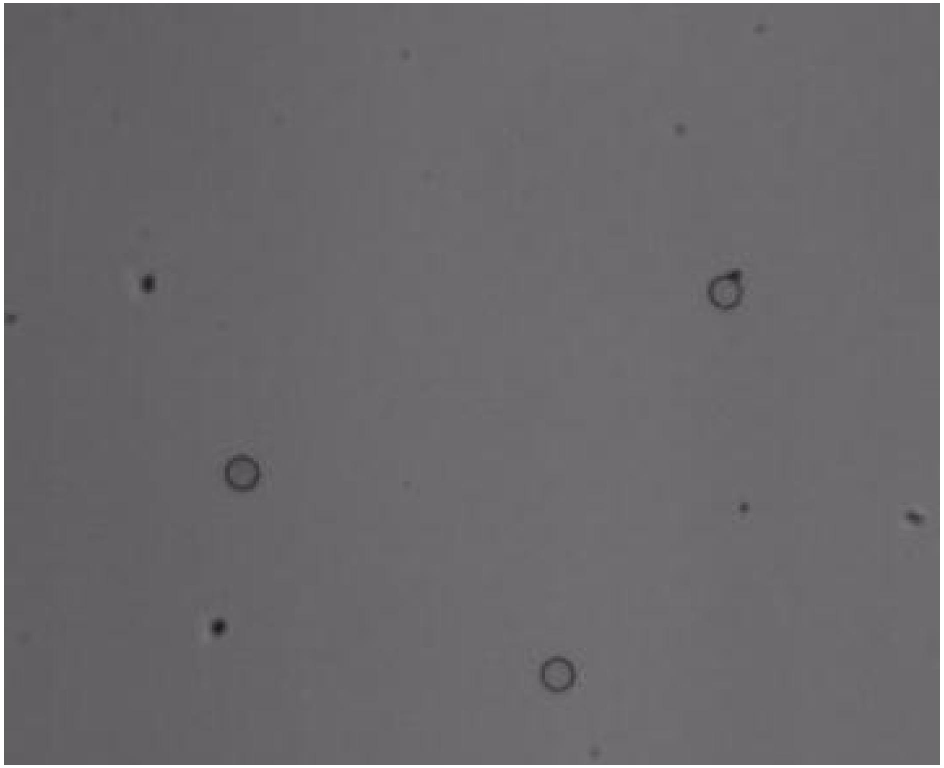
18 ~ 32 nm.

Pinned Contact Lines
Brownian trajectories at planar interface



Pinned contact line

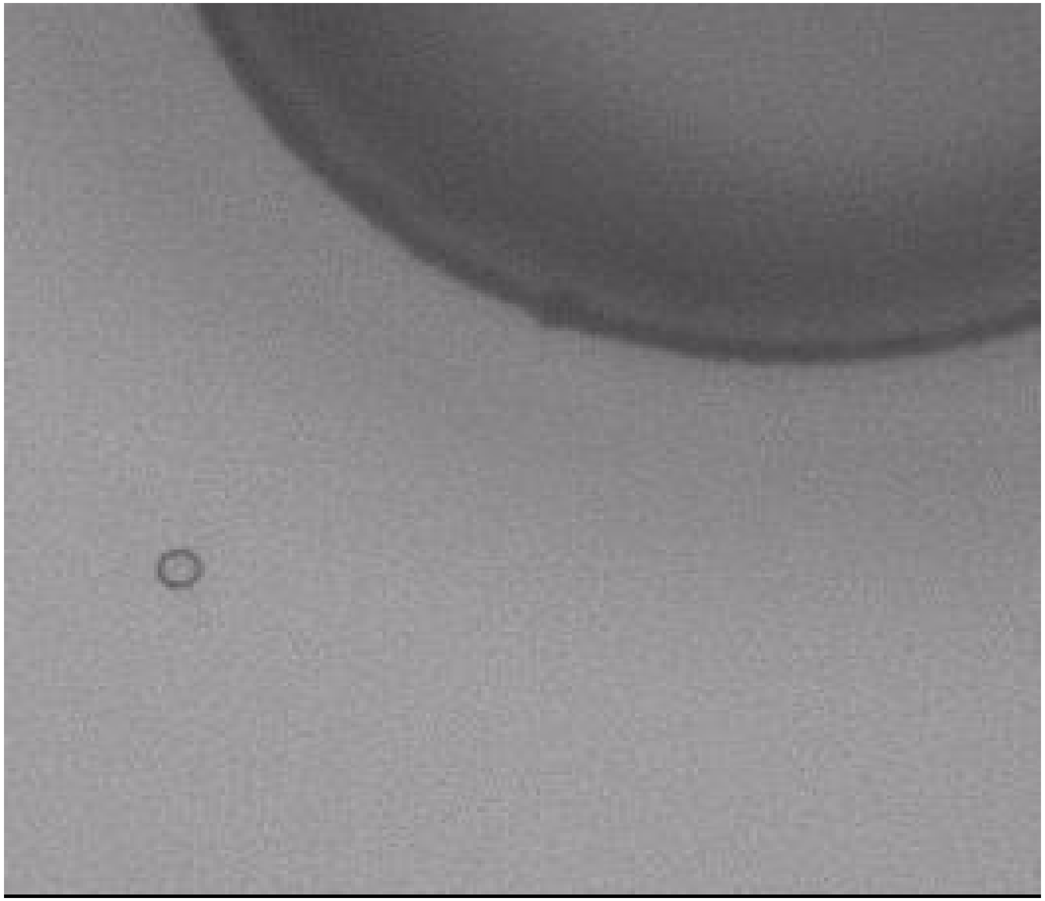


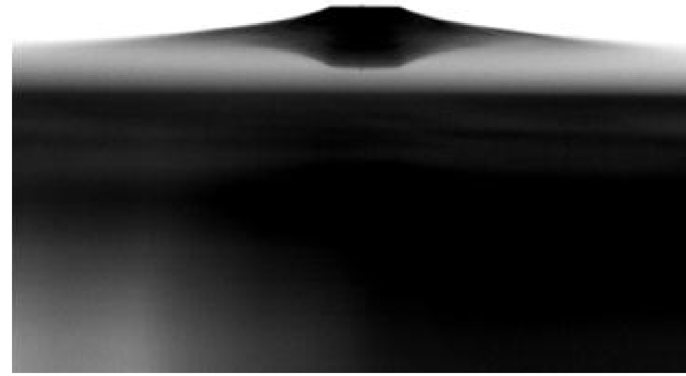


Brownian
trajectories

Planar disk

$$\Delta E = -\int F_{drag} ds = -C_D 6\pi\eta a \int v ds$$

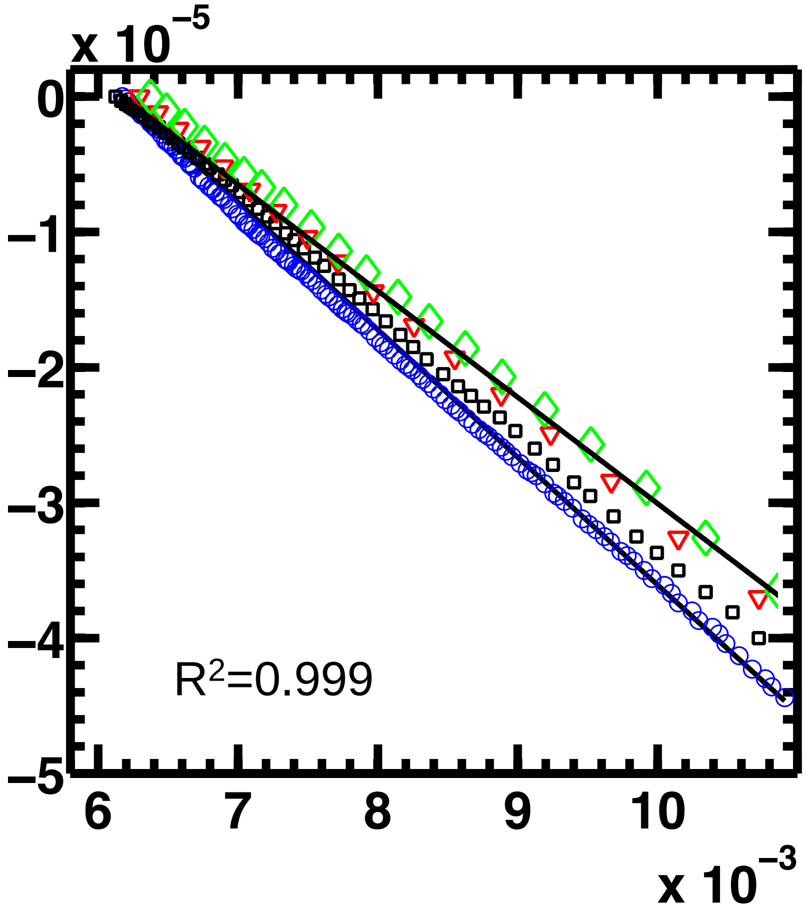




Lamb's drag coeff
(μav=0.002Pa s)

Real time
Disk: 5 micron radius; Post: 125 micron radius

Energy dissipated over trajectory



lines: $h_{qp} = 25nm;\ h_{qp} = 30\ nm$

$$\Delta E = -\gamma\pi \frac{h_{qp} a^2}{2} (\Delta c_f - \Delta c_0)$$

$$-\Delta E_{\exp} = 5.6 \times 10^4 k_B T$$

$$-\Delta A_{LV} \sim 560\ nm^2$$

worst case
Line: R^2=0.999
RMSE=3x10^{-7}

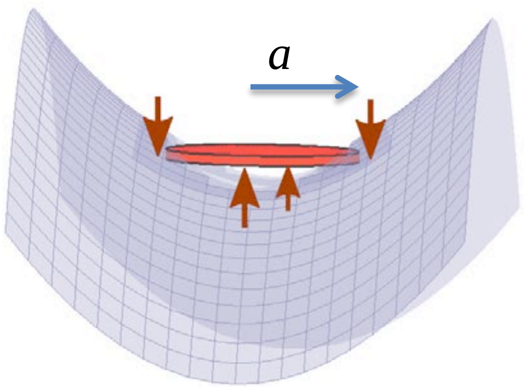
$$15nm < \frac{a^2 \Delta c}{2} < 35nm$$

Analytical shape around the particle

disturbance local to particle; interface a saddle near particle

$$\begin{cases} Bo = \dfrac{\Delta\rho g a^2}{\gamma} \ll 1 \\ \lambda \approx a\Delta c \ll 1; \quad \varepsilon = |\nabla h| \ll 1 \end{cases}$$

Pinned contact line



$$h_{host} = \frac{\Delta c_0}{4} r^2 \cos 2\phi$$

$$\Delta c_0 = \frac{2R_m \tan\Psi}{L_0^2}$$

$$h^{inner}(r,\phi) = h_{qp}\frac{a^2}{r^2}\cos 2\phi + \frac{\Delta c_0}{4}\left(r^2 - \frac{a^4}{r^2}\right)\cos 2\phi$$

$a^2\Delta c \sim 20nm$
$h_{qp} \approx 10-100nm$

$\mathrm{h}_{\mathrm{dist}}(r\sim 20a) = $ (sub) angstrom

Singular perturbation analysis

disturbance local to particle; interface a saddle near particle

Are we certain the we can treat the particle as if it is in an unbounded doman?

How confident are we in this parametrization of the interface in terms of deviatoric curvature of the host?

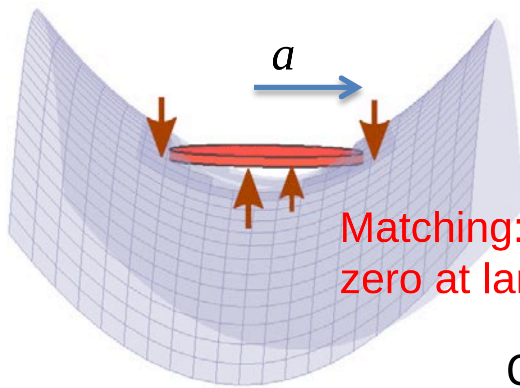
To what order in the small parameter?

dual series expansion

$$\lambda = a\Delta c, \quad \varepsilon = \left|\nabla h\right|$$

Inner Region

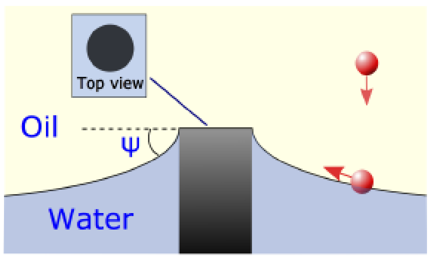
~*a*

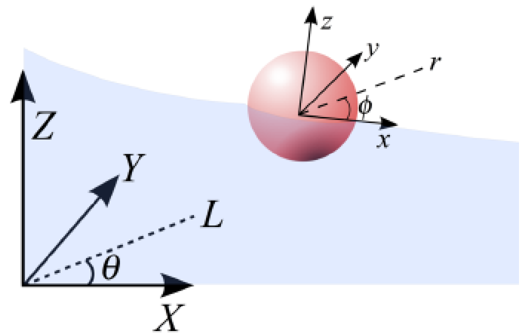


Matching: disturbance zero at large r

Outer Region:
Host interface
Far from particle
~R_c

Inner and outer regions





$$X = L_0 + x + O(\epsilon),$$
$$Y = y,$$
$$Z = Z_0 + z + O(\epsilon),$$

Outer region

$$h^{outer} = H_m - R_m \tan\psi \ln(\frac{\hat{L}}{R_m}).$$

$$\Delta c(L_0) = 2\frac{d^2 h_{outer}}{dL^2}(L_0) = 2\tan\psi \frac{R_m}{L_0^{\ 2}}$$

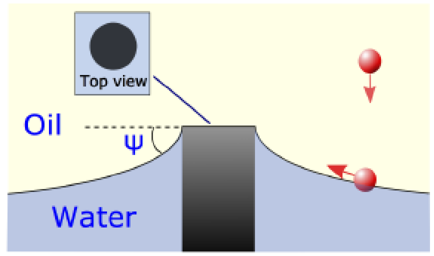
Outer coordinate:; scaled with Rc: $(\hat{X}, \hat{Y}, \hat{Z})$

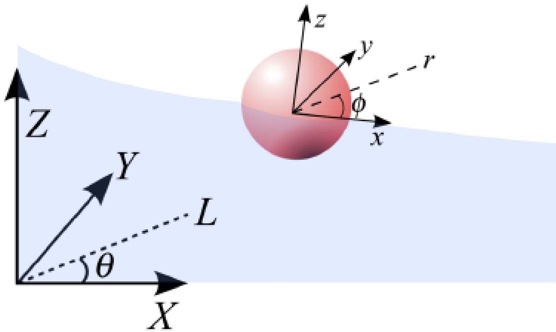
Inner coordinate:; scaled with *a*:

$$(\tilde{x}, \tilde{y}, \tilde{z}); \quad \tilde{z} = \tilde{h}^{inner};$$

$$\text{with slope } \epsilon = -\frac{R_m \tan\psi}{L_0} \text{ with respect to outer coord}$$

Inner and outer regions





$$\hat{h}^{outer} = \frac{H_m}{R_c} - \frac{R_m \tan\psi}{R_c} \ln\left(\frac{\sqrt{(x+L_0)^2 + y^2}}{R_m}\right) - \frac{H_0}{R_c}.$$

$$\lim_{\substack{\lambda \to 0 \\ \tilde{r} \text{ fixed}}} \hat{h}^{outer}(\tilde{r},\phi) = \frac{\lambda^2}{4}\tilde{r}^2 \cos 2\phi + O(\epsilon, \lambda^3)$$

Expand outer solution in terms of inner variables in the limit of small λ.

$$\lim_{\tilde{r} \to \infty} \lambda \tilde{h}^{inner}(\tilde{r},\phi) = \lim_{\substack{\lambda \to 0 \\ \tilde{r} \text{ fixed}}} \hat{h}^{outer}(\tilde{r},\phi).$$

Van Dyke matching condition

Yields far field boundary condition for inner region

$$\lim_{\tilde{r} \to \infty} \tilde{h}^{inner}(\tilde{r},\phi) = \frac{\Delta ca}{4}\tilde{r}^2 \cos 2\phi + O(\epsilon, (\Delta ca)^2).$$

Inner and outer regions

$$h^{\text{uv}} = R_c \hat{h}^{outer} + a\tilde{h}^{inner} - R_c \lim_{\substack{\lambda \to 0 \\ \tilde{r}\ \text{fixed}}} \hat{h}^{outer}$$

$$\eta = h^{\text{uv}} - R_c \hat{h}^{outer} = \frac{h_{qp}}{\tilde{r}^2} \cos 2\phi - \lambda \frac{a}{4\tilde{r}^2} \cos 2\phi + O(\lambda^2).$$

Disturbance:
a decaying function of $\tilde{r}$

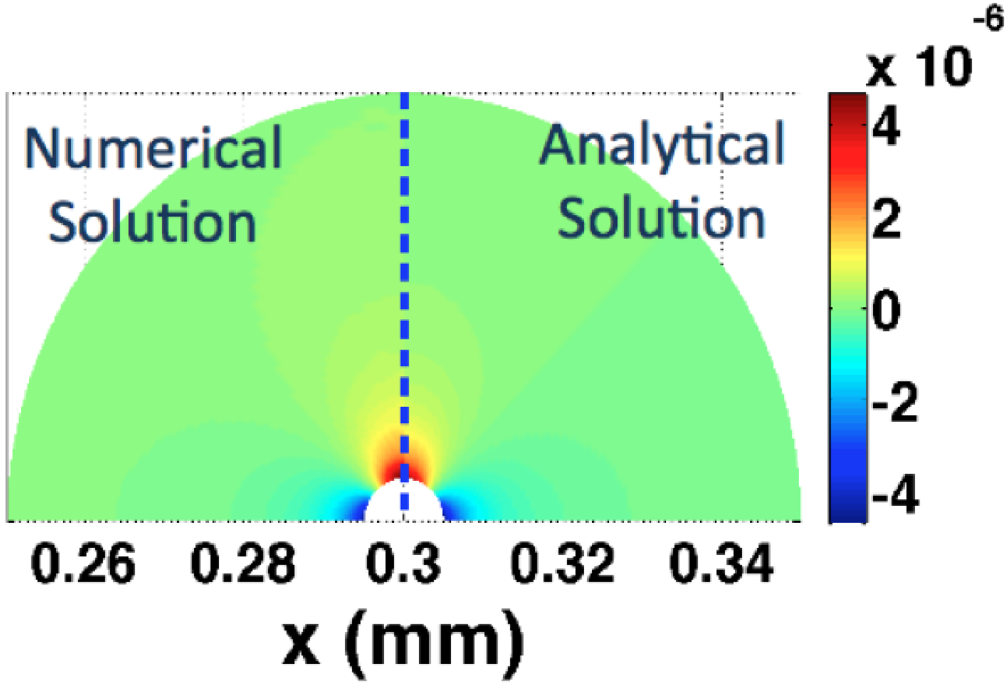
Its value is identically zero in the outer region. T

Thus, the particle results in a ``local'' disturbance which fades over a length scale comparable to its radius a.

Bounds next contribution

Comparison of numerics and analysis

disturbance local to particle; interface a saddle near particle



Agreement to within 2%

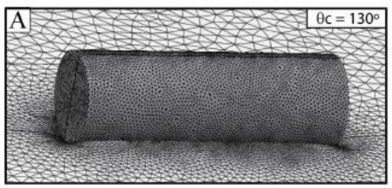
Angstrom scale within ten particle radii

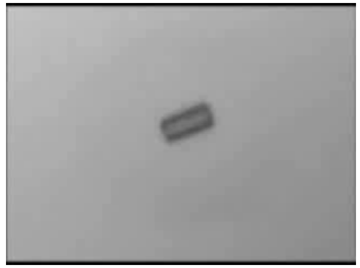
Numerical: Green's function with homogeneous Dirichlet (pinning) BC at the micropost and outer ring introduce the boundary condition at the disk with N capillary charge singularities located at its circumference

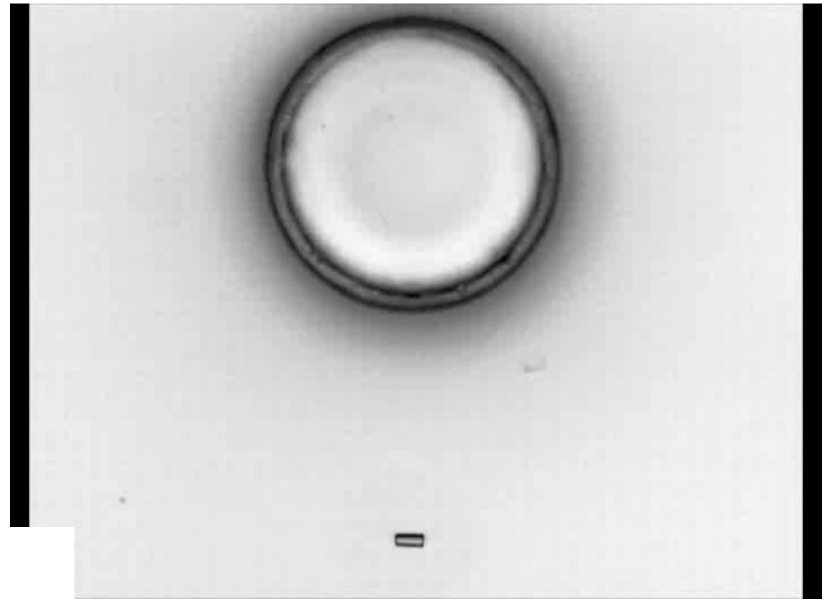
Located at L=3mm from center of micropost

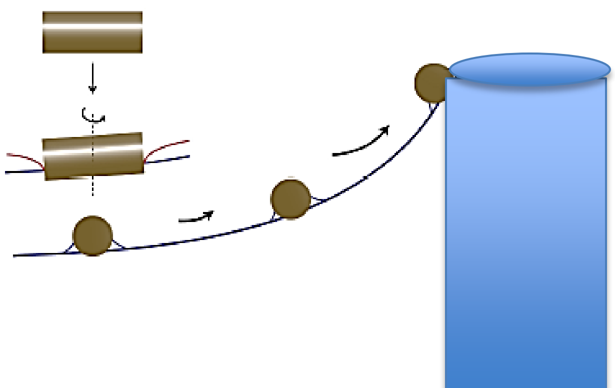
Cylindrical microparticles

10 micron diameter cylinder



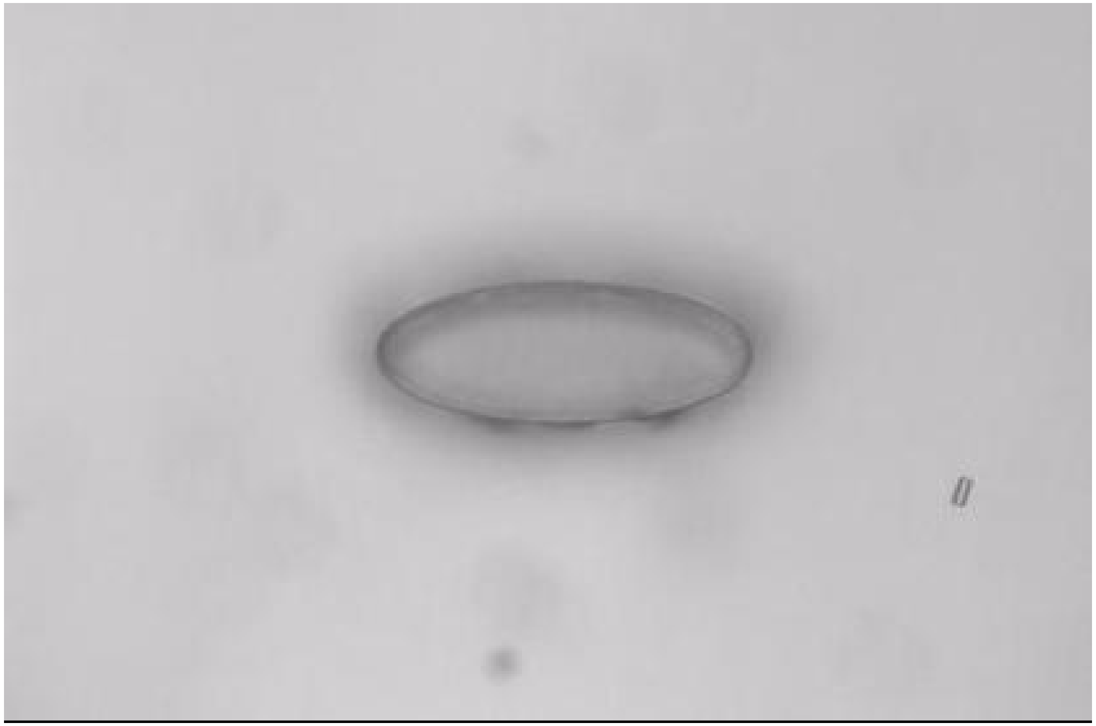






Particles migrate to match their disturbances to their host interface shape

Migration in a Complex Curvature Field

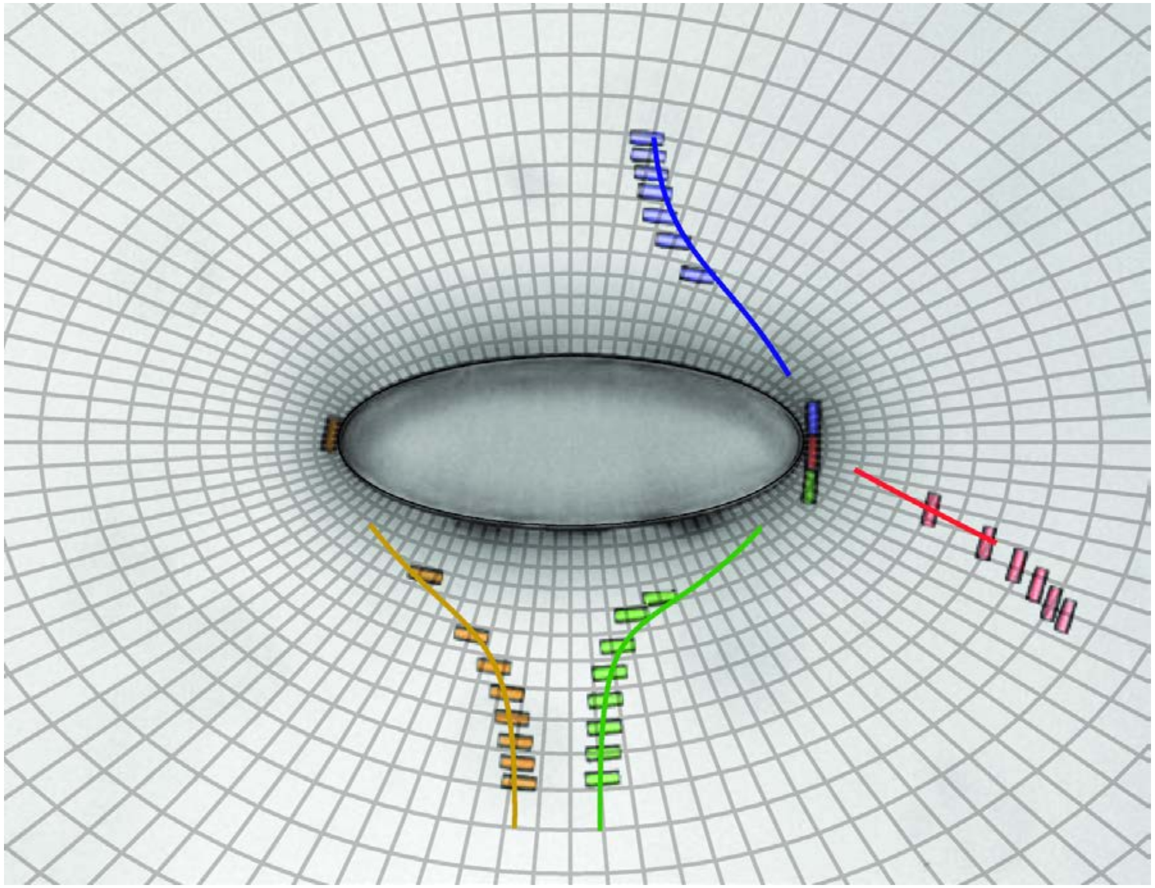


Top view interface around micropost with elliptical cross section

Directed migration towards tips

Let $\Delta c(R, \theta)$

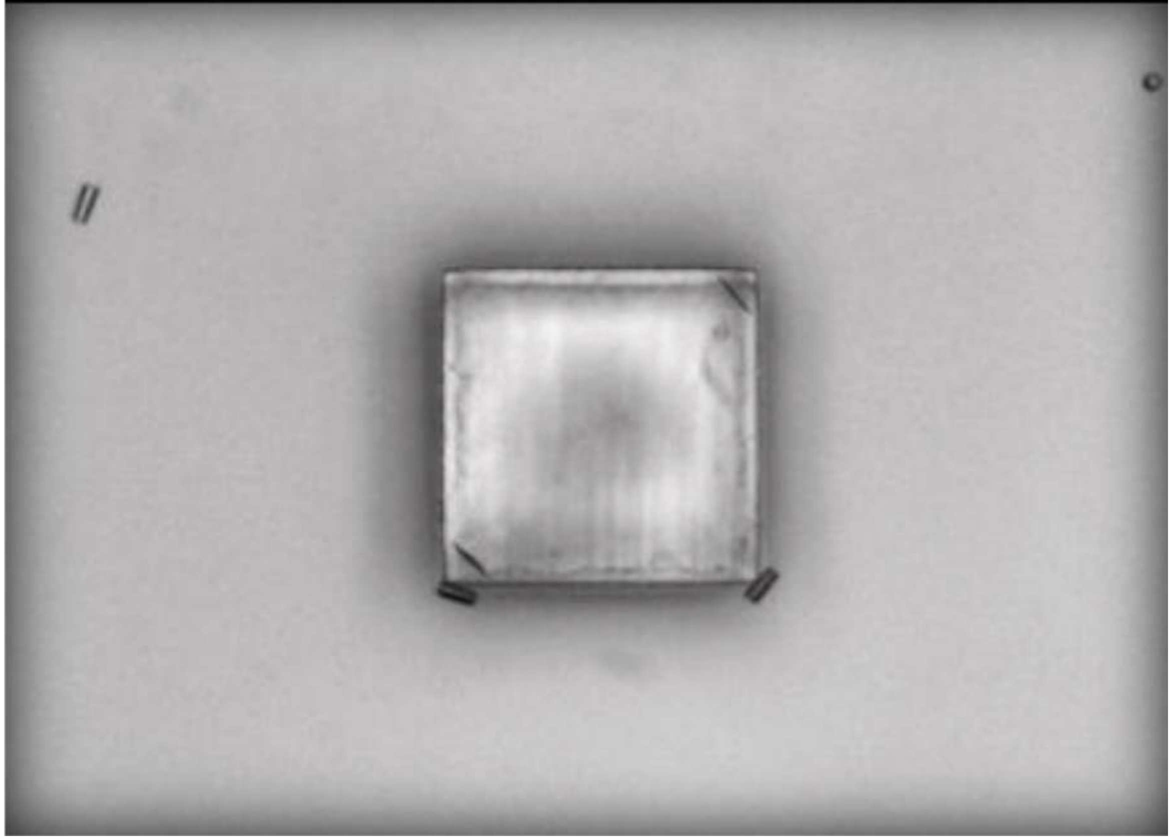
Trajectories in complex curvature field

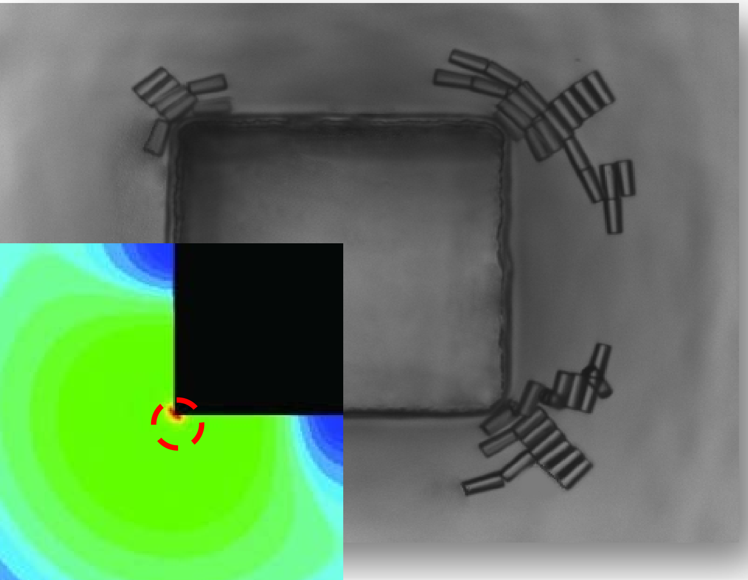


Alignment along principal axes

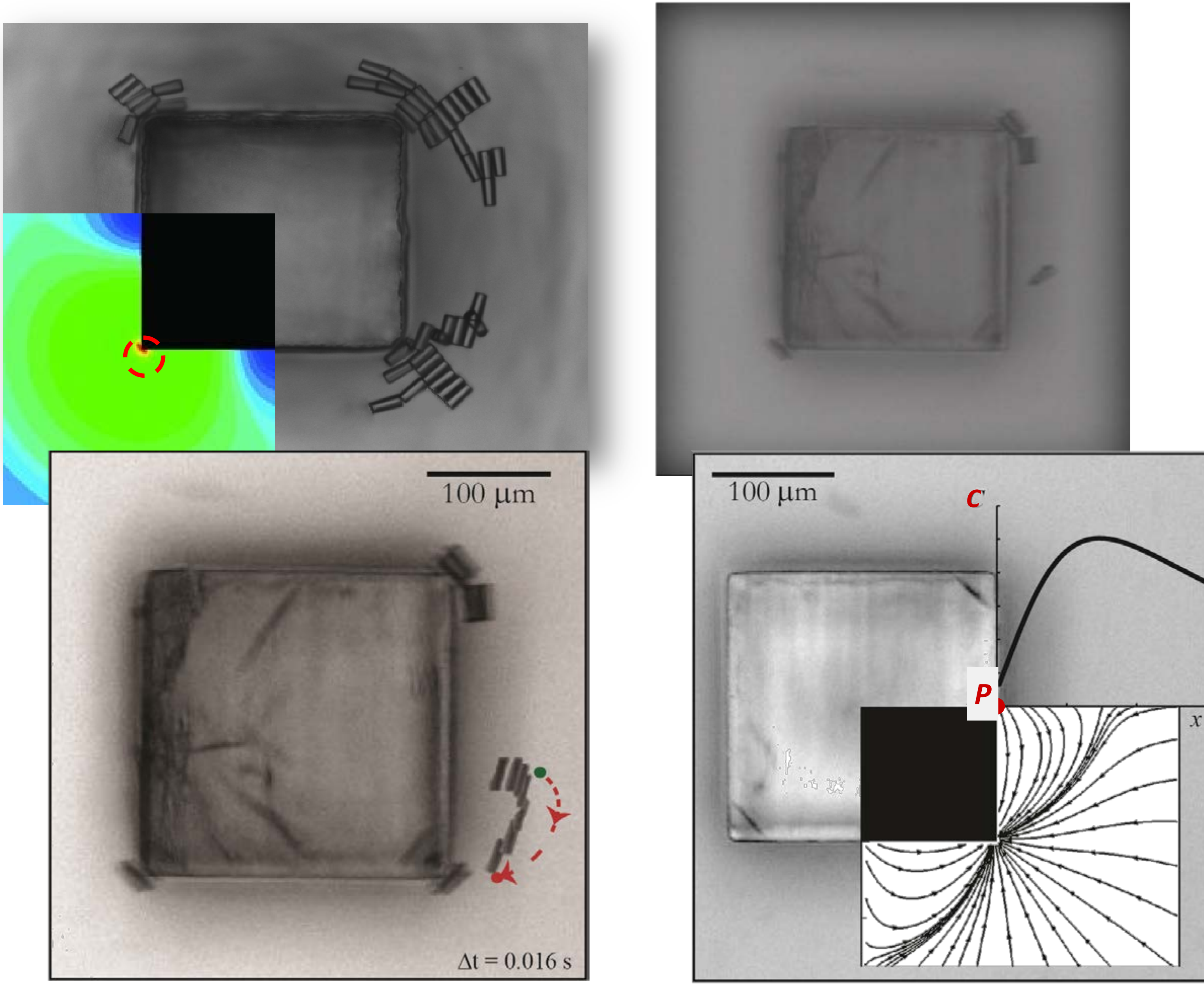
Migration to sites of high curvature

Corners





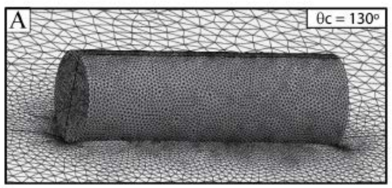
Corners

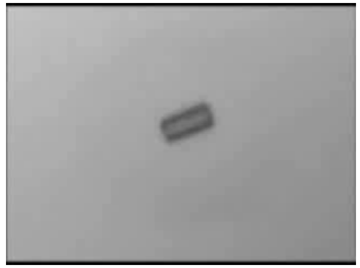


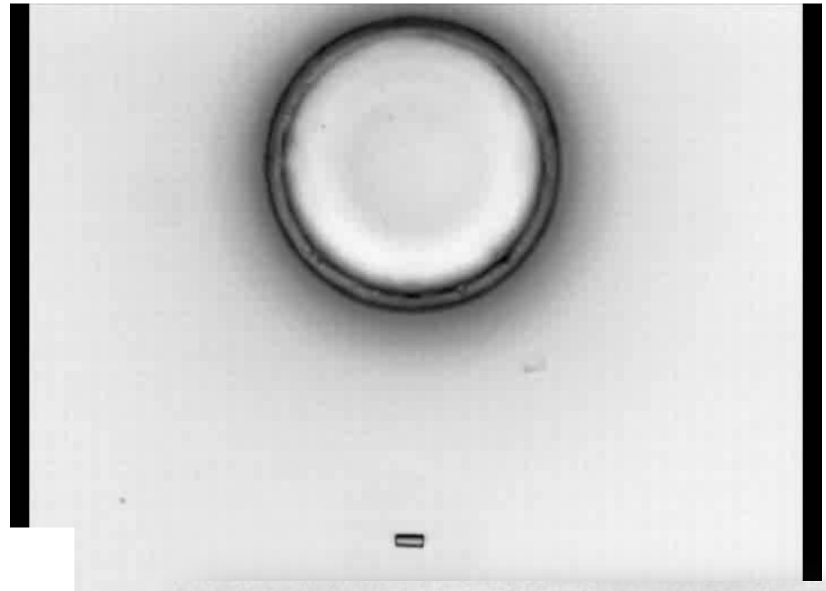
Cavallaro et al PNAS 2011

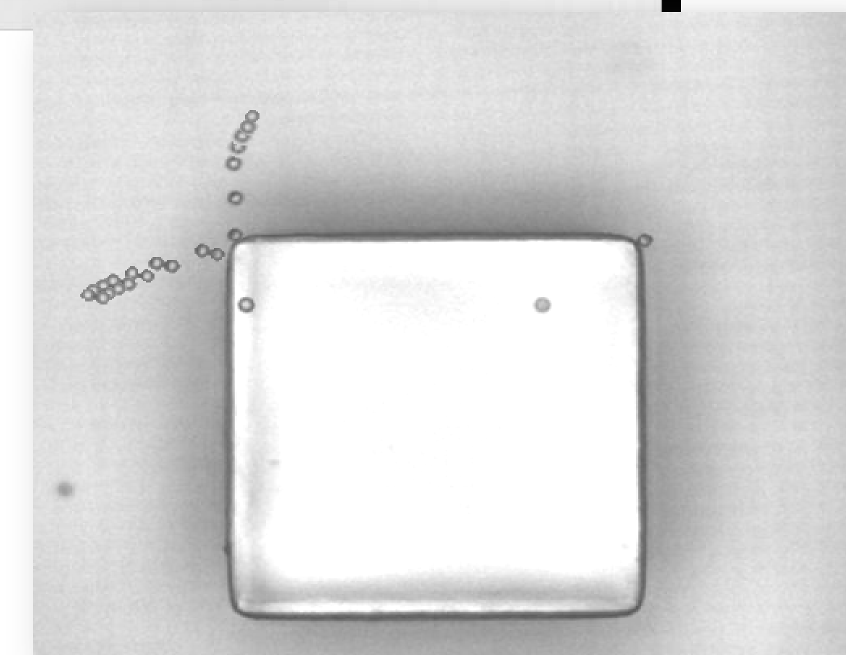
Cylindrical microparticles

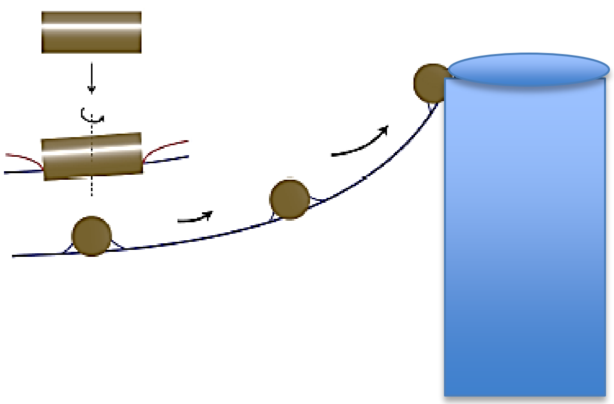
10 micron diameter cylinder





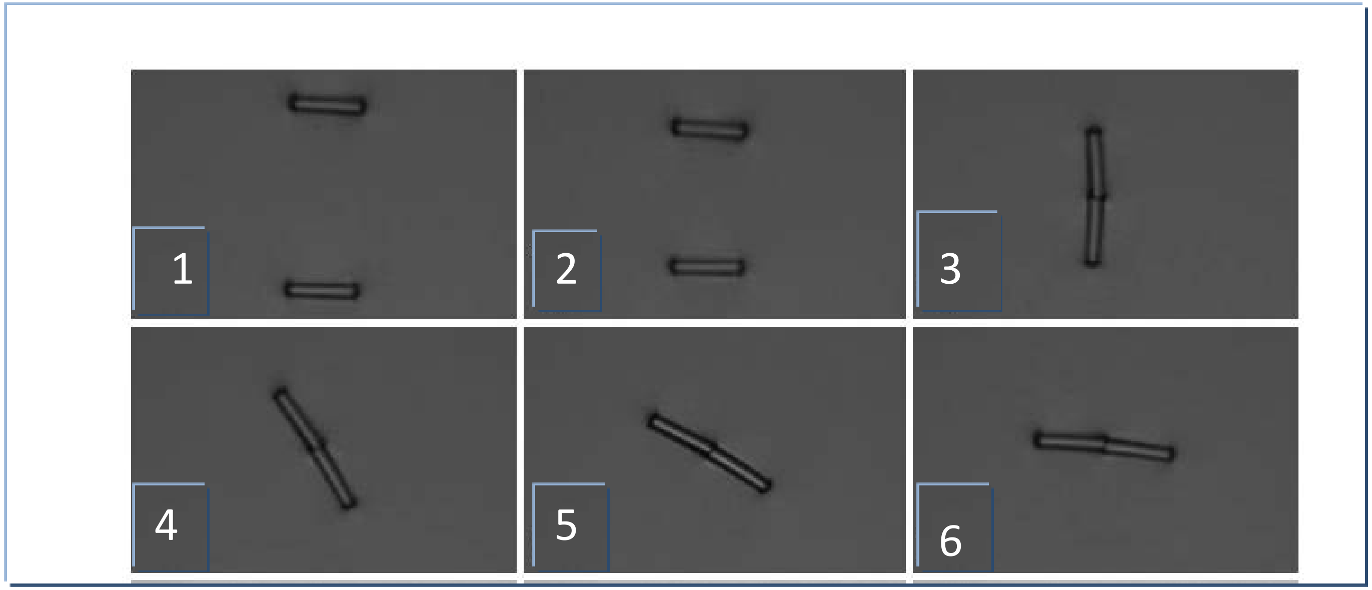




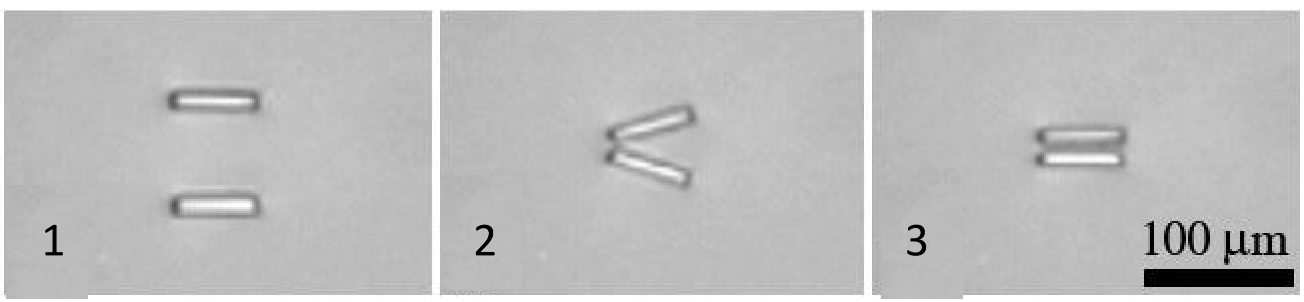


Particles migrate to match their disturbances to their host interface shape

Cylinder assembly on curved interfaces

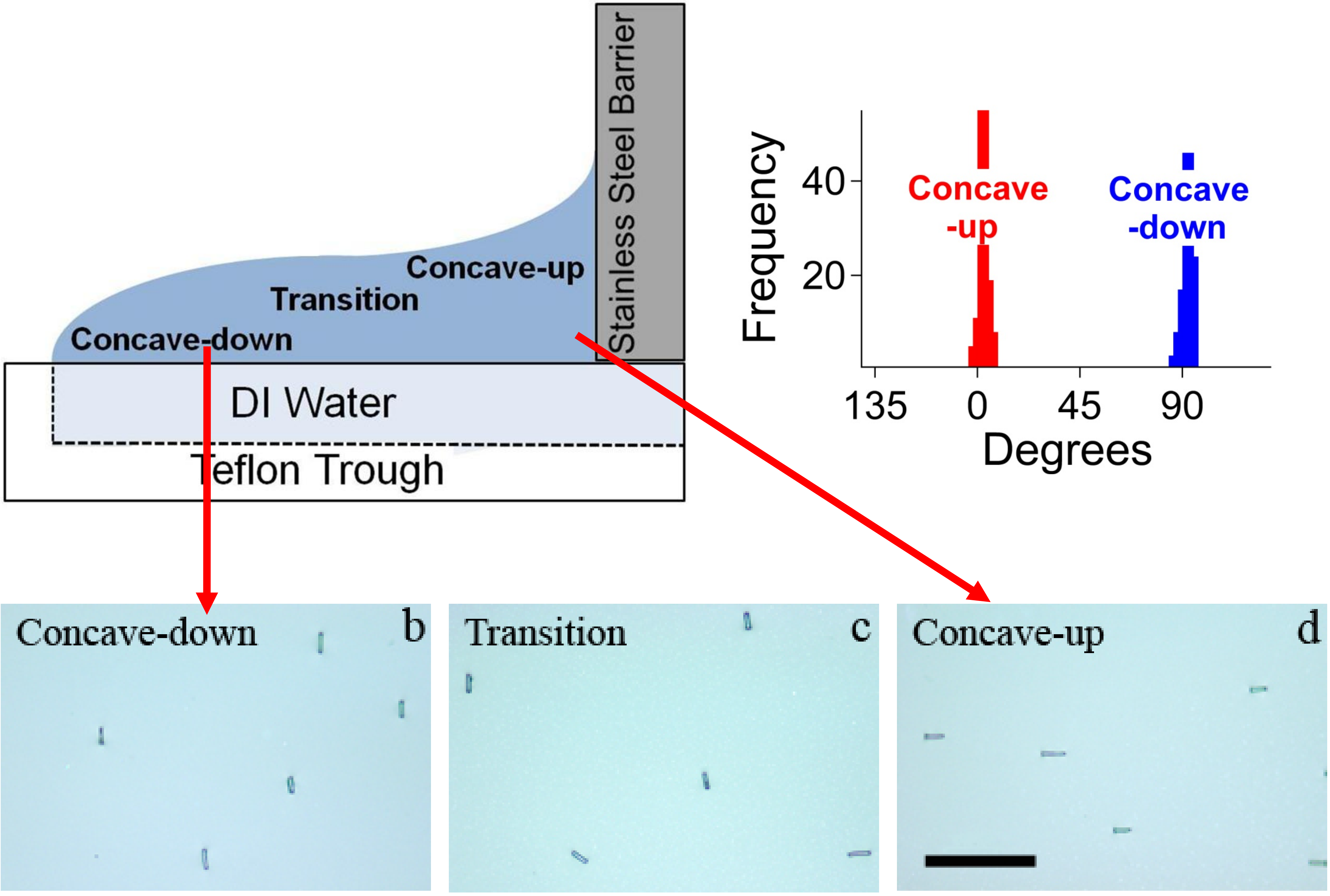


weak curvature



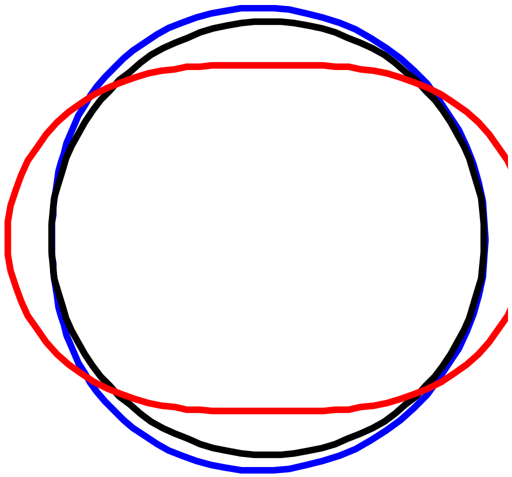
Strong curvature

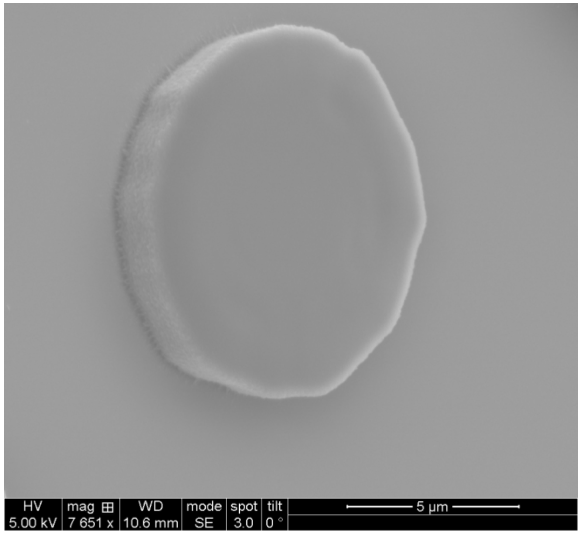
Cylinder alignment on curved interfaces



Perturbed contact line: rough and wavy

Height roughness: $h(r=a) = h_{qp}\dfrac{a^2}{r^2}\cos 2\theta + \ldots$





Domain perturbation

$$r = a\left(1 + \sum_{n=1}^{\infty} \zeta_n \cos(n\phi + \alpha_n)\right)$$

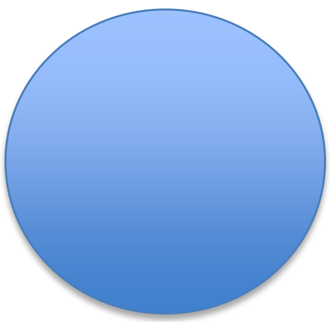
Electrostatic analogies

Grounded disk in an external potential

$$\psi(r=a)=0$$

$\psi(r,\phi)$ analogous to $h(r,\phi)$

U analogous to ΔE



$$\psi(r \geq a)=\psi_0(r^2-\frac{a^4}{r^2})\cos 2\phi,$$
$$\psi(r<a)=0$$

$$\sigma_s=-4\epsilon_0\psi_0 a\cos 2\phi,$$

$$U=\frac{1}{2}\oiint_D \rho(\mathbf{r})\psi(\mathbf{r})dA=\frac{1}{2}\int_a^R\int_0^{2\pi}\sigma_s\delta(r-a)\psi(\mathbf{r})rdrd\phi=0$$

Term by term correspondence to solution of perfect disk on curved interface, sums to zero.

$$U=\epsilon_0\left\{\oiint_{D-P}\frac{(\nabla\psi_{induced})^2}{2}dA+\oiint_{D-P}\nabla\psi_{ext}\cdot\nabla\psi_{induced}dA-\oiint_{P}\frac{(\nabla\psi_{ext})^2}{2}dA\right\}$$

$\psi(r=a)$ finite: the analogy is flawed

$$\psi(r \to \infty) = \psi_0 r^2 \cos 2\phi,$$

$$\psi(r=a) = q_{qp} \cos 2\phi$$

$$\psi^{inside} = q_p \frac{r^2}{a^2} \cos 2\phi,$$

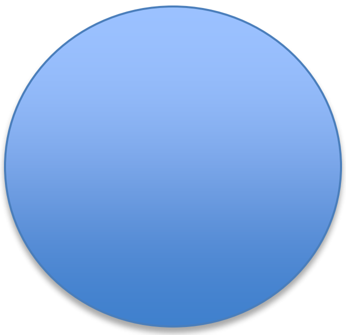
$$\psi^{outside} = q_p \frac{a^2}{r^2} \cos 2\phi + \psi_0 (r^2 - \frac{a^4}{r^2}) \cos 2\phi,$$

$$\psi^{inside}\Big|_{r=a} = \psi^{outside}\Big|_{r=a},$$

$$\mathbf{e}_r \cdot (\nabla\psi^{inside} - \nabla\psi^{outside})\Big|_{r=a} = \frac{\sigma_s}{\epsilon_0},$$

$$\frac{\sigma_s}{\epsilon_0} = 4(\frac{q_p}{a} - \psi_0 a) \cos 2\phi.$$

Example:



A disk with a quadrupolar surface potential:

Requires an electrostatic potential inside disk.

$$U = \frac{1}{2}\int_0^R \int_0^{2\pi} \sigma_s \delta(r-a)\psi(\mathbf{r}) r d\phi dr$$

$$= 2\epsilon_0 (\frac{q_p}{a} - \psi_0 a) \int_0^R \delta(r-a) q_p \frac{r^2}{a^2} r dr \int_0^{2\pi} \cos^2 2\phi \; d\phi = 2\pi\epsilon_0 (q_p^2 - \psi_0 q_p a^2).$$

$$U = -\frac{\epsilon_0}{2} \oint_{\partial(I+P)} (\psi \nabla \psi) \cdot \mathbf{n} \; dl + \frac{\epsilon_0}{2} \oiint_{I+P} (\nabla \psi)^2 dA,$$

$$\oiint_{I+P} (\nabla\psi)^2 dA = \oiint_{P} (\nabla \psi^{inside})^2 dA + \oiint_{I} (\nabla \psi^{outside})^2 dA.$$

$$\oiint_{P} (\nabla \psi^{inside})^2 dA = \int_0^{2\pi} (\cos^2 2\phi + \sin^2 2\phi) d\phi \int_0^a \frac{4q_p^2}{a^4} r^3 dr = 2\pi q_p^2.$$

There is no analogy to the potential inside the disk in the capillarity problem. U is too large owing to the contribution which has no analogy in our system.
HANDLE WITH CARE!