Directed Assembly by Energy Stored in Soft Matter

Kathleen J. Stebe
University of Pennsylvania

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

Aroms: Lennard Jone potential; Born repulsion--thermal

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

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

Directed Assembly

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

Usually $>>\kappa_B T$
Particles distort soft matter

Distortions store energy

This energy can direct particles to assemble

e.g. curvature generating and sensing proteins
Example: 5CB: Nematic Thermotropic Liquid Crystal

\[ \mathbf{n} = \text{director} \]

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

\[ \text{H}_3\text{C} - \overset{\text{CH}}{\text{CH}} - \overset{\text{C}}{\text{C}} - \overset{\text{H}}{\text{H}} \]

\[ T_{CN} = 18^\circ C \quad T_{NI} = 34^\circ C \]
Elastic Distortions & Defects

Fundamental Elastic Distortions

- **splay**
  - \( \text{div } n \neq 0 \)
  - \( E_{\text{splay}} = \frac{1}{2} K_1 [\nabla \cdot n]^2 \)

- **twist**
  - \( \text{curl } n \perp n \)
  - \( E_{\text{twist}} = \frac{1}{2} K_2 [n \cdot (\nabla \times n)]^2 \)

- **bend**
  - \( \text{curl } n \parallel n \)
  - \( E_{\text{bend}} = \frac{1}{2} K_3 [n \times (\nabla \times n)]^2 \)

\[
F' = E_{\text{splay}} + E_{\text{twist}} + E_{\text{bend}}
\]

Topological Defects

- \( s = 1 \)
- \( s = -1 \)
- \( s = \frac{1}{2} \)
- \( s = -\frac{1}{2} \)

\[
s = \frac{\theta}{2\pi}
\]
Elastic Distortions & Defects: rods

Microrod-induced defect structure in LC: DIPOLE*

DP small h; QP large h; DP chaining

Nematic LC
Analogy to electrostatics

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

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

$$n_\mu = \frac{A^\mu}{r} + \frac{p^\mu \cdot r}{r^3} + \frac{c_{ij}^\mu r_i r_j}{r^5} + \ldots$$

Planar anchoring of nematic LC

Homeotropic anchoring

$h=25 \mu m$
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

Parallel dipoles: chain

Anti-parallel dipoles: side-to-side

\[ \Delta E \sim 300-1200kT \]

\[ f_P(r) = \int \frac{\nabla E_P(r)}{2} \cdot v(r) \, dc \]

Stokes Law:

\[ Er << 1; Re << 1 \]
Capillary interactions between particles trapped at fluid interfaces
Cylindrical particles on planar interfaces

$\Delta E \sim 10^7 \text{kT}$

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

$L/2R \sim 2.5$

$L/2R \sim 1.2$

Lewandowski et al, *Langmuir* 2010
Preamble
Length scales

Capillary length = \( \sqrt{\frac{\gamma}{\Delta \rho g}} \)

Particle radius = \( a \)

Geometric length of container = \( L \)

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

Assume:

\[
\begin{align*}
Bo &= \frac{\Delta \rho g a^2}{\gamma} \ll 1 \\
ac &\ll 1; \quad \varepsilon = |\nabla h| \ll 1
\end{align*}
\]

Concept:
Surface tension
Wetting energies
Pinning sites
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)

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

\[ R_1; R_2 \]

\[ c_1 = \frac{1}{R_1}; \quad c_2 = \frac{1}{R_2} \]
Curvature

Decompose into isotropic and traceless (deviatoric) parts:

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

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

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

- **BOWL**
- **SADDLE**
Particles trapped at planar interfaces:
1. equilibrium contact lines
2. pinned contact lines
Particle at equilibrium at a planar interface

\[ E_1 = \gamma_{LS} 4\pi a^2 + \gamma \int \int_{I+P} dxdy \]

\[ dA_{LV} = dxdy; \]
integration domain = \( I + P \)

\[ E_{II} = \gamma_{LS} A_{LSII} + \gamma_{VS} A_{VSII} + \gamma \int \int_I dxdy \]
Particle at equilibrium at a planar interface

\[ \Delta E = E_{II} - E_I = (\gamma_{VS} - \gamma_{LS}) \Delta A_{VS} + \gamma_{LV} \Delta A_{LV} \]

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

\[ \Delta A_{LV} = -\int \int_P dx dy = -\pi a^2 \sin^2 \theta_0 \]

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

Pieranski’s trapping energy

\[ E_{\text{planar}} = E_2 - E_1 = \gamma_{LS} A_{LSII} + \gamma_{VS} A_{VSII} - \gamma \iint dx dy - \gamma_{LS} 4\pi a^2 \]

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

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

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

\[ = \gamma a^2 (2 \cos \theta_0 - 2 \cos^2 \theta_0 - \sin^2 \theta_0) \]

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

\[ = -\gamma a^2 (1 - \cos \theta_0)^2 \]

Comment on absolute value
Particle at equilibrium at a planar interface

\[ \Delta E_{\text{planar}} = E_{II} - E_I = -\gamma_{LV} \pi a^2 \left(1 - \left|\cos \theta_0\right|\right)^2 \]

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:
\[ \nabla^2 h = 0; \quad \text{multipole expansion} \]

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

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

\[ h = b_0 \ln r \]

\[ t = -l e_\phi \]

\[ n = e_r - \frac{b_0}{a} e_z \]

\[ m_k = -(e_{21k} e_{n1} + e_{23k} e_{n3}) \]

\[ m = e_r + \frac{b_0}{a} e_z \]

\[ F = \gamma f \int_{C} m ds \]

\[ m = e_r + \frac{b_0}{a} e_z \]

\[ F_z = \gamma \frac{b_0}{a} (2\pi a) = 2\pi \gamma b_0 \]
Dipolar deformation is zero absent external torque

\[ h = b_1 \frac{a}{r} \cos \phi \]

\[ m = e_r - \frac{b_1}{a} \cos \phi e_z \]

\[ e_R = e_r + \frac{b_1}{a} \cos \phi e_z \]

\[(e_R \times m)_k = e_{13k} \left( -\frac{b_1}{a} \cos \phi \right) + e_{31k} \frac{b_1}{a} \cos \phi \]

\[(e_R \times m) = 2 \frac{b_1}{a} \cos \phi e_{\phi} \]

\[ T = \gamma \oint_C e_R \times m \, ds = 2ayb_1 e_y \]
What if the contact line is pinned?

Particle disturbs the interface:

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

\[ dA_{LV} \approx \left[ 1 + \frac{\nabla h \cdot \nabla h}{2} \right] dx dy \]

\[ E_{II} = \gamma_{LS} A_{LSII} + \gamma_{VS} A_{VSII} + \gamma \int \int_{I} dA_{LV} - \gamma \int \int_{P} dA_{LV} \]

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

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

\[ E_{\text{dist}, hqp} = \gamma_{LV} \int_I \nabla h_{hqp} \cdot \nabla h_{hqp} \frac{dxdy}{2} \]

\[ \nabla h_{qp} = \frac{\partial h_{qp}}{\partial r} \mathbf{e}_r + \frac{1}{r} \frac{\partial h_{qp}}{\partial \theta} \mathbf{e}_\theta \]

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

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

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

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

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

\[ 2A_{\text{self particle}} = \left( 2h_{qp} \right)^2 \int_a^\infty \frac{a^4}{r^6} rdrd\theta \]

\[ A_{\text{self particle}} = 4h_{qp}^2 \pi a^4 \int_a^\infty r^{-5} dr = \pi h_{qp}^2 \]
Trapping of particles on interfaces: non-spherical shapes
\( \Lambda = 6; \ R = 10\mu m \)

**Shape of interface around isolated cylinder**

- **Simulation**: 
  - Interface topology satisfying contact angle not unique.
  - Surface evolver simulation, const P, Neumann conditions far field.

- **Minimum surface energy configuration**

- **Isoheight contours**

- **Quadrupole in ellip coord**

- **Excess area map**
Model roughness

Scale bar 50 microns
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?

Focus: saddle-shaped surfaces

\[ a \Delta c \ll 1 \]

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

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

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

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

\[ \Delta A_{LV} = \Delta A_{LV; \text{planar}} + \Delta A_{LV; \Delta c} \]

Two cases: pinned contact line; equilibrium contact lines (see arxiv, Sharifi-Mood, Liu, KJS)
Pinned contact line: shape of interface with particle

\[ \begin{cases} a \Delta c \ll 1 \\ |\nabla h| \ll 1 \end{cases} \]

\[ h_{\text{host}} = \frac{\Delta c}{4} r^2 \cos 2\phi \]

\[ \nabla^2 h = 0 \]

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

\[ h(r \to \infty) = h_{\text{host}} \]

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

\[ h = h_{\text{host}} + \eta_{\text{ind}} + \eta_{qp} \]
$\Delta A_{LV}$: Pinned contact line

\[ \Delta A_{LV} = \Delta A_{LV, \text{planar}} - \iint_P \left( \frac{\nabla h_{\text{host}} \cdot \nabla h_{\text{host}}}{2} \right) \, dx dy + \iint_I \left( \frac{\nabla \eta \cdot \nabla \eta}{2} \right) \, dx dy + \iint_I \left( \nabla \eta \cdot \nabla h_{\text{host}} \right) \, dx dy \]

the increased area of hole under the particle = the increased area of interface from $\eta_{\text{ind}}$

\[ \iint_P \left( \frac{\nabla h_{\text{host}} \cdot \nabla h_{\text{host}}}{2} \right) \, dx dy = \iint_I \left( \frac{\nabla \eta_{\text{ind}} \cdot \nabla \eta_{\text{ind}}}{2} \right) \, dx dy \]

\[ \gamma \iint_I \left( \frac{\nabla \eta_{\text{hqp}} \cdot \nabla \eta_{\text{hqp}}}{2} \right) \, dx dy = E_{\text{dist}, hqp, \text{planar}} = \pi h_{qp}^2 \]

\[ \iint_I \left( \nabla \eta_{\text{hqp}} \cdot \nabla \eta_{\text{ind}} \right) \, dx dy = -\frac{\pi}{2} \Delta c a^2 h_{qp} \]

\[ \iint_I \left( \nabla \eta_{\text{hqp}} \cdot \nabla h_{\text{host}} \right) \, dx dy = 0; \quad \iint_I \left( \nabla \eta_{\text{hqp}} \cdot \nabla h_{\text{host}} \right) \, dx dy = 0^{**} \]

**typically reported as $-\frac{\pi a^4 \Delta c^2}{8}$ owing to appropriate neglect of outer contour.
$\Delta E(\Delta c)$: Pinned contact line

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

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

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

\[ h_2 = h_2 \big|_{r_1=0} + \mathbf{r} \cdot \nabla h_2 \big|_{r_1=0} + \mathbf{r} \cdot \frac{\nabla \nabla h_2}{2} \big|_{r_1=0} + \ldots \]
Pair interaction: Method of reflections

Particle 1 experiences far field boundary condition created by particle 2

\[ h_2 = h_2 \bigg|_{r_1=0} + \mathbf{r} \cdot \nabla h_2 \bigg|_{r_1=0} + \mathbf{r} \cdot \frac{\nabla \nabla h_2}{2} \bigg|_{r_1=0} + \ldots \]

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

treatment differs from literature

\[ \nabla^2 h_1 = 0 \]
\[ h_1(r = a) = h_{qp1} \cos 2(\phi - \alpha_1) , \]
\[ h_1(r_1 \to \infty) = \frac{3h_{qp2}a^2}{r_{12}^4} r^2 \cos 2(\phi + \alpha_2) \]

\[ h_1 = \frac{3h_{qp2}a^2}{r_{12}^4} r^2 \cos 2(\phi + \alpha_2) + \eta_1 \]
\[ \eta_1 = -\frac{3h_{qp2}a^2}{r_{12}^4} \frac{a^4}{r^2} \cos 2(\phi + \alpha_2) + h_{qp1} \frac{a^2}{r^2} \cos 2(\phi - \alpha_1) \]
\[ \eta_1 = \eta_{ind} + \eta_{qp} \]
\[ \eta = \left(\frac{-a^2 \Delta c}{4} + h_{qp}\right) \frac{a^2}{r^2} \cos 2\phi \]
\[ \Delta c \text{ from particle 2} = \frac{12h_{qp2}a^2}{r_{12}^4} \cos 2(\phi + \alpha_2) \]
Pair interaction

Here we respect bc at particle and in far field

\[ \Delta E = -\gamma \pi a^2 \frac{h_{particle}(a) \Delta c}{2} \]

\[ \Delta E = -\gamma \pi a^2 \frac{12 h_{qp2} h_{qp1} a^2}{r_{12}^4} \cos 2(\alpha_1 + \alpha_2) \]

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

1. Expose resist through mask
2. Develop photoresist
3. Sonicate in ethanol to free particles
Cylindrical particles on planar interfaces

\[ r_{12init} \sim 180 \mu m \]

\[ L/2R \sim 2.5 \]

\[ L/2R \sim 1.2 \]

Lewandowski et al, *Langmuir* 2010
Surface area decreases when deformations overlap

**Far field interactions**

\[
A_{LV} \approx \int_S 1 + \frac{\nabla h \cdot \nabla h}{2} \ dS \sim A_{\text{plane}} + A_{\text{excess}}
\]

**Interaction Energy**

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

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

**Here- method of reflections**

**Force of Attraction**

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

\[
F_{12} \sim r_{AB}^{-5}
\]

Excess area drives interactions

*but no preferred orientation*
Far field: Quadrupolar Attraction: power law

\[ r_{12} = C (t - t_c)^\alpha \]

\[ \alpha = \frac{1}{6} \]

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

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

\[ dt \sim r_{12}^5 dr_{12} \]

\[ \Delta E(r_{12}) \propto r^{(2 - \frac{1}{\alpha})} \]

\[ (2 - \frac{1}{\alpha}) = -4 \]

\[ \alpha = \frac{1}{6} \]
Extract magnitude of far field interaction energy

Viscous dissipation

\[ \Delta E^{\text{Drag}} = -6\pi \mu R C_D \int_{r_f}^{r_i} v(r') dr' = -2.16 \pm 0.65 \times 10^5 kT \]

\[ 0.6 \Delta E^{\text{Drag}} = -2.24 \pm 0.67 \times 10^5 kT \]

Capillary interaction energy

\[ \Delta E \approx -12\pi \gamma H_p^2 \left( 1 - \frac{(L/D - 1)^2}{(L/D + 1)^2} \right) R^4 \left( \frac{1}{r_{12,f}^4} - \frac{1}{r_{12,i}^4} \right) = -0.985 \times 10^5 kT \quad \text{predicted} \]
\( \Lambda = 6; R = 10 \mu m \)

**Shape of interface around isolated cylinder**

- **Simulation**
  - Interface topology satisfying contact angle not unique
  - Surface evolver simulation, const P, Neumann conditions far field

- **Environmental SEM**

- **Minimum surface energy configuration**

- **Isoheight contours**

- **Quadrupole in ellip coord**

**Graphs:**

- Interferometry vs Analytical for different values of \( r \):
  - \( r = 10R \)
  - \( r = 20R \)
  - \( r = 40R \)

**Legend:**

- Excess area map
  - 0.017
  - 0.013
  - 0.003
Quadrupoles in Elliptical Coordinates
Near field Torque

Rotation: very local; decays steeply

\[ T_{torque} \sim \frac{\Delta E}{\Delta \theta} \sim \frac{1}{r_1^6} \]

Analysis and experiment

Euler Scheme

Trajectory computed as:

\[ x^{n+1} = x^n + \frac{\Delta t}{6\pi \mu R f_T} \left( \frac{\partial E}{\partial x} \right)^\kappa \]

\[ \theta^{n+1} = \theta^n + \frac{\Delta t}{8\pi \mu R^2 f_\theta} \left( \frac{\partial E}{\partial \theta} \right)^\kappa \]

(used experimentally measured drag coeffs \( f_T \) & \( f_\theta \))

Lewandowski et al. Langmuir 2010
Capillary assembly strongly dependent on shape

Capillary energy landscape for ellipsoids

\[ T = -\frac{\partial E}{\partial \phi} \]

\[ T = \kappa C \]

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

\[ \kappa \sim 2RG = 0.003\gamma R^3 \]

Modest torque to bend the chain
\[ T \sim 10^3 kT \]
Capillary energy landscape for cylinders

\[ E \sim 10^7 \text{kT} \]

\[ \frac{E}{\gamma R^2} \]

bond angle \( \phi (\degree) \)

Energy barrier for different assembly configurations

Capillary Bridge

HINGING MOTION

steric constraint

\( \phi \)
Yield Torque: chain of cylinders

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

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

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 role. Waviness can give near field repulsion. Corners, sharp edges, can cement very strong bonds and preferred orientations.
Curvature driven motion
Planar disk

\[ \Delta E = - \int F_{\text{drag}} \, ds = -C_D \pi \eta a \int v ds \]

Lamb’s drag coeff
(\( \mu \nu = 0.002 \text{Pa s} \))

Real time
Disk: 5 micron radius; Post: 125 micron radius
$\Delta E(\Delta c): \text{Pinned contact line}$

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

$\Delta c(\text{position})$

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

$h_p = 30 - 35 \text{nm}$

$a = 5 \mu m$

$\theta_0 = 90^0$

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

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

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

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

Lewandowski et al. (KJS) 2008
Cavallaro et al (KJS) PNAS 2011
Lu et al (KJS) JCIS 2015
Planar disks

disk: $a = 5 \mu m$

$\delta a = 225 \pm 55 \text{ nm}$

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

AFM

Roughness:

RMS

18 ~ 32 nm.
Pinned Contact Lines
Brownian trajectories at planar interface
Planar disk

\[ \Delta E = - \int F_{\text{drag}} \, ds = -C_D \int \pi \eta a \, v \, ds \]

Lamb’s drag coeff
(\( \mu a v = 0.002 \text{Pa s} \))

Real time
Disk: 5 micron radius; Post: 125 micron radius
Energy dissipated over trajectory

\[ \Delta E = -\gamma \pi \frac{h_{ap} a^2}{2} (\Delta c_f - \Delta c_0) \]

\[ -\Delta E_{\text{exp}} = 5.6 \times 10^4 k_B T \]

\[ -\Delta A_{LV} \sim 560 \text{ nm}^2 \]

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

lines: \( h_{ap} = 25\text{nm}; \ h_{ap} = 30 \text{nm} \)

\[ 15\text{nm} < \frac{a^2 \Delta c}{2} < 35\text{nm} \]
Analytical shape around the particle

disturbance local to particle; interface a saddle near particle

\[ \begin{align*}
B_0 &= \frac{\Delta \rho g a^2}{\gamma} \ll 1 \\
\lambda &= a \Delta c \ll 1; \quad \varepsilon = |\nabla h| \ll 1
\end{align*} \]

\[ h^{\text{inner}}(r, \phi) = h_{qp} \frac{a^2}{r^2} \cos 2\phi + \frac{\Delta c_0}{4} (r^2 - \frac{a^4}{r^2}) \cos 2\phi \]

\[ a^2 \Delta c \approx 20 \text{nm} \]

\[ h_{qp} \approx 10 - 100 \text{nm} \]

\[ h_{\text{dist}}(r \sim 20a) = (\text{sub}) \text{ angstrom} \]
Singular perturbation analysis

disturbance local to particle; interface a saddle near particle

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

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?

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

Matching: disturbance zero at large \( r \)

Outer Region:
Host interface
Far from particle
\( \sim R_c \)

Inner Region
\( \sim a \)
Inner and outer regions

Outer region

\[ h_{\text{outer}} = H_m - R_m \tan \psi \ln \left( \frac{L}{R_m} \right). \]

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

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

Inner coordinate; scaled with \( a \):

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

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

\[ X = L_0 + x + O(\epsilon), \]
\[ Y = y, \]
\[ Z = Z_0 + z + O(\epsilon), \]
Inner and outer regions

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

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

\[ \lim_{\tilde{r} \to \infty} \lambda \hat{h}_{\text{inner}} (\tilde{r}, \phi) = \lim_{\lambda \to 0} \hat{h}_{\text{outer}} (\tilde{r}, \phi). \]

Van Dyke matching condition

Yields far field boundary condition for inner region

\[ \lim_{\tilde{r} \to \infty} \tilde{h}_{\text{inner}} (\tilde{r}, \phi) = \frac{\Delta c a}{4} \tilde{r}^2 \cos 2\phi + O(\epsilon, (\Delta c a)^2) . \]


Inner and outer regions

\[ h^{uv} = R_c \hat{h}^{\text{outer}} + a \hat{h}^{\text{inner}} - R_c \lim_{\lambda \to 0} \lambda \to 0 \hat{h}^{\text{outer}} \]

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

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

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

Particles migrate to match their disturbances to their host interface shape
Directed migration towards tips

Migration in a Complex Curvature Field

Top view interface around micropost with elliptical cross section

Let $\Delta c(R, \theta)$
Trajectories in complex curvature field

Alignment along principal axes

Migration to sites of high curvature
Corners
Cylindrical microparticles

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

[Diagram showing the alignment of cylinders on different interfaces: DI Water, Transition, Stainless Steel Barrier, Concave-up, Concave-down.]

Frequency distribution for Concave-up and Concave-down orientations.

Images labeled 'Concave-down a', 'Concave-down b', 'Transition c', 'Concave-up d'.
Perturbed contact line: rough and wavy

Height roughness:
\[ h(r = a) = h_{qp} \frac{a^2}{r^2} \cos 2\theta + ... \]

Domain perturbation
\[ r = a(1 + \sum_{n=1}^{\infty} \zeta_n \cos(n\phi + \alpha_n)) \]
Electrostatic analogies
Grounded disk in an external potential

\[ \psi(r, \phi) \text{ analogous to } h(r, \phi) \]

\[ U \text{ analogous to } \Delta E \]

\[ \psi(r \geq a) = \psi_0(r^2 - \frac{a^4}{r^2})\cos 2\phi, \]

\[ \psi(r < a) = 0 \]

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

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

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

\[ U = \epsilon_0 \left\{ \iint_{D-P} \frac{(\nabla \psi_{\text{induced}})^2}{2} dA + \iint_{D-P} \nabla \psi_{\text{ext}} \cdot \nabla \psi_{\text{induced}} dA - \iiint_P \frac{(\nabla \psi_{\text{ext}})^2}{2} dA \right\} \]
\( \psi (r = a) \) finite: the analogy is flawed

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

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

\[
\psi_{\text{inside}} = q_p \frac{r^2}{a^2} \cos 2\phi,
\]

\[
\psi_{\text{outside}} = q_p \frac{a^2}{r^2} \cos 2\phi + \psi_0 (r^2 - \frac{a^4}{r^2}) \cos 2\phi,
\]

\[
\psi_{\text{inside}} \bigg|_{r=a} = \psi_{\text{outside}} \bigg|_{r=a},
\]

\[
\mathbf{e}_r \cdot (\nabla \psi_{\text{inside}} - \nabla \psi_{\text{outside}}) \bigg|_{r=a} = \frac{\sigma_s}{\epsilon_0},
\]

\[
\frac{\sigma_s}{\epsilon_0} = 4 \left( \frac{q_p}{a} - \psi_0 a \right) \cos 2\phi.
\]

Example:

A disk with a quadrupolar surface potential:

Requires an electrostatic potential inside disk.
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!