

Effective interactions between colloidal particles at the surface of a liquid drop

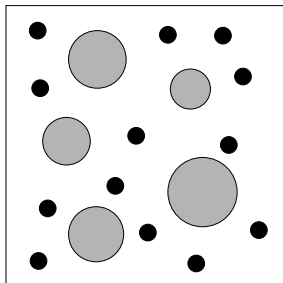
Jan Guzowski

Instytut Chemii Fizycznej PAN, Warszawa

IPPT, Warszawa, 09.11.2011

Pickering Emulsions

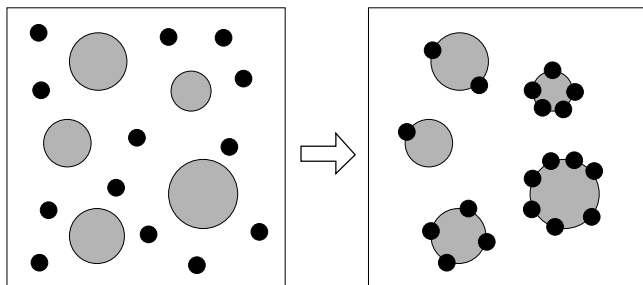
- emulsion + colloidal particles
- particles get trapped at the surface of droplets



- applications: stabilization of emulsions, engineering of functional particles

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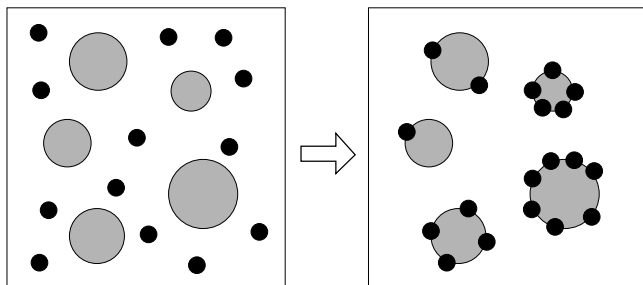
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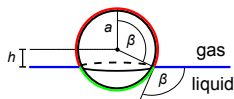
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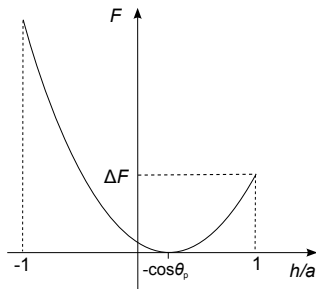
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Stability of a colloidal particle at the interface

- macroscopic picture: interplay of surface energies
- contributions from three possible interfaces: $F = \gamma_{pl}S_{pl} + \gamma_{pg}S_{pg} + \gamma_{lg}S_{lg}$
- rough estimate: undeformable flat interface $\Rightarrow F(h) = \pi\gamma a^2(h/a + \cos\theta_p)^2$, where $\cos\theta_p = (\gamma_{pg} - \gamma_{pl})/\gamma_{lg}$

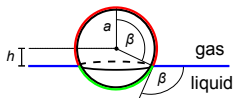


a	ΔF [$k_B T$]
10nm	10^3
100nm	10^5
$1\mu\text{m}$	10^7

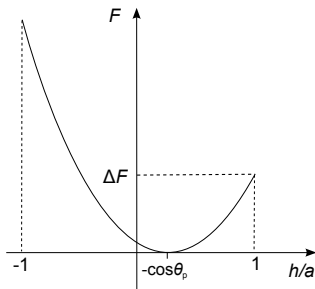


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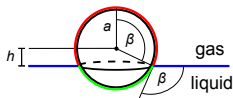


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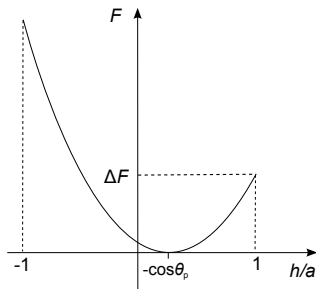


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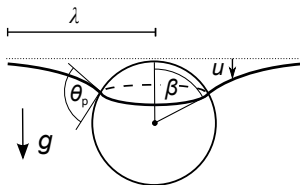
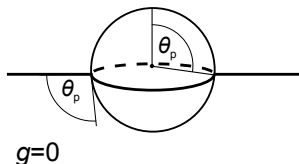


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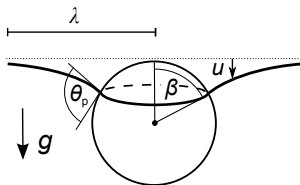
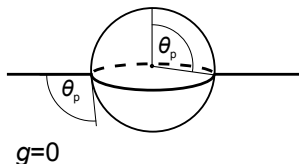
Generic case: single particle at a flat interface

- particle pulled by the force $f = \text{weight} - \text{buoyancy}$
- interface effectively pinned by gravity at the distance $\lambda = \sqrt{\gamma/\Delta\rho g}$ (capillary length)



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- the capillary equation for $|\nabla_{\parallel} u| \ll 1$ (balance of capillary and hydrostatic pressures across the interface)

$$-\gamma \nabla_{\parallel}^2 u + \frac{\gamma}{\lambda^2} u = 0$$

- the corresponding Green's function $G(\mathbf{x}, \mathbf{x}') = G(|\mathbf{x}, \mathbf{x}'|)$ obeying the condition $G(r \rightarrow \infty) = 0$ reads

$$G(r) = (1/2\pi)K_0(r/\lambda) \sim \begin{cases} \ln(\lambda/r) & \text{for } r \ll \lambda \\ r^{-1/2}e^{-r/\lambda} & \text{for } r \gg \lambda \end{cases}$$

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Effective description, limit $\lambda \rightarrow \infty$

- particle replaced by an effective pressure distribution $\Pi(\mathbf{x})$
- for $\lambda \rightarrow \infty$ Poisson equation $-\gamma \nabla_{\parallel}^2 u = \Pi(\mathbf{x})$
- in terms of complex variables $u(\mathbf{x}) = \text{Re}V(z)$ with $V(z) = (2\pi\gamma)^{-1} \int d^2\mathbf{x}' \Pi(z') \ln[\lambda/(z - z')]$
- for $\Pi(z')$ localized around the origin one can use the Taylor expansion

$$2\pi\gamma V(z) = \tilde{Q}_0 \ln(\lambda/z) + \sum_{n=1}^{\infty} \tilde{Q}_n n^{-1} z^{-n}$$

- with the multipoles $\tilde{Q}_n := \int d^2\mathbf{x}' \Pi(z') z'^n = Q_n e^{i\phi_n}$ so that $Q_0 =$ total external force, $Q_1 =$ total external torque; $Q_{n \geq 2}$ correspond to free particles
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Capillary interactions

- two particles at distance d , effective pressure $\Pi = \Pi_1 + \Pi_2$
- free energy

$$F = \int d^2\mathbf{x} \left[\frac{\gamma}{2} (\nabla_{\parallel} u)^2 - \Pi(\mathbf{x})u(\mathbf{x}) \right] = -\frac{1}{2\gamma} \int d^2\mathbf{x} \int d^2\mathbf{x}' \Pi(\mathbf{x})G(\mathbf{x}, \mathbf{x}')\Pi(\mathbf{x}')$$

- $F = F_{1,self} + F_{2,self} + \Delta F(d)$
- multipole expansion yields

$$\Delta F(d) = -\frac{1}{\gamma} \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} Q_{1,n} Q_{2,n'} g_{nn'} \cos(n\varphi_{1n} + n'\varphi_{2n'}) \times \begin{cases} \ln(\lambda/d) & n = n' = 0, \\ d^{-n-n'} & \text{otherwise} \end{cases}$$

- in general $Q_{i,n} = Q_{i,n}(d)$ (feedback $u \rightarrow \Pi$), many-body interactions!
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Spherical interfaces

- assume small radial deformations $v(\Omega) = (r(\Omega) - R_0)/R_0$ and incompressibility of liquid \Rightarrow free energy functional:

$$\mathcal{F}[\{v(\Omega)\}] = \gamma R_0^2 \int_{\Omega_0} d\Omega \left[\frac{1}{2} (\nabla_a v)^2 - v^2 - (\pi(\Omega) + \mu)v \right] + O(v^3, (\nabla_a v)^3)$$

- with $\int d\Omega v(\Omega) = 0$; condition $\delta\mathcal{F} \stackrel{!}{=} 0$ yields $-\nabla_a^2 v - 2v = \pi(\Omega) + \mu$
- free energy $F = \min_{\{v(\Omega)\}} \mathcal{F}$ in terms of the corresponding Green's function G reads

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- at small separations $G(\bar{\theta}) \xrightarrow{\bar{\theta} \rightarrow 0} -(2\pi)^{-1} \ln(\bar{\theta}) = -(2\pi)^{-1} \ln(r/R_0)$

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Expansion in spherical harmonics

- capillary equation

$$[l(l+1) - 2]v_{lm} = \pi_{lm} + \mu\delta_{l0} \text{ with}$$

$$X_{lm} = \int d\Omega X(\Omega) Y_{lm}(\Omega)$$

- $l = 0$: incompressibility $v_{00} = 0 \Rightarrow \mu = \pi_{00}$
- $l = 1$: translations v_{1m} undefined, assume fixed center of mass $v_{1m} = 0$
- free energy in terms of irreducible representation of rotation group

$$\Delta F = -\gamma R_0^2 \sum_{l \geq 2} \sum_{m=-l}^l \sum_{m'=-l}^l \pi_{1,lm} \pi_{2,lm'} \frac{(-1)^{m'}}{l(l+1) - 1} d_{m,-m'}^l(\bar{\theta}) e^{i(m\phi_1 + m'\phi_2)}$$

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$$\Delta F = -\gamma R_0^2 \sum_{l \geq 2} \sum_{m=-l}^l \sum_{m'=-l}^l \pi_{1,lm} \pi_{2,lm'} \frac{(-1)^{m'}}{l(l+1) - 1} d_{m,-m'}^l(\bar{\theta}) e^{i(m\phi_1 + m'\phi_2)}$$

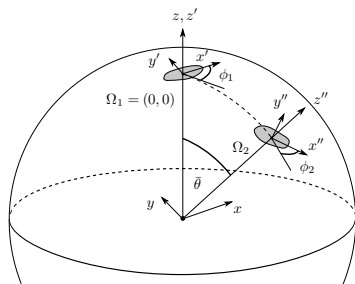
Expansion in spherical harmonics

- capillary equation
 $[l(l+1) - 2]v_{lm} = \pi_{lm} + \mu\delta_{l0}$ with
 $X_{lm} = \int d\Omega X(\Omega) Y_{lm}(\Omega)$
- $l = 0$: incompressibility $v_{00} = 0 \Rightarrow \mu = \pi_{00}$
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Limit of small particles

- in the limit $a, a' \ll R_0$ one has $\Delta F = \sum_{n,n'=0}^{\infty} \Delta F_{nn'}$ with $n = |m|$ and

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Numerical calculations

- surface free energy minimized by using software Surface Evolver based on the gradient descent method
- minimized expression:

$$\begin{aligned}\mathcal{F}[\{\mathbf{r}(\Omega)\}, h_i, \boldsymbol{\psi}_i; \bar{\theta}, \phi_i, f_i, T_i, \theta_{p,i}, a_i, V_l, \lambda_0] = \\ = \gamma S_{lg} + \sum_{i=1,2} (-\gamma \cos \theta_{p,i} S_{pl,i} - f_i h_i - \mathbf{T}_i \cdot \boldsymbol{\psi}_i) - \lambda_0 (V - V_l).\end{aligned}$$

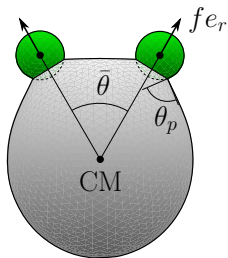
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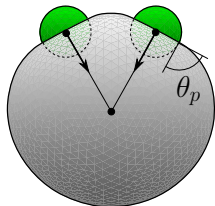
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Results: monopoles

- smooth spherical particles, external radial forces $f = \gamma a Q_0$, fixed CM

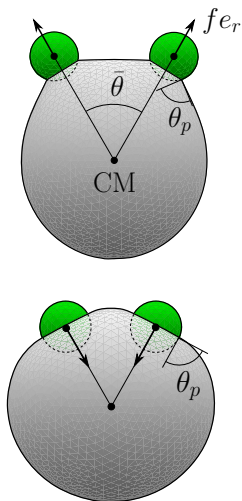


$$\frac{\Delta F_{00}(\bar{\theta})}{\gamma a^2} = -Q_0^2 G(\bar{\theta}) = \frac{Q_0^2}{4\pi} \left[\frac{1}{2} + \frac{4}{3} \cos \bar{\theta} + 2 \cos \bar{\theta} \ln \left(\sin \frac{\bar{\theta}}{2} \right) \right]$$

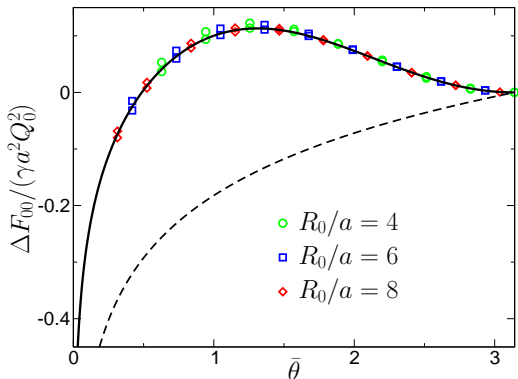


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Results: dipoles

- three metastable branches for three different orientational configurations

$$\Delta F_{11}(\bar{\theta}, \phi_1, \phi_2) = \gamma a^2 \frac{Q_1^2}{8\pi} \left(\frac{a}{R_0} \right)^2 \begin{cases} -f_+(\bar{\theta}) + f_-(\bar{\theta}), & \text{for } \bar{\theta} < \bar{\theta}_0, & \uparrow \uparrow \\ -f_+(\bar{\theta}) - f_-(\bar{\theta}), & \text{for } \bar{\theta}_0 < \bar{\theta} < \bar{\theta}_1, & \leftarrow \rightarrow \\ f_+(\bar{\theta}) - f_-(\bar{\theta}), & \text{for } \bar{\theta} > \bar{\theta}_1, & \uparrow \downarrow \end{cases}$$

- where $f_-(\bar{\theta}_0) = 0$ and $f_+(\bar{\theta}_1) = 0$ and

$$f_+(\theta) := \frac{1}{\sin^2(\theta/2)} - 4 \sin^2 \frac{\theta}{2} \ln \left(\sin \frac{\theta}{2} \right) - \frac{20}{3} \sin^2 \frac{\theta}{2} + 2,$$

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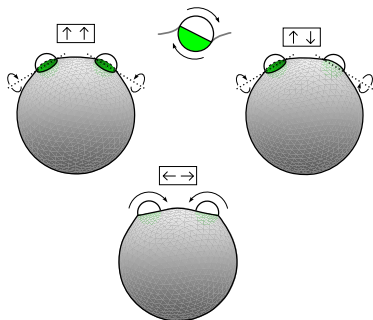
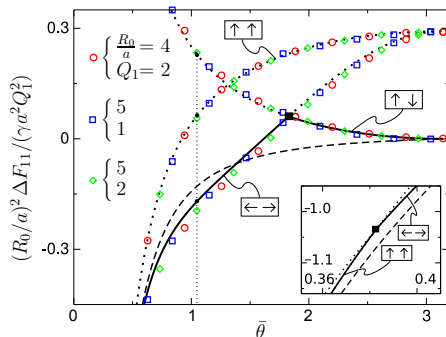
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Results: dipoles

- pinned contact lines, external torques $T = \gamma a^2 Q_1$, fixed CM

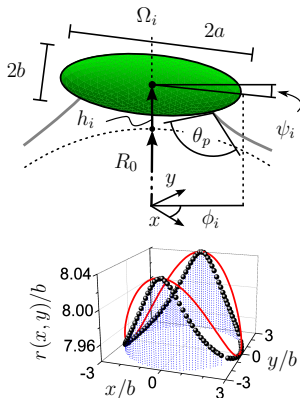
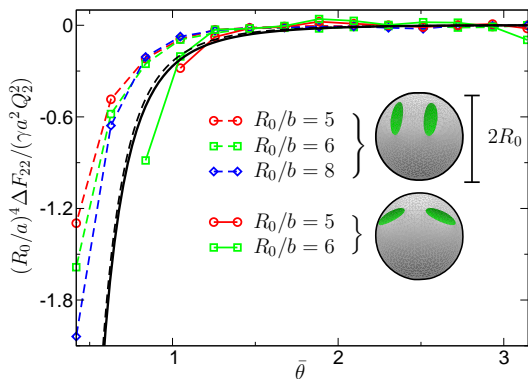


Results: free spheroidal particles

- free, smooth prolate spheroids; approximation:

$$Q_2 = Q_2(R_0) \simeq 2\pi\Delta r|_{\theta=a/R_0}/a$$

$$\Delta F_{22}(\bar{\theta}, \phi_1, \phi_2) = -\gamma a^2 \frac{3Q_2^2}{64\pi} \left(\frac{a}{R_0}\right)^4 \frac{1}{\sin^4(\bar{\theta}/2)}$$

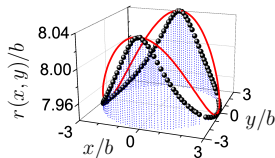
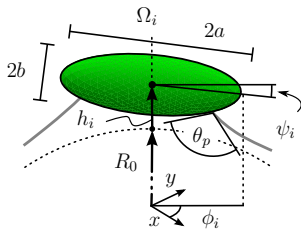
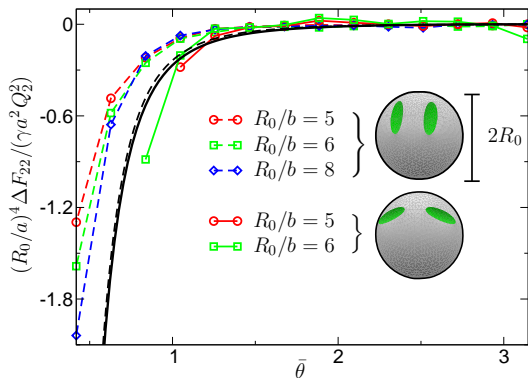


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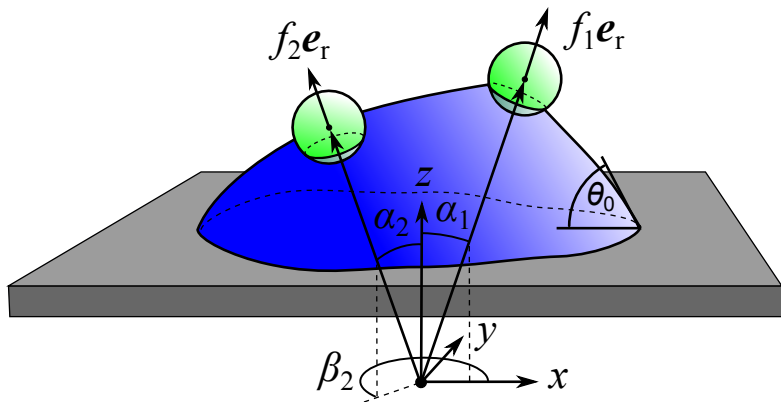
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Sessile drops

- free energy depends on the contact angle θ_0 and boundary conditions of either a free ($\sigma = A$) or a pinned ($\sigma = B$) contact line at the substrate



Sessile drops: free energy

- after subtracting self-energies $F_{i,self}$ one gets

$$\begin{aligned}\Delta F_\sigma^{(N)} &:= F_\sigma^{(N)}(\Omega_1, \dots, \Omega_N, \theta_0) - \sum_{i=1}^N F_{i,self} = \\ &= \sum_{i=1}^N \Delta F_\sigma^{(1)}(\theta_i, \theta_0) + \sum_{i < j} V_\sigma(\Omega_i, \Omega_j, \theta_0)\end{aligned}$$

- substrate potential $\Delta F_\sigma^{(1)}$ and pair-potential V_σ :

$$\Delta F_\sigma^{(1)} = -\frac{f_i^2}{2\gamma} [G_{\sigma,reg}(\Omega_i, \Omega_i) - G_{\sigma,reg}(0, 0)]$$

$$V_\sigma = -\frac{f_i f_j}{2\gamma} [G_\sigma(\Omega_i, \Omega_j) + G_\sigma(\Omega_j, \Omega_i)],$$

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Sessile drops: Green's functions

- for $\Omega \in \Omega_0$ Green's functions G_σ satisfy

$$-(\nabla_a^2 + 2)G_\sigma(\Omega, \Omega', \theta_0) = \delta(\Omega, \Omega') + \Delta_\sigma(\Omega, \Omega', \theta_0)$$

- functions $\Delta_\sigma(\Omega, \Omega', \theta_0)$ corresponding to μ and π_{CM} determined from the force balance and incompressibility condition $\int_{\Omega_0} d\Omega G_\sigma(\Omega, \Omega') = 0$
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$$\begin{aligned}(\sin \theta_0 \partial_\theta G_A(\Omega, \Omega') - \cos \theta_0 G_A(\Omega, \Omega'))|_{\Omega \in \partial\Omega_0} &= 0, \\ G_B(\Omega, \Omega')|_{\Omega \in \partial\Omega_0} &= 0.\end{aligned}$$

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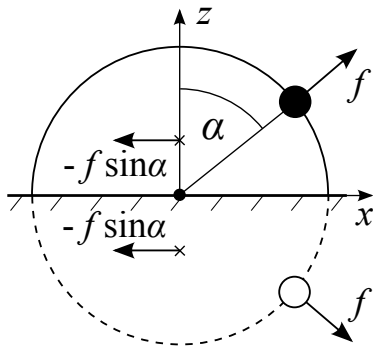
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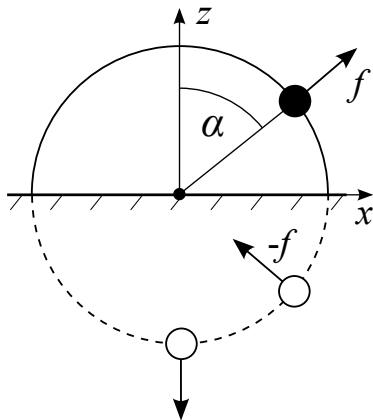
Sessile drops: special case $\theta_0 = \pi/2$

- f images

free c.l.

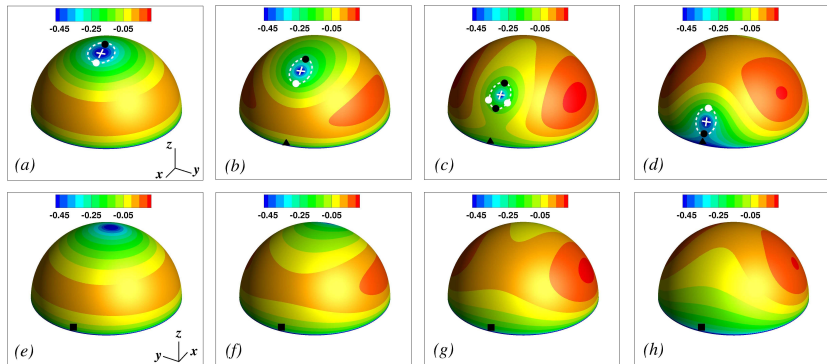


pinned c.l.



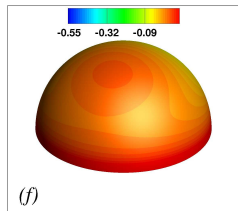
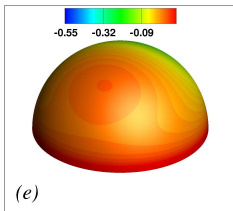
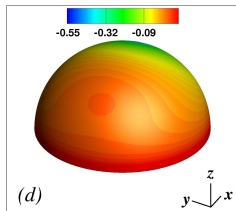
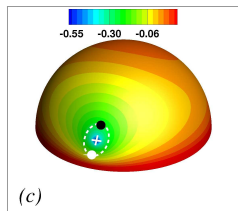
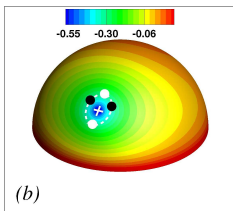
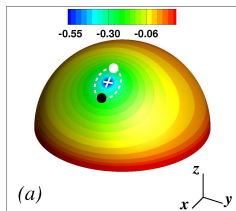
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- interactions between **monopoles** and **dipoles** on spherical interface are non-monotonic and much different than on a flat interface
- interactions between **spheroids** are quite similar
- importance of **curvature** only in case of external fields
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