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

Jan Guzowski

Instytut Chemii Fizycznej PAN, Warszawa

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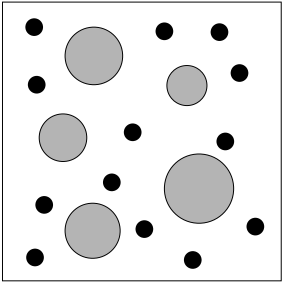
# Pickering Emulsions

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



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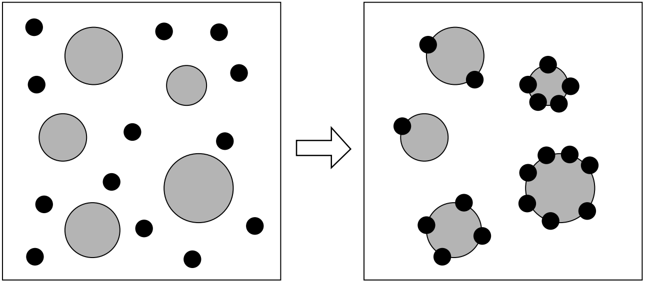

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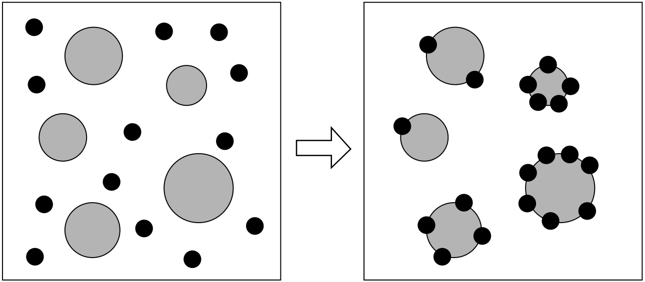

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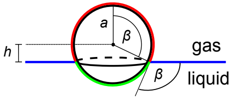
# Stability of a colloidal particle at the interface

- 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 $\cos\theta_p = (\gamma_{pg} - \gamma_{pl})/\gamma_{lg}$

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| 10nm | $10^3$ |
| 100nm | $10^5$ |
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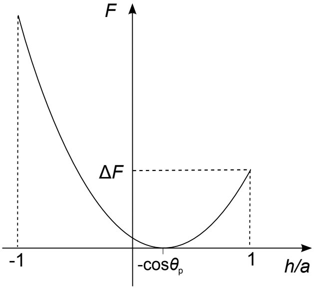

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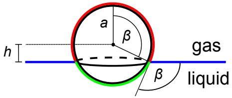


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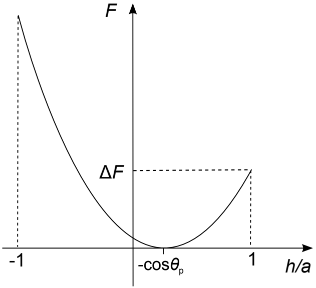

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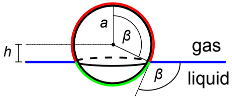


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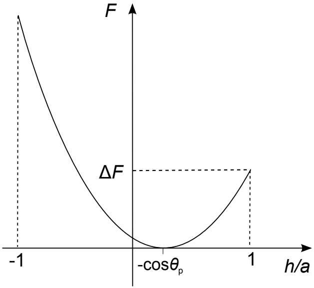
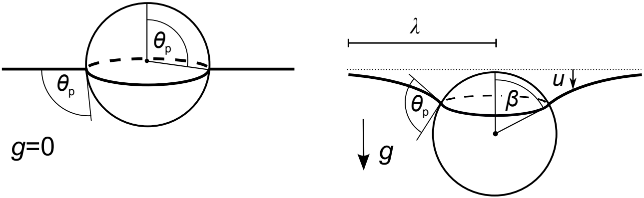


# Generic case: single particle at a flat interface

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



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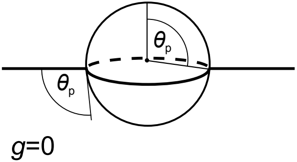


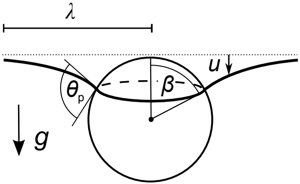

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- the capillary equation for $|\nabla_{\parallel} u| \ll 1$ (balance of capillary and hydrostatic pressures across the interface)

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

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

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

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- particle replaced by an effective pressure distribution $\Pi(\mathbf{x})$
- for $\lambda \to \infty$ Poisson equation $-\gamma \nabla_{||}^2 u = \Pi(\mathbf{x})$
- in terms of complex variables $u(\mathbf{x}) = \mathrm{Re} V(z)$ 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

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

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

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- in general $Q_{i,n} = Q_{i,n}(d)$ (feedback $u \to \Pi$), 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 $-\nabla_a^2 v - 2v = \pi(\Omega) + \mu$
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# 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 $v_{00} = 0 \Rightarrow \mu = \pi_{00}$
- $l = 1$: translations $v_{1m}$ undefined, assume fixed center of mass $v_{1m} = 0$
- free energy in terms of irreducible representation of rotation group

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

# Expansion in spherical harmonics

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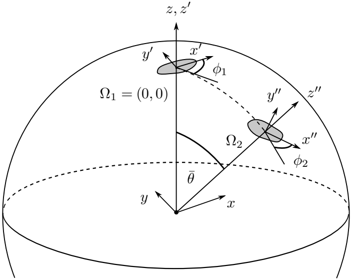


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- in the limit $a, a' \ll R_0$ one has $\Delta F = \sum_{n,n'=0}^{\infty} \Delta F_{nn'}$ with $n = |m|$ and

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- $Q_{i,n}$ are capillary multipoles on the locally flat interface, i.e., defined on the plane tangent to the unit sphere at $\Omega_i$
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# Numerical calculations

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

$$\mathcal{F}[\{\mathbf{r}(\Omega)\}, h_i, \psi_i; \bar{\theta}, \phi_i, f_i, T_i, \theta_{p,i}, a_i, V_l, \lambda_0] =$$

$$= \gamma S_{lg} + \sum_{i=1,2} (-\gamma \cos\theta_{p,i} S_{pl,i} - f_i h_i - \mathbf{T}_i \cdot \boldsymbol{\psi}_i) - \lambda_0 (V - V_l).$$

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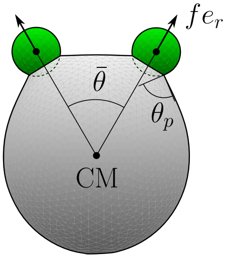
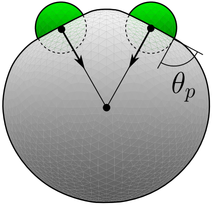
# Results: monopoles

- 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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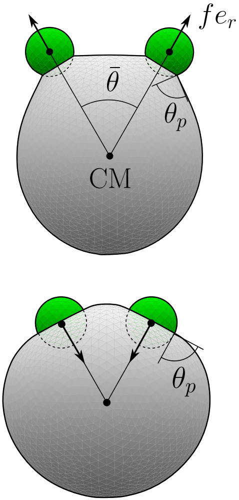


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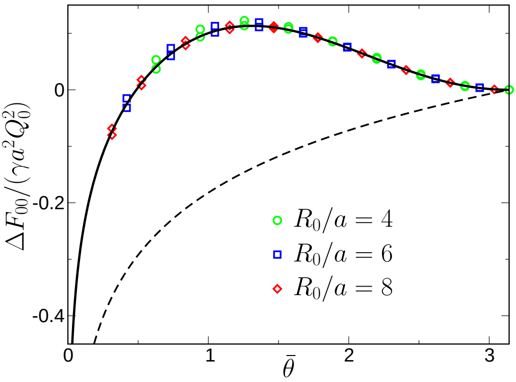

# Results: dipoles

- three metastable branches for three different orientational configurations

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

- 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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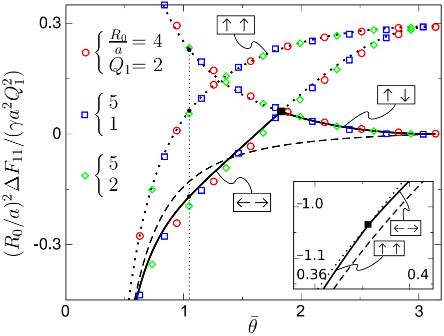
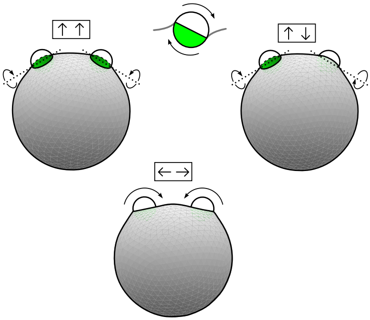
# Results: dipoles

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

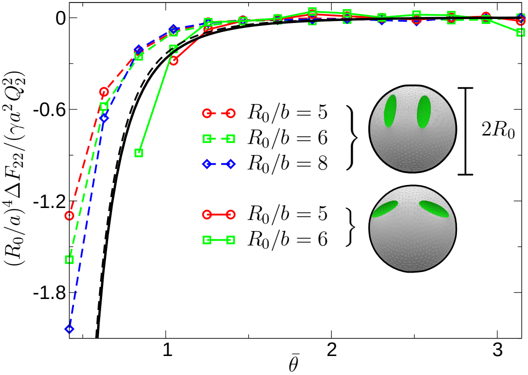


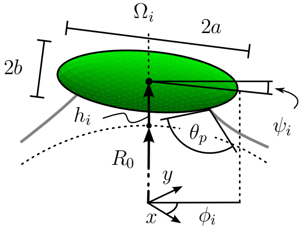



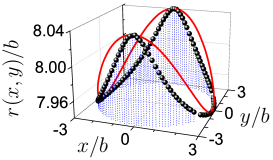
# Results: free spheroidal particles

- 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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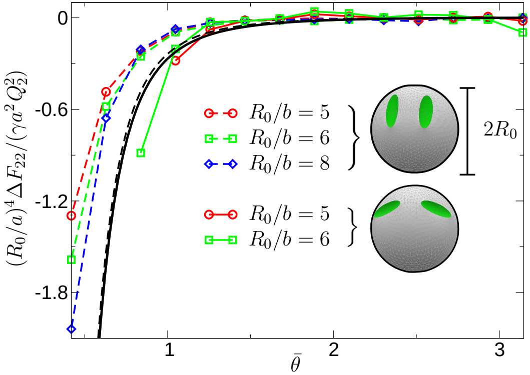
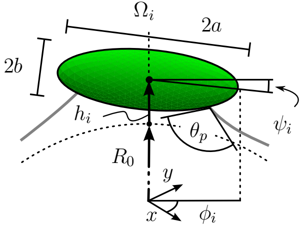
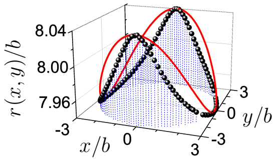
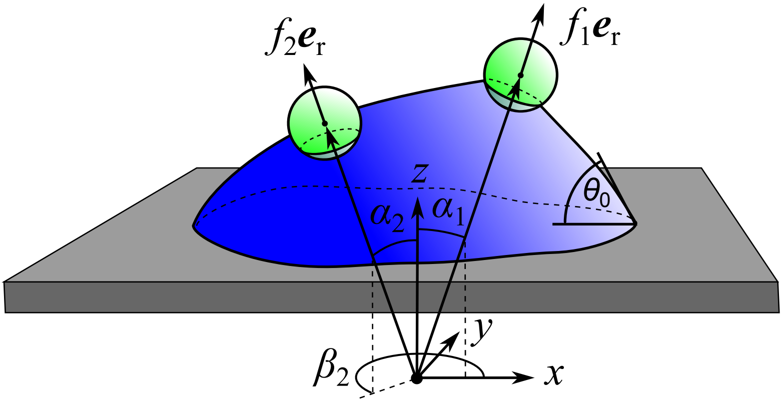


# Sessile drops

- free energy depends on the contact angle $\theta_0$ 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

$$\Delta F_\sigma^{(N)} := F_\sigma^{(N)}(\Omega_1, \ldots, \Omega_N, \theta_0) - \sum_{i=1}^{N} F_{i,self} =$$

$$= \sum_{i=1}^{N} \Delta F_\sigma^{(1)}(\theta_i, \theta_0) + \sum_{i<j} V_\sigma(\Omega_i, \Omega_j, \theta_0)$$

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

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

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# Sessile drops: Green's functions

- for $\Omega \in \Omega_0$ Green's functions $G_\sigma$ 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 $\mu$ and $\pi_{CM}$ determined from the force balance and incompressibility condition $\int_{\Omega_0} d\Omega \, G_\sigma(\Omega, \Omega') = 0$
- with boundary conditions:

$$\begin{aligned}(\sin\theta_0 \partial_\theta G_A(\Omega, \Omega') - \cos\theta_0 G_A(\Omega, \Omega'))|_{\Omega \in \partial\Omega_0} &= 0, \\ G_B(\Omega, \Omega')|_{\Omega \in \partial\Omega_0} &= 0.\end{aligned}$$

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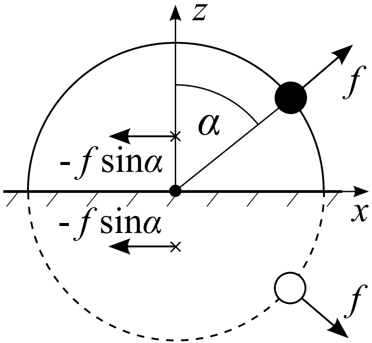
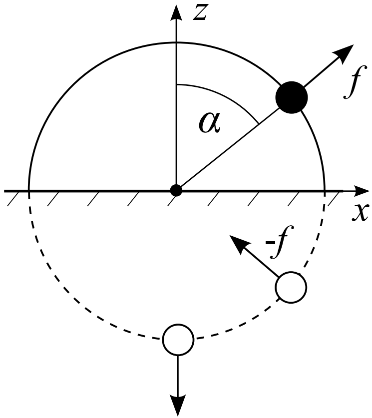
# Sessile drops: special case $\theta_0 = \pi/2$

- f images

free c.l.




pinned c.l.



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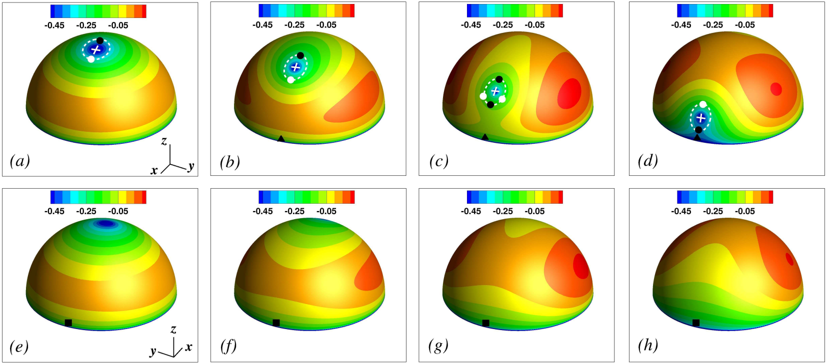
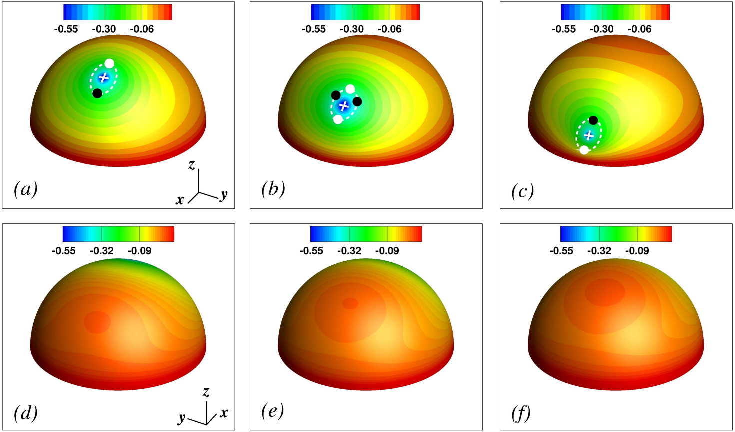


# Sessile drops: special case $\theta_0 = \pi/2$

- $\gamma \Delta F_B^{(2)}/(f_1 f_2) =$



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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
- the effects of boundary conditions on the substrate for monopoles are long-ranged and independent of $R_0$
- the effective confining potential depends qualitatively on the boundary conditions
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