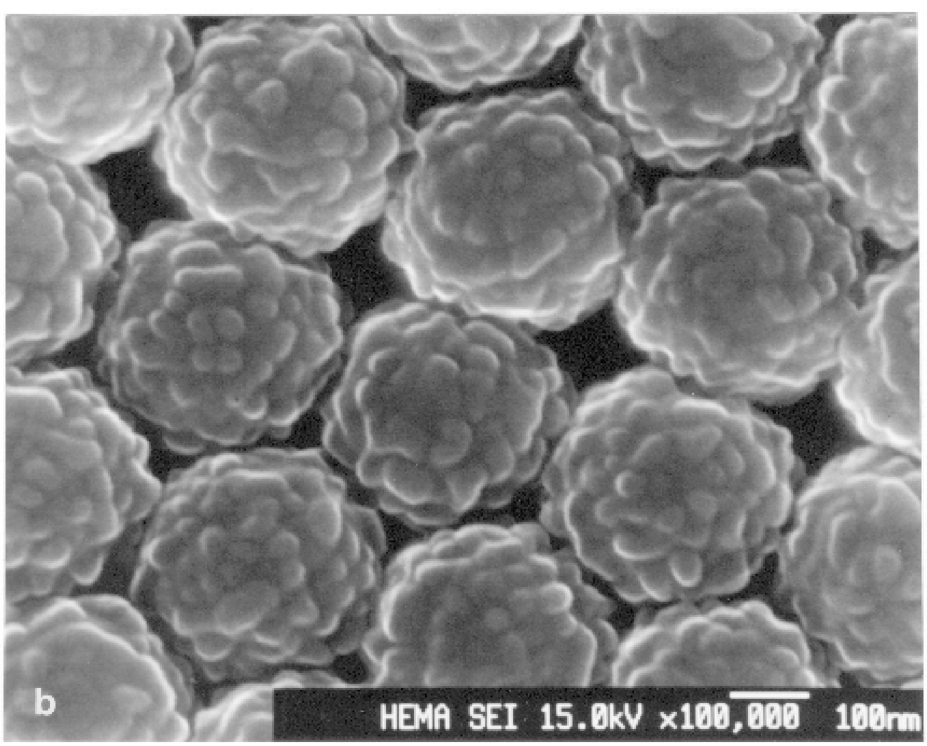
Capillary Interactions between Rough-Edged Particles, Captive at a Fluid Interface, and Rheology of Particulate Monolayers

Peter A. Kralchevsky, K. D. Danov and N. D. Denkov

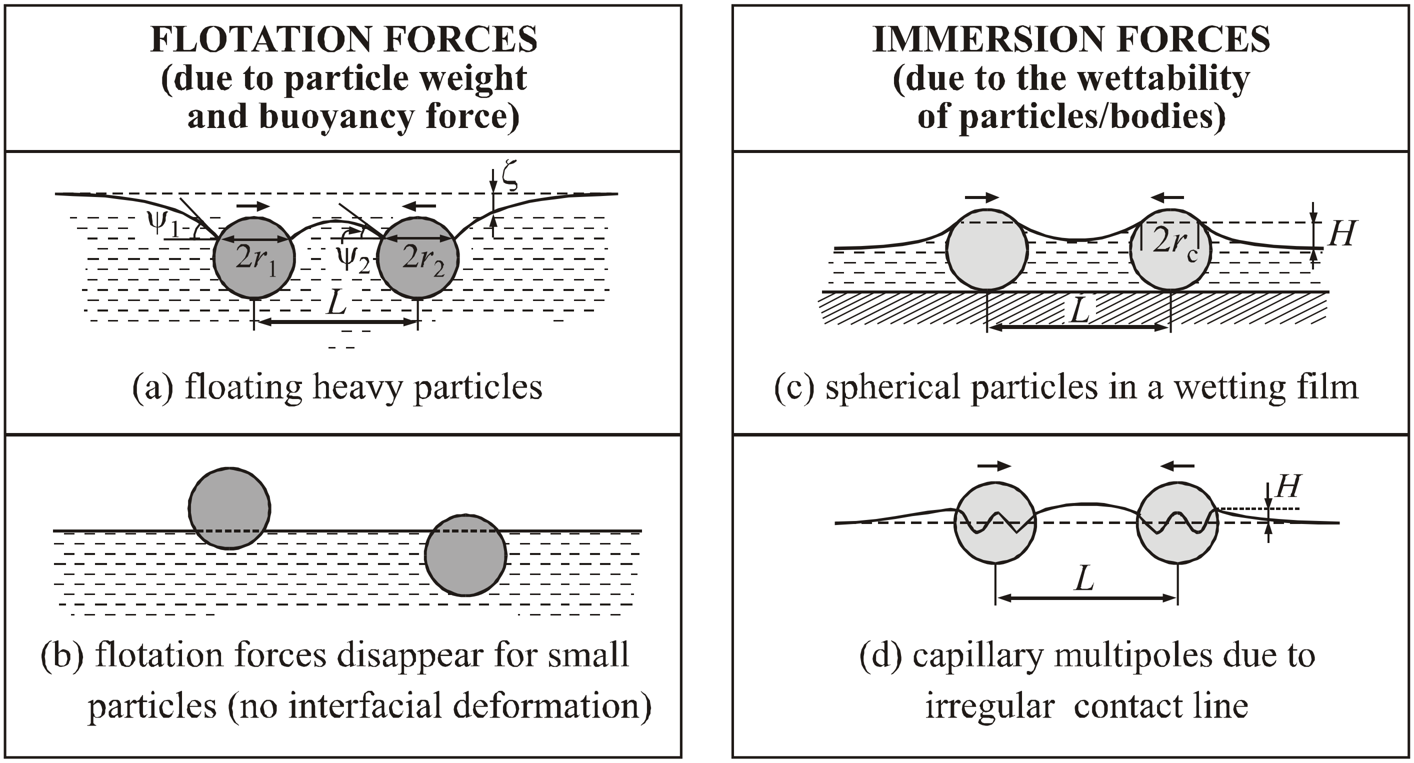
Laboratory of Chemical Physics & Engineering

Faculty of Chemistry, University of Sofia, BULGARIA



Rough-edged particles have undulated contact line when attached to a fluid interface.

Copolymer latex particles (PS/HEMA) produced by Cardoso et al. [1]



Meniscus around particles of <u>undulated</u> contact line:

$$\zeta(r,\varphi) = \sum_{m=0}^{\infty} \mathrm{K}_m(qr)\,(A_m \cos m\varphi + B_m \sin m\varphi)$$

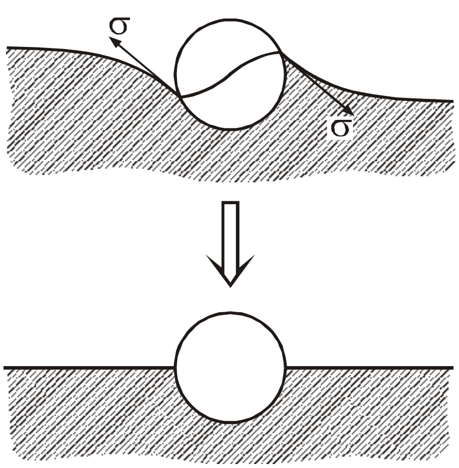
Analogy with electrostatics: ***m*** **= 0 – "capillary charges"**

m **= 1 – "capillary dipoles"**

m **= 2 – "capillary quadrupoles"**

m **= 3 – "capillary hexapoles"**

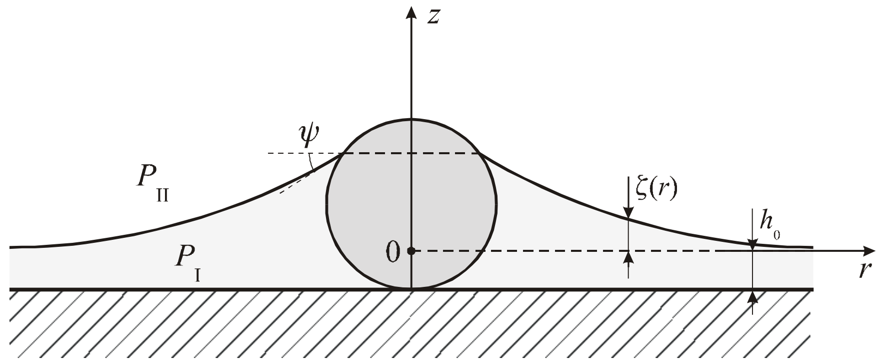
..



The capillary force spontaneously rotates a floating particle to annihilate its dipole moment (*m* = 1)

⇒ The leading multipole orders are the charges and quadrupoles.

"Capillary Charges"

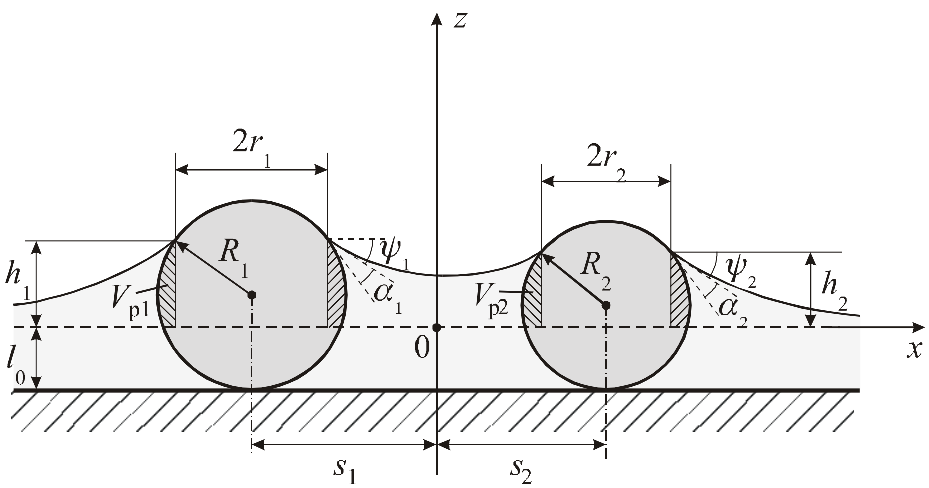


Equation for the meniscus shape (Linearized Laplace equation):

$$\nabla_{\mathrm{II}}^2 \zeta = q^2 \zeta, \qquad q^2 \equiv \frac{\Delta\rho g}{\sigma} + \frac{-\Pi'}{\sigma}$$

Helmholtz type equation (possesses solutions finite at infinity):

$$\zeta_1(r) = Q_1 \mathrm{K}_0(qr), \qquad\qquad Q_1 = r_1 \sin\psi_1$$



Superposition Approximation

Interaction energy:

$$\Delta W = -2\pi\sigma Q_1 Q_2 \mathrm{K}_0(qL)$$

Interaction force:

$$F = -2\pi\sigma Q_1 Q_2\, q\, \mathrm{K}_1(qL)$$

$(L = s_1 + s_2)$

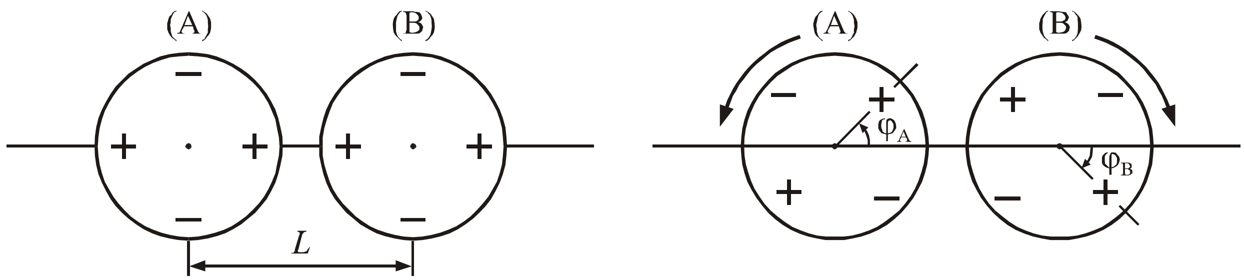
$$F = -2\pi\sigma \frac{Q_1 Q_2}{L} \qquad \text{for} \quad r_k << L << q^{-1}$$

(2D analogue of the Coulomb law in electrostatics)

$Q_k = r_k \sin\psi_k \qquad (k = 1, 2)$ – **"Capillary Charge"**

characterizes the interfacial deformation caused by the respective particle [2]

Interaction between "Capillary Quadrupoles"



(a) (b)

The signs "+" and "–" symbolize convex and concave local deviations of the contact line from planarity. (a) Initial state. (b) After rotation of the respective particles at angles φ_A and $\varphi_B = -\varphi_A$.

Asymptotic formula, Stamou et al. [3]:

$$\Delta W(L) = -12\pi\sigma H^2 \cos(2\varphi_A + 2\varphi_B)\frac{r_c^4}{L^4}, \qquad (m = 2;\ L >> 2r_c)$$

***H* – amplitude of the undulation of the contact line**

r_c –average contact line radius

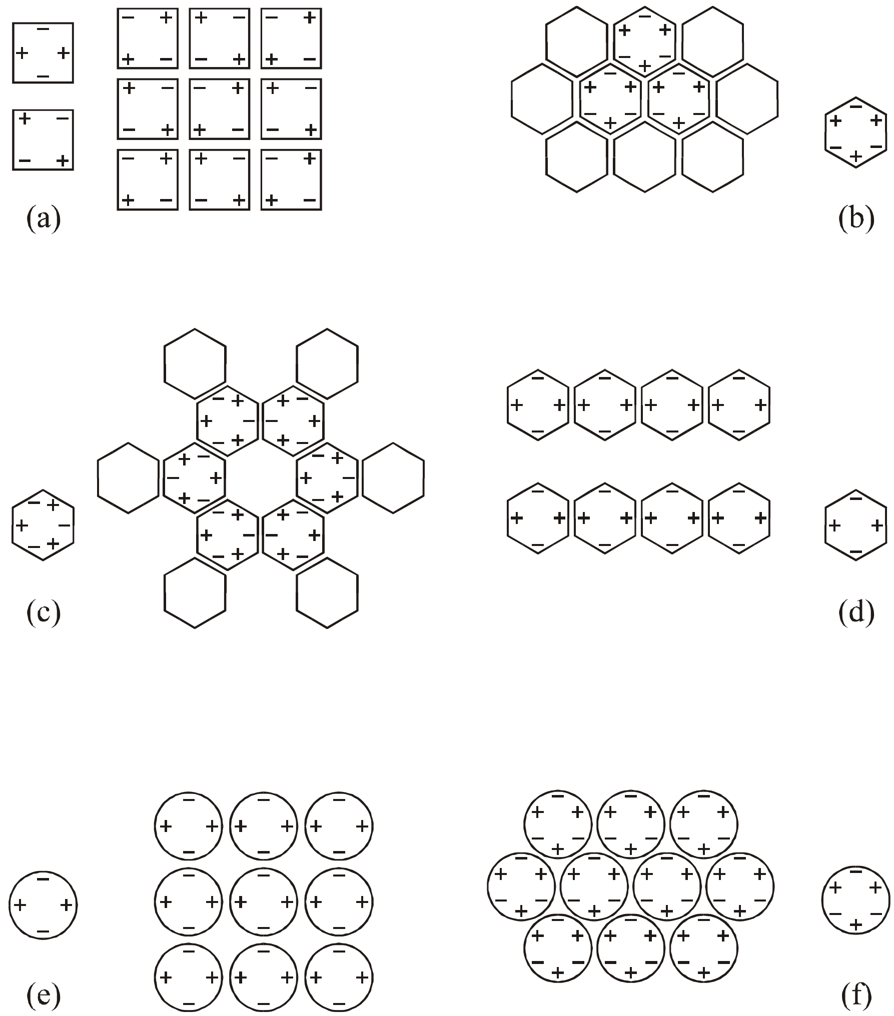
Particles in contact ($L/r_c = 2$); optimal orientation, $\cos(2\varphi_A + 2\varphi_B) = 1$:

$$\Delta W = -(3/4)\pi\sigma H^2$$

For σ = 35 mN/m: ΔW becomes greater than the thermal energy *kT* for undulation amplitude $H > 2.2$ Å.

⇒ Even a minimal roughness of the contact line could be sufficient to give rise to a significant capillary attraction, which may produce 2D aggregation of the colloidal particles

Structures from Capillary Multipoles



2D arrays formed by capillary quadrupoles (*m* = 2) and hexapoles (*m* = 3)

Signs "+" and "–" denote positive and negative "capillary charges": convex and concave local deviations of the meniscus shape from planarity at the contact line.

(a) Quadrupoles of square shape form tetragonal close-packed array.

(b) Hexapoles with hexagonal shape form a close-packed array if the charges are located on the corners;

(c) Porous (opened) hexagonal array is formed when the charges are located on the hexagon sides.

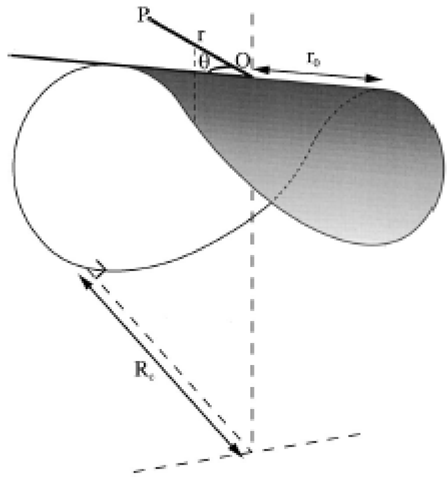
(d) Quadrupoles having the shape of hexagons form linear aggregates.

(e) Quadrupoles having circular shape will form square array;

(f) Circular hexapoles can form close-packed hexagonal array.

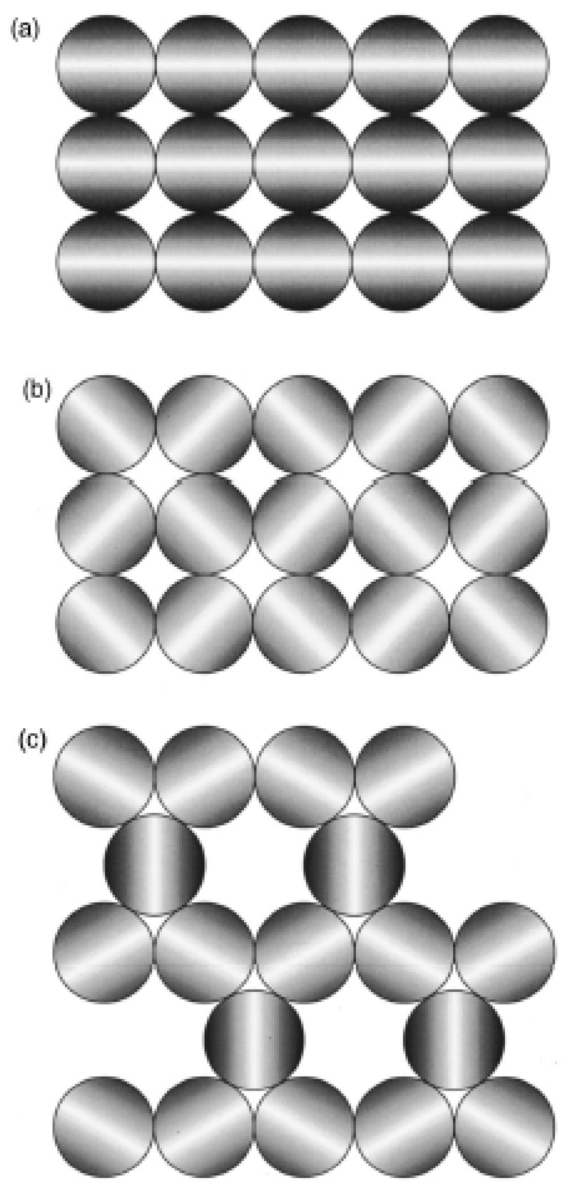
see refs. [4] and [5]

Example for Quadrupoles: Curved Disks



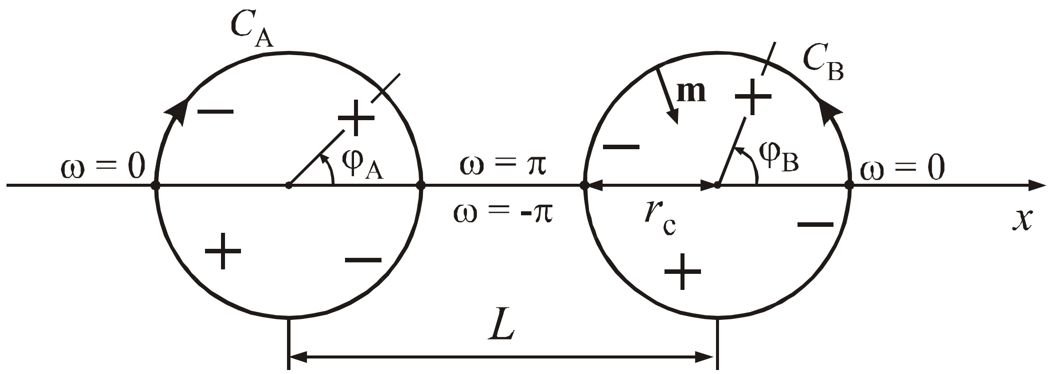
Experiments of Brown et al. [6]: photolithography-fabricated curved disks, having one hydrophilic and one hydrophobic side.

Structures formed from curved disks



Exact Theory of Quadrupole-Quadrupole Capillary Force

(P. Kralchevsky, N. Denkov, K. Danov, ***Langmuir*** **17** (2001) 7694–7705)



Interaction energy:

$$W(L) = \pi\sigma\left[(H_A^2 + H_B^2)S(L) - H_A H_B G(L)\cos(2\varphi_A + 2\varphi_B)\right]$$

where

$$S(L) = \tfrac{1}{2}(1-\varepsilon)^2 \sum_{n=1}^{\infty} n\,[n-1-(n+1)\varepsilon]^2\,\varepsilon^{n-2}\left(1 + \frac{2\varepsilon^{2n}}{1-\varepsilon^{2n}}\right)$$

$$G(L) = (1-\varepsilon)^2 \sum_{n=1}^{\infty} n\,[n-1-(n+1)\varepsilon]^2\,\frac{2\varepsilon^{2n-2}}{1-\varepsilon^{2n}}$$

$$\varepsilon = \frac{1}{[x+(x^2-1)^{1/2}]^2}, \qquad x = \frac{L}{2r_c}$$

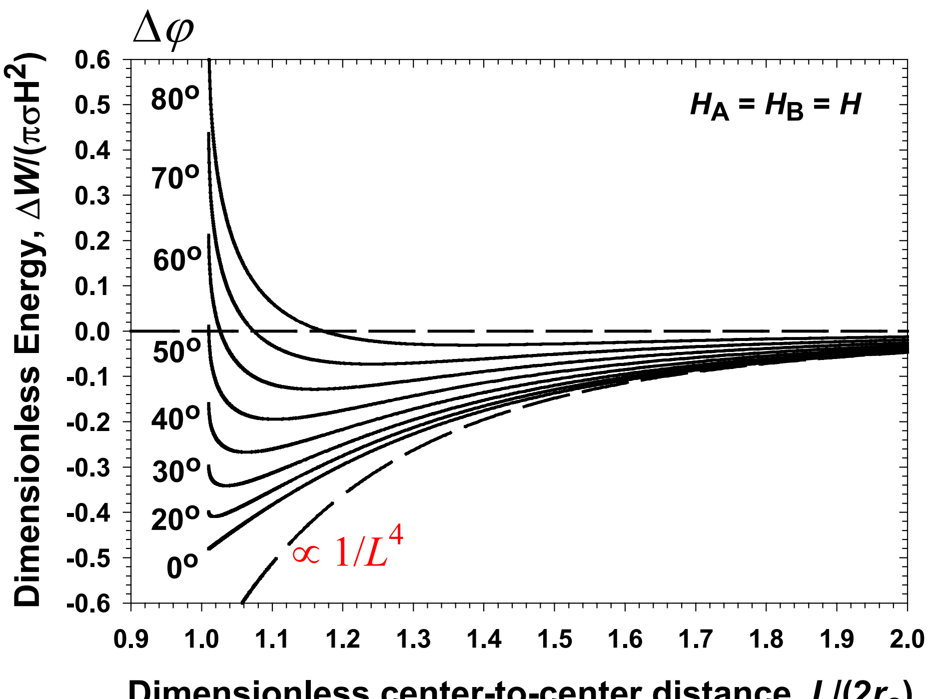
Capillary Charges | **Capillary Quadrupoles**

$F \propto 1/L$ | $F \propto 1/L^5$

⇒ **the quadrupole–quadupole interaction has a shorter range of action;**

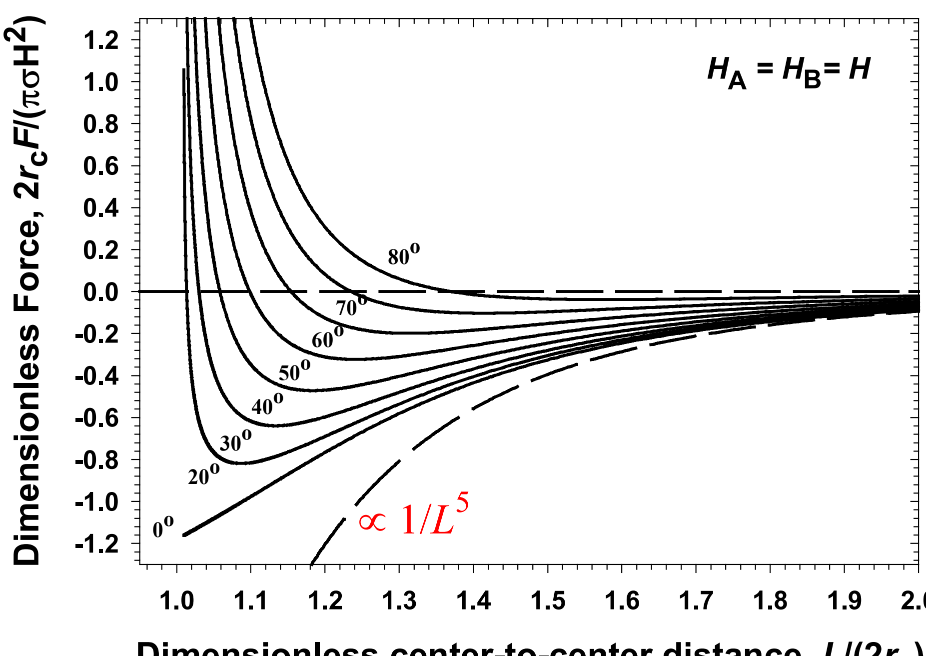
⇒ **it may affect the rheology of particle monolayers in a Langmuir trough.**

Interaction Energy and Force



(a)

$$\Delta\varphi = 2\varphi_A + 2\varphi_B$$



(b)

The curves correspond to different values of the phase angle $\Delta\varphi$;

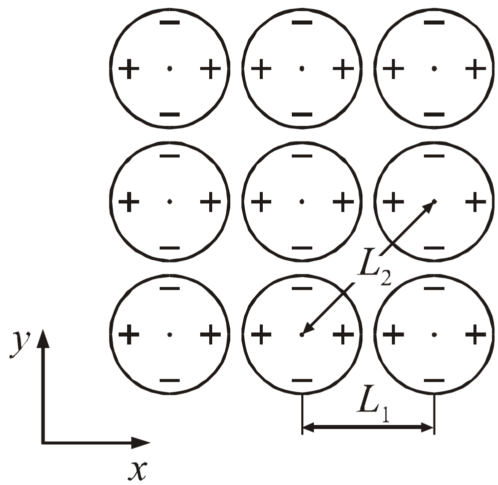
Two similar particles: $H_A = H_B = H$; for $\Delta\varphi > 13°$ – minimum;

The dashed curves –long-distance asymptotic expressions, $\Delta\varphi = 0$.

Rheology of Particulate Monolayers

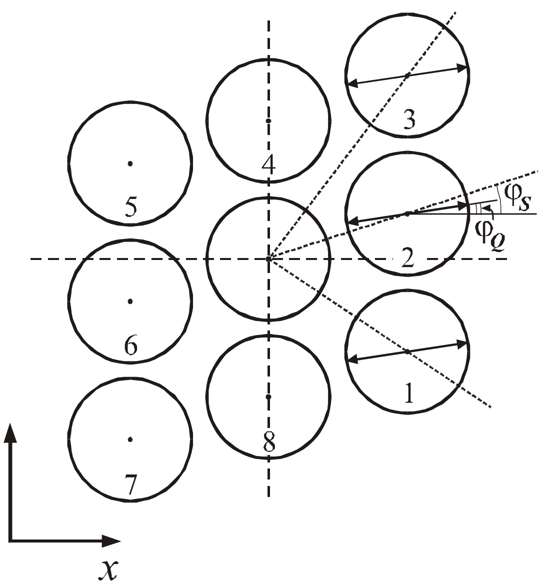
(the monolayer response to deformations)

(a) Dilatation:



L_1 and L_2 are the distances between first and second neighbors

(b) Shear:
(along the y-axis)



The angles φ_S and φ_Q characterize the shear, and particle rotation

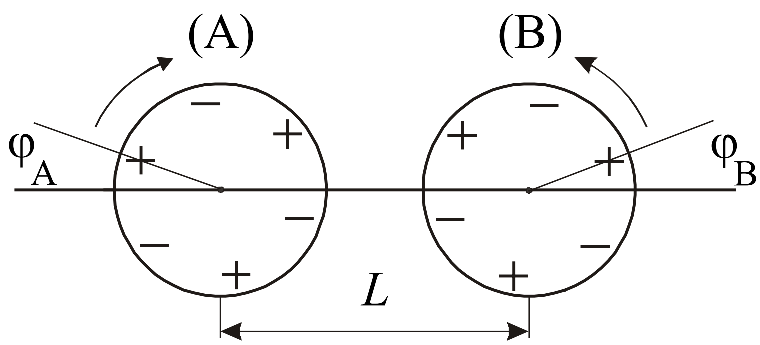
Yield Stress: $$\tau^* = -0.137\,\sigma\left(\frac{H}{r_c}\right)^2$$ **(small effect)**

Shear Elasticity: $$E_S = 23\sigma\left(\frac{H}{r_c}\right)^2 \qquad (L_1 = 2r_c)$$ **(considerable effect)**

$(E_S/\tau^* \approx 169)$

With $H/r_c = 0.1$ and $\sigma = 70$ mN/m one estimates $E_S \approx 16.1$ mN/m [7]

Capillary Multipoles of Arbitrary Order: Interactions



General Expression for the Interaction Energy:

$$\frac{W(L)}{\pi\sigma} = H_A^2 S_A(L) + H_B^2 S_B(L) - H_A H_B G(L)\cos(m_B\varphi_B - m_A\varphi_A)$$

m_A, m_B – **multipole orders;**

H_A, H_B – **amplitudes of the contact-line undulations;**

φ_A, φ_B – **angles of rotation with respect to the equilibrium state;**

$$S_Y(L) = \sum_{n=1}^{\infty} \frac{n}{2} \frac{\cosh[n(\tau_A+\tau_B)]}{\sinh[n(\tau_A+\tau_B)]} A^2(n, m_Y, \tau_Y), \qquad Y = A, B.$$

$$G(L) \equiv \sum_{n=1}^{\infty} \frac{n}{\sinh[n(\tau_A+\tau_B)]} A(n, m_A, \tau_A) A(n, m_B, \tau_B)$$

$A(n,m,\tau)$ – **a known function**

Asymptotic Multipole Interactions for $L >> r_A, r_B$

Type of Interaction	(m_A, m_B)	Interaction Energy $\Delta W(L)$ for $r_A, r_B << L << q^{-1}$
charge – quadrupole	(0, 2)	$-\frac{\pi}{2}\sigma Q_A H_B \cos[2(\varphi_B - \pi)]\left(\frac{r_B}{L}\right)^2$
charge – multipole	$(0, m_B)$	$-\frac{\pi}{2}\sigma Q_A H_B \cos[m_B(\varphi_B - \pi)]\left(\frac{r_B}{L}\right)^{m_B}$
quadrupole – quadrupole	(2, 2)	$-12\pi\sigma H_A H_B \cos[2(\varphi_A - \varphi_B)]\frac{(r_A r_B)^2}{L^4}$
quadrupole – hexapole	(2, 3)	$24\pi\sigma H_A H_B \cos(2\varphi_A - 3\varphi_B)\frac{r_A^2 r_B^3}{L^5}$
quadrupole – octupole	(2, 4)	$-40\pi\sigma H_A H_B \cos(2\varphi_A - 4\varphi_B)\frac{r_A^2 r_B^4}{L^6}$
hexapole – hexapole	(3, 3)	$-60\pi\sigma H_A H_B \cos(3\varphi_A - 3\varphi_B)\frac{r_A^3 r_B^3}{L^6}$
hexapole – octupole	(3, 4)	$120\pi\sigma H_A H_B \cos(3\varphi_A - 4\varphi_B)\frac{r_A^3 r_B^4}{L^7}$
multipole – multipole	(m_A, m_B)	$-G_s \pi\sigma H_A H_B \cos(m_A\varphi_A - m_B\varphi_B)\frac{r_A^{m_A} r_B^{m_B}}{L^{(m_A+m_B)}}$

$$G_s = 2(-1)^{(m_A + m_B)} \sum_{n=1}^{\min(m_A, m_B)} \frac{m_A! m_B!}{(m_A - n)!(m_B - n)! n!(n-1)!}$$

SUMMARY AND CONCLUSIONS

1. **<u>Particles with undulated contact line</u> can be theoretically described as "capillary multipoles".**
2. **The angular dependence of the force between "quadrupoles" leads to a considerable <u>shear elasticity</u> of particle monolayers.**
3. **If capillary interaction is present, as a rule, its <u>energy is much greater than *kT*</u>, and causes particle aggregation and ordering.**

References

[1] A.H. Cardoso, C.A.P. Leite, F. Galembeck, "*Latex particle self-assembly and particle microchemical symmetry: PS/HEMA latex particles are intrinsic dipoles*," Langmuir 15 (1999) 4447.

[2] P.A. Kralchevsky, K. Nagayama, "*Particles at Fluid Interfaces and Membranes*", Elsevier, Amsterdam, 2001 (book: 14 chapters, 654 pages).

[3] D. Stamou, C. Duschl, D. Johannsmann, "*Long-range attraction between colloidal spheres at the air-water interface: The consequence of an irregular meniscus.*" Phys. Rev. E, 62 (2000) 5263-5272.

[4] N. Bowden, I.S. Choi, B.A. Grzybowski, G.M. Whitesides, "*Mesoscale self-assembly of hexagonal plates using lateral capillary forces: Synthesis using the capillary bond.*" J. Am. Chem. Soc. 121 (1999) 5373-5391.

[5] P.A. Kralchevsky, N.D. Denkov, "*Capillary forces and structuring in layers of colloid particles*", Current Opinion in Colloid & Interface Sci. 6 (2001) 383-401.

[6] A.B.D. Brown, C.G. Smith, A.R. Rennie, "*Fabricating colloidal particles with photolithography and their interactions at an air-water interface*." Phys. Rev. E, 62 (2000) 951-960.

[7] P. A. Kralchevsky, N. D. Denkov, and K. D. Danov, *"Particles with an undulated contact line at a fluid interface: Interaction between capillary quadrupoles and rheology of particulate monolayers"*, Langmuir 17 (2001) 7694–7705.