CONEX Program

COOPERATION AND NETWORKING FOR EXCELLENCE

Project Title:

Emulsions with Nanoparticles for New Materials

Short Project Title: EMMA

Partners:

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Nano-structured materials – "hot topic" in the materials science:

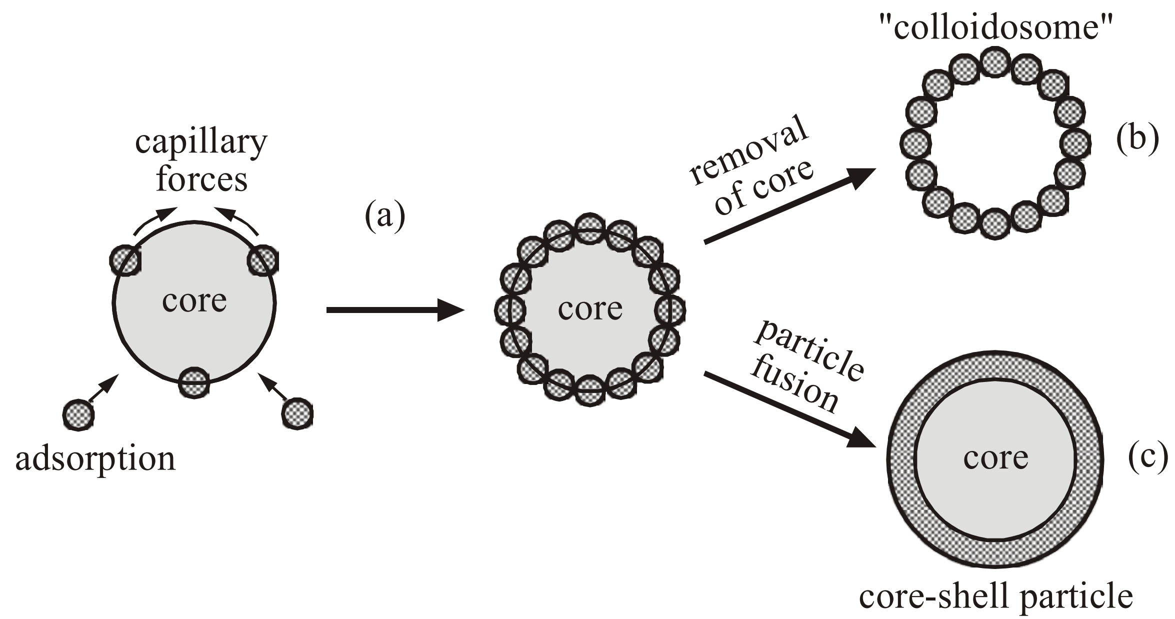
- **nanostructured surfaces for photoelectrochemical and photocathalytic processes;**
- **paint coatings of new optical properties;**
- **structured nanoporous materials using colloid crystal templates;**
- **preparation of core-shell colloid particles of various structures and compositions;**
- **micro-capsules for encapsulation of drugs, enzymes, minerals, dyes, phase-change materials;**
- **micro-reaction cages.**

The main purpose of the project:

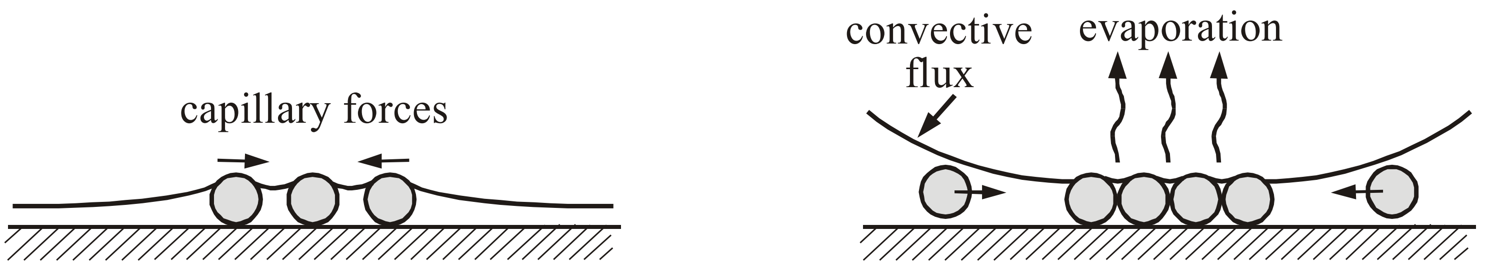
Use of emulsions stabilized by solid particles

for fabrication of nano-composites (colloidosomes, microcapsules, core-shell and composite particles), nano-structured surfaces and porous layers

by using emulsion droplets as precursors and/or templates



(a) Particle assembly on emulsion drops to produce (b) “colloidosome” or (c) “core-shell” particles



(d) Nucleus formation
by capillary forces

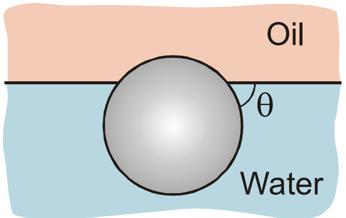
(e) 2D crystal growth due to
evaporation driven convective flux

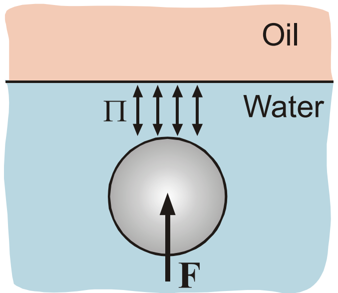
Formation of particulate layers from colloid particles (including colloidosomes and core-shell particles) by the method of convective self-assembly.

Formation of Pickering Emulsions (Emulsions Stabilized by Solid Particles)

⇒ **The solid particles form a shell protecting the emulsion drops against coalescence;**

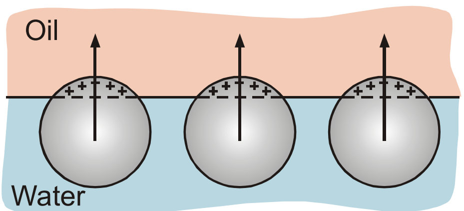
⇒ **The adsorption energy of the particles is very high, but they could encounter a barrier to adsorption;**

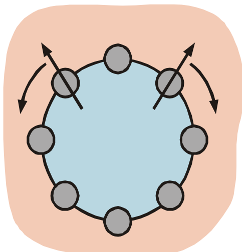


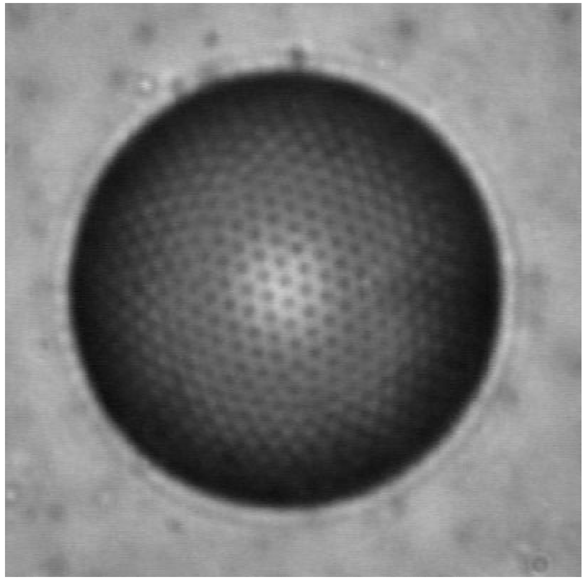


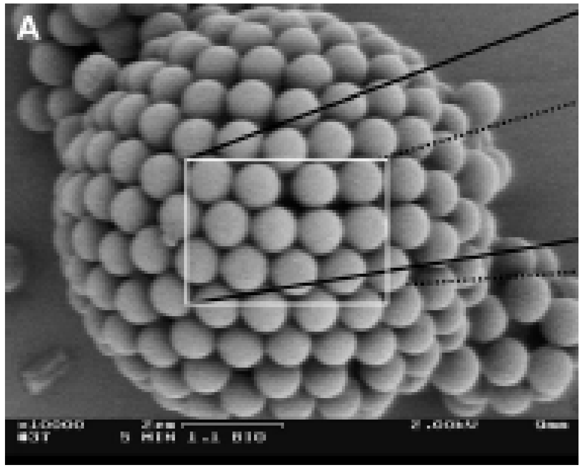
$$W_{ads} = \pi R_P^2 \sigma_{OW} \left(1 - \cos\theta\right)^2 >> kT$$

⇒ **A balance of electrostatic repulsion and capillary attraction lead to particle packing and ordering.**









Kinds of Capillary Forces between Particles:

Lateral Capillary Forces:

$$F = -2\pi\sigma Q_1 Q_2\, q\, K_1(qL)$$

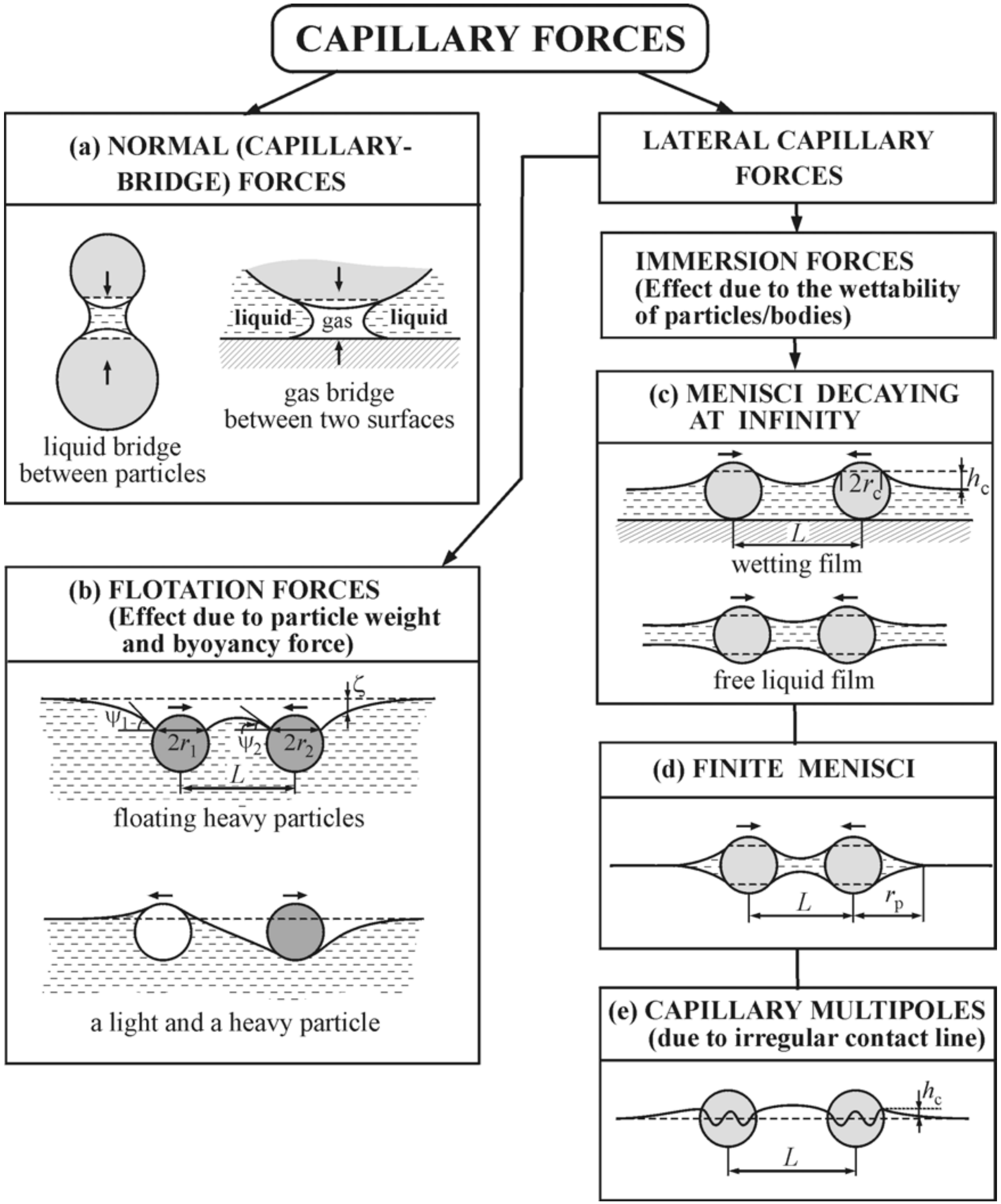
$$F = -2\pi\sigma \frac{Q_1 Q_2}{L} \qquad \text{for} \quad r_k << L << q^{-1}$$

(2D analogue of the Coulomb law in electrostatics)

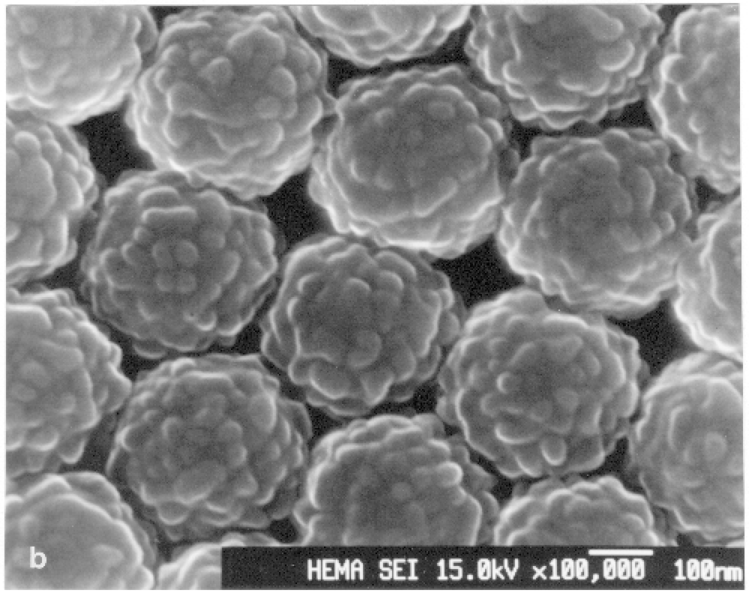
$$Q_k = r_k \sin\psi_k = \frac{F_N^{(k)}}{2\pi\sigma} \qquad (k = 1, 2)$$

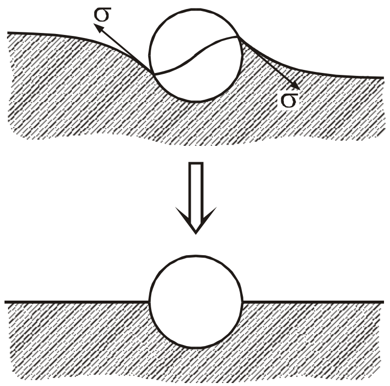
– **"Capillary Charge"**

(characterises the interfacial deformation caused by the respective particle)



New Aspects of Capillary Forces: (1) Interaction between Capillary Multipoles





(the particles in Pickering emulsions are often rough-edged)

Meniscus around particles of undulated 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"

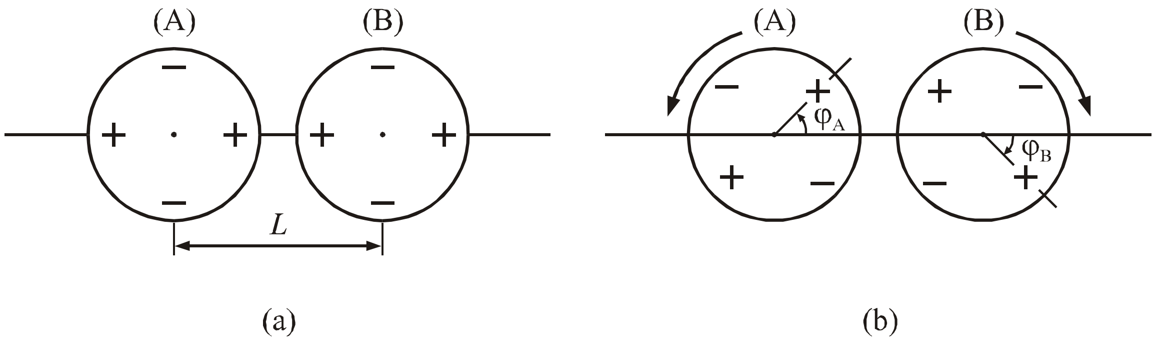
m = 3 – "capillary hexapoles"

...

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

⇒ The leading multipole orders are the charges and quadrupoles.

Interaction between "Capillary Quadrupoles"



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 $\varphi_B = -\varphi_A$.

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

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

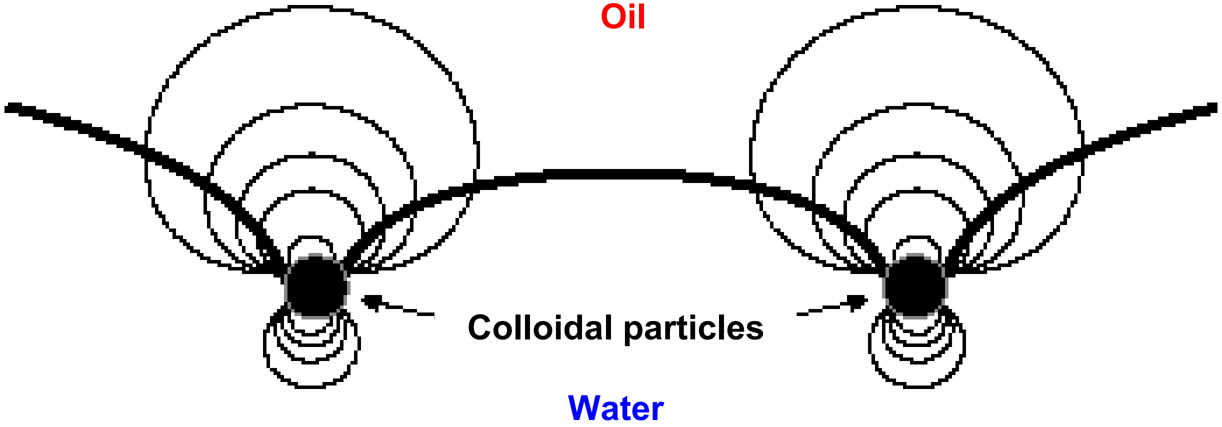
$$\Delta W = -(3/4)\pi\sigma H^2$$

For $\sigma = 35$ 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.

New Task: Derive general expressions for all types of capillary multipoles; rheology of particle monolayers

<u>New Aspects</u>: (2) <u>Electric-Field Induced Capillary Forces</u>



The electric force pushes each particle toward the water phase.

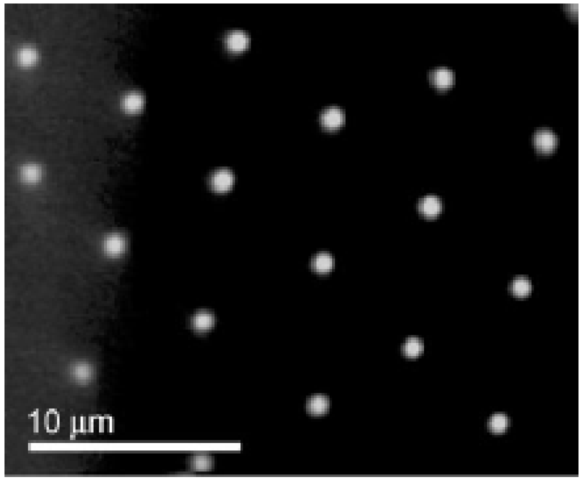
The overlap of the interfacial distortions around the two particles leads to a strong lateral capillary attraction.

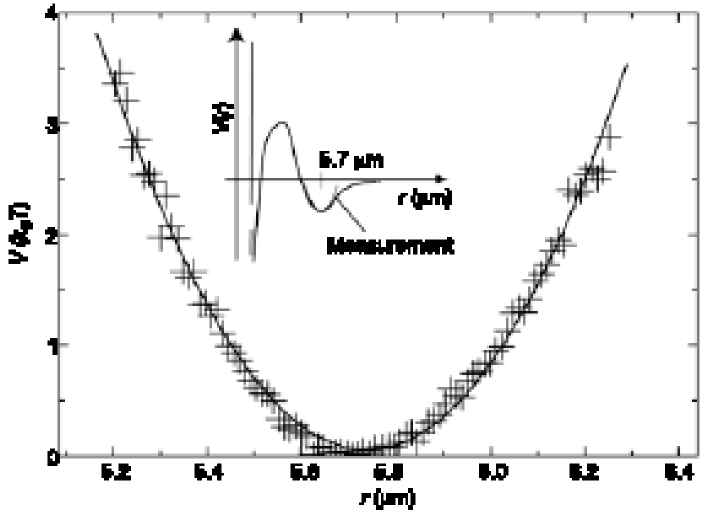
D. Weitz et al. Nature (2002): <u>A rather universal effect</u>, appears with particles from nm to mm size!

<u>New Task</u>: Develop a rigorous theory of:

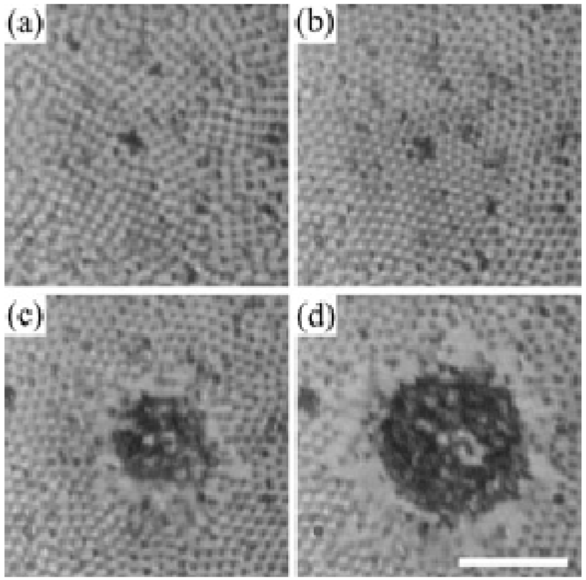
(1) electro-dipping force;

(2) lateral capillary and electric force





New Aspects: (3) Particles at Meniscus of Non-uniform Curvature

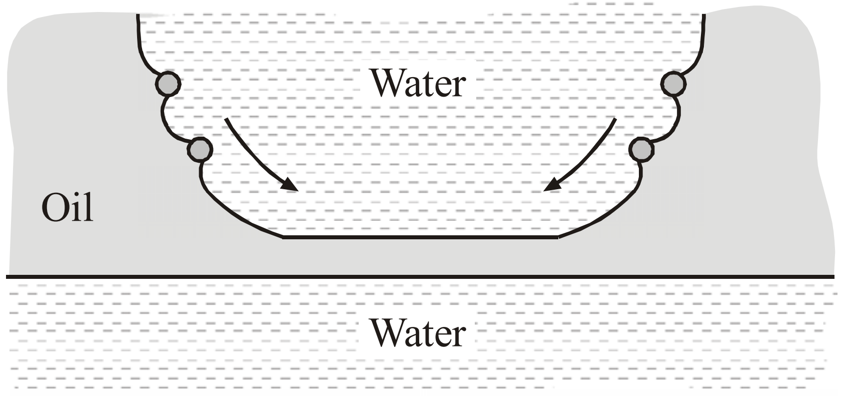


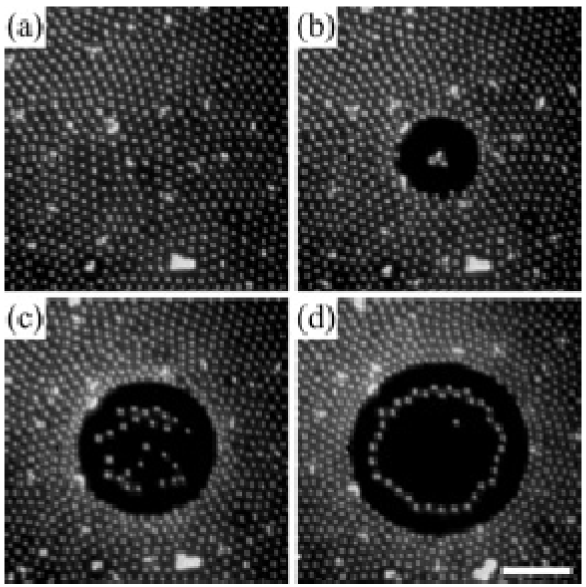
Water

in

Oil

(Fuller et al.)

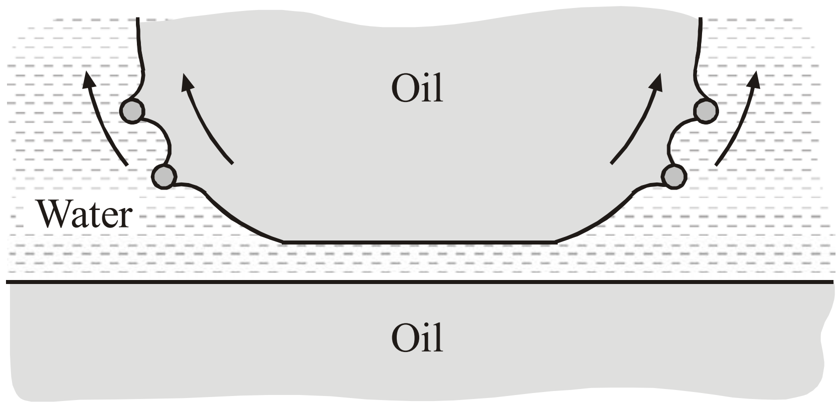




Oil

in

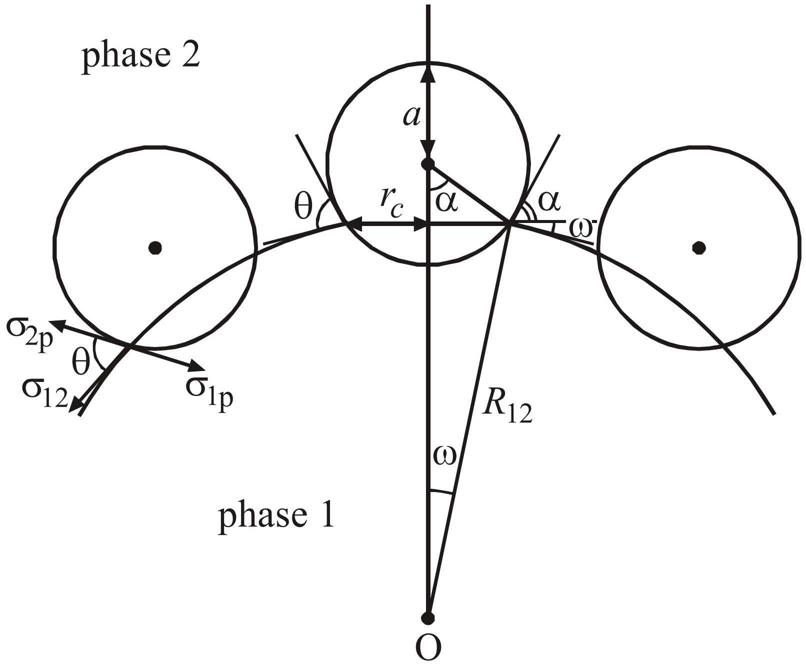
Water



Possible explanation: The particles can be (1) attracted or (2) repelled from the flat zone. Electro-dipping force operative.

Task: Investigate this effect

Thermodynamic Aspects of Production of Pickering Emulsions



Interfacial Work of Emulsification:

$$W = \sigma_{12}A_{12} + \sigma_{1p}A_{1p} + \sigma_{2p}A_{2p} + N_b\sigma_{2p}4\pi a^2$$

Direct Emulsion: $(\varepsilon = a/R_{12})$

$$W_d = \frac{3\sigma_{12}V_1}{a}\varepsilon\{(1-\varphi_a b) + \varepsilon\varphi_a[f(\theta)(1-\varphi_a b) - 2b\cos\theta]\}$$

Reverse Emulsion:

$$W_r = \frac{3\sigma_{12}V_2}{a}\varepsilon\{(1-\varphi_a b) + \varepsilon\varphi_a[g(\theta)(1-\varphi_a b) + 2b\cos\theta]\}$$

$\Delta W = W_d - W_r$, **provides an Emulsification Criterion (which emulsion will form upon agitation):**

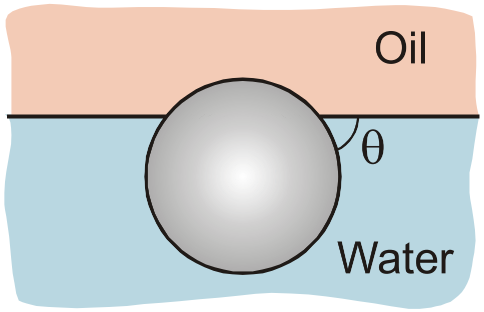
$\Delta W < 0 \quad \Rightarrow$ **the direct emulsion is formed;**

$\Delta W > 0 \quad \Rightarrow$ **the reverse emulsion is formed.**

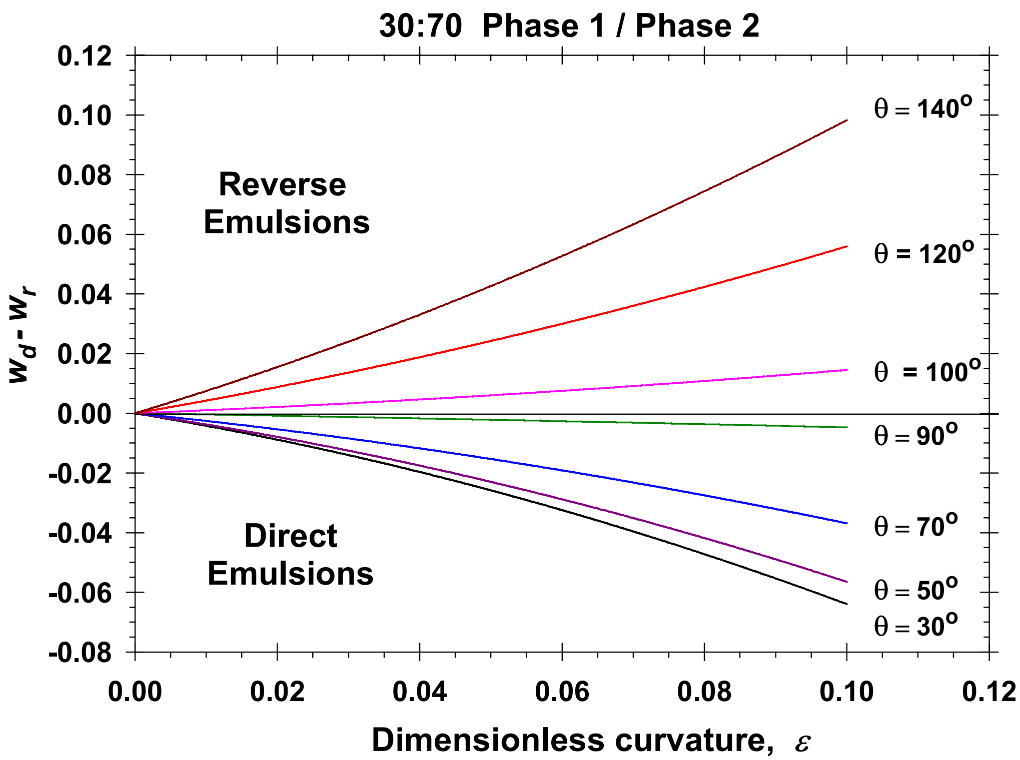
Calculated Work of Emulsification:

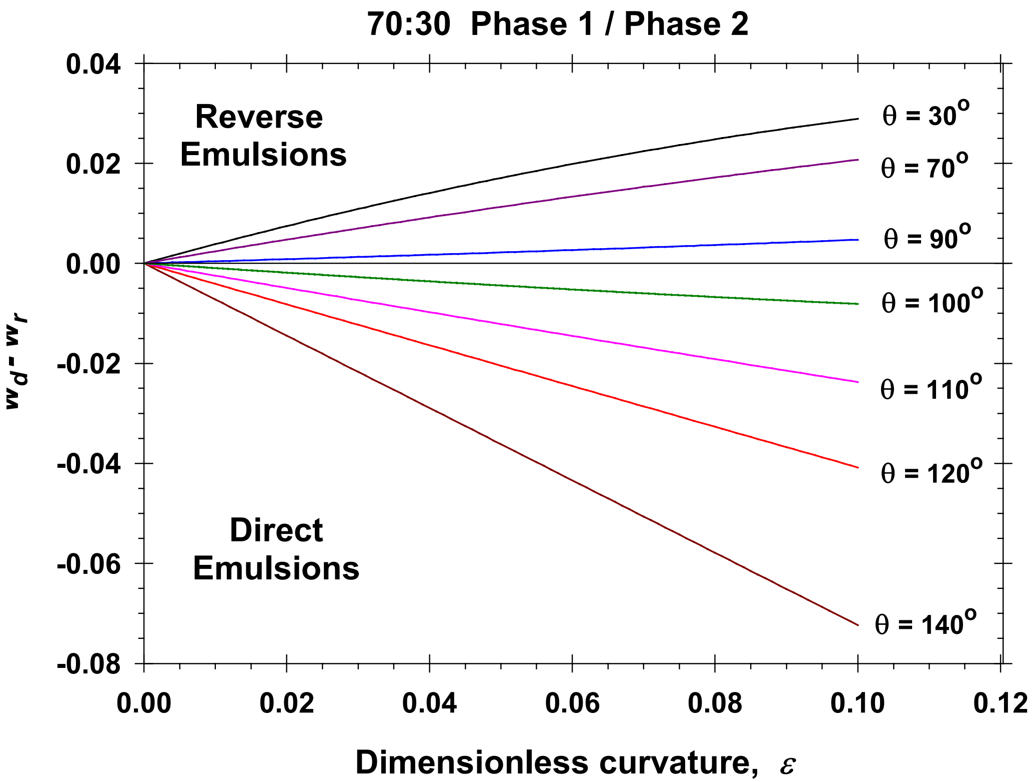
$W_d - W_r < 0 \;\Rightarrow$ **the direct emulsion is formed;**

$W_d - W_r > 0 \;\Rightarrow$ **the reverse emulsion is formed.** $(\varepsilon = a/R_{12})$



Catastrophic phase inversion (?)





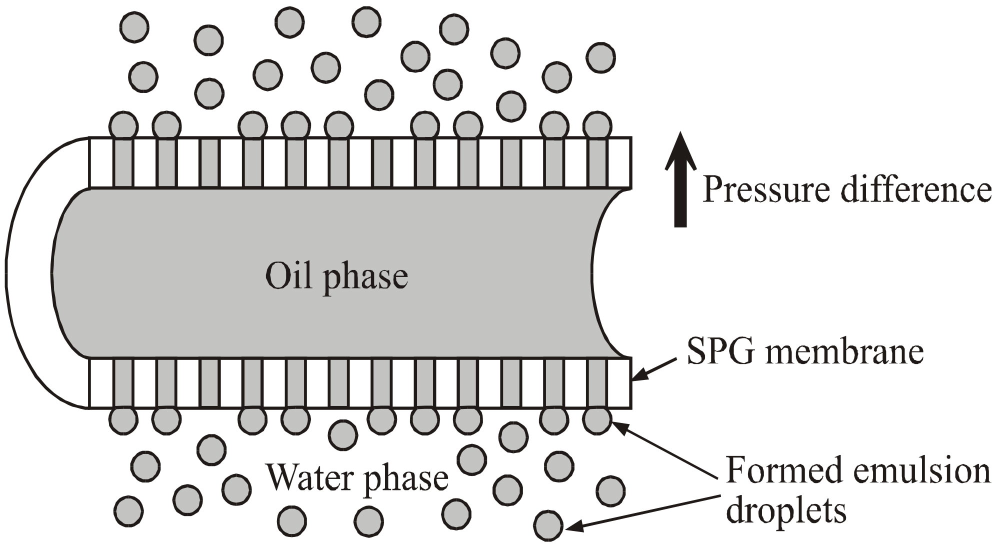
Membrane Emulsification

Porous glass or ceramic membrane

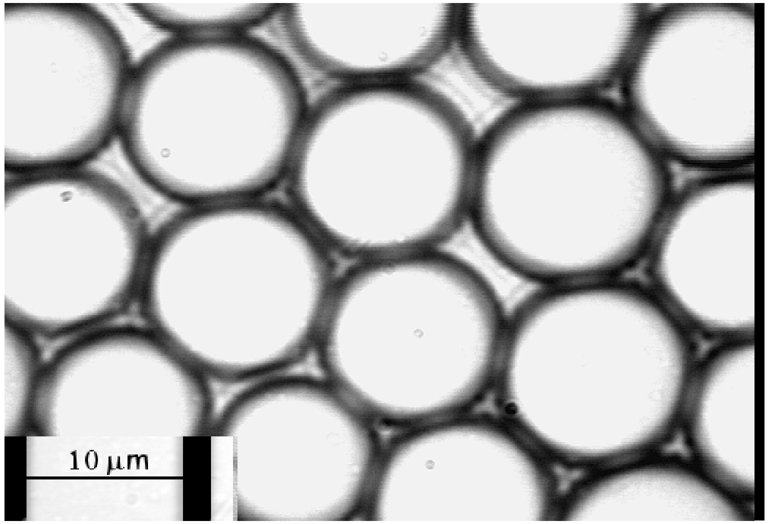
New Task:
Apply this method to Pickering emulsions

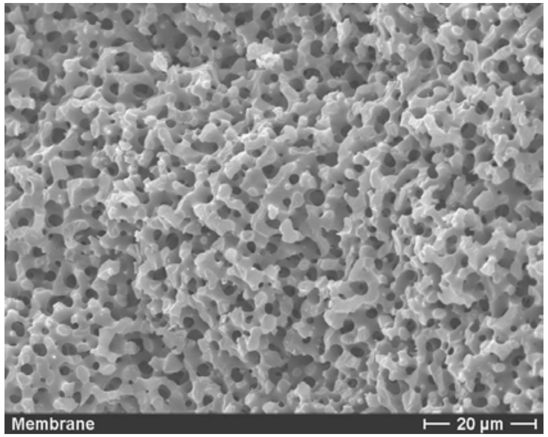
Produced monodisperse common emulsion:

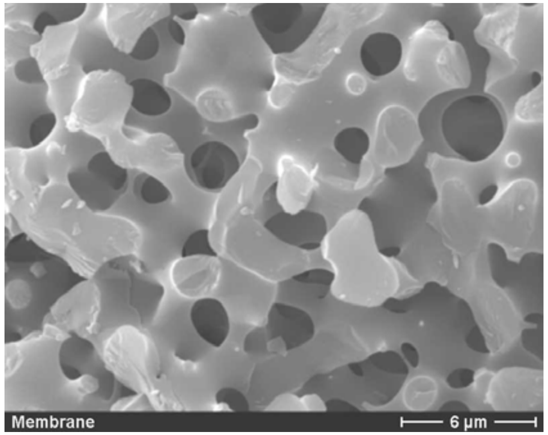
(pore diameter 3.2 μm)



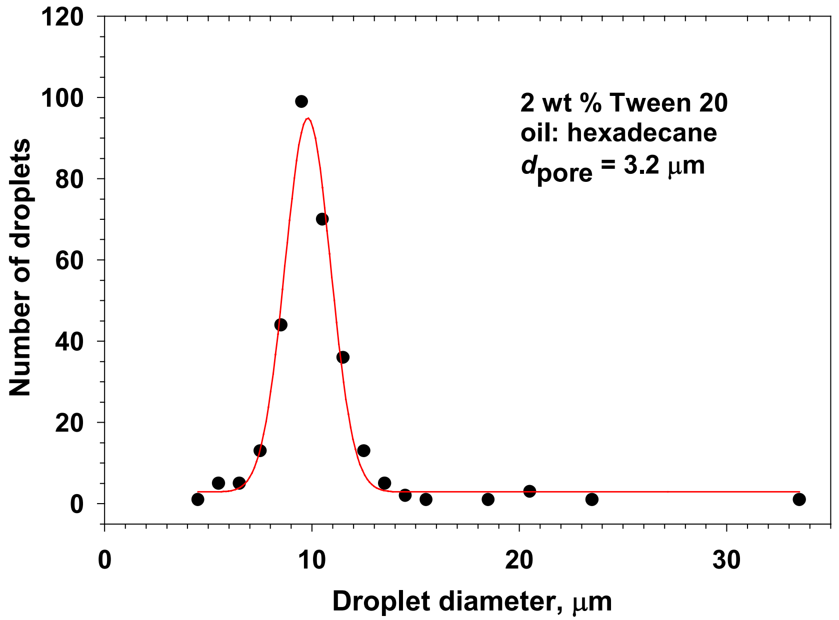
Surface of a membrane with 2 μm pore size

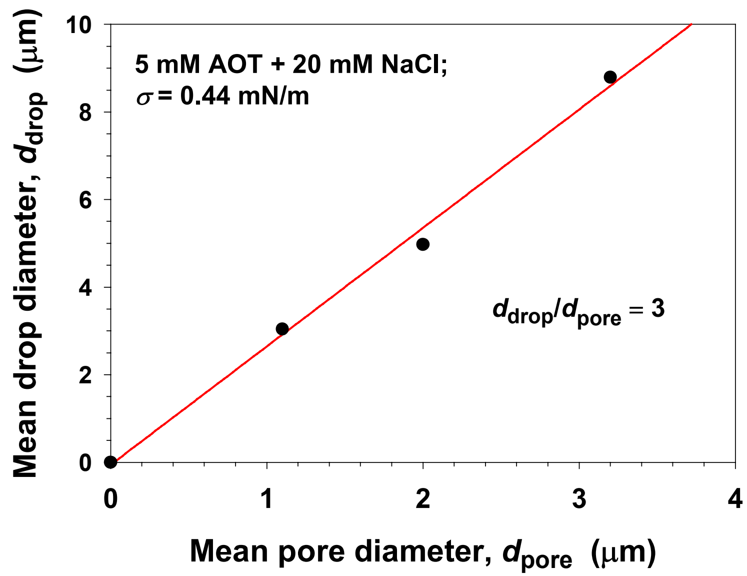




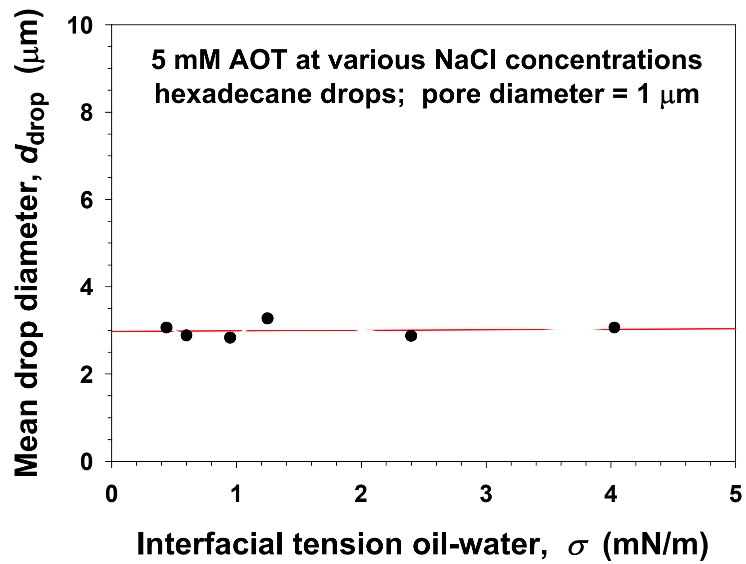


Oil-in Water Emulsions Obtained by Hydrophilic Membranes





Typically $d_{drop}/d_{pore} \approx 3$



d_{drop}/d_{pore} is independent of the pore size

d_{drop}/d_{pore} is independent of the interfacial tension

Basic Question:

Why $d_{drop}/d_{pore} \approx 3$?

(irrespective of pore size, interfacial tension and viscosity of the liquid phases?)

Theoretical Analysis:

Condition for Detachment of a Growing Drop from a Pore

KEY:

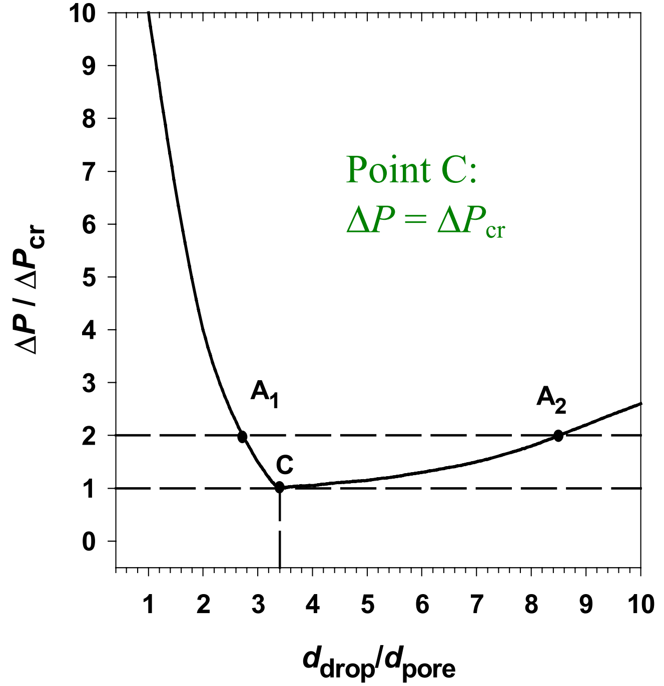
Analogy: detachment of a pendant drop

- **Steady state growth: $F_{tot} = 0$;**
- **At a given size the drop profile becomes unstable;**
- **The critical value of the body (gravitational) force is:**

$$F_{cr} = \sigma d_{drop} \lambda(x)$$

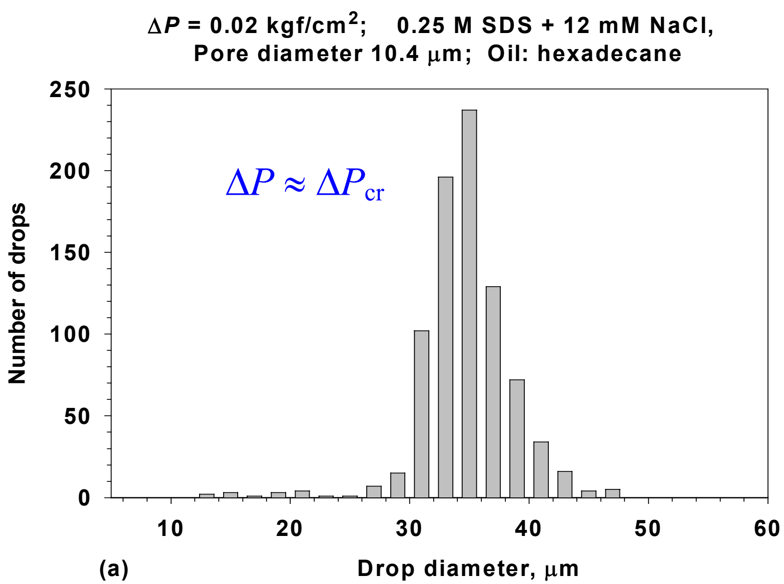
$x = d_{drop}/d_{pore}$ **$\lambda(x)$ – known universal function**

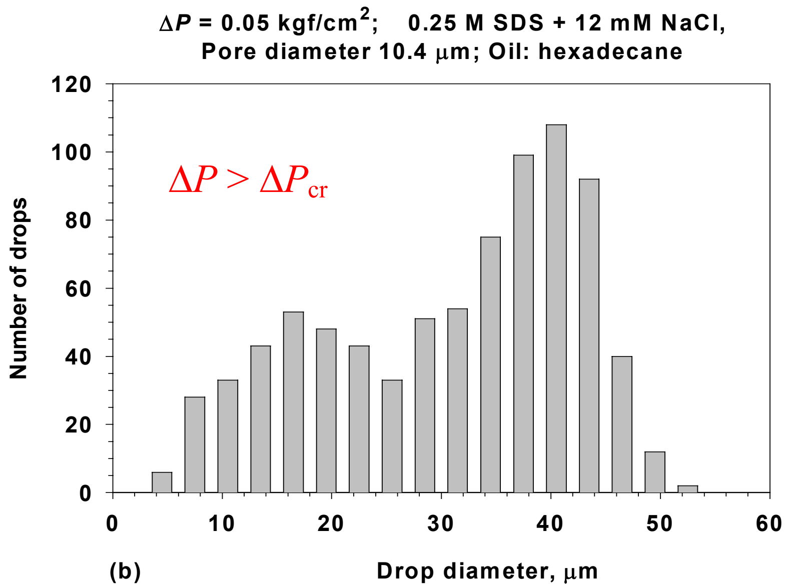
$\lambda(x) \propto (V_{max})^{2/3}$; V_{max} **– dimensionless maximum drop volume**



- For $\Delta P < \Delta P_{cr}$ emulsion drops are not released from the membrane.
- For $\Delta P > \Delta P_{cr}$ drops with two different sizes, corresponding to the points A_1 and A_2, ⇒ two-peak drop-size distribution;
- For $\Delta P = \Delta P_{cr}$ (point C) monodisperse drops are produced with $d_{drop}/d_{pore} \approx 3$.

⇒ $d_{drop}/d_{pore} \approx 3$ (monodisperse drops), irrespective of the type of the oily and aqueous phases, interfacial tension, bulk viscosities, surfactant adsorption kinetics, etc.





Summary of the New Tasks:

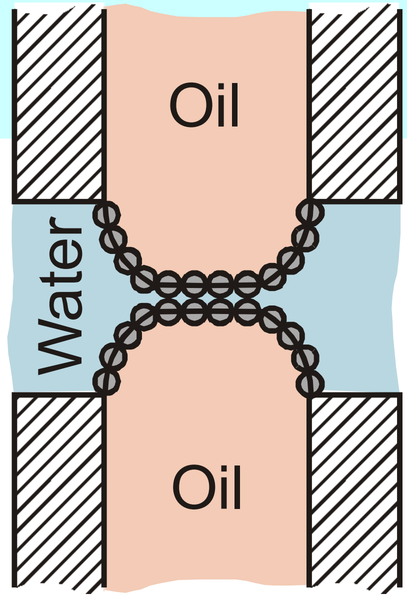
(1) Derive general expressions for all types of capillary multipoles;

rheology of particle monolayers;

(2) Develop a rigorous theory of:

(a) electro-dipping force;

(b) lateral capillary and electric force.



(3) Investigate the External-Meniscus driven capillary force and its importance for the coalescence in Pickering emulsions

(4) Formulate a thermodynamic criterion for obtaining direct/reverse Pickering emulsion and check it against experiment

(5) Develop a hydrodynamic theory of membrane emulsification and apply this method to produce experimentally Pickering emulsions.