COST P21: Student Training School

Physics of droplets: Basic and Advanced Topics

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Experimental methods for characterization of interfaces and thin films

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Contents

Single Surfaces

- ◎ **Basic properties and measured parameters:**

  Surface energy & tension

  Rheological parameters (i.e. elasticity, viscosity)

  Composition

- ◎ **Experimental methods:**
  - **Force measurement → force per unit length**
  - **Optical methods: Shape determination (ADSA); reflectivity determination (ellipsometry); optical and/or mass density measurement, etc.**
  - **Combined methods: shape in outer inertial or electric field.**

Thin Liquid Films

- ◎ **Basic properties and measured parameters:**

  Kinetics of film thinning, i.e. *h*(*t*)

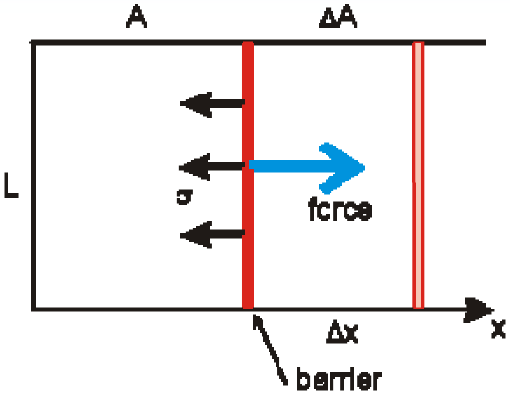
  Interaction energy between the surface of the film

  Composition of the films

- ◎ **Experimental methods:**
  - **Optical & Force/Pressure measurements**
  - **Cells and devices**

Single Surfaces

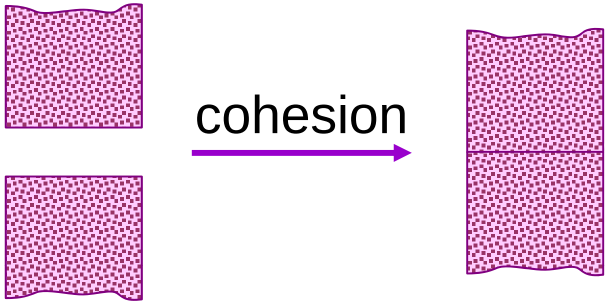
Fluid surfaces



Force per unit length: $$\sigma \equiv \frac{1}{L}\frac{\Delta W}{\Delta x}$$

surface tension =
surface excess energy per unit area

Solid surfaces: surface energy ≠ surface tension usually


cohesion


adhesion

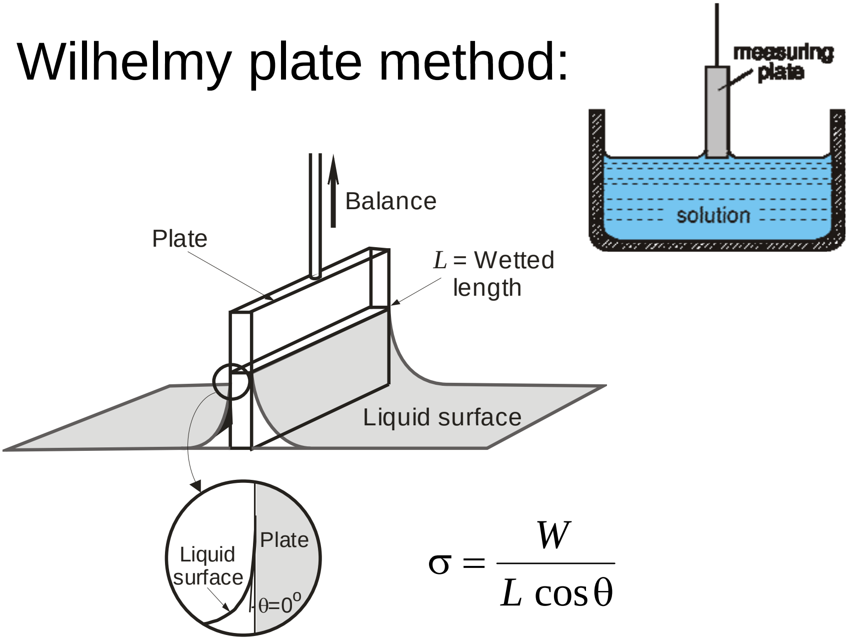
Work for cohesion $W_{coh} = 2\sigma_1$

Work for adhesion $W_{adh} = \sigma_1 + \sigma_2 - \sigma_{12}$

Force measuring methods for single surfaces

FORCE/weight measurement ⇒ Surface tension calculation

- Wilhelmy plate method:

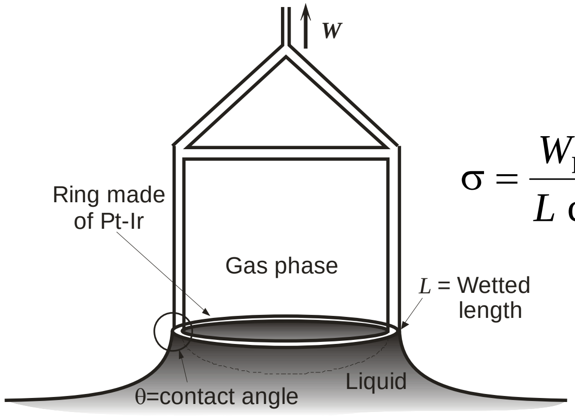


$$\sigma = \frac{W}{L\cos\theta}$$

Usually the liquid fully wets (contact angle θ=0) the surface of a probe object, e.g. a vertical plate (Wilhelmy, 1863)

The plate: (i) platinum (porous); (ii) glass (especially roughened); (iii) paper (in the Langmuir troughs; (iv) open frame (for cationics)

- Du Noüy ring method:



$$\sigma = \frac{W_{\max}}{L\cos\theta}$$

W_{max} - maximum value of the weight of the liquid meniscus to be detached from a contact surface with a defined perimeter, L, e.g. a horizontal ring (Du Noüy, 1919):

The ring: platinum

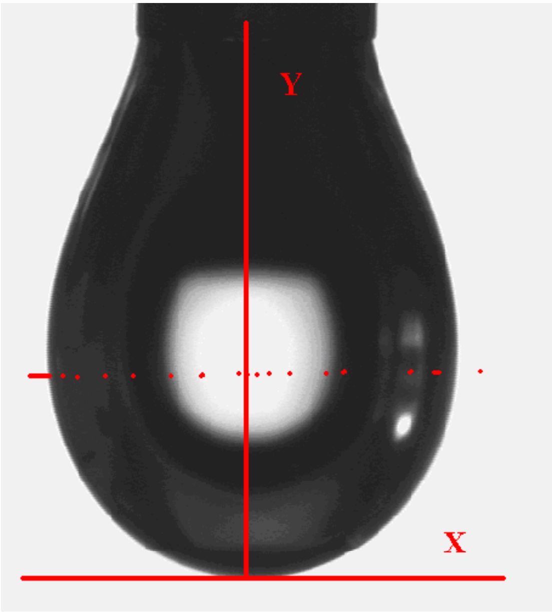
- Other probe objects: sphere; cylinder; fiber; …

Optical methods for single surfaces

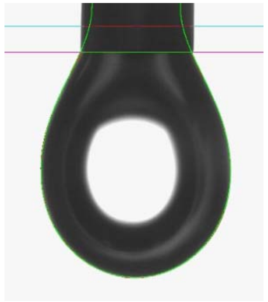
Optical determination of the SHAPE of fluid surface for fit with Laplace equation ⇒ surface tension calculation

Under mechanical equilibrium the balance of the capillary and gravitational forces determine the shape

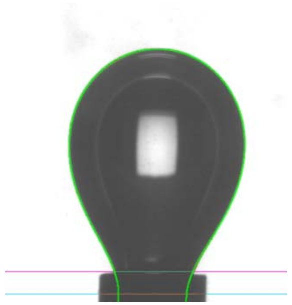
- ADSA method (Axisymmetric Drop Shape Analysis, Rotenberg, Boruvka, Neumann, J Colloid Interface Sci 1983):



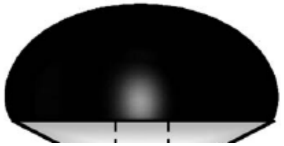
$$\sigma\left[\frac{y''}{(1+y'^2)^{2/3}}+\frac{y'}{x(1+y'^2)^{1/2}}\right]=\Delta\rho g y+\frac{2\sigma}{R}$$



pendant drop

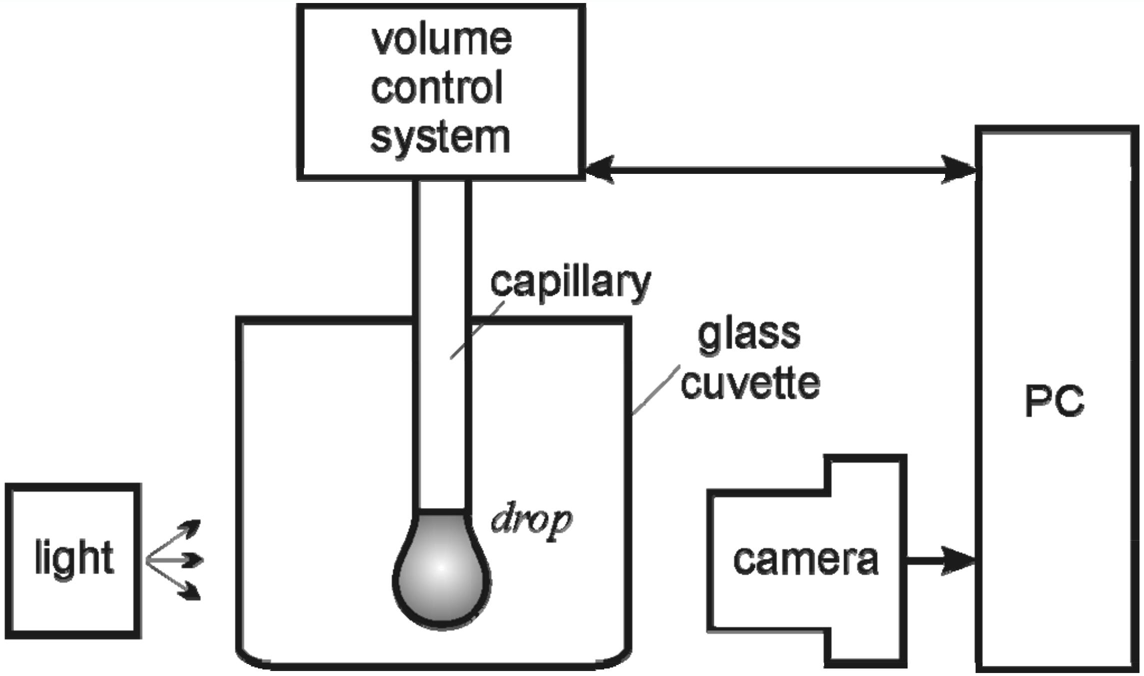


rising bubble



sessile drop

Practical realization of ADSA methods



Important parameters:

- Optical alignment of the system

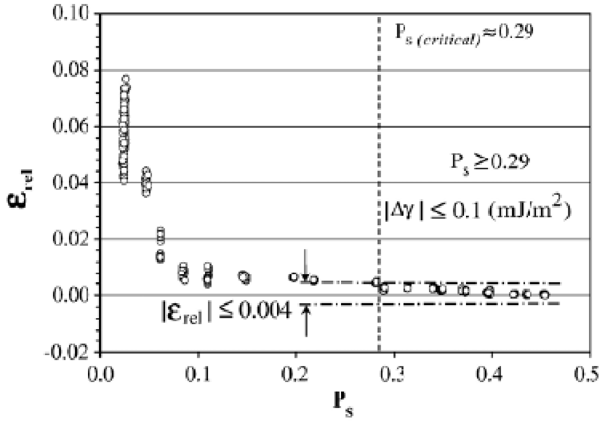
  → true axisymmetric shape

- Aspect ratio accounting

  → true axisymmetric shape

- “Good” shape factor, $B=\Delta\rho R^2 g/\sigma$,

  i.e. comparable gravity and capillary forces

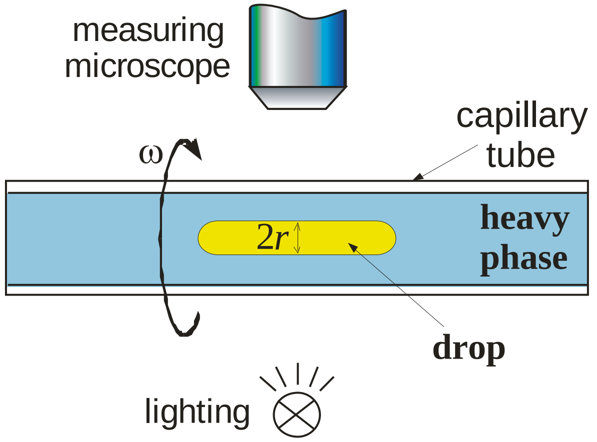


(For very detailed consideration : Hoorfar & Neumann, Adv. Colloid Interface Sci. 121 (2006) 25)

Optical methods for single surfaces

Optical determination of the Shape of fluid surface under additional force field (for very low σ)

- Spinning drop method: $10^{-6} – 10^{1}$ mN/m



$$\sigma = \frac{1}{4} r^3 \Delta\rho\,\omega^2$$

r – radius of the spinning drop,

$\Delta\rho$ – density difference between the drop and the outer (heavy) phases.

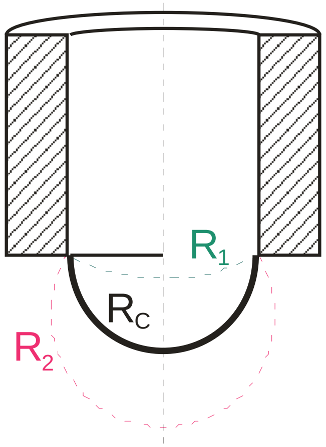
ω – angular velocity, up to 1000 s^{-1}.

- The electrowetting method (external electric field) – lecture of Prof. van den Ende

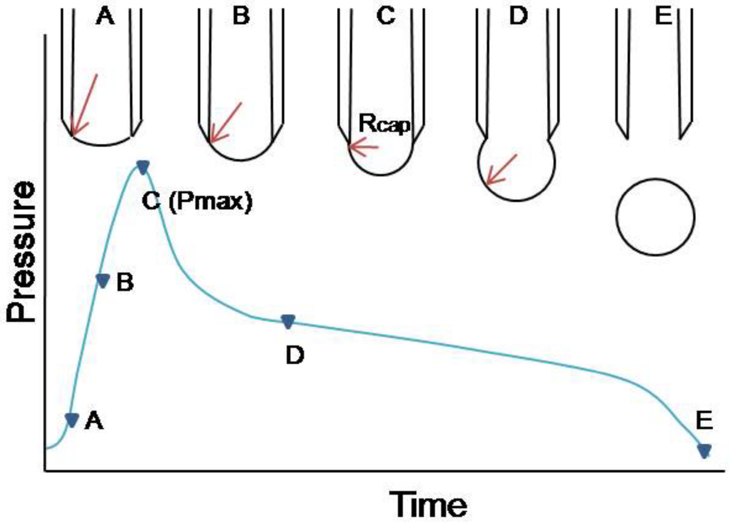
Pressure methods for single surfaces

Direct measurement of the pressure inside a spherical <u>bubble</u> ⇒ determination of the surface tension

- Maximum Bubble Pressure Method:



$$\sigma = \frac{P_{\max} R_c}{2}$$

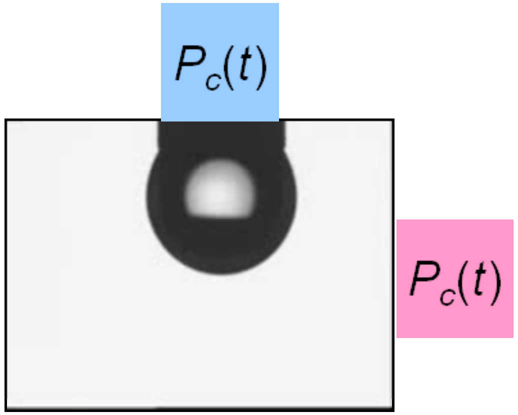


The practical realization of the method does not include optical observation but relies on preliminary determination of the capillary radius (i.e. calibration procedure)

Pressure methods for single surfaces

Direct measurement of the pressure inside a spherical <u>drop/bubble</u>

- Capillary pressure tensiometry (CPT):



$$\sigma = \frac{P_c R_d}{2}$$

Capillary pressure, *P_c*, is determined by using pressure transducer, which is connected either to:

<u>the inner (drop) fluid</u>

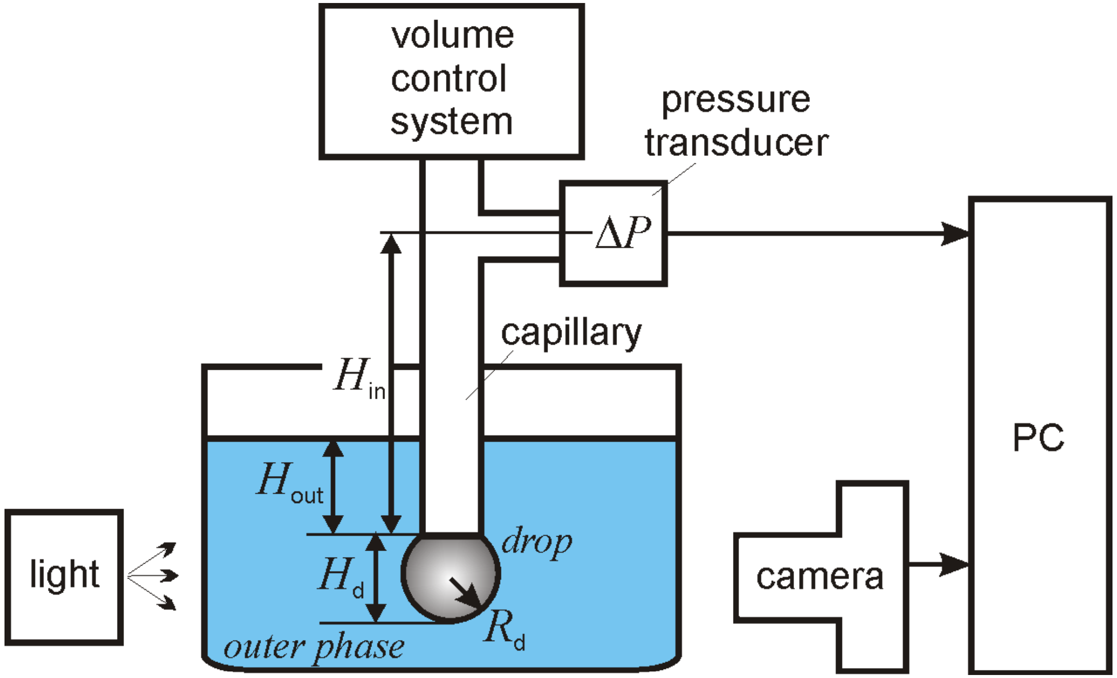
(Liggieri et al., 1990; Horozov et al. 1993; Nagarajan & Wasan, 1993),

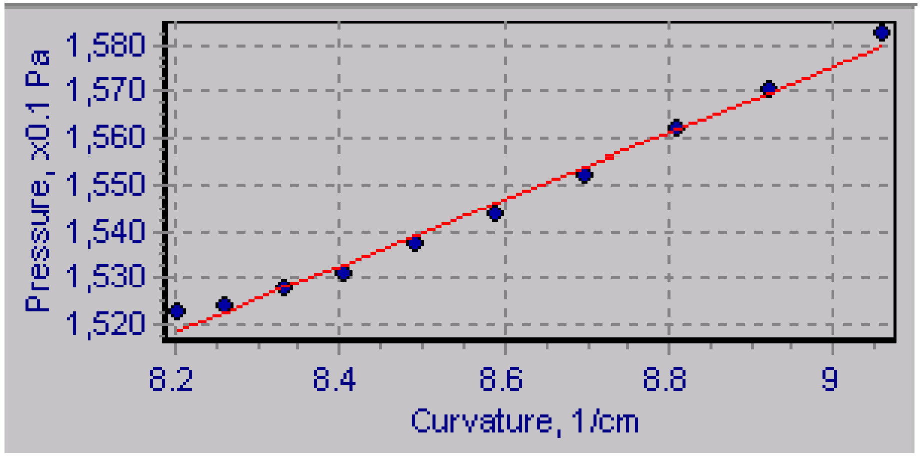
<u>or to the outer fluid</u>

(Lunkenheimer & Kretzschmar, 1975, Wantke et al. 1993, Liggieri et al. 1998).

The practical realization of the method does include optical observation and complex preliminary calibration procedure.

Practical realization of the CPT method





One measures:

$$P_M = P_0 + P_{DH} + P_C$$

$$= P_0 + \Delta\rho g H_D + 2\sigma\frac{1}{R_D}$$

Linear dependence:

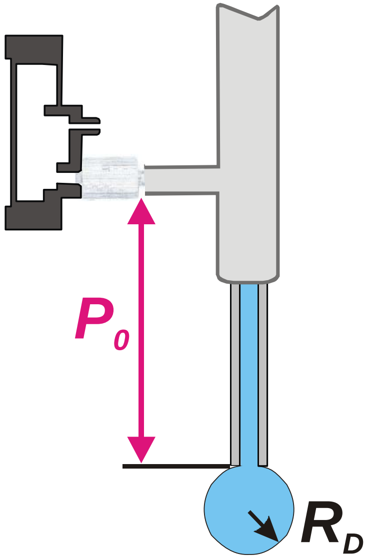
$$P_M \sim 2\sigma\frac{1}{R_D}$$

Linear regression through the data (P_i, R_i^{-1}) ensures best precision!

Accuracy & sensibility of the CPT method

$$P_M = P_0 + P_{DH} + P_C$$

$$\sigma \sim \frac{P_M R_D}{2}$$



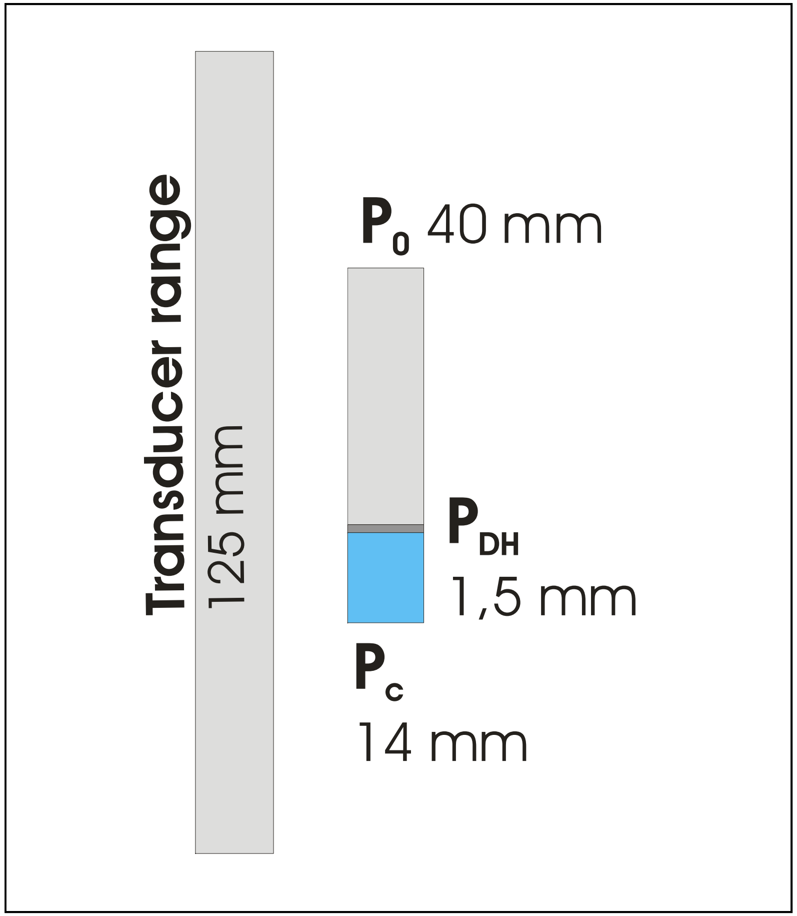
Example system 1:

- $\sigma = 70$ mN/m
- $R_d = 1$ mm,
- $\Delta\rho = 1$ g/cm^3

Estimation:

For 1% precision of σ:

~ ± 1 Pa -> 0,1 mm H_2O !!!



Example system 2:

- $\sigma = 30$ mN/m
- $R_d = 0.3$ mm
- $\Delta\rho = 1$ g/cm^3

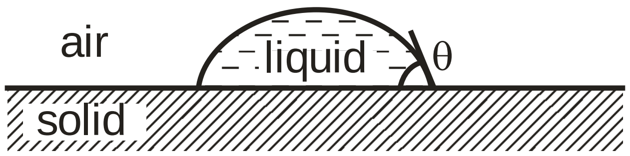
Example system 3:

- $\sigma = 10$ mN/m
- $R_d = 0.3$ mm
- $\Delta\rho = 0.1$ g/cm^3

Measurement in vibration isolated and temperature controlled environment is recommended !!!

Methods for solid surfaces

Optical determination of contact angle and shape of fluids wetting solid surfaces → determination of the surface energy



$$\sigma_L\left(1+\cos\theta\right)=W_{SL}$$ Young-Dupré equation

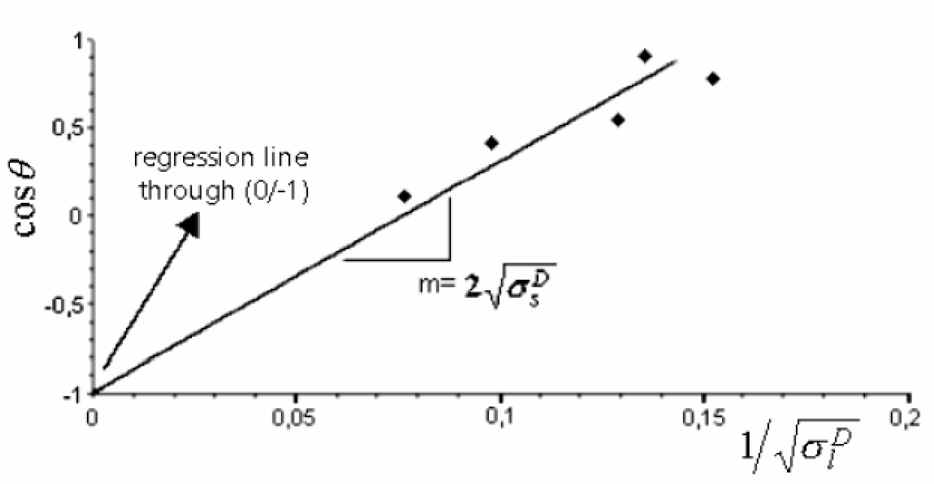
$$W_{SL} = \sigma_L + \sigma_S - \sigma_{SL}$$

$$\sigma_S - \sigma_{SL} = \sigma_L \cos\theta$$ Young equation

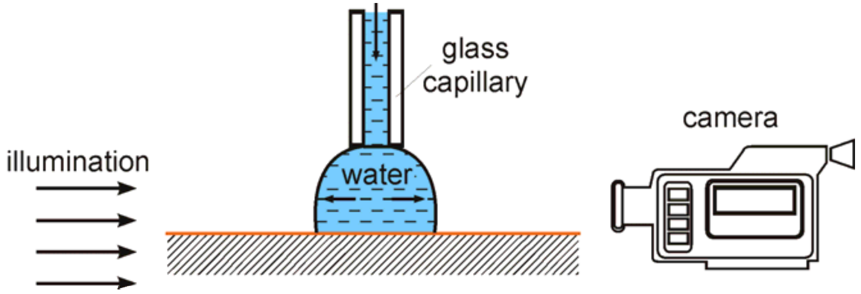
Girifalco&Good (1957): for the case of dispersion interaction between the molecules:

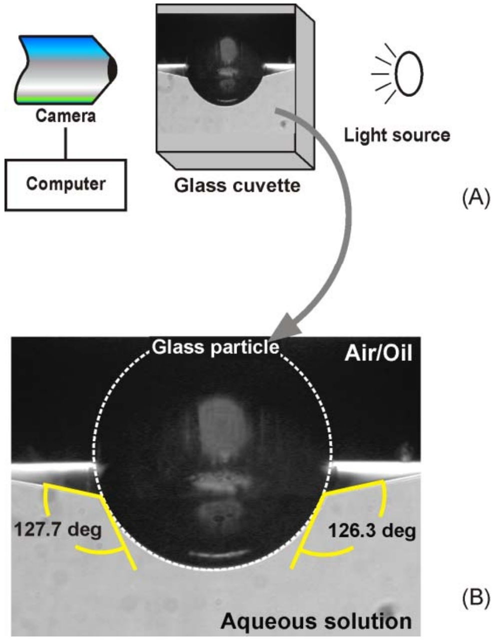
$$\sigma_{SL} = \sigma_S + \sigma_L - 2\sqrt{\sigma_S^D\,\sigma_L^D}$$

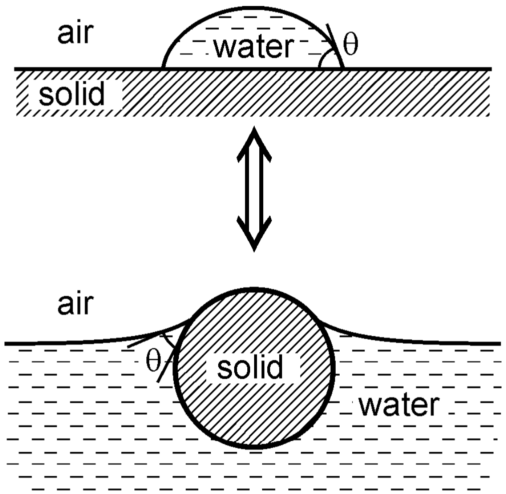
$$\cos\theta = -1 + 2\frac{\sqrt{\sigma_S^D}}{\sqrt{\sigma_L^D}}$$

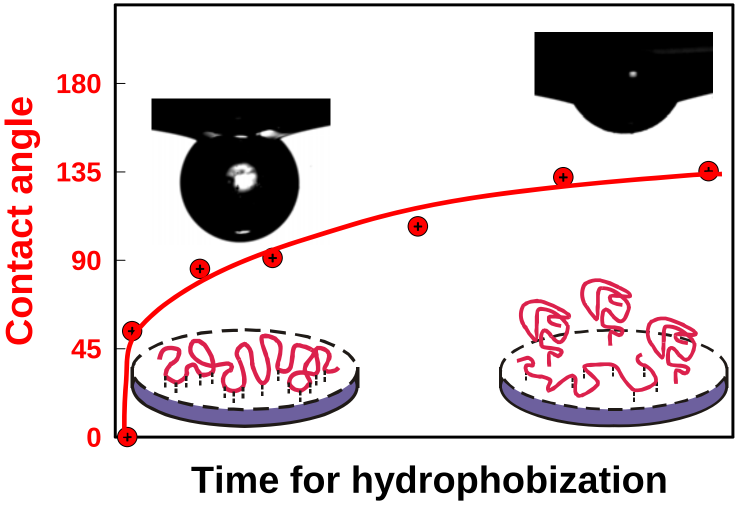


Practical realization of the contact angle measurement



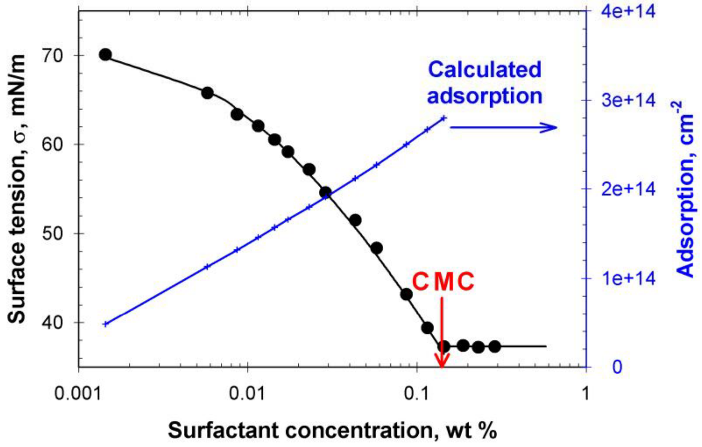




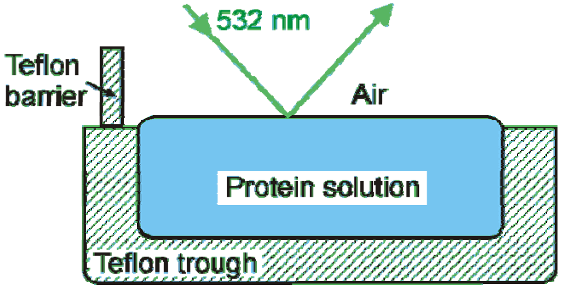


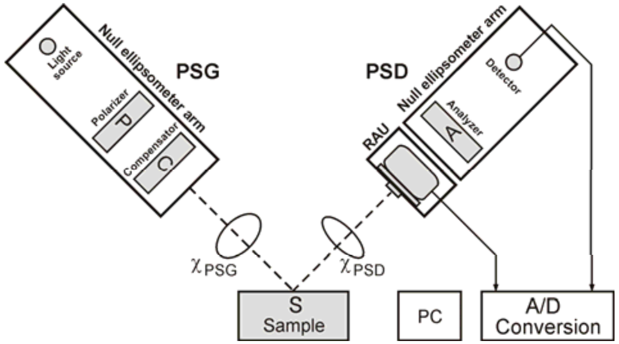
Determination of the surface composition

- **From surface tension isotherm – after fitting the experimental dependence σ(C) with a suitable adsorption model**



- **After "direct" ellipsometric measurement**





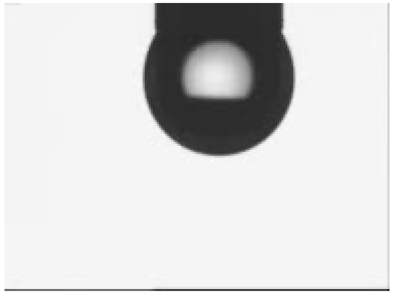
- **Quartz crystal microbalance**
- **SEM / TEM for solid surfaces or after applying e.g. Langmuir-Blodgett technique for liquid surfaces**
- **Other …**

Methods for surface rheological measurements

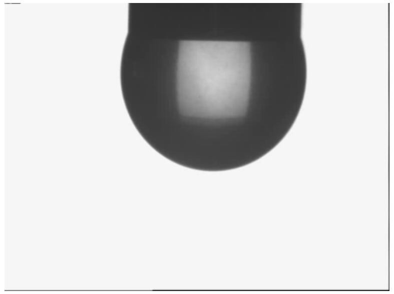
Drops surfaces:

Oscillating deformed drop
(ODM/DSA)

Oscillating spherical drop
(SDA/CPT)

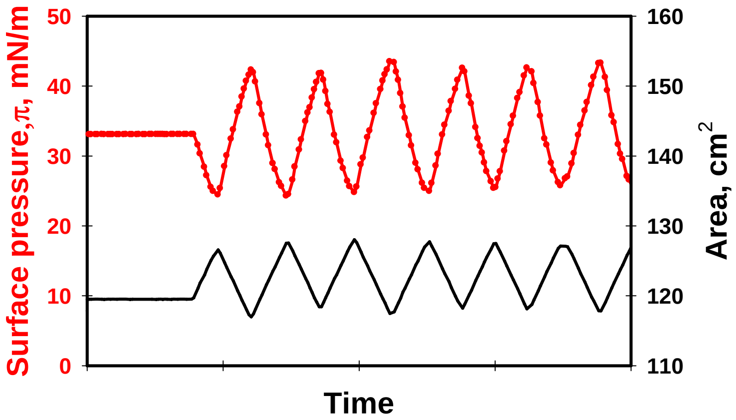


Expanding spherical drop
(EDM/CPT)

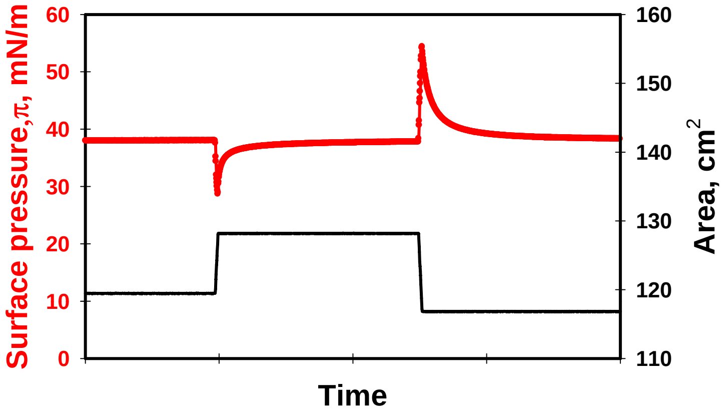


Flat surfaces (e.g. in a Langmuir trough)

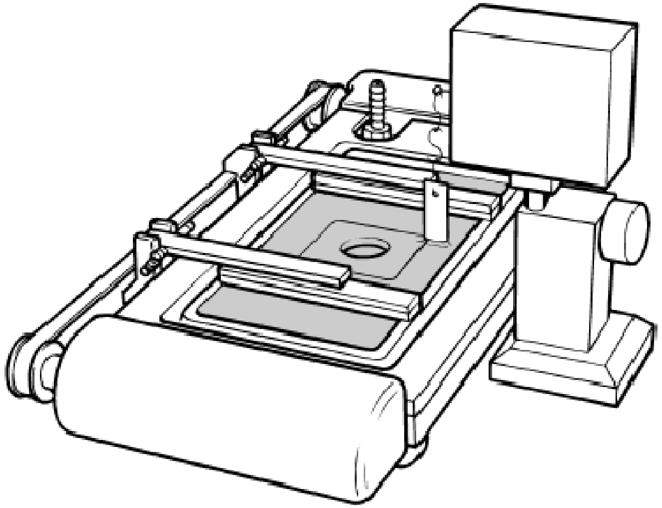
Triangle oscillations



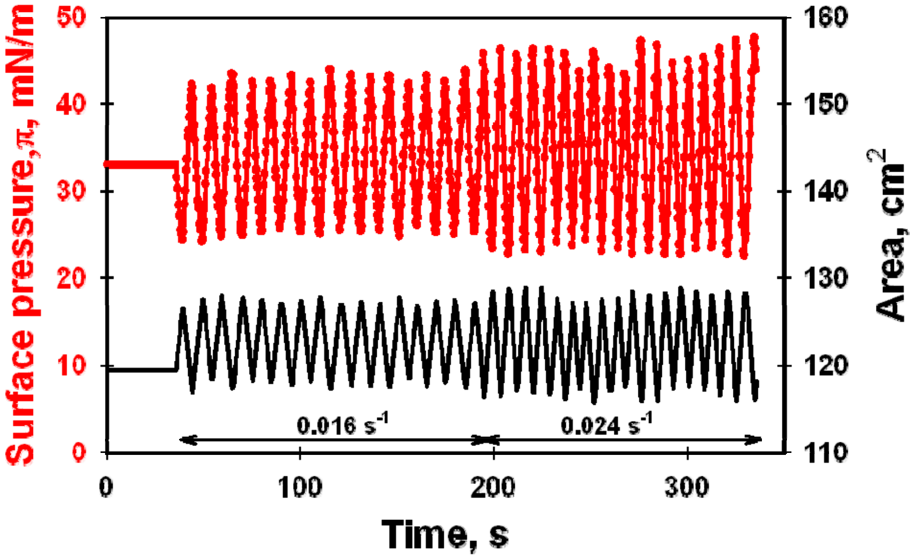
Stress-relaxation



Langmuir trough

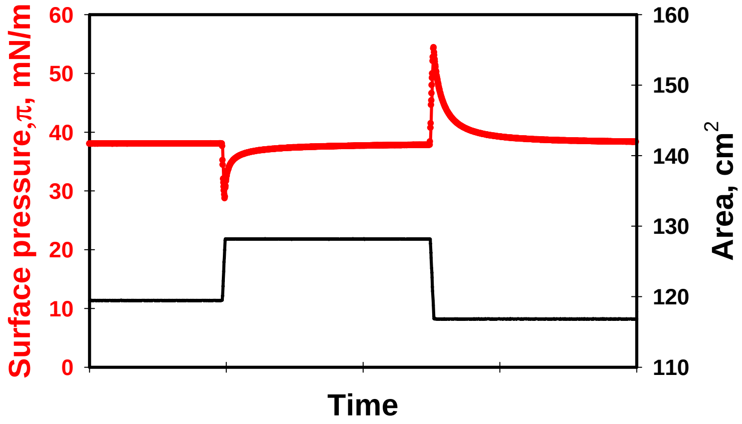


Periodic deformation



$$-\Delta\pi = \Delta\sigma(t,\alpha) \Rightarrow E'(\omega),\ E''(\omega)$$

Stress relaxation



Rheological law: *E*, η

Kelvin model

$$\tau = -\Delta\pi = \Delta\sigma = E_{\mathrm{V}}\alpha + \eta_{\mathrm{V}}\dot{\alpha}$$

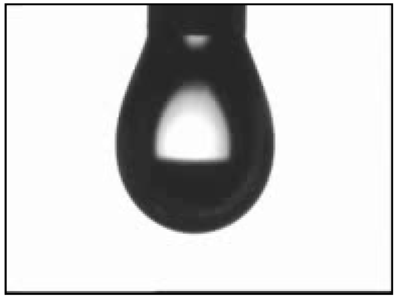
Maxwell model

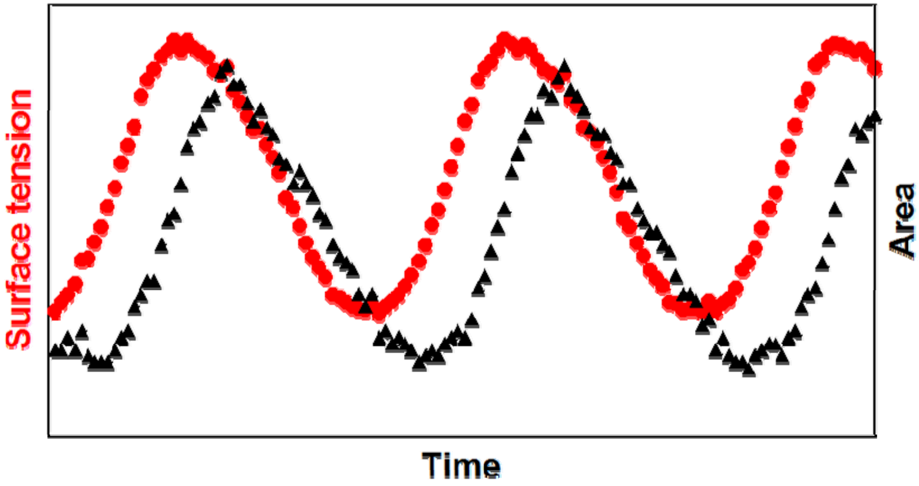
$$\frac{\dot{\tau}}{E_{\mathrm{M}}} + \frac{\tau}{\eta_{\mathrm{M}}} = \dot{\alpha}$$

Surface rheological parameters after sinusoidal oscillations

Area, *A*, of a pendant drop oscillates: $A(t) = A_0 + \Delta A \sin(\omega t)$

ADSA method gives the resulting change of the surface tension σ(t): $\sigma(t) = \sigma_0 + \Delta\sigma \sin(\omega t + \varphi)$





At small ΔA/A (for linear response):

$$\boxed{E^*(\omega) = \frac{\Delta\sigma}{\Delta A / A} e^{i\varphi}}$$

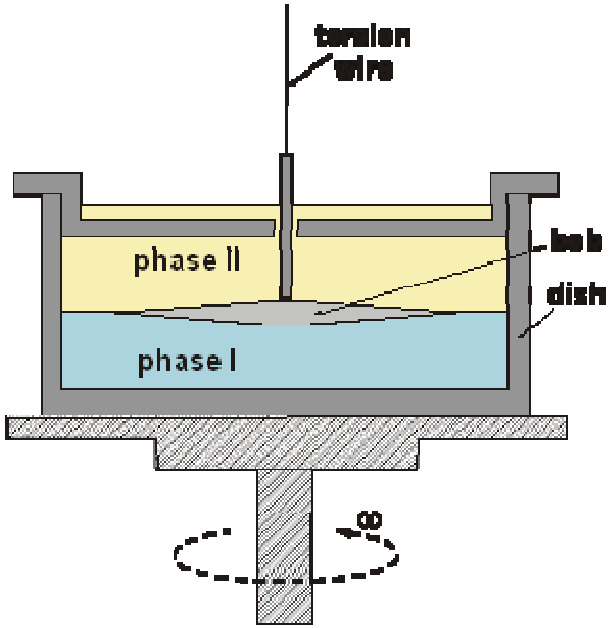
$E^*(\omega)$ - interfacial visco-elasticity

E' - elastic (storage) modulus

E'' - viscous (loss) modulus

Surface shear rheology

- Surface shear rheometer:



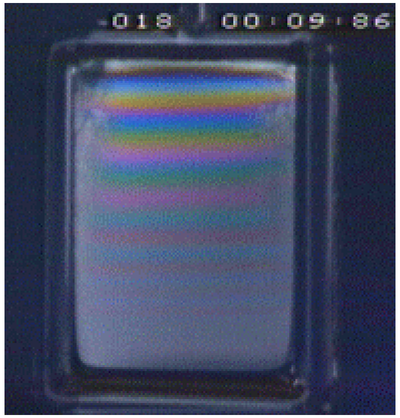
measurement of the force exerted by a deformed interfacial layer on a torsion pendulum.

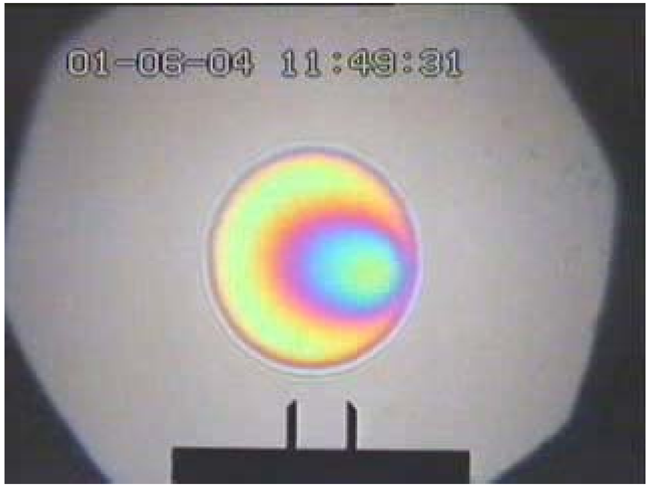
Other methods:

- Oscillating needle
- Deep channel
- Floating particle technique
- others …

Most recent review in:
Interfacial Rheology,
R. Miller & L. Liggieri Eds.,
VSP Brill, Leiden, 2009.

Thin liquid films

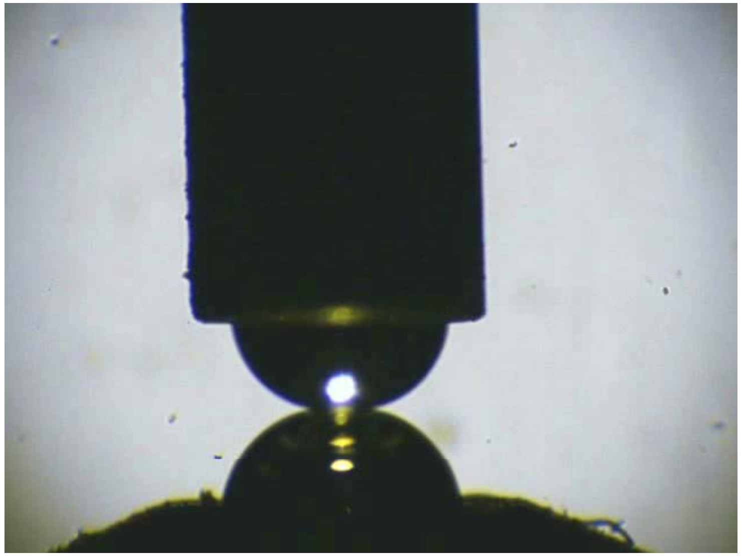




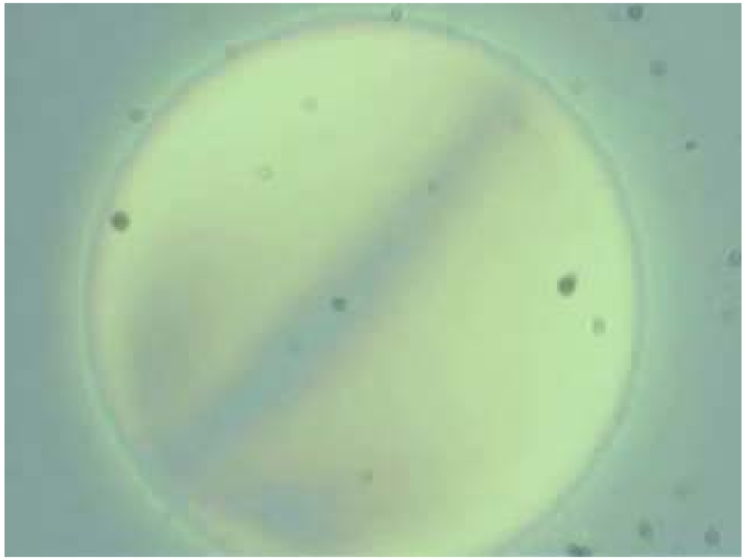
Nice colored pictures provide information for the:

- interactions between the film surfaces,
- mobility of the surfaces,
- impact of the fluid (viscosity and structure) between the surfaces

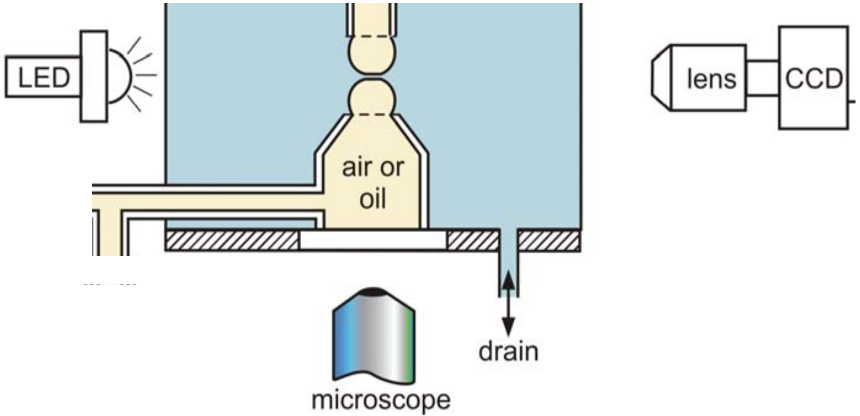
Film formation upon bubble collision



side observation

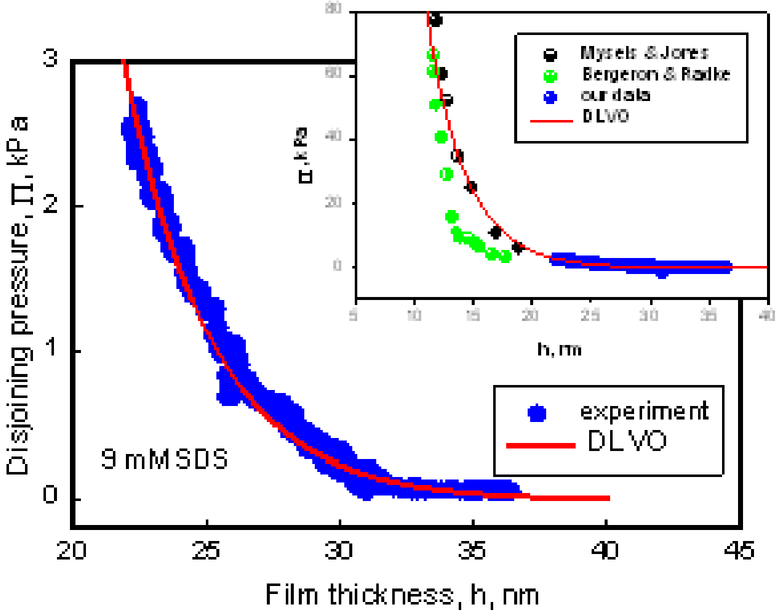


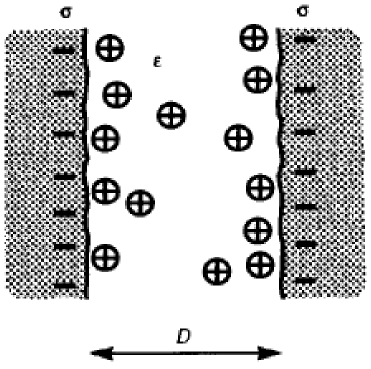
film observation



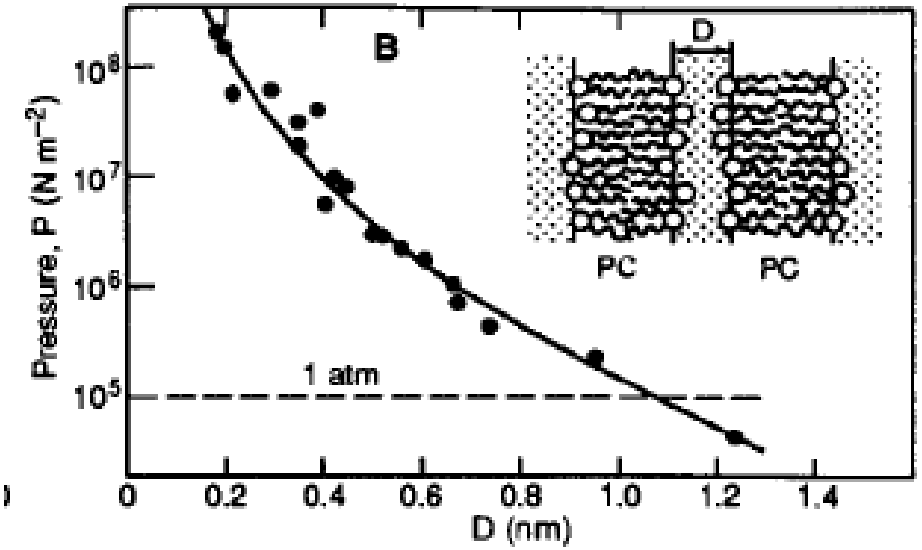
Thin liquid films ↔ surface force techniques

Main aim – to determine experimentally the **Force** and/or **Energy (distance) law** between surfaces

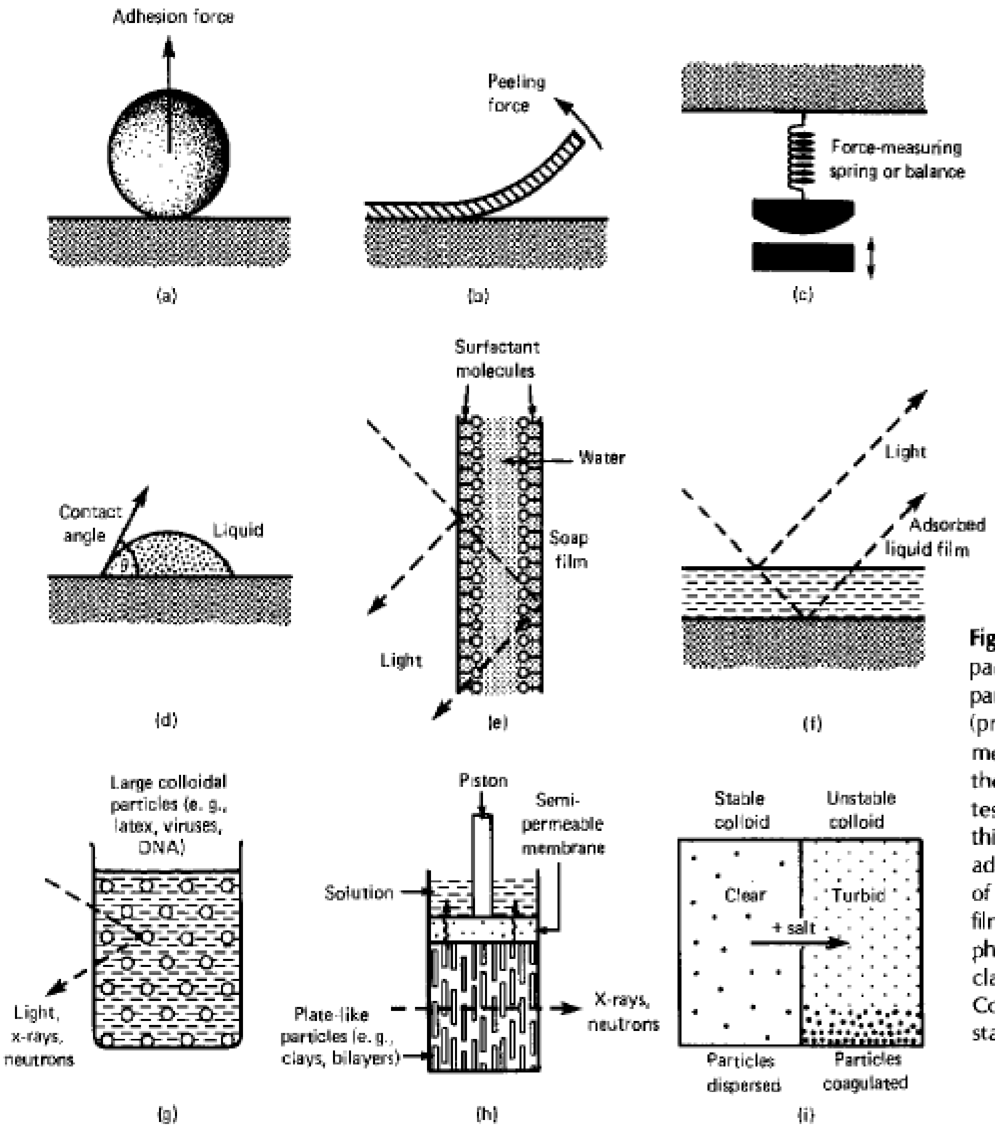




The experimental dependence should be further compared with theoretical predictions in order to describe quantitatively the surface forces!



Different techniques for different objects



Independent measurement/determination of 2 parameters:

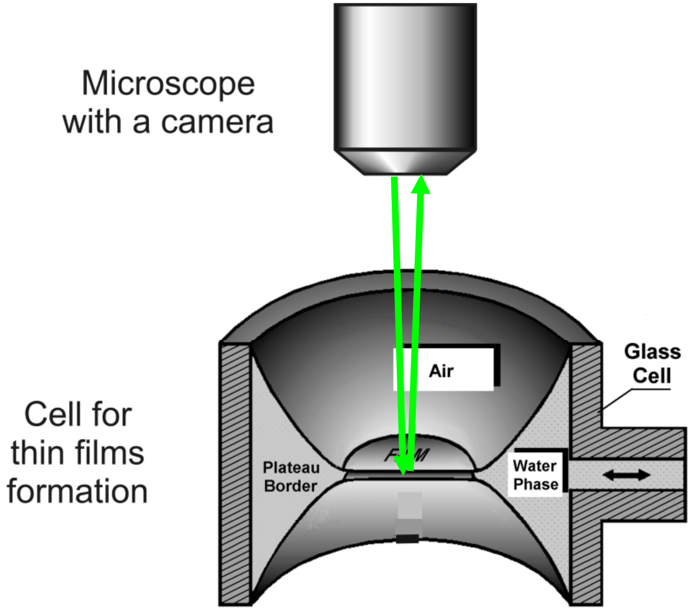
1. Force or pressure
2. Distance

$\Rightarrow \Pi(h)$, $W(h)$, $F(h)$, etc.

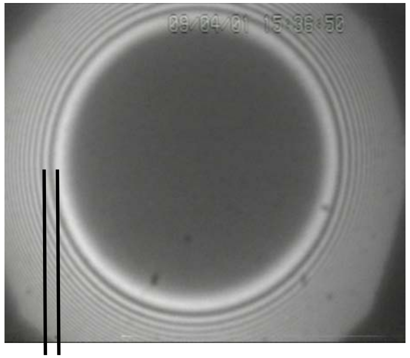
Fig. 10.6. Different types of measurements that provide information on the forces between particles and surfaces. (a) Adhesion measurements (practical applications: xerography, particle adhesion, powder technology, ceramic processing). (b) Peeling measurements (practical applications: adhesive tapes, material fracture and crack propagation). (c) Direct measurements of force as a function of surface separation (practical applications: testing theories of intermolecular forces). (d) Contact angle measurements (practical applications: testing wettability and stability of surface films, detergency). (e) Equilibrium thickness of thin free films (practical applications: soap films, foams). (f) Equilibrium thickness of thin adsorbed films (practical applications: wetting of hydrophilic surfaces by water, adsorption of molecules from vapour, protective surface coatings and lubricant layers, photographic films). (g) Interparticle spacing in liquids (practical applications: colloidal suspensions, paints, pharmaceutical dispersions). (h) Sheet-like particle spacings in liquids (practical applications: clay and soil swelling behaviour, microstructure of soaps and biological membranes). (i) Coagulation studies (practical application: basic experimental technique for testing the stability of colloidal preparations).

Israelachvili, 1992

Optical interference from thin liquid films



optical interference:



$\Delta h = \lambda/2n \approx 203$ nm

Cells of Scheludko-Exerowa (1959),
Mysels (1964)

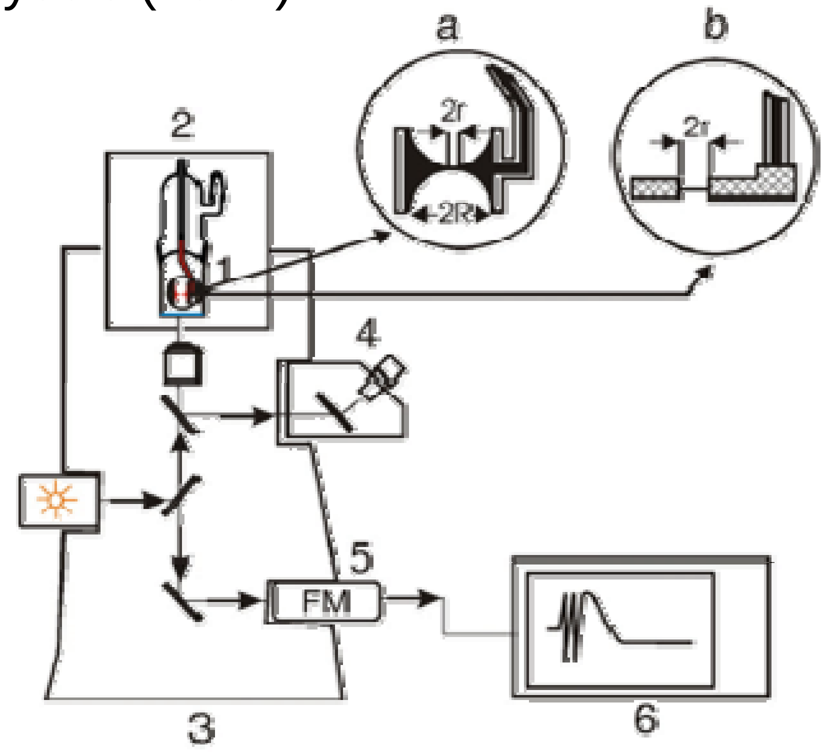
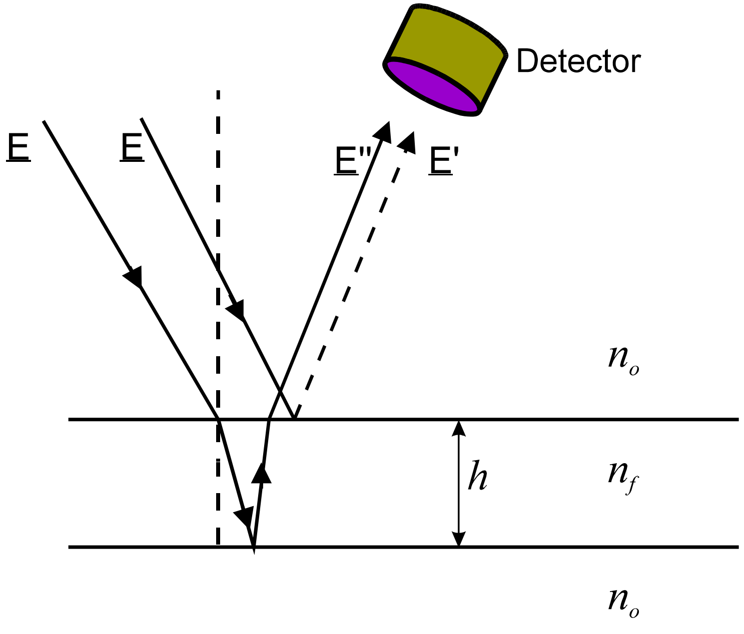


Fig. 2. Schematic of the microinterferometric technique. 1 — measuring cell; 2 — thermostating device; 3 — microscope; 4 — light source; 5 — photomultiplier; 6 — recording device. (a) — film holder of the Scheludko–Exerowa cell; (b) — film holder of the Exerowa–Scheludko porous plate cell.

Cohen & Exerowa, ACIS 134–135 (2007) 24

Interferometric method for thickness determination – homogeneous film



$$\underline{E}' = R\underline{E}_0\, e^{i(\underline{k}\underline{r} - wt)}$$

$$\underline{E}'' = R\underline{E}_0\, e^{i(\underline{k}\underline{r} - wt + \Delta)}$$

$\underline{E}_0$ - amplitude of the incident beam,
$\underline{k}$ - wave vector in a point $\underline{r}$,
ω - wave frequency,
Δ - phase difference between the two beams.

For incident beam perpendicular to the interface: $R = \dfrac{n_f - n_0}{n_f + n_0}$

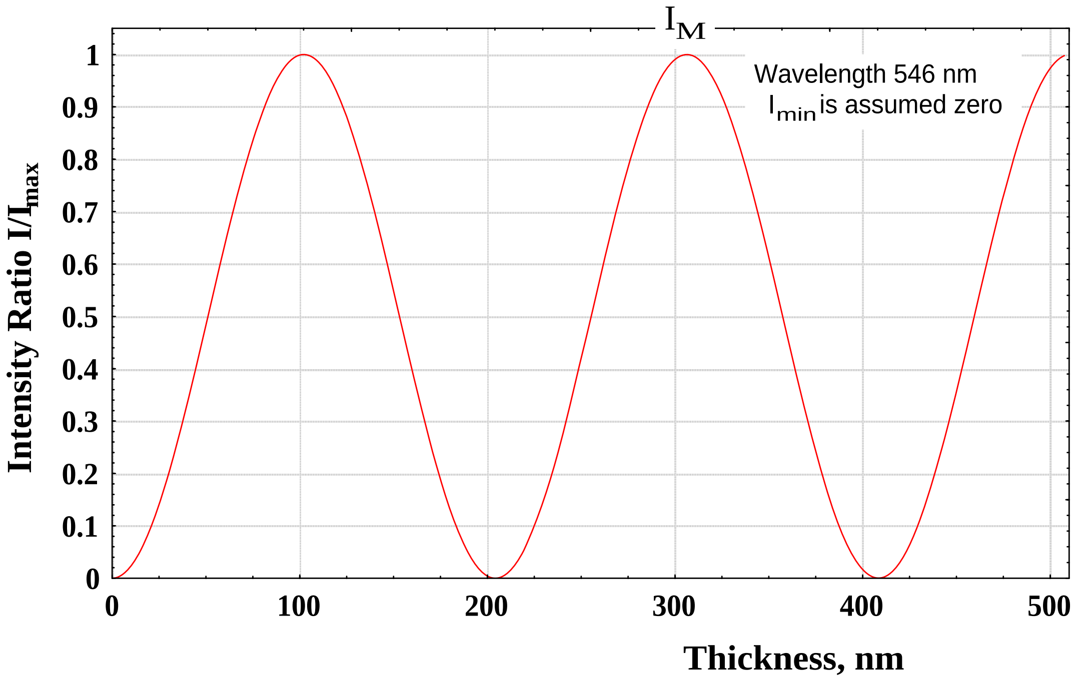
Superposition of the two beams: $\underline{E}_{\text{int}} = \underline{E}' + \underline{E}'' = R\underline{E}_0 e^{i(\underline{k}\underline{r} - wt)}\left(1 + e^{i\Delta}\right)$

Intensity, $I \sim E^2 \Rightarrow I = |R|^2 I_0 (1 + \cos\Delta)$ $\Delta = 2hn_f 2\pi/\lambda - \pi$

Interferometric method for thickness determination

$$I = |R|^2 I_0 \left(1+\cos\Delta\right)$$

$$\Delta = 2hn_f 2\pi/\lambda - \pi$$



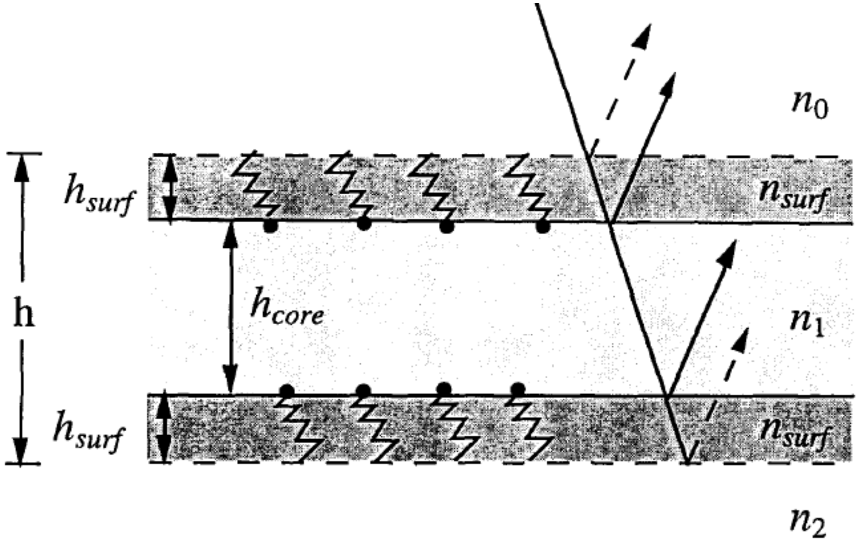
max: $2hn_f 2\pi/\lambda - \pi = 2m\pi$, m = 0, 1, 2, ... $\Rightarrow h = \lambda/4n_f,\ 3(\lambda/4n_f)$,

min: $2hn_f 2\pi/\lambda - \pi = (2m - 1)\pi$, m = 0, 1, 2, ... $\Rightarrow h = \lambda/2n_f,\ 2(\lambda/2n_f)$,

$$h = \frac{\lambda}{2\pi n_f}\left(k\pi \pm \arcsin\sqrt{\beta\frac{I - I_{\min}}{I_{\max} - I_{\min}}}\right)$$

$$\beta = \left(1 + \frac{4R^2\left(1 - \frac{I - I_{\min}}{I_{\max} - I_{\min}}\right)}{(1-R^2)^2}\right)^{-1}$$

Interferometric method for thickness determination – three layer model



$$h = h_w - 2\left(\frac{n_{\mathrm{surf}}^2 - n_1^2}{n_1^2 - n_0^2}\right)h_{\mathrm{surf}}$$

$$r_1 = \frac{n_1 - n_0}{n_1 + n_0}$$

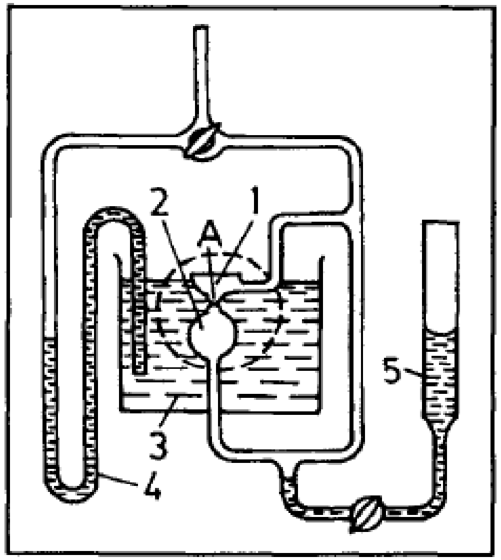
$$r_2 = \frac{n_2 - n_1}{n_2 + n_1}$$

I^r_{max}/I_0 and I^r_{min}/I_0 expressions for various combinations of refractive indices

	1. $n_0 < n_1 < n_2$ or 2. $n_0 > n_1 > n_2$	3. $n_0 < n_1 > n_2$ or 4. $n_0 > n_1 < n_2$
I^r_{max}/I_0	$\left(\frac{r_1 + r_2}{1 + r_1 r_2}\right)^2$	$\left(\frac{r_1 - r_2}{1 - r_1 r_2}\right)^2$
I^r_{min}/I_0	$\left(\frac{r_1 - r_2}{1 - r_1 r_2}\right)^2$	$\left(\frac{r_1 + r_2}{1 + r_1 r_2}\right)^2$

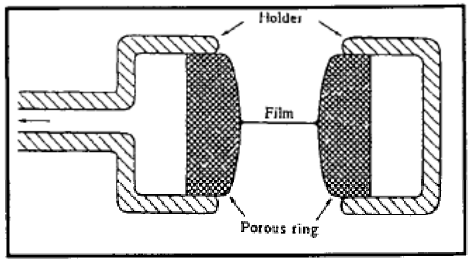
Thin films setups for precise pressure determination in a large pressure range

Derjaguin & Titievskaya, 1954



Film between two bubbles

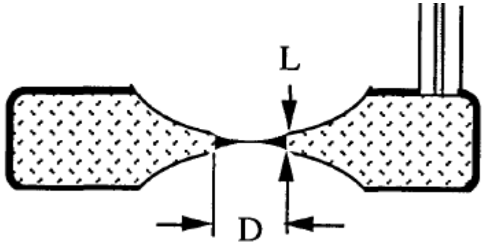
Mysels, 1964



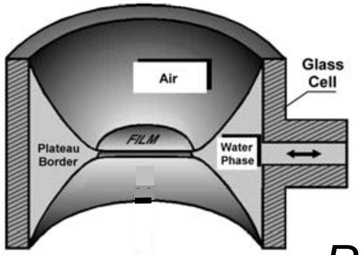
Porous glass for very high pressure

$R_c \sim 10\ \mu m \Rightarrow P_c \sim 5$ kPa

Bergeron, 1992



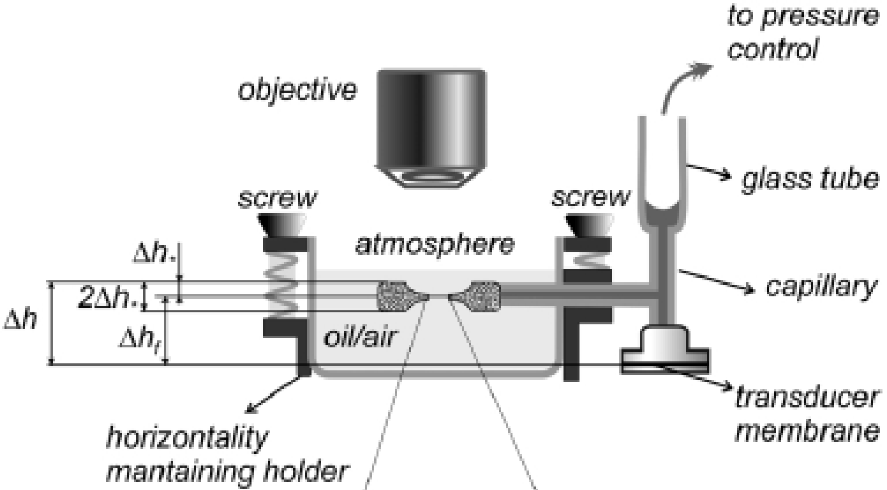
From very low to very high pressure



$$P_c = \frac{2\gamma R_c}{R_c^2 - r_f^2 \cos\varphi}$$

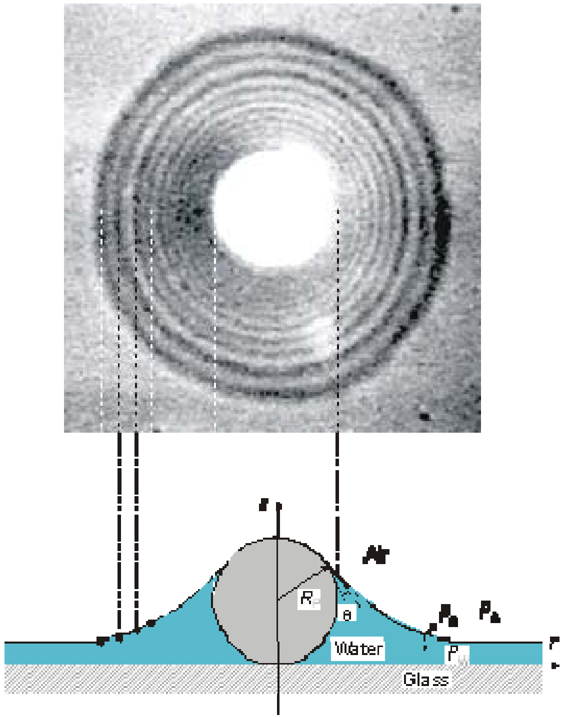
Toshev & Ivanov, 1975

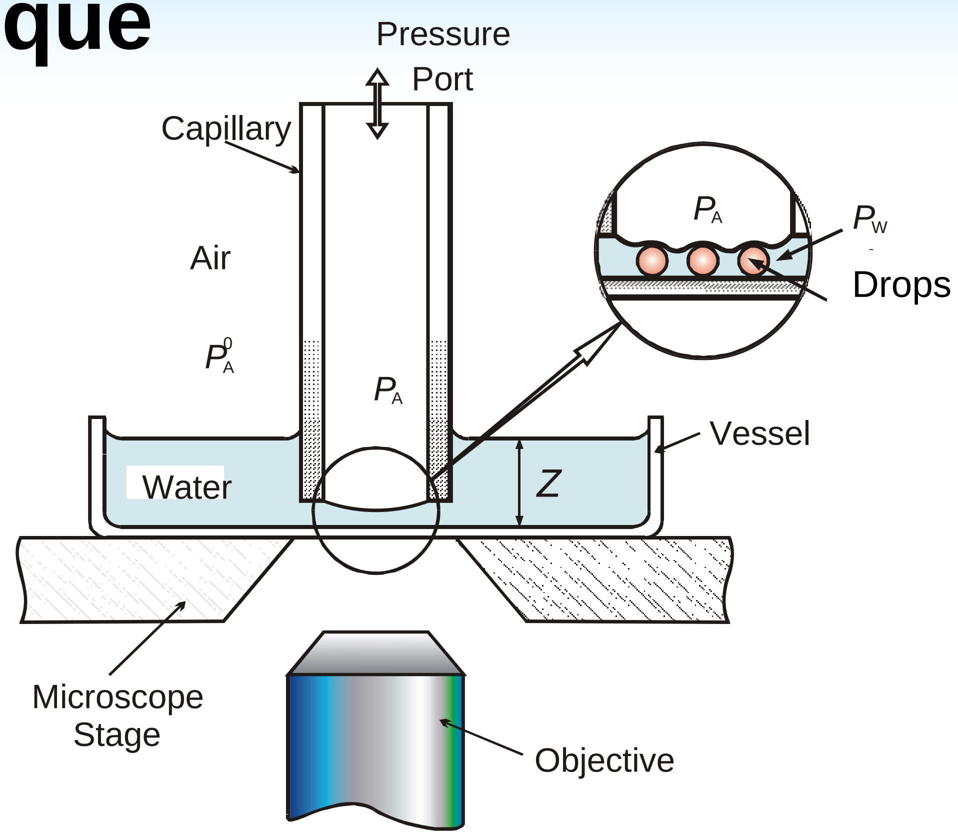
$R_c \sim 1$ mm $\Rightarrow P_c \sim 50$ Pa



Dimitrova et al., 2004 – emulsion films

Film trapping technique

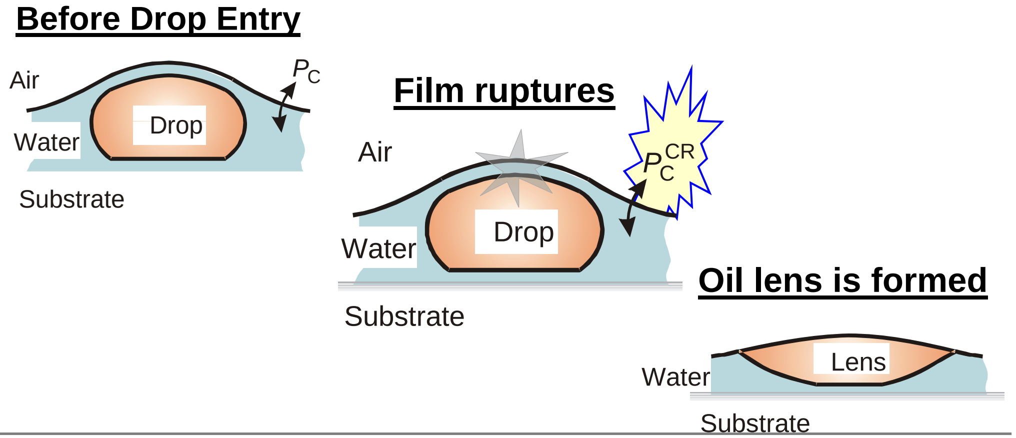




Hadjiiski et al. 1996 – contact angle of micronsized particles

Ivanov et al. 1998 - energy of adhesion of human T cells

Hadjiiski et al 2001, 2002 - entry barriers of antifoam droplets


Before Drop Entry

Film ruptures

Oil lens is formed