Lecture 7

Contact angle phenomena and wetting

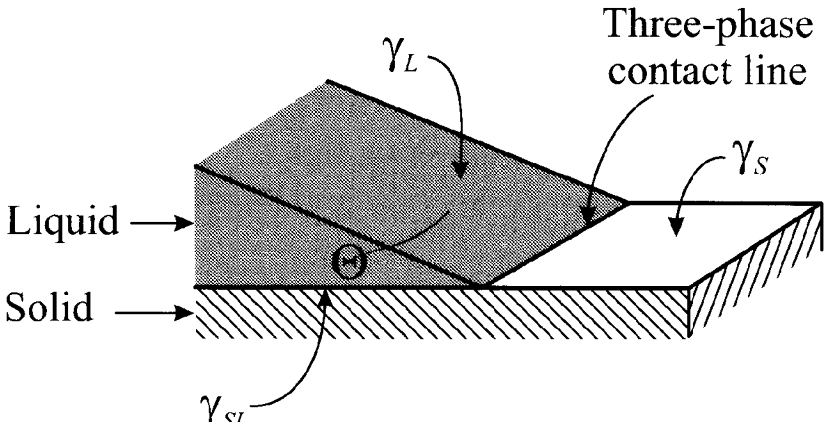
Young's equation

- Drop on the surface
  - complete spreading
  - Establishing finite contact angle

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL}$$

$\gamma_S - \gamma_{SL} > 0$ partial wetting

$\gamma_S - \gamma_{SL} < 0$ no wetting



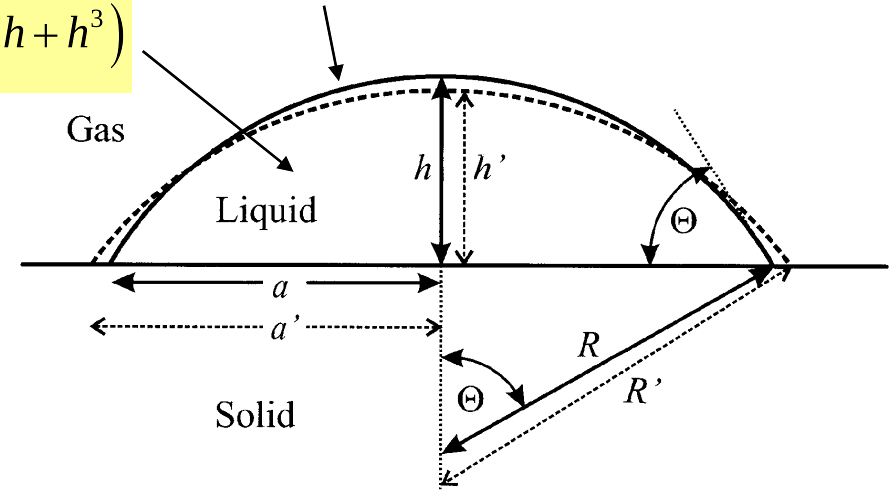
Young’s equation

- Derivation from the equilibrium condition

$$dG = \left(\gamma_{SL} - \gamma_S\right) dA_{SL} + \gamma_L dA_L = 0 \qquad \text{at} \qquad dV = 0$$

$$A_L = \pi\left(a^2 + h^2\right)$$

$$V_L = \frac{\pi}{6}\left(3a^2h + h^3\right)$$



$$dA_{SL} = 2\pi a da$$

$$\left.\begin{aligned} dA_L &= \frac{\partial A_L}{\partial a} da + \frac{\partial A_L}{\partial h} dh = 2\pi a da + 2\pi h dh \\ dV_L &= \frac{\partial V_L}{\partial a} da + \frac{\partial V_L}{\partial h} dh = \pi a h da + \frac{\pi}{2}\left(a^2 + h^2\right) dh = 0 \end{aligned}\right\} \qquad dA_L = 2\pi a \cos\theta da$$

Line tension

- For small drops (<10µm) an additional energy of the wetting line should be taken into account

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL} - \frac{\kappa}{a}$$

- Estimate:
  - at a rim a molecule has 2 bonds less (assuming simple cubic)
  - for cyclohexane:

$$\kappa = \frac{\Delta_{vap} U}{3 N_A a_{mol}} = 3 \cdot 10^{-11}\, {}^{J}\!/_{m}$$

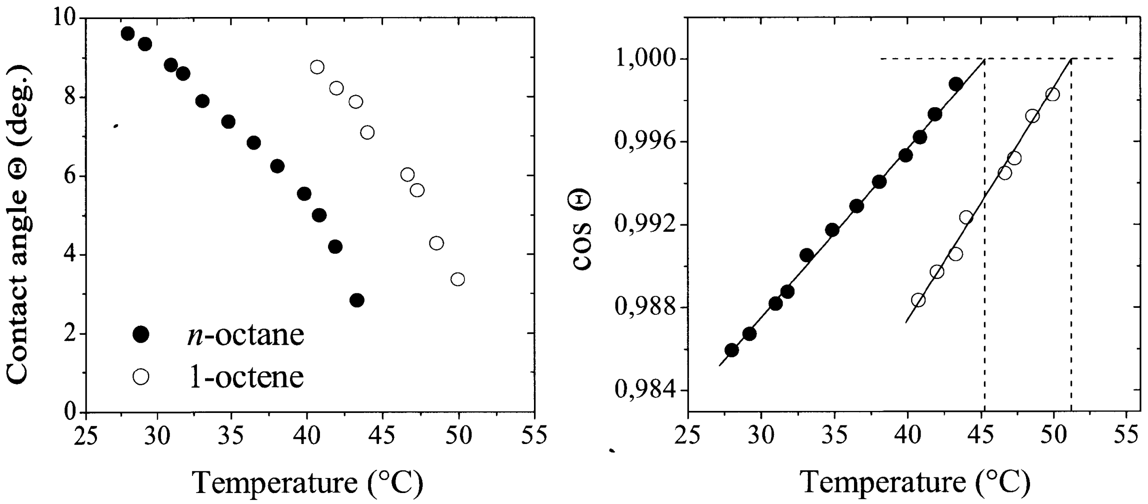
Complete wetting

- If $\gamma_S > \gamma_{SL} + \gamma_L$

  Gibbs free energy is decreased by forming a continuous film on the surface

- Spreading coefficient: $S = \gamma_S - \gamma_{SL} - \gamma_L$

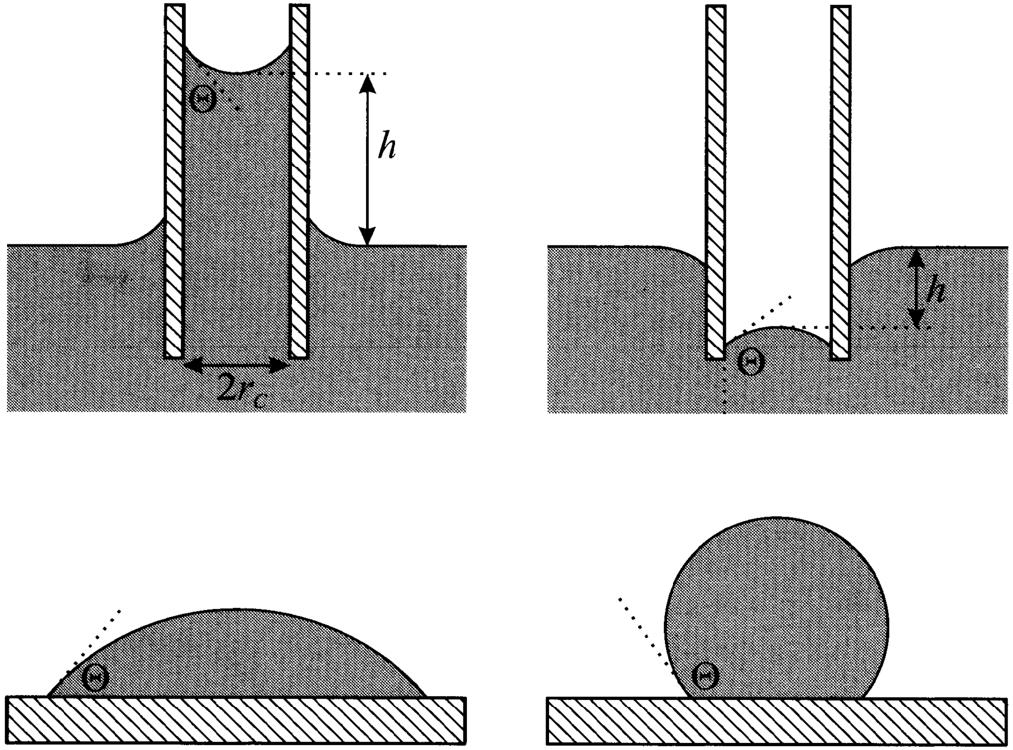
- Contact angle decreases with temperature due to drop in γ_L.
- At wetting temperature Tw, S=0 and complete wetting is reached.



Capillary rise

- If capillary is dipped in a liquid, the liquid meniscus will either rise or lower due to surface tension

$$h = \frac{2\gamma_L \cos\theta}{r_c g \rho}$$

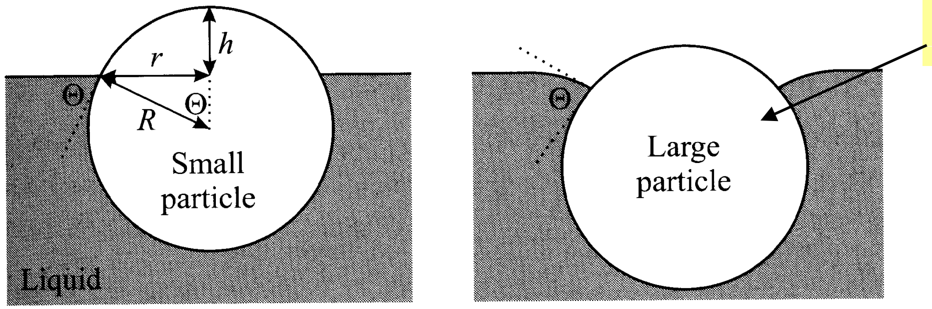


Indeed:

$$dG = -2\pi r_C dh \cdot \left(\gamma_S - \gamma_{SL}\right) + 2\pi r_C{}^2 \rho g h dh$$

Particles at liquid-gas interface

- For small particles (i.e. neglecting the gravity) the equilibrium position at the interface is determined by the surface tension

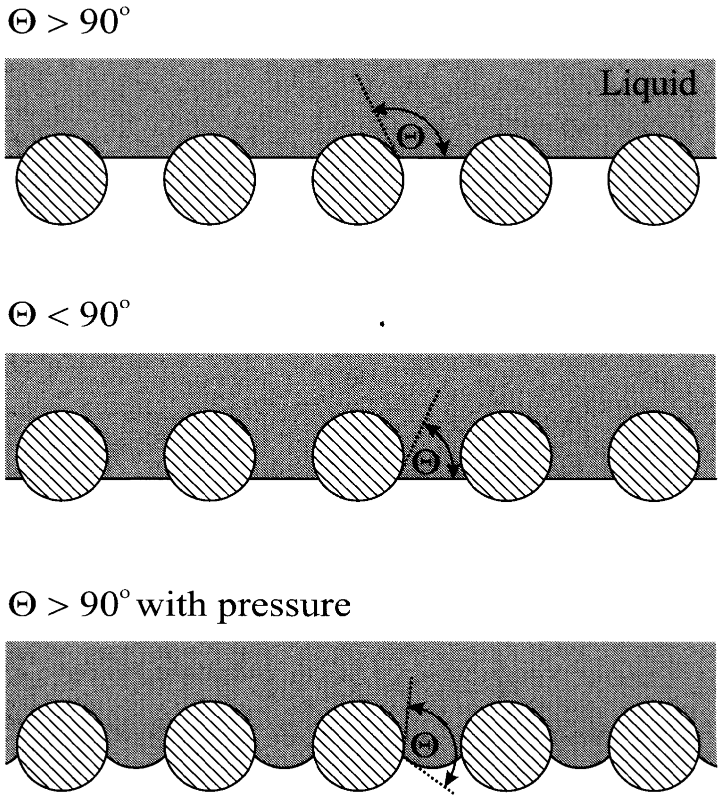


typically >100µm

Works both ways: flotation and stabilization of emulsion by solid particles

Network of fibers

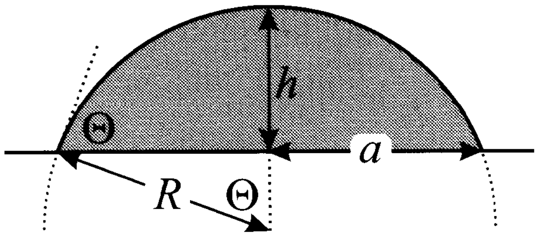
- Network of fibers with final wetting angle will prevent water from passing through; some pressure has to be applied to let it through



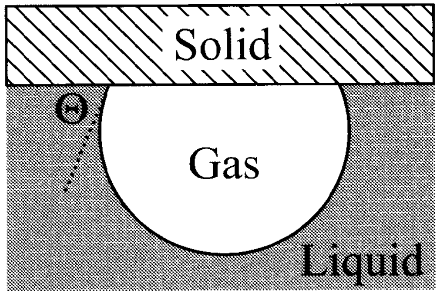
Measurement of the contact angle

- The most common technique is observation of sessile drop with a microscope

$$\tan\left(\frac{\theta}{2}\right) = \frac{h}{a}$$



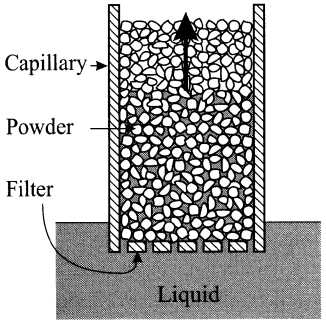
Sessile drop



Sessile bubble.

- or by using a Wilhelmy plate

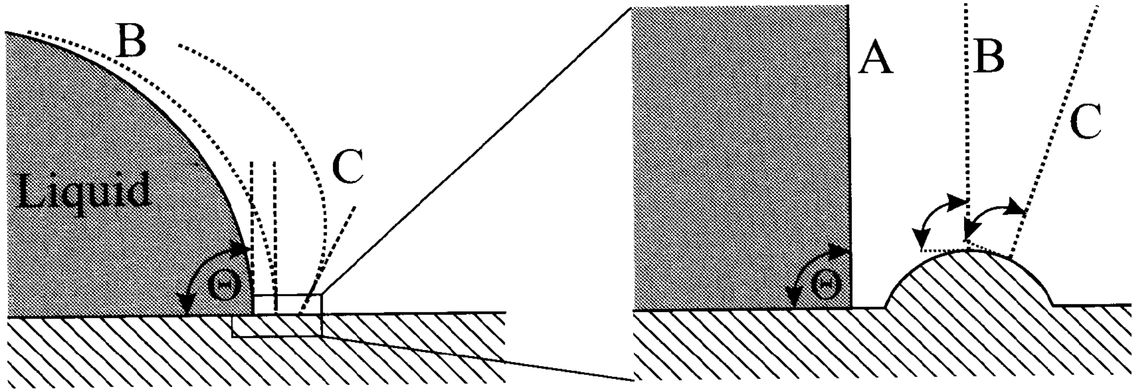
- Wetting properties of powders can be detrmined from capillary rise



- Note, the contact angle depends strongly on the surface contamination

Hysteresis in contact angle measurements

- If we increase or decrease e.g. droplet volume a hysteresis in the angle will be observed
- Usually: $\theta_{adv} > \theta_{rec}$

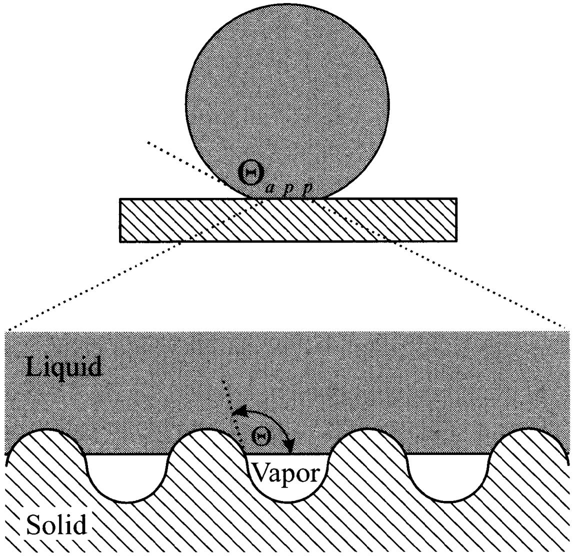


- Causes for the contact angle hysteresis:
  - surface roughness
  - heterogeneity of the surface (resulting in pinning of a droplet)
  - absorbing dissolved substances
  - mechanical deformation of the surface due to surface tension
  - adsorption/desorption of liquid molecules at the interface (work required!)

Surface roughness and heterogeneity

- Roughness increases the actual surface area and therefore decreases the apparent wetting angle for hydrophilic surface and increases it for a hydrophobic surface (**Wenzel law**)

$$\cos\theta_{app} = R_{rough} \cdot \cos\theta$$

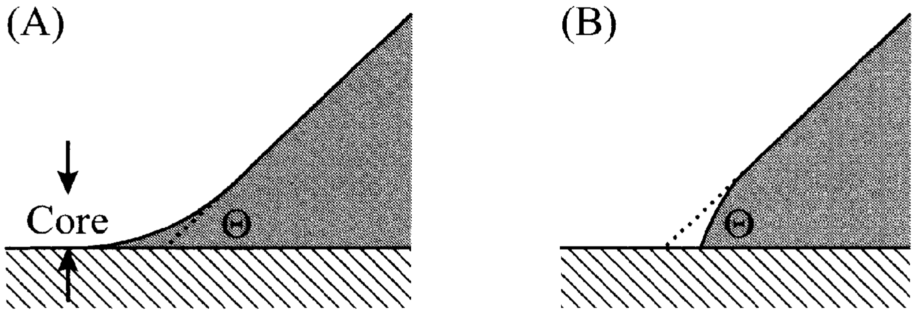


- Heterogeneous surfaces: **Cassie equation**

$$\cos\theta_{app} = f_1 \cdot \cos\theta_1 + f_2 \cdot \cos\theta_2$$

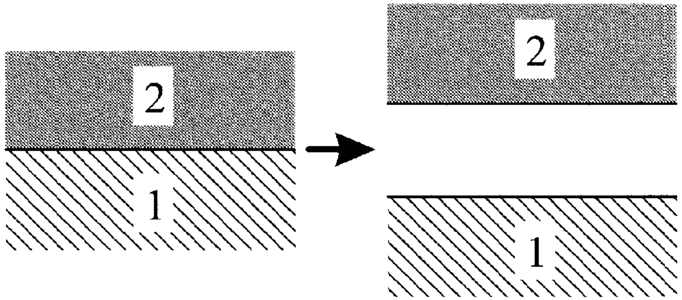
Theory aspects

- Surface tension at solid-air and solid-liquid interfaces strongly depend on the surface preparation (e.g. deformation)
- Experimentally only advancing and receding angles can be determined
- Macroscopic (Young's) contact angle is different from a microscopic one (caused by van der Waals and DL-forces, at distances <100nm)



Theory aspects

- Surface tension at solid-liquid is the most difficult to be accessed by the experiment
- Though it can be estimated based on the properties of clean interfaces (Girifalco, Good and Fowkes model)



$$w = \gamma_1 + \gamma_2 - \gamma_{12}$$

$$w = \frac{A_{12}}{12\pi D_0^2} \approx \frac{\sqrt{A_{11}A_{22}}}{12\pi D_0^2}$$

recall

$$A_H = \frac{3}{4}kT\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \\ + \frac{3h}{4\pi}\int_{v1}^{\infty}\left(\frac{\varepsilon_1(iv) - \varepsilon_3(iv)}{\varepsilon_1(iv) + \varepsilon_3(iv)}\right)\left(\frac{\varepsilon_2(iv) - \varepsilon_3(iv)}{\varepsilon_2(iv) + \varepsilon_3(iv)}\right)dv$$

$$\gamma_{11} = \frac{A_{11}}{24\pi D_0^2} \quad \text{and} \quad \gamma_{11} = \frac{A_{11}}{24\pi D_0^2}$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1\gamma_2}$$

Dynamics of wetting

- Typical measurement geometries

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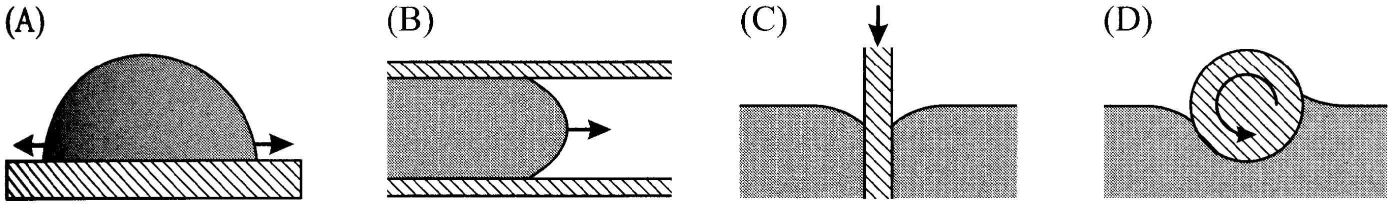
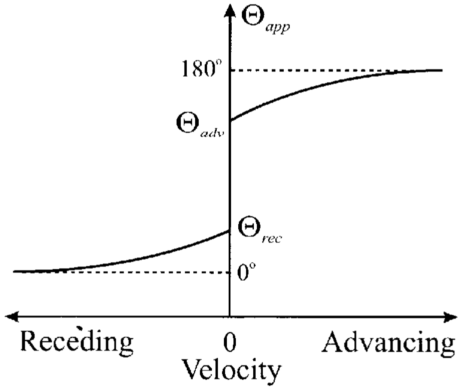


- Apparent contact angle depends also on the speed and viscosity, that can be combined into a
- Capillary number:

$$Ca = \frac{v\eta}{\gamma_L}$$

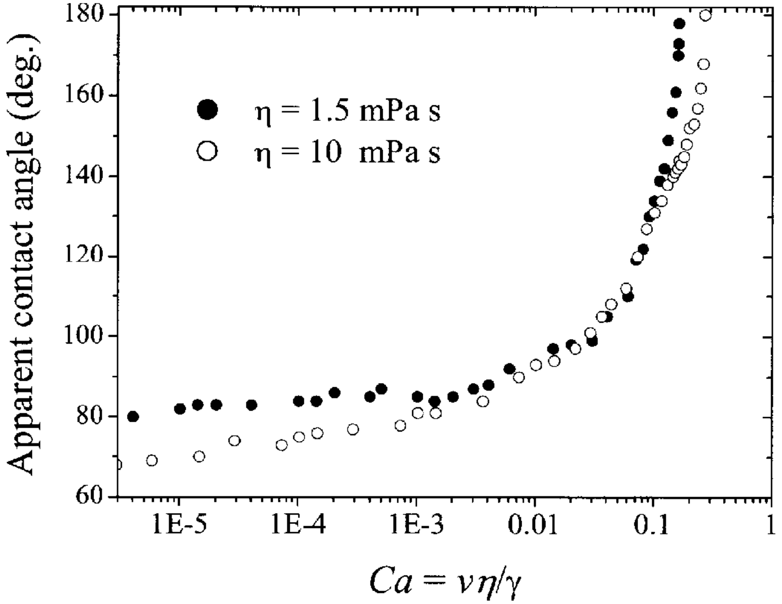
Dynamic of wetting and dewetting

- Apparent contact angle vs. speed



- Apparent advancing angle vs. capillary number for two mixtures of glycerol/water

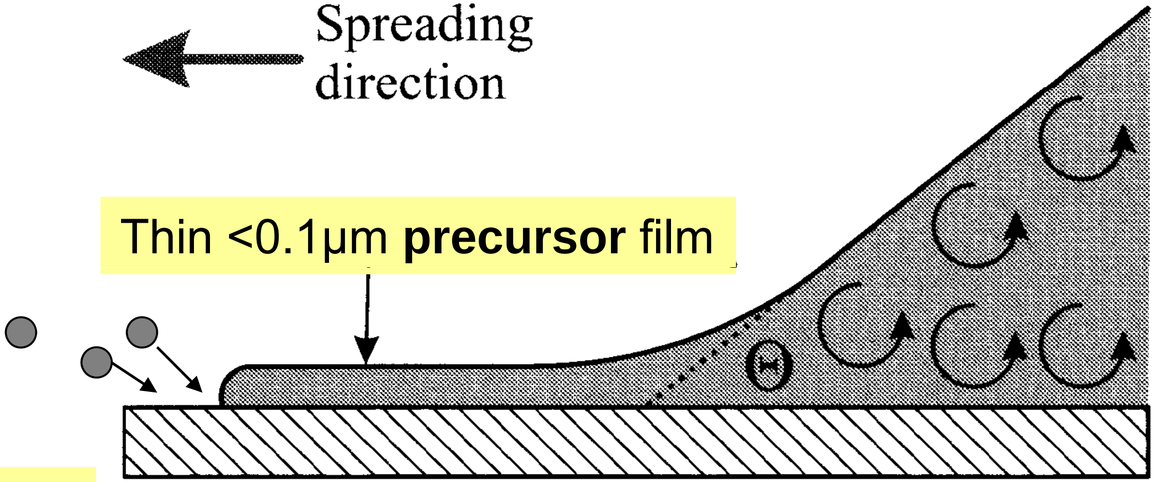
Despite 7 times difference in viscosity, capillary number is a good parameter for both liquids



Dynamics of wetting

- Liquid spreading on a solid surface

movement of the drop. Heat is dissipated by eddies



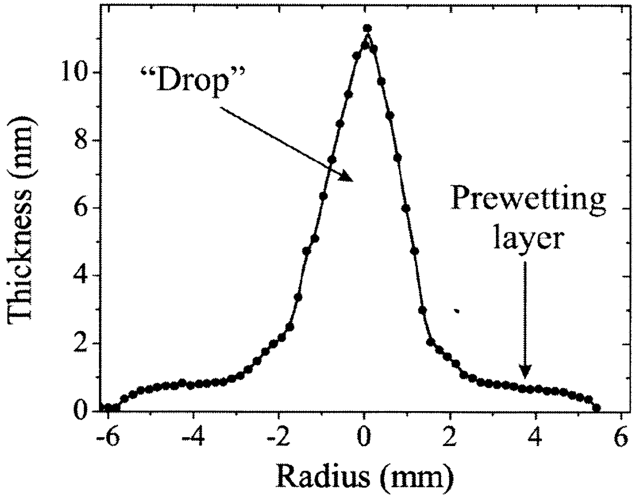
Thin <0.1µm **precursor** film

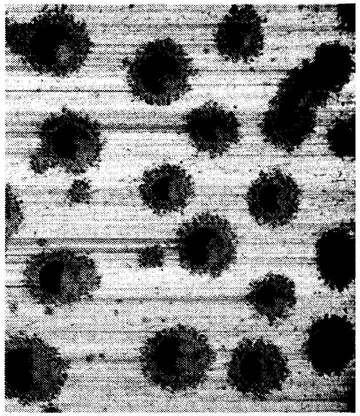
binding of molecules at the front of the precursor film

Dynamics of wetting: examples

- Spreading of PDMS drops on Si surface

Ellipsometer profile, 19h after deposition:

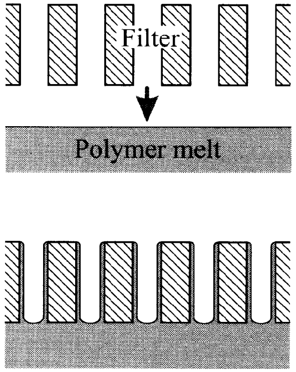


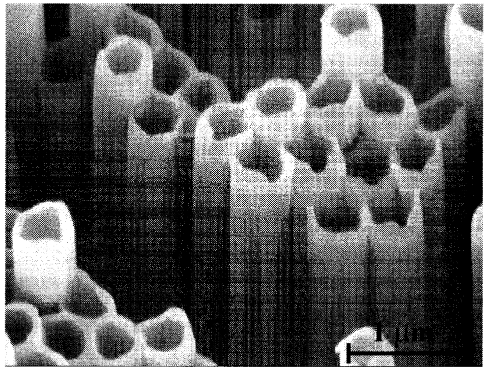


AFM image of PDMS drops on Si surface

- Fabrication of polymer nanotubes using precursor film

Brief dipping of the alumina filter in a polystyrol melt

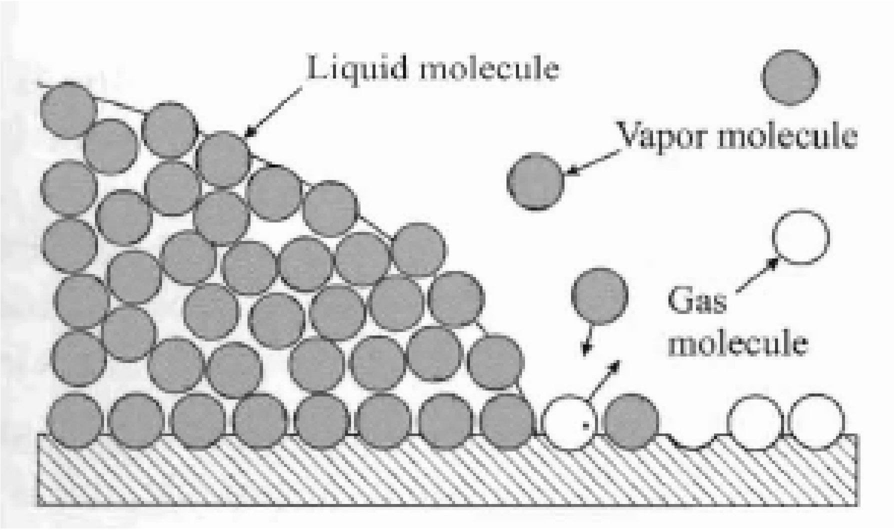




SEM image of the nanotubes (scale 1µm)

Dynamics wetting: mechanism

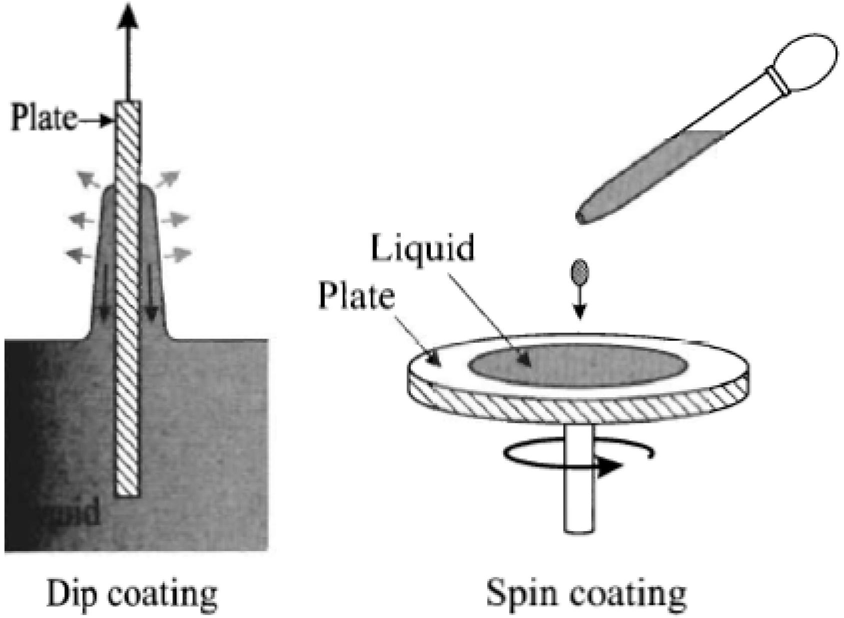
- The wetting kinetics is determined by absorption of the precursor film molecules e.g. finding the binding sites and displacing the gas molecules
- Maximum wetting speed and minimum dewetting speed can be predicted based on the modelling (e.g. for water v_{max}=5-10 m/s



Polymer deposition and Dewetting

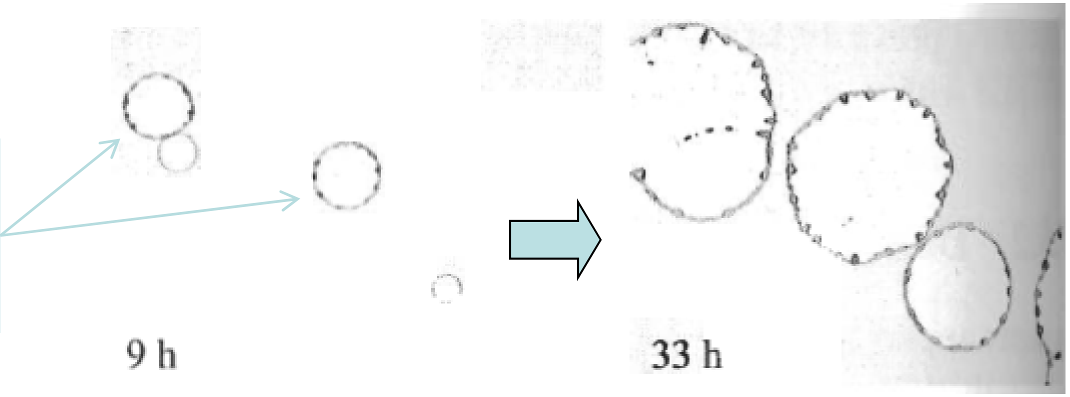
- Many films are metastable or stable above certain thickness

- polymers are typically deposited either by **dip or spin coating**
- if wetting angle θ=0, the film is thermodynamically stable
- if wetting angle θ>0, the film is metastable and the holes will be formed spontaneously above the glass transition temperature



Dip coating

Spin coating



spontaneous formation of holes

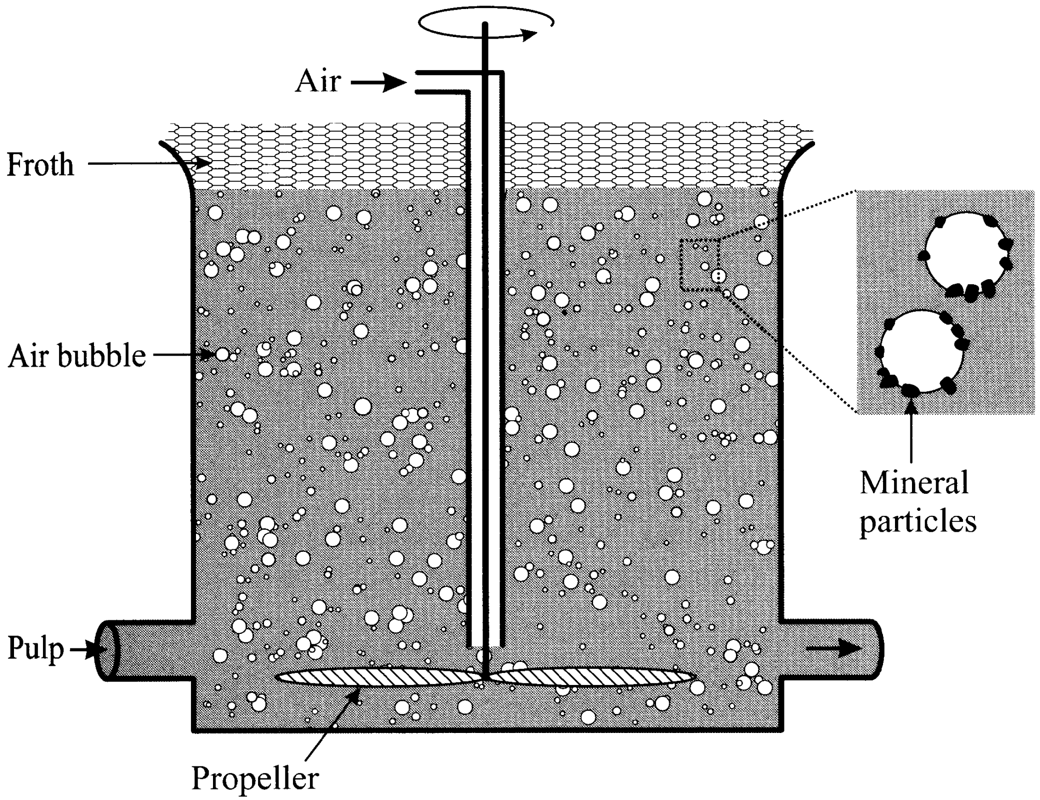
dewetting of a 28nm polystyrene film on Si at 121 ºC

Flotation

- Flotation is a method to separate solid particles from each other based on their wetting properties

Technology

- crushing into small particles (<0.1mm) and mixing with water (pulp)
- bubbling air through
- the higher the wetting angle the better particles attach to a bubble
- specifically adsorbed surfactants (”collectors”) can be used to improve efficiency

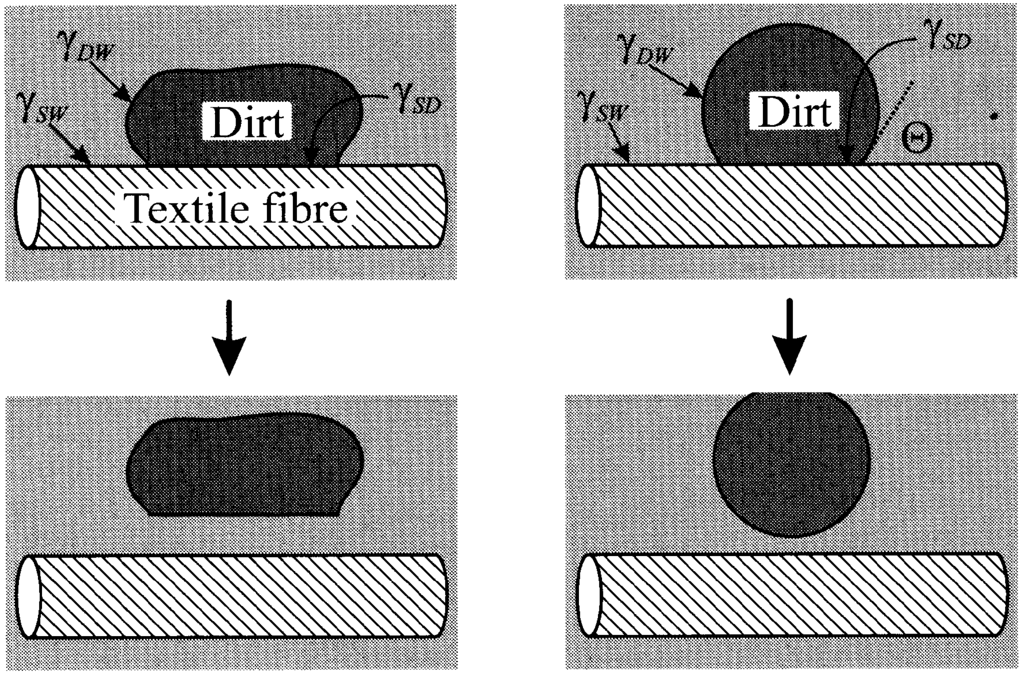


Detergency

- Detergency: theory and praxis of removing foreign material from solids by surface-active substrates

Mechanism:

- Dirt-Solid interface is replaced by Dirt-Water and Water-Solid interfaces after addition of detergent
- Dirt particles are suspended in water preventing aggregation and flocculation (e.g. electrostatically)

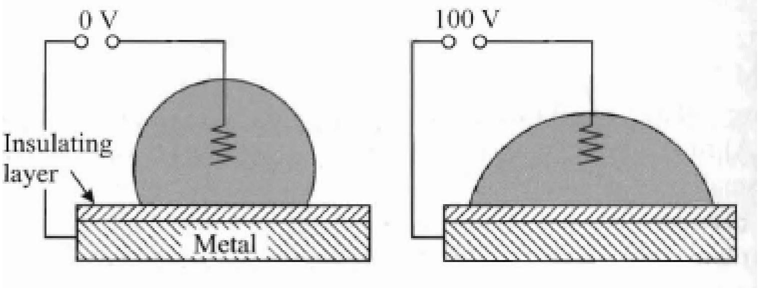


$$\Delta G = A(\gamma_{DW} + \gamma_{SW} - \gamma_{SD}) \leq 0$$

$$\gamma_{SD} \leq \gamma_{DW} + \gamma_{SW}$$

Adjustable wetting

- Electrowetting



$$\cos\theta = \cos\theta_0 + \frac{\varepsilon\varepsilon_0 U^2}{2h\gamma_L}$$

- Photoswitching of hydrophobic/hydrophilic state (e.g. azobenzene)

- Electrical field controlled conformation of SAM layer

Problems

End of chapter problems:

- ch.7.1
- ch.7.2
- ch.7.3