Surfaces and Interface Effects

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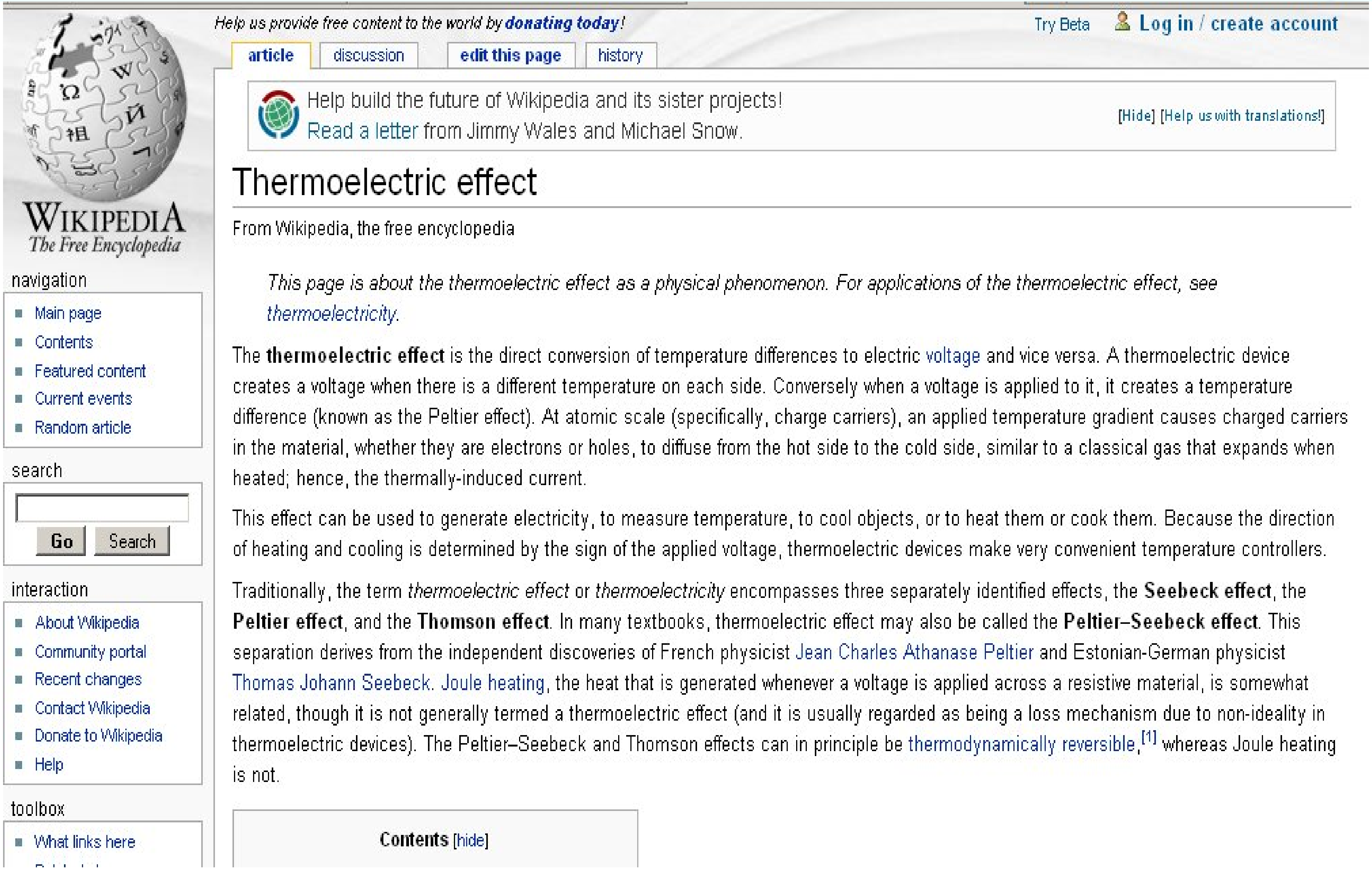
Course Website: **nanoHUB.org**
Compass.illinois.edu

About Final Project

- You are asked to create an entry of nanotechnology topic on Wikipedia

- Recommended Contents:
  - Background and History
  - Basic Principles
  - Size effect
  - Materials, Applications
  - Recent advancements
  - Links

Wikipedia Example



Help build the future of Wikipedia and its sister projects!
Read a letter from Jimmy Wales and Michael Snow.

Thermoelectric effect

From Wikipedia, the free encyclopedia

This page is about the thermoelectric effect as a physical phenomenon. For applications of the thermoelectric effect, see thermoelectricity.

The **thermoelectric effect** is the direct conversion of temperature differences to electric voltage and vice versa. A thermoelectric device creates a voltage when there is a different temperature on each side. Conversely when a voltage is applied to it, it creates a temperature difference (known as the Peltier effect). At atomic scale (specifically, charge carriers), an applied temperature gradient causes charged carriers in the material, whether they are electrons or holes, to diffuse from the hot side to the cold side, similar to a classical gas that expands when heated; hence, the thermally-induced current.

This effect can be used to generate electricity, to measure temperature, to cool objects, or to heat them or cook them. Because the direction of heating and cooling is determined by the sign of the applied voltage, thermoelectric devices make very convenient temperature controllers.

Traditionally, the term *thermoelectric effect* or *thermoelectricity* encompasses three separately identified effects, the **Seebeck effect**, the **Peltier effect**, and the **Thomson effect**. In many textbooks, thermoelectric effect may also be called the **Peltier–Seebeck effect**. This separation derives from the independent discoveries of French physicist Jean Charles Athanase Peltier and Estonian-German physicist Thomas Johann Seebeck. Joule heating, the heat that is generated whenever a voltage is applied across a resistive material, is somewhat related, though it is not generally termed a thermoelectric effect (and it is usually regarded as being a loss mechanism due to non-ideality in thermoelectric devices). The Peltier–Seebeck and Thomson effects can in principle be thermodynamically reversible,[1] whereas Joule heating is not.

Contents [hide]

Proposal Presentation

- Date: Oct 12-Oct 16
- Every one is given 15 minutes for your presentation:
  - What's your topic?
  - Why it is interesting?
  - What's the nanoscience principle?
  - Who are the heros in this area?
  - What would be the potential applications?

Organization of Coming Lectures

- Coupled Charge-Mass Transport in Fluid
  - Electrokinetic Phenomena
- **Surface and Interface Interactions**
  - Contact Angle, Effect on Melting and Condensation, Wetting on surface textures
- Friction, Lubrication and Adhesion

Conduction of Ions in Fluids

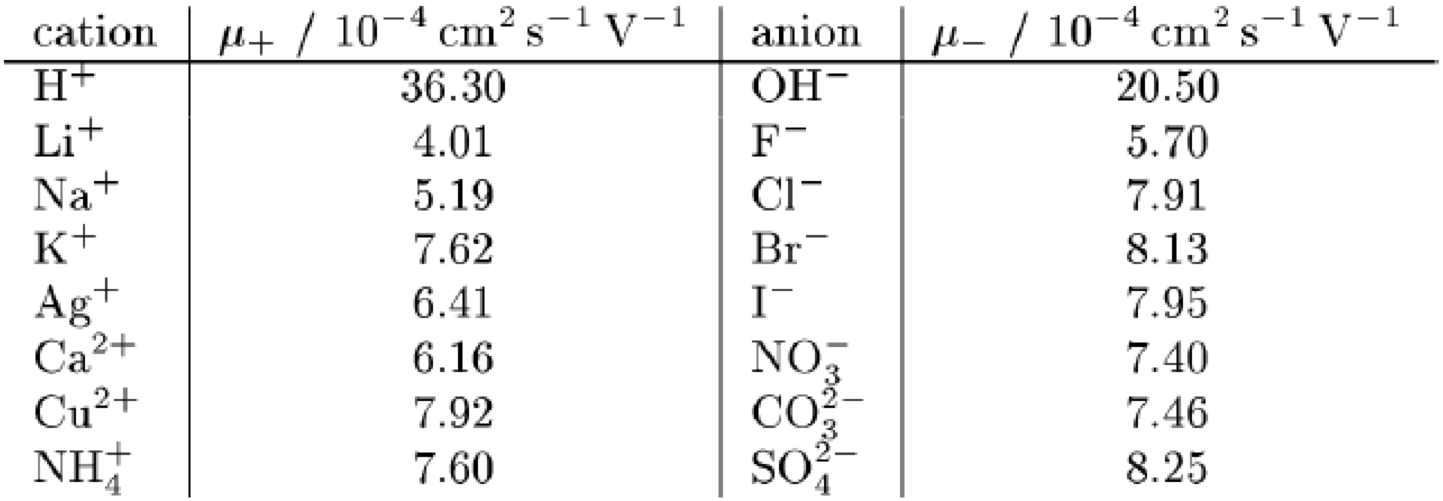
$$J_{ion} = \frac{\partial}{\partial z}\left(eZ\frac{k_B T n_{ion}\langle\tau\rangle}{m_{ion}}\right) + F_z\frac{eZ n_{ion}\langle\tau\rangle}{m_{ion}}$$

Mobility:

$$\mu_{ion} = \frac{eZ\langle\tau\rangle}{m_{ion}}$$

Conductivity:

$$\sigma_{ion} = eZ\mu_{ion}n_{ion}$$



cation	μ_+ / $10^{-4}\,\mathrm{cm}^2\,\mathrm{s}^{-1}\,\mathrm{V}^{-1}$	anion	μ_- / $10^{-4}\,\mathrm{cm}^2\,\mathrm{s}^{-1}\,\mathrm{V}^{-1}$
H^+	36.30	OH^-	20.50
Li^+	4.01	F^-	5.70
Na^+	5.19	Cl^-	7.91
K^+	7.62	Br^-	8.13
Ag^+	6.41	I^-	7.95
Ca^{2+}	6.16	NO_3^-	7.40
Cu^{2+}	7.92	CO_3^{2-}	7.46
NH_4^+	7.60	SO_4^{2-}	8.25

Table 2.1. Ionic mobilities μ_i in water solution at $T = 298\,\mathrm{K}$

From: Jens Ducrée, http://www.myfluidix.com/

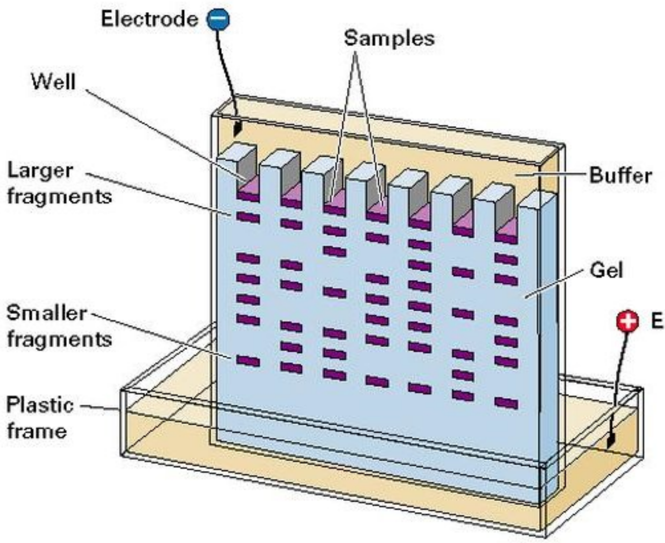
Applications of Ion Migration

Gel Electrophoresis:

- Separation of larger molecules with smaller ones by their mobility in gels

- Competing with diffusion so low diffusivity preferred

- For 15-20 cm long gel, the separation time is about hours



http://www.cbs.dtu.dk/staff/dave/roanoke/genetics980211.html

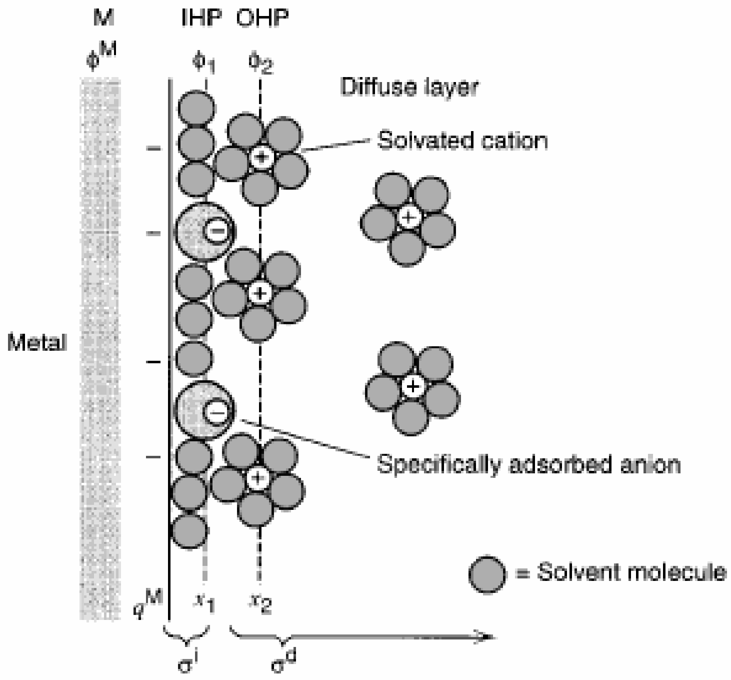
$$\mu_{ion} = \frac{eZ\langle\tau\rangle}{m_{ion}}$$

Electric Double Layer

Poisson Equation due to space charges

$$\nabla^2 U(\vec{r}) = \sum \frac{e}{\varepsilon} Z_{ion} c_{ion}(\vec{r})$$

$$\sum e Z_{ion} c_{ion}(\vec{r}) = eZ(n_+ - n_-)$$



Presence of space charges due to thermal excitation:

$$c_{ion} = c_0 \exp(-eZ_{ion} U(\vec{r})/k_B T)$$

Debye Length

$$\lambda_D = \sqrt{\frac{k_B T / 2}{e^2 \sum c_i Z_i^2 / \varepsilon\varepsilon_0}}$$

Thermal Energy

Electrostatic Energy density

- A rough measure of the characteristic length for potential decay

- Calculated with the ionic strength of the bulk fluid

E.G. 1M HCl @300K:

λ_D = 13.8 nm

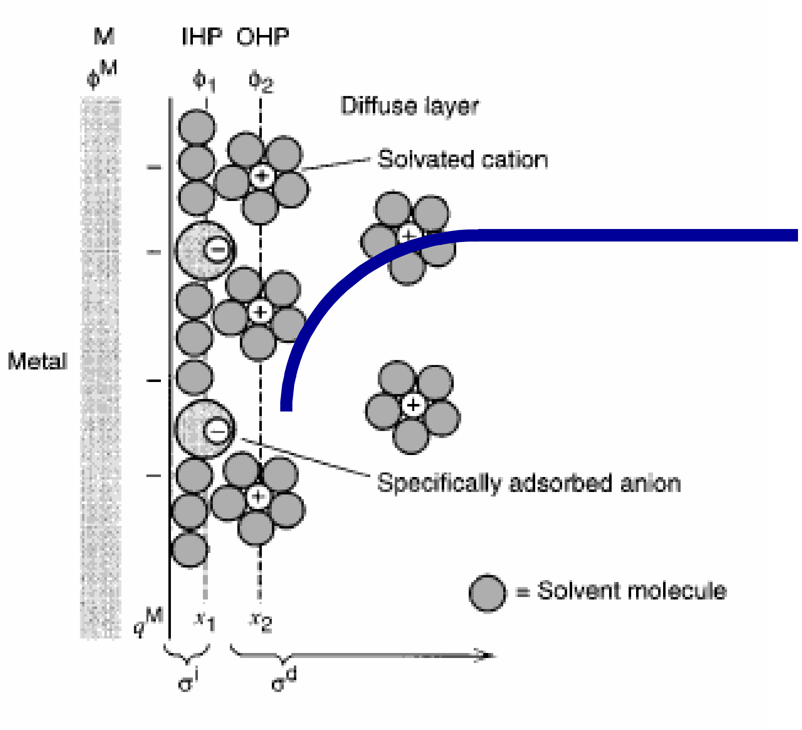
1nM HCl@300K:

λ_D = 435 μm

Electro-Osmotic Effect

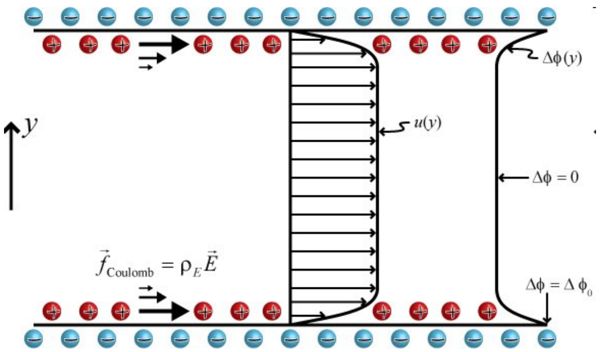
- In the diffuse layer, there is a net charge that moves according to external field

- Electric field induced ion flow also moves the fluid, following a flat velocity profile (plug flow)



$$v_{EOF} = \frac{zeE}{\eta}\lambda c_0$$

Electro-Osmotic Flow



www.kirbyresearch.com/.../etc/textbook/mae28.jpg

Plug-flow profile:

Very important for mixing and pumping in microdevices

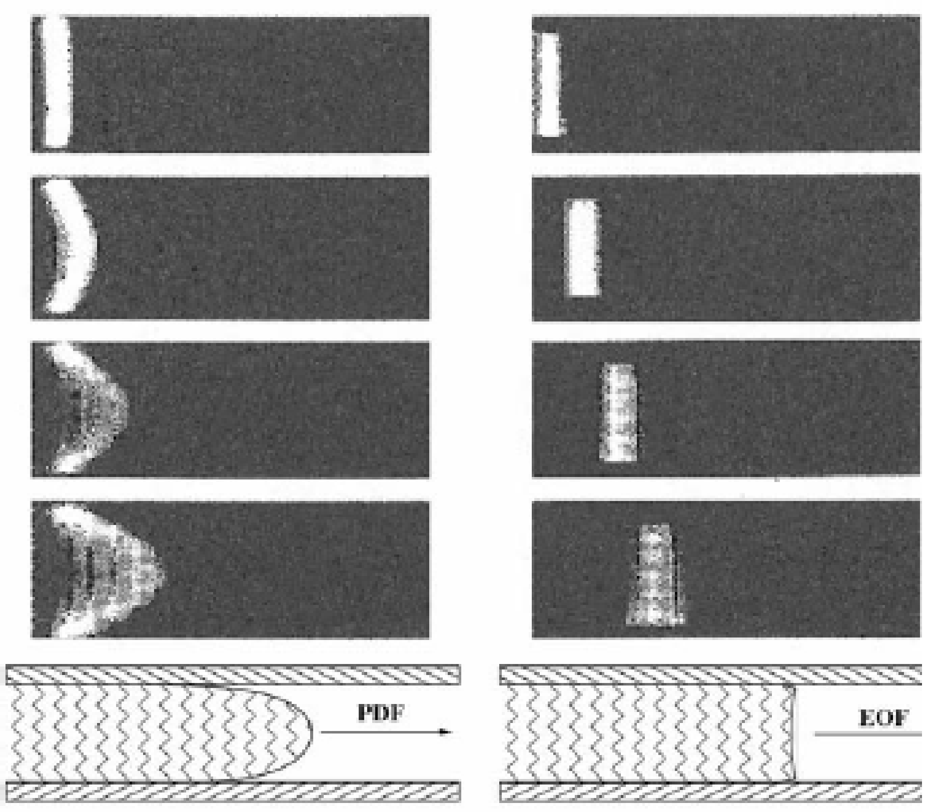


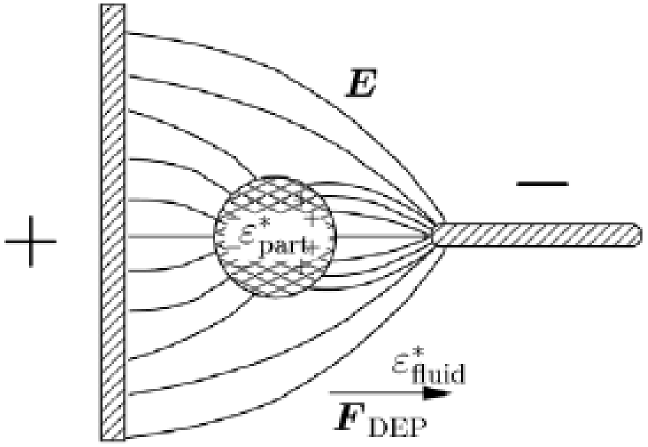
Fig. 3.42. Velocity profiles in pressure-driven and electroosmotic flow and expe mental observations recorded in 33-ms time frames

From: Jens Ducrée, •http://www.myfluidix.com/

Dielectrophoresis, etc

- Particles become polarized under electric field

- When E field is not uniform, there is a net force on particle



$$F \propto \underbrace{\alpha(\omega)}_{\text{Frequency dependent polarizability}}\underbrace{V}_{\text{Particle volume}}\underbrace{(\nabla E^2)}_{\text{E field gradient}}$$

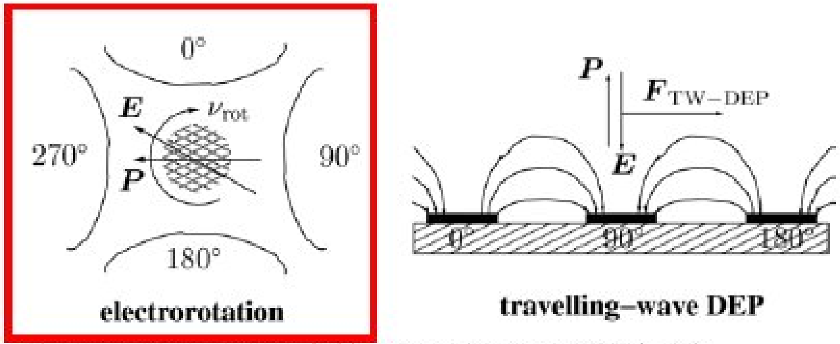
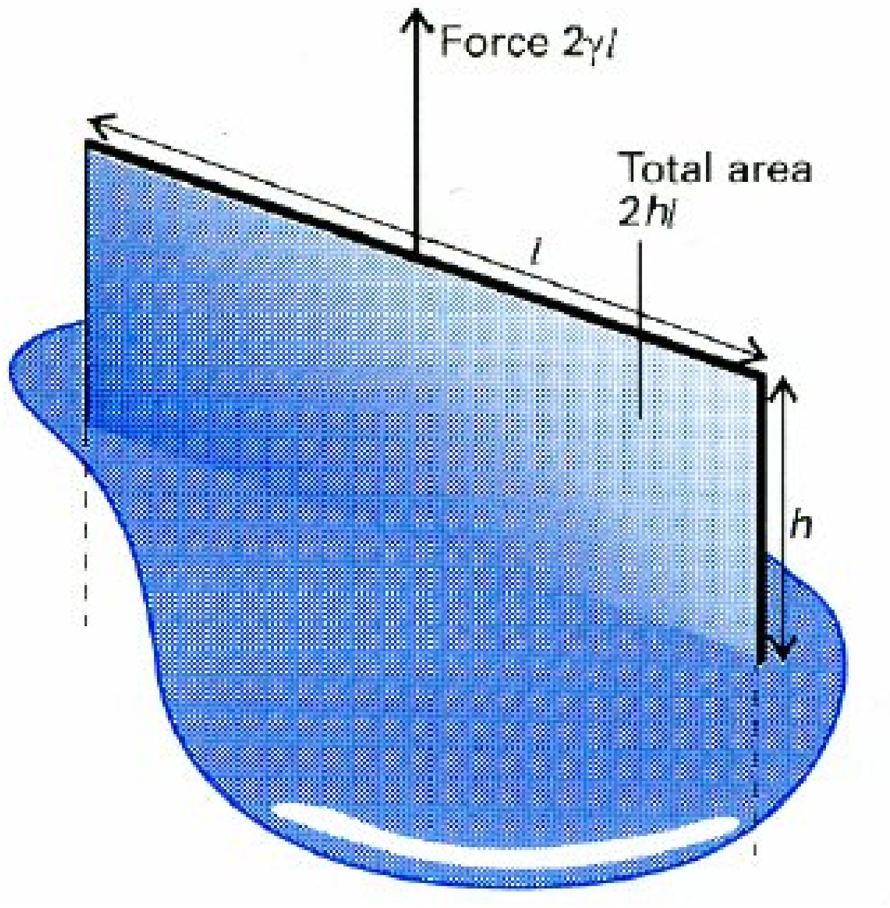


Fig. 3.47. Electrorotation (left) and travelling wave DEP (right)

From: Jens Ducrée, •http://www.myfluidix.com/

Surface and Surface Tension

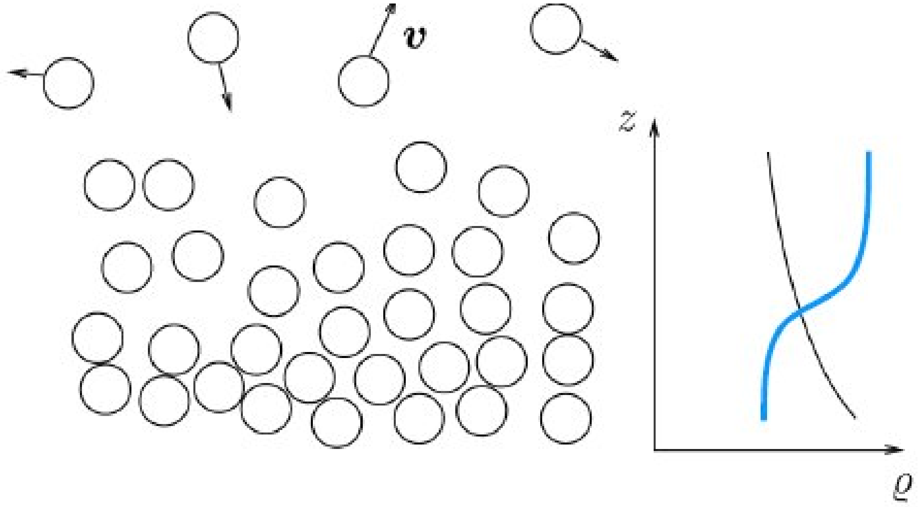
- Surface tension: a thermodynamic property



- $dG=\gamma dA$, $dF=\gamma dl$
- Unit : J/m^2 or N/m

Surface tension is generally restricted to liquid; Surface free energy generally applies to liquids and solids

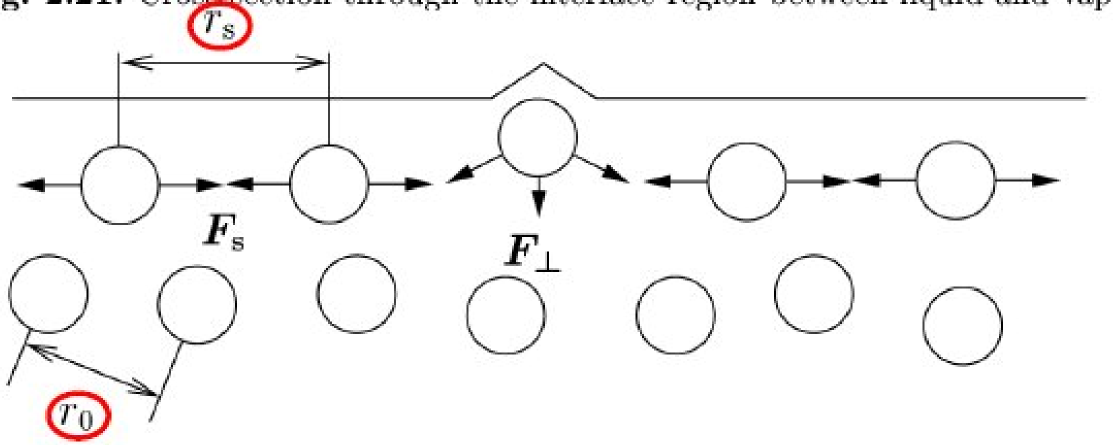
Molecular Picture of Surface Tension



Density distribution

Surface Potential

Fig. 2.21. Cross section through the interface region between liquid and vapor

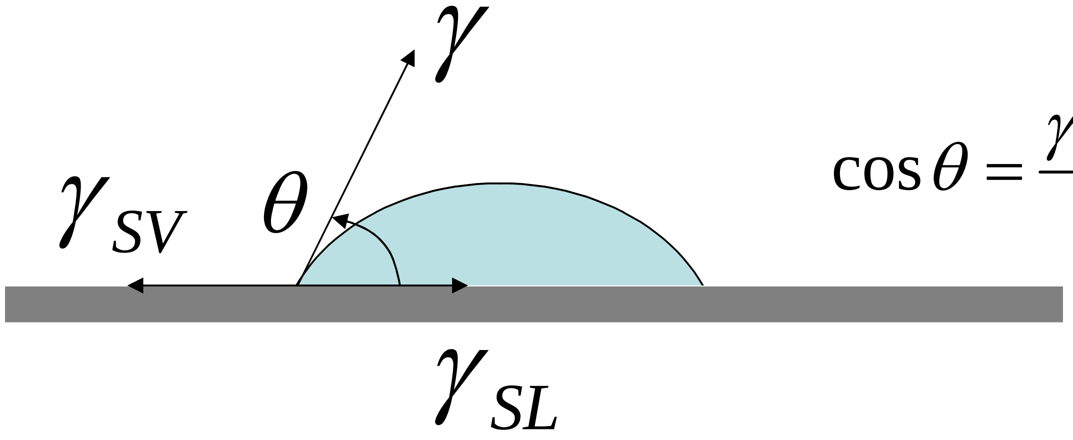


Surface forces

Fig. 2.22. Force $F_\perp$ on molecule moved perpendicular to surface plane results from perpendicular components $F_\perp$ of forces F_s acting in surface plane

From: Jens Ducrée, http://www.myfluidix.com/

Contact Angle: Young's Equation



$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma}$$

- Young's equation to relate the surface forces at the three-phase contact line to the apparent contact angle for an ideal surface.

$\theta =$ Young's angle for a smooth surface

where

the interfacial energies

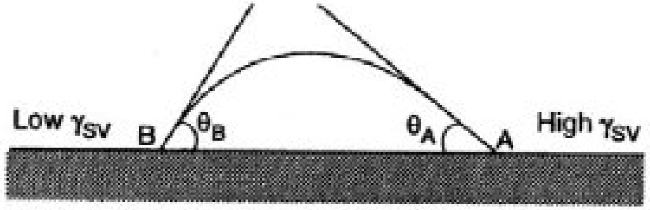
γ_{SV} : solid - vapor

γ_{SL} : solid - liquid

γ : liquid - vapor

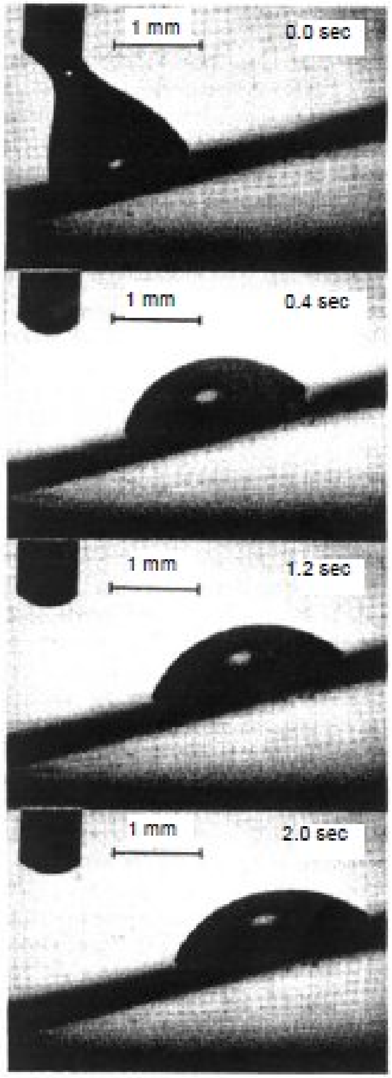
How to Make Droplet Run Uphill

Produce a gradient in water wettability



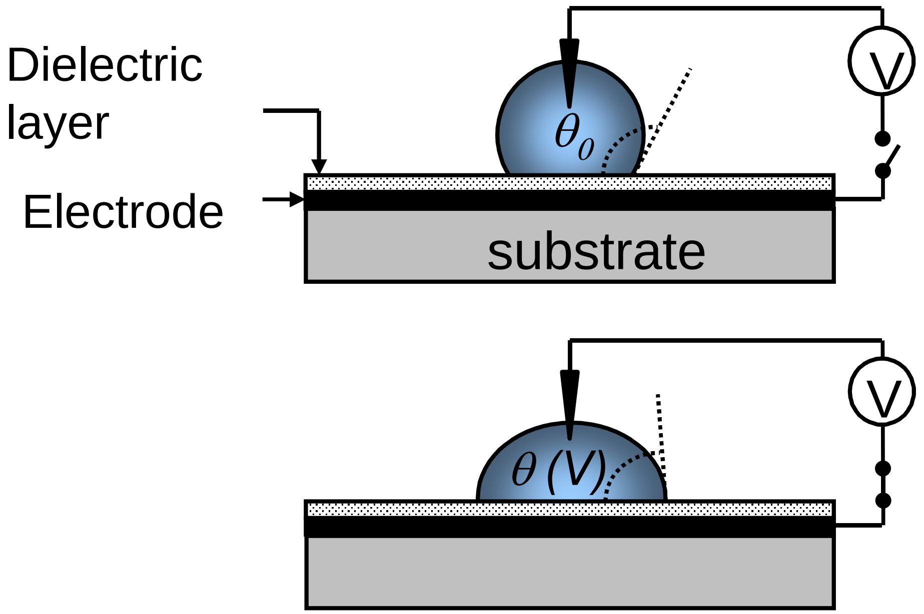
$$dF = [(\gamma_{sv} - \gamma_{sl})_A - (\gamma_{sv} - \gamma_{sl})_B]dx$$
$$= \gamma_{lv}\,(\cos\theta_A - \cos\theta_B)\,dx$$

Chaudhury, M. K.; Whitesides, G. M. *Science* **1992**, *256*, 1539.



Electro- wetting

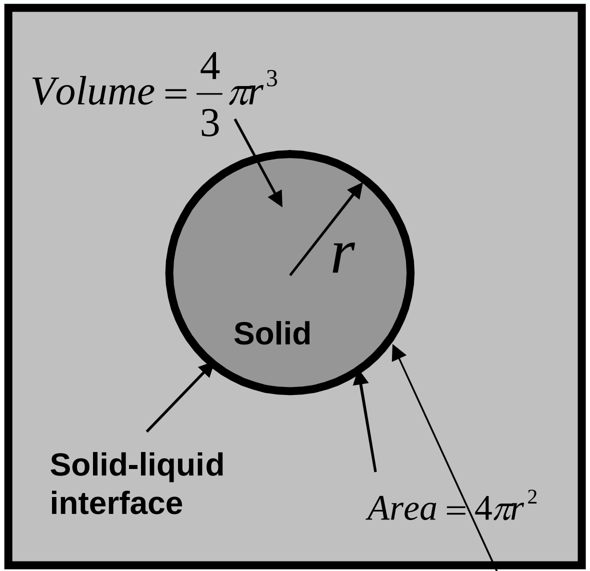
An electrostatic energy build up on the solid-liquid interface (Electric double layer):



$$\gamma_{SL} = \gamma_{SL,0} + \frac{1}{2}CV^2$$

$$\boxed{\cos\theta(V) = \cos\theta_o - \frac{1}{2}\frac{\varepsilon_o\varepsilon}{\gamma\ t}V^2}$$

Effect of Surface Energy: Nucleation/Melting



Volume (Bulk) Free Energy – stabilizes the nuclei (releases energy)

$$\Delta G_V = \frac{4}{3}\pi r^3 \Delta G_\upsilon$$

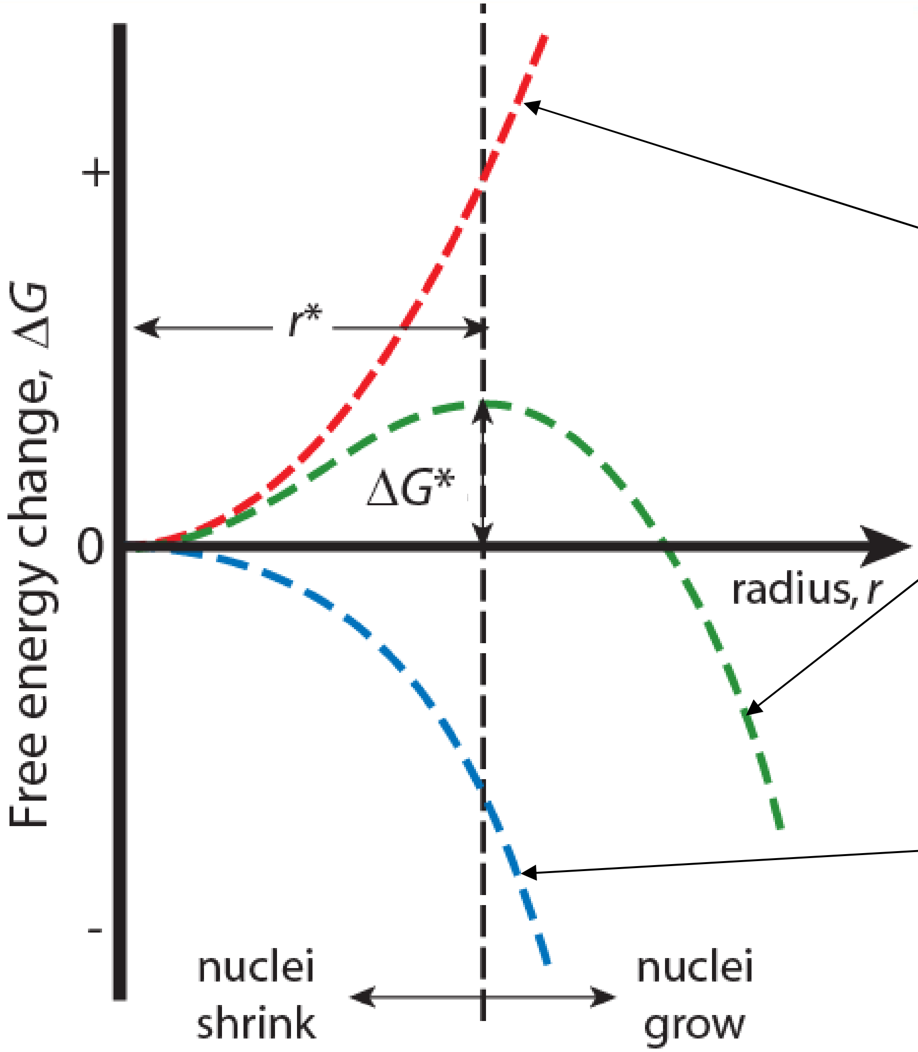
$$\Delta G_\upsilon = \frac{\text{volume free energy}}{\text{unit volume}}$$

Surface Free Energy- destabilizes the nuclei (it takes energy to make an interface)

$$\Delta G_S = 4\pi r^2 \gamma$$

γ = surface tension between solid-liquid interface

Surface Effect & Homogeneous Nucleation



Surface Free Energy-

$$\Delta G_S = 4\pi r^2 \gamma$$

γ = surface tension

ΔG_T = Total Free Energy

$= \Delta G_S + \Delta G_V$

Volume (Bulk) Free Energy

$$\Delta G_V = \frac{4}{3}\pi r^3 \Delta G_\upsilon$$

r^* = critical nucleus: nuclei < r^* shrink; nuclei>r^* grow (to reduce energy)

Adapted from Fig.10.2(b), *Callister 7e.*

Homogeneous Nucleation (Cont')

The total energy change

$$\Delta G = -\frac{4}{3}\pi \mathrm{r}^3 \, \Delta \, \mathrm{G}_\mathrm{v} + 4\pi \, \mathrm{r}^2 \, \gamma$$

Find critical radius for maximum free energy change

$$\frac{d(\Delta G)}{dr} = \frac{4}{3}\pi\Delta G_v(3r^2) + 4\pi\gamma(2r) = 0$$

The newly formed nucleus is stable only when its radius exceeds a critical size

$$\boxed{r^* = -\frac{2\gamma}{\Delta G_v}}$$

And the energy barrier that a nucleation process must overcome

$$\boxed{\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}}$$

Solidification/Melting

$$\boxed{r^* = \frac{-2\gamma T_m}{\Delta H_S \Delta T}}$$

r^* = critical radius

γ = surface free energy

T_m = melting temperature

ΔH_S = latent heat of solidification

$\Delta T = T_m - T$ = supercooling

Note: ΔH_S = strong function of ΔT

γ = weak function of ΔT

$\therefore$ r^* decreases as ΔT increases

For typical ΔT r^* ca. 100Å

Bulk gold melts at 1,064°C.

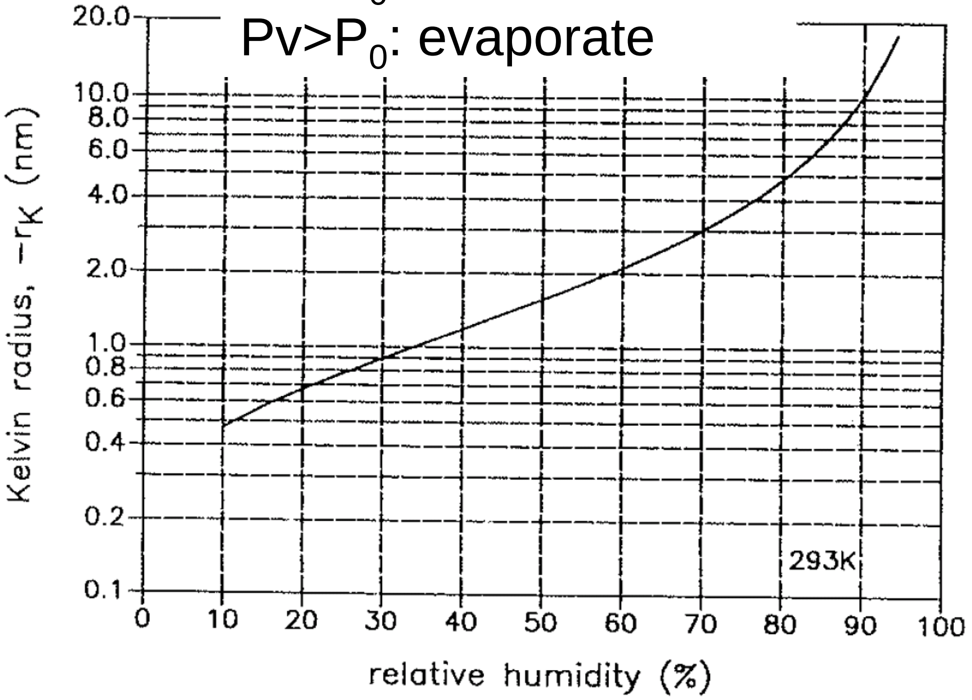
3nm gold nanoparticles melts at 300°C!

Size Effect in Evaporation/ Condensation

Kelvin Equation: The change in vapor pressure due to a meniscus with radius *r* (e.g. in a capillary or over a droplet)

$$\frac{2\gamma}{r} = nk_B T \ln\left(\frac{P_v}{P_0}\right)$$

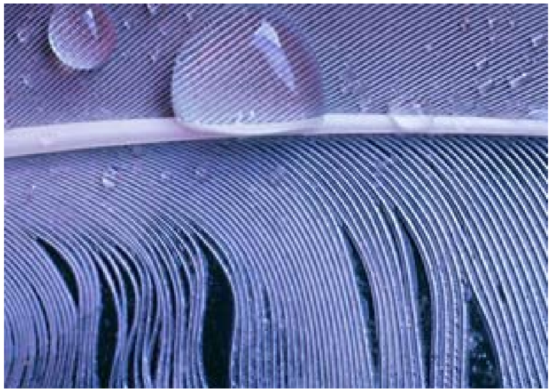
$Pv<P_0$: condense;
$Pv>P_0$: evaporate



- The surface tension of water is γ = 74mN/m at T = 293 K which gives the parameter γ/nkT = 0.54 nm.
- Therefore we obtain for a Kelvin radius of **100 nm (concave),** Pv/P_0 = 0.9.

Wetting on Textured Surfaces

- Nature has provided some water repelling examples from which we can learn.
  - Bird feathers
  - Lotus leaves
  - Water walking insects such as water striders and some types of spiders



http://chemistry.org/

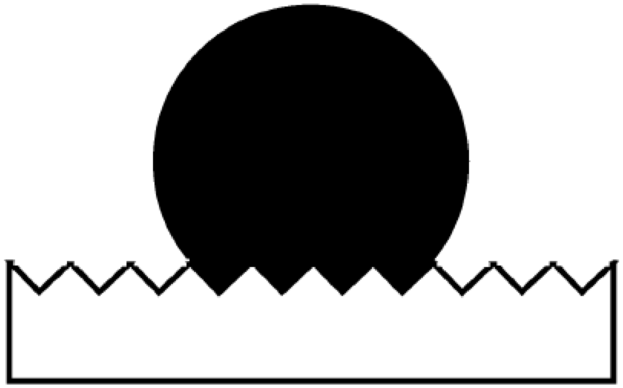
http://www.treehugger.com/files/lotus-leaf.jpg

http://www-math.mit.edu/~dhu/Striderweb/striderweb.html

Wetting on Textures: Wenzel Model

- Wenzel [2] showed that the apparent contact angle for homogeneous systems with surface roughness is modified in the following way:

$$\cos\theta_W = r\cos\theta$$



Marmur, *Wetting on hydrophobic rough surfaces: To be heterogeneous or not to be* [3]

θ_W = Apparent contact angle for a Wenzel drop

$r \equiv \text{surface roughness} = \dfrac{\text{actual surface area}}{\text{geometric surface area}}$

θ = Young's angle for a smooth surface

Illustration of a drop in the Wenzel state on a rough surface; note homogeneous contact area

Inhomogeneous Wetting

- Cassie and Baxter [4] developed the following relation, sometimes referred to as Cassie's Law, to predict the apparent contact angle for heterogeneous systems based on wetted fractional areas

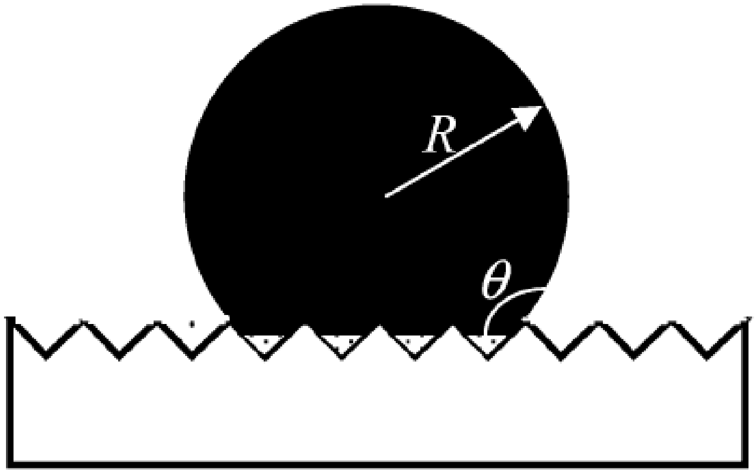
$$\cos\theta_C = \phi_s\left(r_w \cos\theta + 1\right) - 1$$

θ_C = Apparent contact angle for a Cassie drop

ϕ_s = Wetted area fraction on the horizontal projected plane

r_w = Surface roughness of the wetted area

θ = Young's angle for a smooth surface

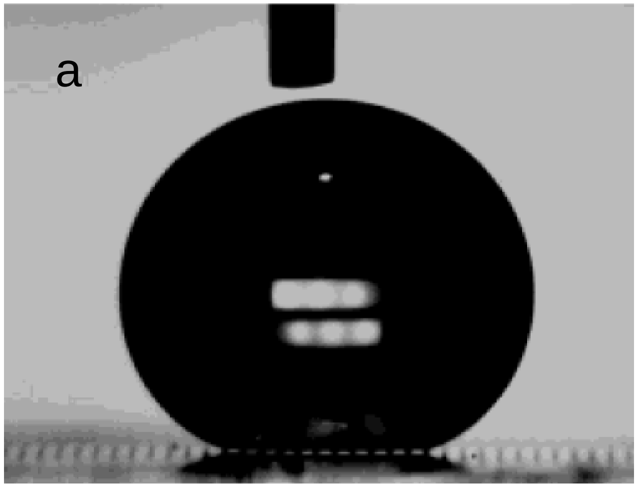


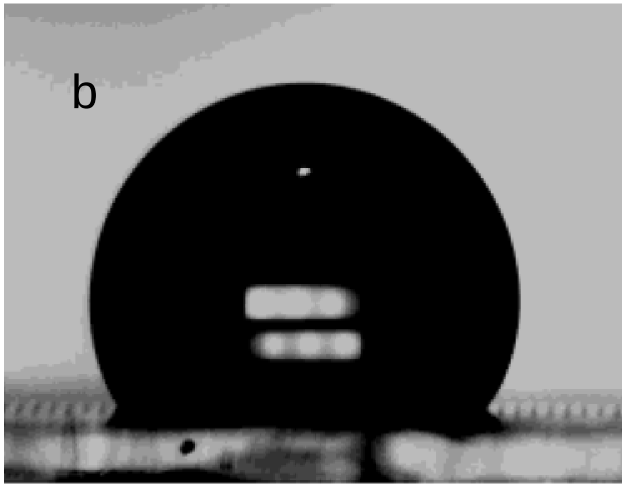
Marmur, *Wetting on hydrophobic rough surfaces: To be heterogeneous or not to be* [3]

Illustration of a drop in the Cassie state on a rough surface; note heterogeneous contact area

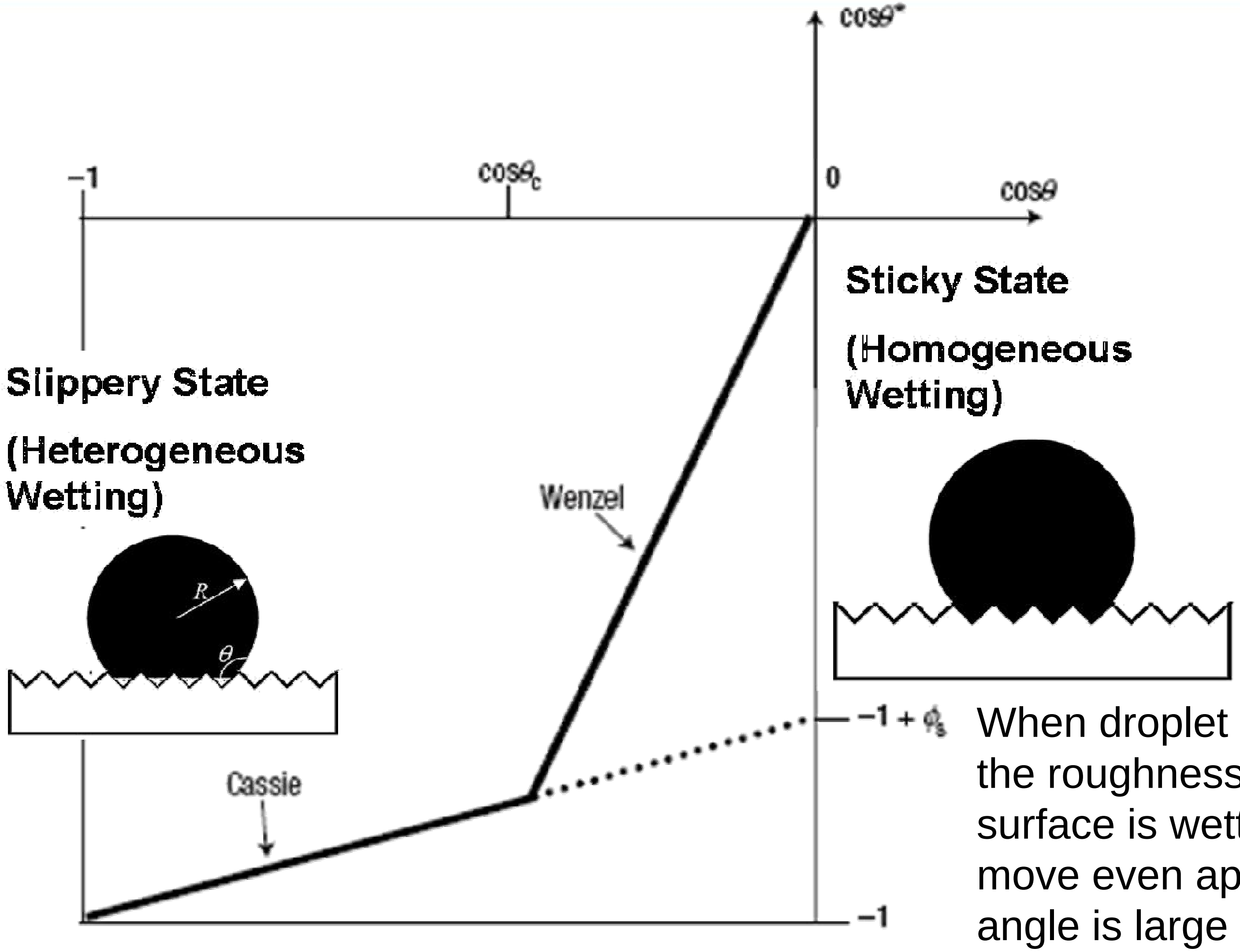
Cassie and Wenzel States

- Here are a pair of excellent micrographs from Patankar showing actual droplets in the Cassie state (a) and the Wenzel state (b)
- Note, however, that they are sitting on exactly the same surface, indicating transitions are possible





Sticky or Slippery Surfaces?



When droplet is comparable to the roughness and the original surface is wetting, it may not move even apparent contact angle is large

Additional Readings

- Jacob N. Israelachvili, ***Intermolecular and Surface Forces***, Chapt 11, Academic Press, 2nd Edition, 1992
- Jens Ducrée, online resources for micro- and nanofluidic technologies,Chap. 2.7 & 3.7 http://www.myfluidix.com/