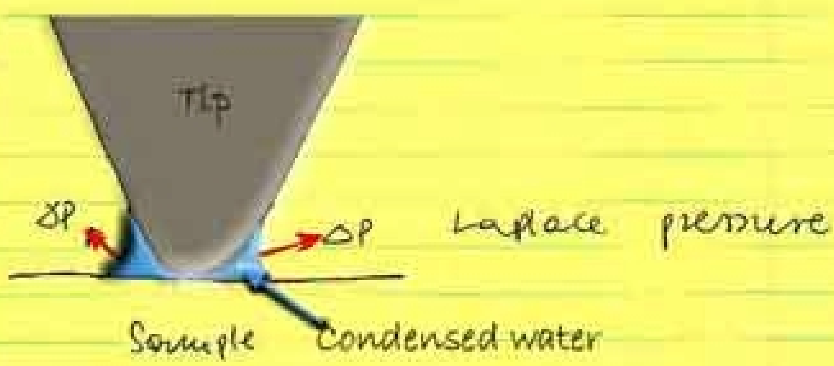
Capillary forces

If the AFM is operated in the atmosphere containing water vapor, and the surfaces of the tip and of the sample are well wetted by water, we may have to deal with additional force pulling the tip towards the sample. This force will be caused by the capillary action of water condensing in the nanoscale cavity formed by the tip and the surface



Laplace pressure.

Consider the equilibrium of a spherical hallow bubble of radius r:

Total surface free energy

$$G = 4\pi r^2 \gamma$$

$$dG = 8\pi r \gamma \, dr$$ → change due to change in radius by dr

Why the bubble does not shrink to $r \to 0$?
The pressure of air (vapor) inside balances the surface tension force

$$dG = dw$$

where dw - work against the pressure difference ΔP between the inside and outside.

work performed against the pressure difference ΔP between the inside and outside

$$dw = \Delta P \cdot 4\pi r^2 dr$$

In equilibrium

$$dw = dG$$

$$\Delta P \, 4\pi r^2 dr = 8\pi r \gamma dr$$

$$\boxed{\Delta P = \frac{2\gamma}{r}}$$ Laplace pressure

The pressure exerted by the curved surface on gas trapped inside the bubble.

Laplace pressure is also responsible for the rise of liquids inside capillaries

Capillary rise

r<o (concave menuscus!)

capillary pressure

$$\Delta P = P_g - P_l = \frac{2\gamma}{r}$$

contact angle

Perfect wetting ($\theta = 0$)

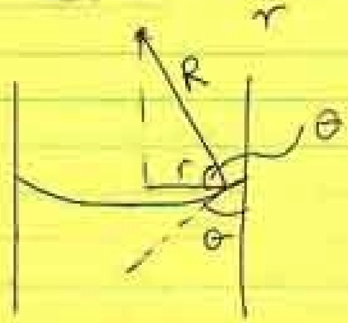
$r = r_c$

r_c - capillary radius

r - meniscus radius.

if $\theta > 0$

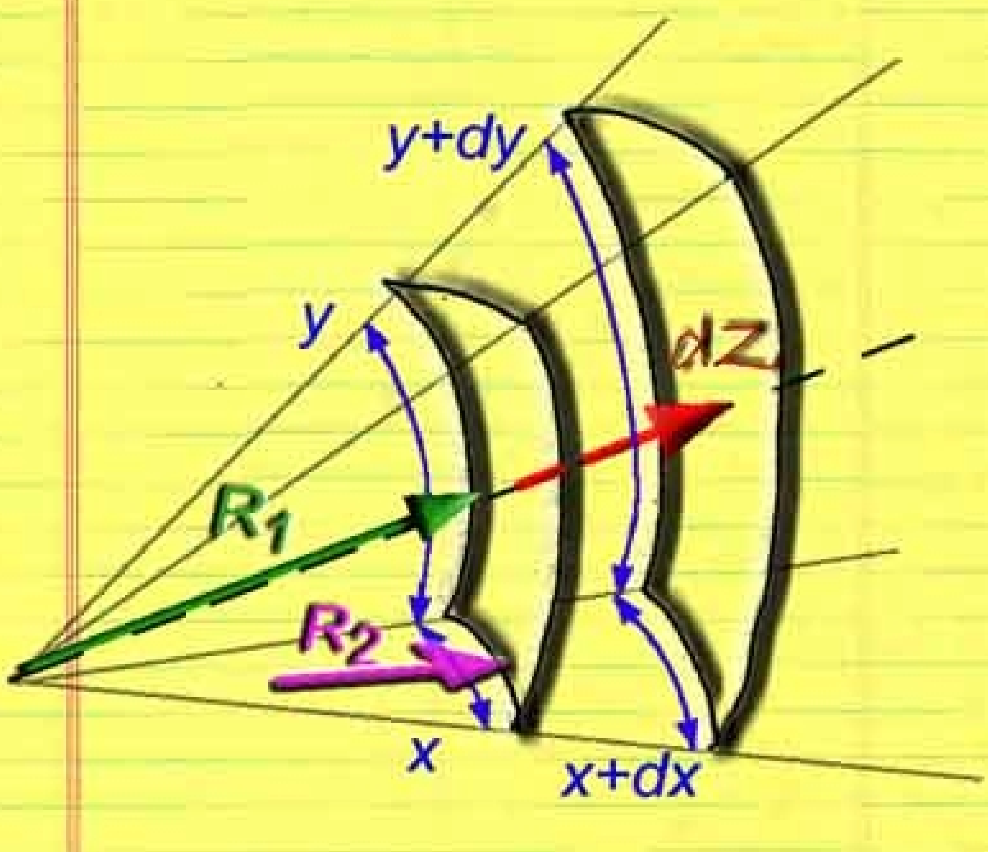
$$\Delta P = \frac{2\gamma \cos\theta}{r}$$



$$R = \frac{r}{\cos\theta}$$

General case: Young-Laplace equation.

Consider the arbitrary curved surface. In order to describe such a surface we need in general two radii of curvature



If the section is small enough, the radii R_1, R_2 can be treated as constant

The change of area upon displacement of the surface by dz outward

$$\Delta A = (x+dx)(y+dy) - xy = x\,dy + y\,dx$$

The work done in forming this additional area

$$W_A = \gamma\,(x\,dy + y\,dx)$$

Work performed by Laplace pressure

$$W_P = \underbrace{\Delta P\, x y}_{\text{force}}\ \underbrace{dz}_{\text{displacement.}}$$

From similar triangles

$$\frac{y}{R_1} = \frac{y+dy}{R_1+dz} \qquad \frac{x}{R_2} = \frac{x+dx}{R_2+dz}$$

taking this into account, and demanding that at equilibrium $W_A = W_P$

we obtain

$$\boxed{\Delta P = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)}$$

this reduces to

$$\boxed{\Delta P = \frac{2\sigma}{R}}$$

for a sphere, for which $R_1 = R_2 = R$

capillary condensation

Consider the equilibrium between volume of liquid bounded by a curved surface and its vapor.

Additional pressure acting on liquid (Laplace pressure, ΔP) will change its vapor pressure.

In equilibrium chemical potentials of liquid and its vapor are equal

$$\mu(l) = \mu(g)$$

liquid vapor (gas)

The same is true with the change of chemical potential due to the action of Laplace pressure

$$\Delta\mu(l) = \Delta\mu(g)$$

For a pure substance

$\mu = G_m \leftarrow$ molar Gibbs energy

For a liquid

$(dG = Vdp - SdT)$

$$\Delta G_m(\ell) = \int_{p^*}^{p^*+\Delta P} V_m(\ell)\,dp = V_m(\ell)\,\Delta P$$

p^* - pressure above flat surface

$V_m(\ell)$ - molar volume of a liquid (nearly constant)

For vapor treated as an ideal gas

$$V_m(g) = \frac{RT}{P}$$

p_c - vapor pressure of liquid subjected to ΔP

$$\Delta G_m(g) = \int_{p^*}^{p_c} \frac{RT}{P}\,dp = $$

$$= RT \ln\left(\frac{p_c}{p^*}\right)$$

Thus:

$$(*) \quad \Delta P = \frac{RT}{V_m(\ell)} \ln\left(\frac{p_c}{p^*}\right)$$

and since $\Delta P = \frac{2\gamma}{r}$ (surface tension)

$$(**) \quad \boxed{\frac{1}{r} = \frac{RT}{2\gamma V_m(\ell)} \ln\left(\frac{p_c}{p^*}\right)}$$

Kelvin equation

Eqn. (*) describes the change of a vapor pressure of a liquid subjected to ΔP. (Positive pressure squeezes out the molecules of liquid into gas phase, increasing its vapor pressure. Negative pressure will "suck out" the molecules from vapor phase)

Eqn. (**) provides the value of curvature of meniscus which can exist in equilibrium with vapor at pressure p_c.

Meniscus with positive curvature (e.g. such as in a spherical droplet) can be in equilibrium only with vapor under the pressure $p_c > p^*$. If $p_c = p^*$ $r \to \infty$ which means that formation of droplets is energetically unvarable.

Example 1:

What is the equilibrium radius of water droplet at 20°C and vapor pressure $p_c = 1.1\,p^*$?

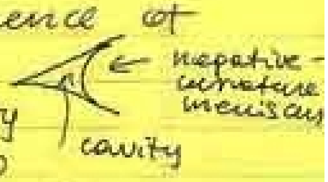
For water at 20°C

$\gamma = 73\ \mathrm{mJ/m^2}$

$V_m = 18 \times 10^{-6}\ \mathrm{m^3}$ $\Rightarrow \dfrac{\gamma V_m}{RT} = 0.54\ \mathrm{nm}$

$$r = \frac{1}{2}\,\frac{\gamma V_m}{RT}\cdot\frac{1}{\ln\left(\frac{p_c}{p^*}\right)} = 2.83\ \mathrm{nm}$$

The ability to form meniscus with negative curvature arising in the presence of nanoscale cavities provides the opportunity to condense vapor into liquid even at vapor pressures below the saturated vapor pressure, $p_c < p^*$. This condensation is referred to as capillary condensation.



Example 2

How small should be the cavity in order to facilitate capillary condensation of water at 20°C from vapor at $p_c/p^* = 0.5$ (50% relative humidity)?

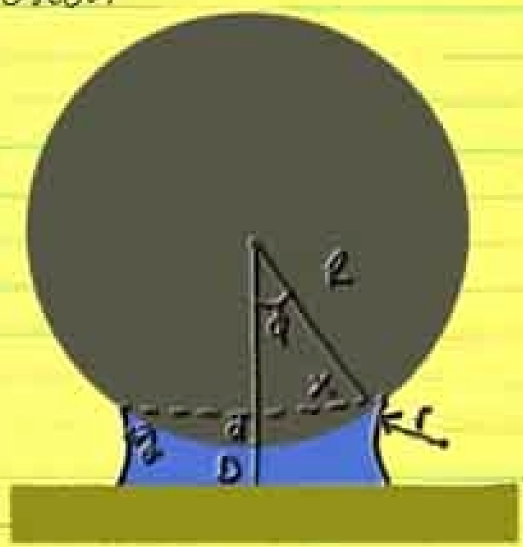
Using the solution from EX. 1 the radius of concave meniscus has to be equal to

$$r = \frac{1}{2} \cdot 0.54 \text{ nm} \frac{1}{\ln(0.5)} =$$

$$= -0.38 \text{ nm}$$

Thus the cavity has to have the diameter of $\sim 2r \approx$ ≈ 0.8 nm.

The effect of Laplace pressure of water condensed between the tip and the sample on adhesion



$$P = \gamma_L \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

the pressure acts on the area

$\pi x^2 \approx 2\pi R d$ (Chord theorem).

$$F \approx 2\pi R d \left(\gamma_L / r_1 \right)$$

$$d \approx 2 r_1 \cos\theta$$

$$F \approx 4\pi R \gamma_L \cos\theta$$

More on capillary forces in AFM…

Effect of Water on Lateral Force Microscopy in Air

Richard D. Piner and Chad A. Mirkin*

6864 *Langmuir* **1997,** *13,* 6864-6868

Thin-film friction and adhesion studies using atomic force microscopy

Bharat Bhushan a) and Chetan Dandavate

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