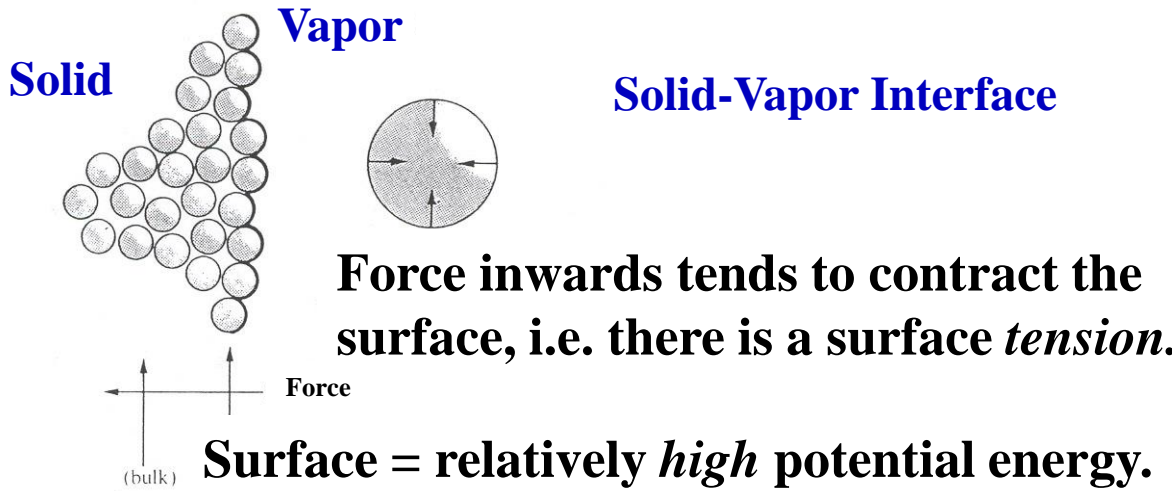


# Chap. 16C.2(a) Solid-Vapor Interface => Surface Tension ( $\alpha - \beta$ Interface)

- Its potential energy would be lowered if the surface area is reduced, and so the molecules are under the influence of a force.
- This force is reducing total surface area, and we term it a tension, the surface tension.



Force inwards tends to contract the surface, i.e. there is a surface *tension*.

Surface = relatively *high* potential energy.

Bulk = relatively *low* potential energy.

Microscopic basis of surface tension.

Dangling Bonds

ppt 16-1 = *handwave argument*

Surface Tension = Interfacial Gibbs Free Energy

# *Interface Equilibrium – Si (001) Surface*

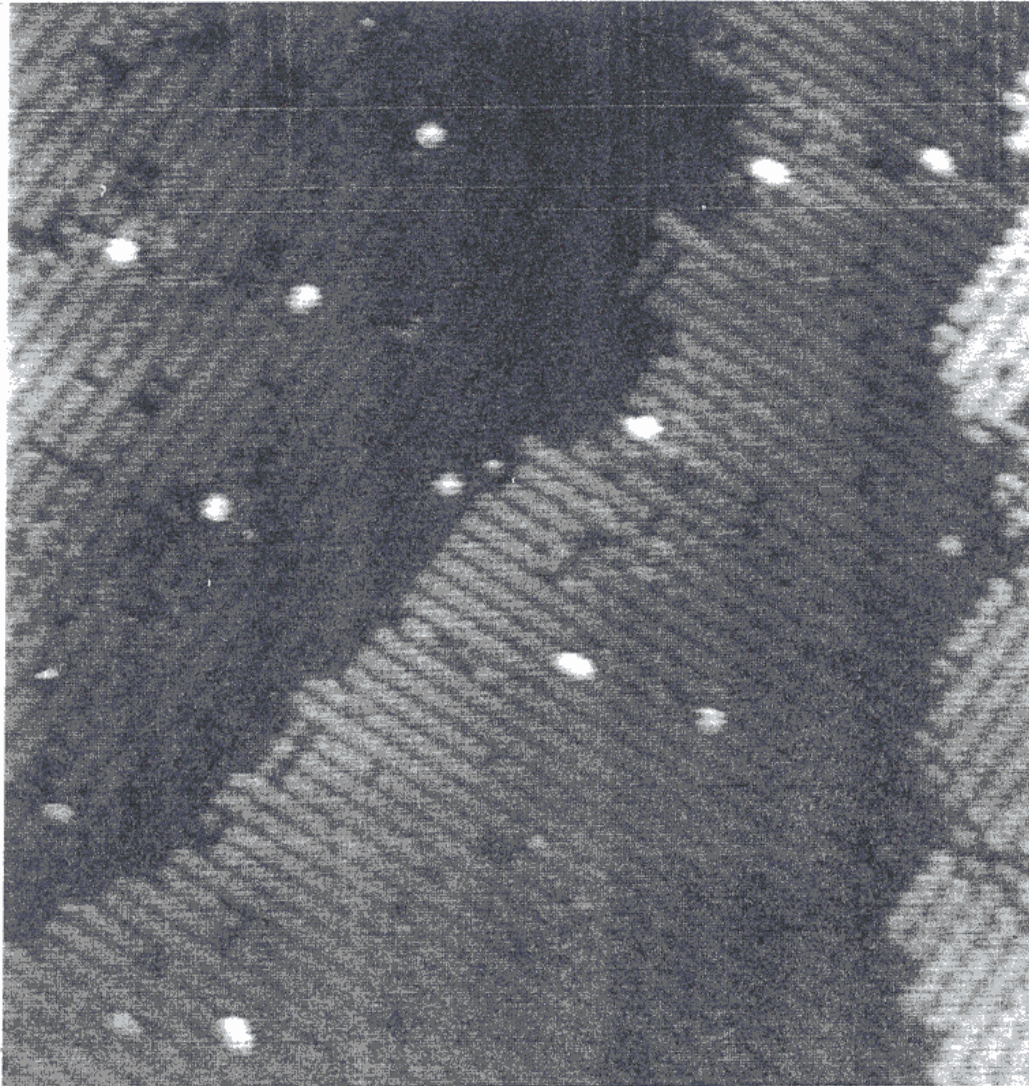


FIGURE 1. A SCANNING tunneling microscope image of a silicon (001) surface after the deposition of a small amount of Si at room temperature. The image shows two single-layer steps (the jagged interfaces) separating three terraces. Because of the tetrahedral bonding configuration in the silicon lattice, dimer row directions are orthogonal on terraces joined by a single-layer step. The area pictured is  $30 \times 30$  nm.

Liquids (or solids) assume a shape that minimizes their surface area because it enables the maximum number of molecules to be in the **bulk** rather than **surface**.

$$\gamma = \text{surface tension}$$

(~16C.5)

$$\underline{dG = -SdT + Vdp + \gamma d(\text{area})}$$

(~16C.6)

At constant pressure and temperature,

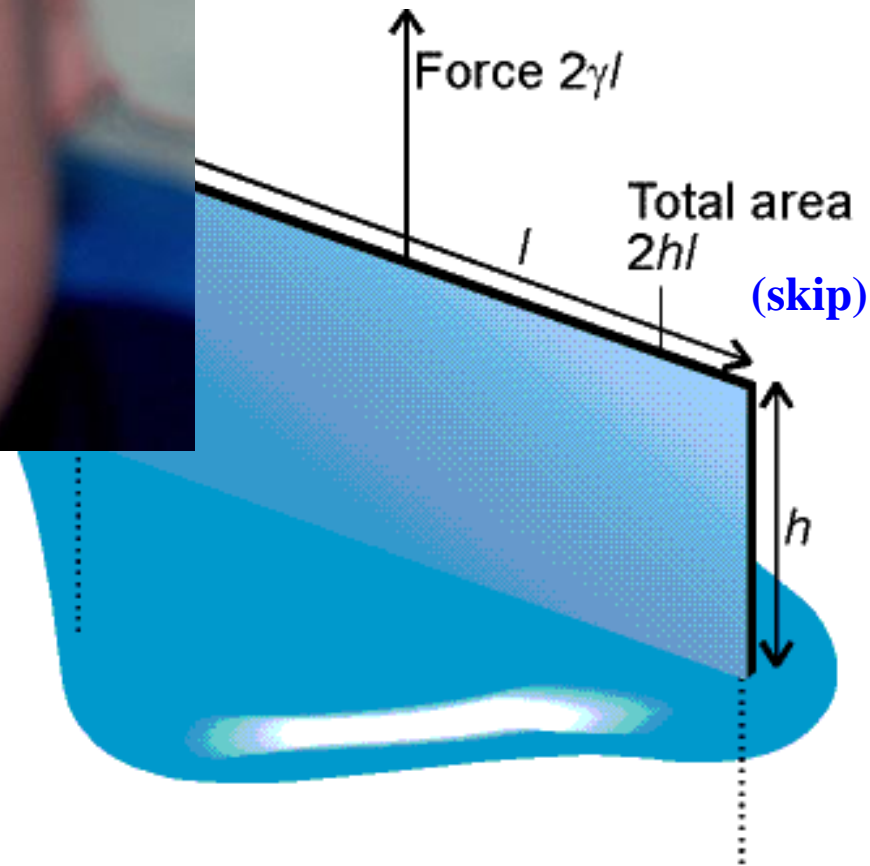
$$dG = \gamma d(\text{area})$$

*ppt 16-3 = exact*

$dG < 0 \Rightarrow d(\text{area}) < 0$  : which means that surfaces have a natural tendency to contract.

$$G' \equiv G'_{\alpha} + G'_{\beta} + \gamma A$$

Surface Tension = Interfacial Gibbs Free Energy



**Figure 16C.6 (skip)**

The model used for calculating the work of forming a liquid film when a wire of length  $l$  is raised and pulls the surface with it through a height  $h$ .



# Humanity's Top Ten Problems for the Next 50 Years

**1. ENERGY**

**2. WATER**

**3. FOOD**

**4. ENVIRONMENT**

**5. POVERTY**

**6. TERRORISM & WAR**

**7. DISEASE**

**8. EDUCATION**

**9. DEMOCRACY**

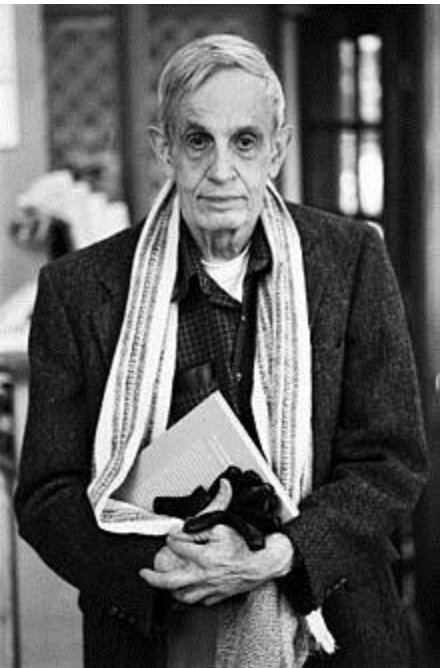
**10. POPULATION**

**Prof. R. E. Smalley (1943 – 2005)**



**2019      7.6 Billion People**

**2050      ~10 Billion People**



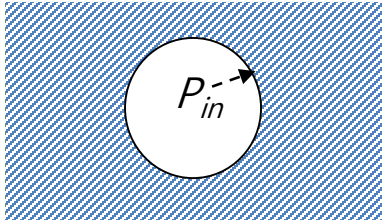
# *Prof. John Nash* **A Beautiful Mind**

**2001 영화**

| <b>John Forbes Nash, Jr.</b> |  |
|------------------------------|--|
| Born                         | June 13, 1928<br>Bluefield, West Virginia, U.S.                                  |
| Died                         | May 23, 2015 (aged 86)<br>Monroe Township, Middlesex County,<br>New Jersey, U.S. |
| Nationality                  | American   |
| Fields                       | •Mathematics<br>•Economics   |
| Institutions                 | •Massachusetts Institute of Technology<br>•Princeton University                  |

***Spent several years at psychiatric hospitals.***

Consider a bubble (or cavity).



$P_{in}$  : the pressure inside the cavity

$P_{out}$  : the outside pressure

The internal pressure is due to the sum of the outside pressure  $P_{out}$  and the surface tension.

The change in surface area when the radius of a sphere changes from  $r$  and  $r + dr$  is

$$d\sigma = 4\pi(r + dr)^2 - 4\pi r^2 \cong 8\pi r dr \quad dr^2 \text{ is ignored}$$

$$\therefore dw = \gamma d\sigma = 8\pi r \gamma dr$$

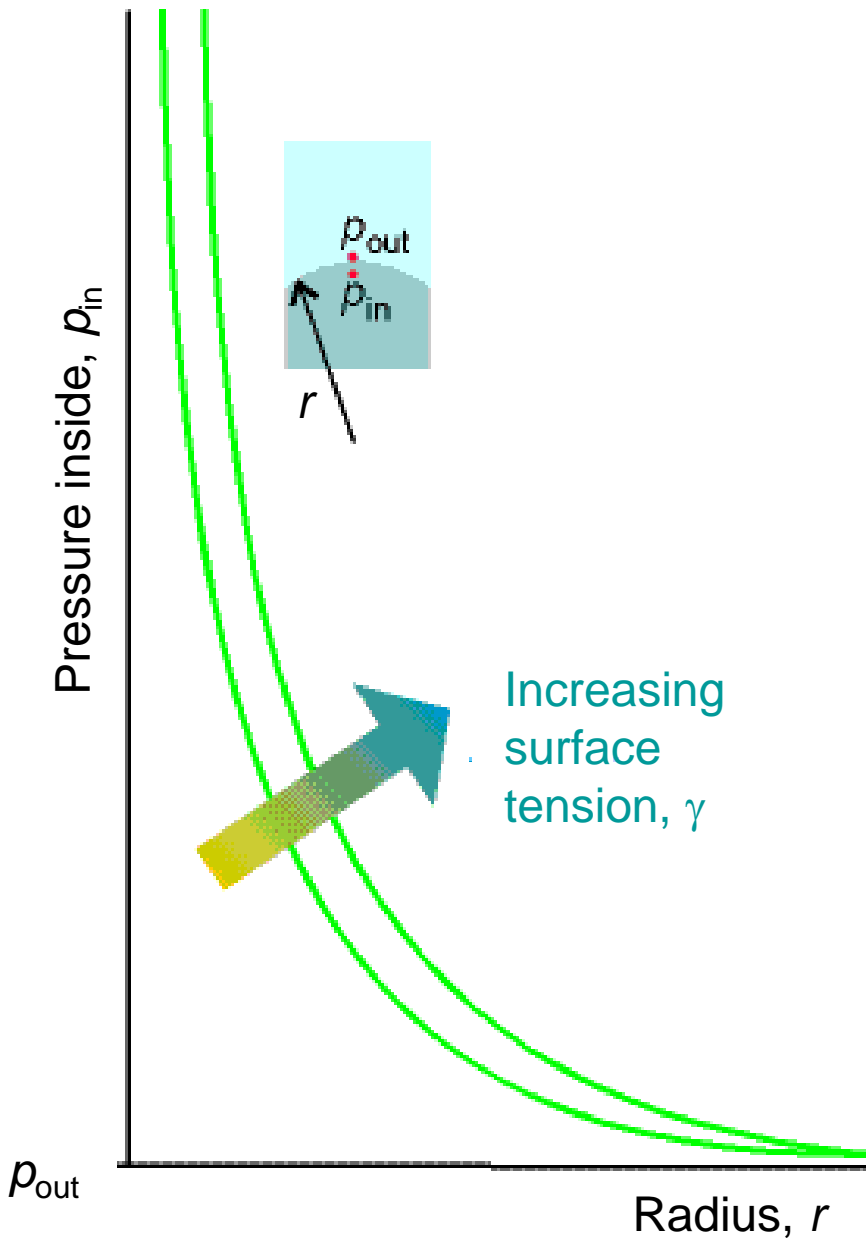
$\therefore$  As force  $\times$  distance is work, the force opposing stretching through the distance  $dr$  at this radius  $= 8\pi r \gamma$ .

$$\therefore 4\pi r^2 p_{in} = 4\pi r^2 p_{out} + 8\pi r\gamma$$

$$p_{in} - p_{out} = \frac{2\gamma}{r} \quad \text{Laplace equation}$$

**Note:** The Laplace equation shows that the pressure inside a curved surface is always greater than the pressure outside, but the difference decreases to zero as the radius of curvature becomes infinite.





$$p_{in} - p_{out} = \frac{2\gamma}{r}$$

**Figure 4.22**

The dependence of the pressure inside a curved surface on the radius of the surface, for two different values of the surface tension.

## Consider droplets.

At equilibrium, the chemical potentials of a vapor and its liquid are equal.

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

Let the pressure on the system be increased. If the pressure on the liquid changes by  $dp(l)$ , then the change in the pressure of its vapor,  $dp(g)$  will be such that

$$V_m(g)dp(g) = V_m(l)dp(l) \quad (\text{at constant } T)$$

$$\because d\mu = V_m dp - S_m dT \Rightarrow d\mu = V_m dp \quad \text{at constant pressure}$$

Assuming that the vapor is ideal,  $V_m(g) = \frac{RT}{p(g)}$ .

$$\frac{RT}{p(g)} dp(g) = V_m(l)dp(l) \Rightarrow \frac{dp(g)}{p(g)} = \frac{V_m(l)dp(l)}{RT}$$

On integration with boundary condition of  $p^*(g)=p^*(l)$ , when the pressure exerted on the liquid is the normal pressure  $p^*$ , i.e.,  $p(g)=p^*$  and  $p(l)=p^*$ ,

$$\int_{p^*}^p \frac{dp(g)}{p(g)} = \frac{1}{RT} \int_{p^*}^{p^*+\Delta p} V_m(l) dp(l)$$

$$\ln \frac{p}{p^*} = \left( \frac{V_m}{RT} \right) \{ (p^* + \Delta p) - p^* \} = \frac{V_m \Delta p}{RT} \rightarrow p = p^* \exp \left( \frac{V_m \Delta p}{RT} \right)$$

One way of increasing the pressure on the liquid is to disperse it as droplets. The pressure differential across a curved surface is  $2\gamma/r$ .

$$p(\text{mist}) = p(\text{bulk}) \exp \left\{ V_m(l) \frac{2\gamma}{rRT} \right\} \quad \text{Kelvin equation}$$

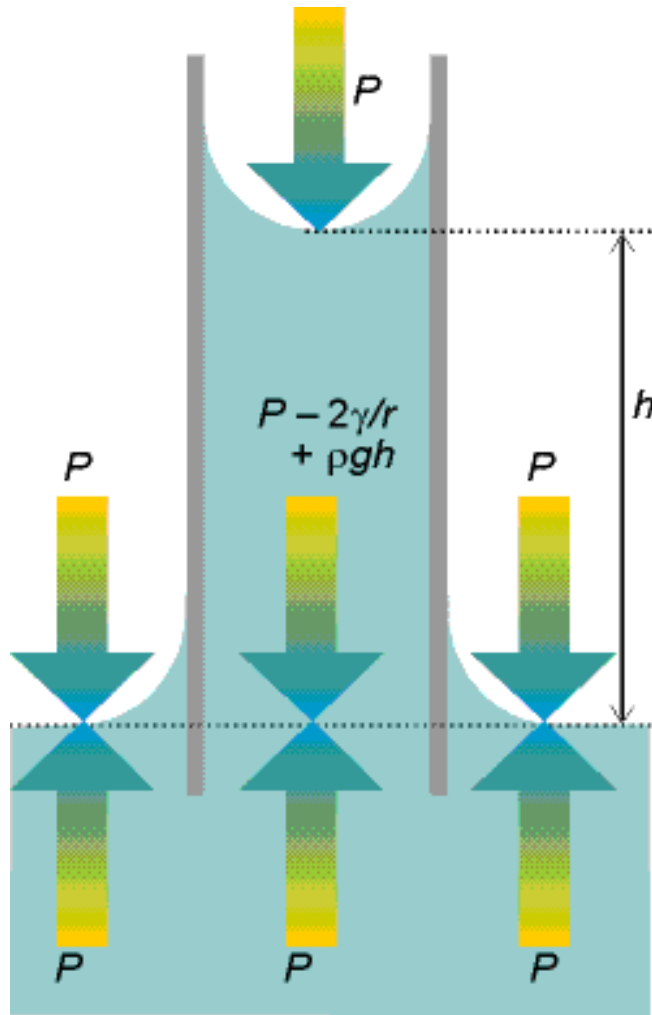
where  $p(\text{mist})$  is the vapor pressure of a sample of mist with droplet radius  $r$  and  $p(\text{bulk})$  is the pressure of a plane surface of the same material.

The pressure exerted by a column

$$p = \rho gh \quad \rho : \text{liquid density}$$

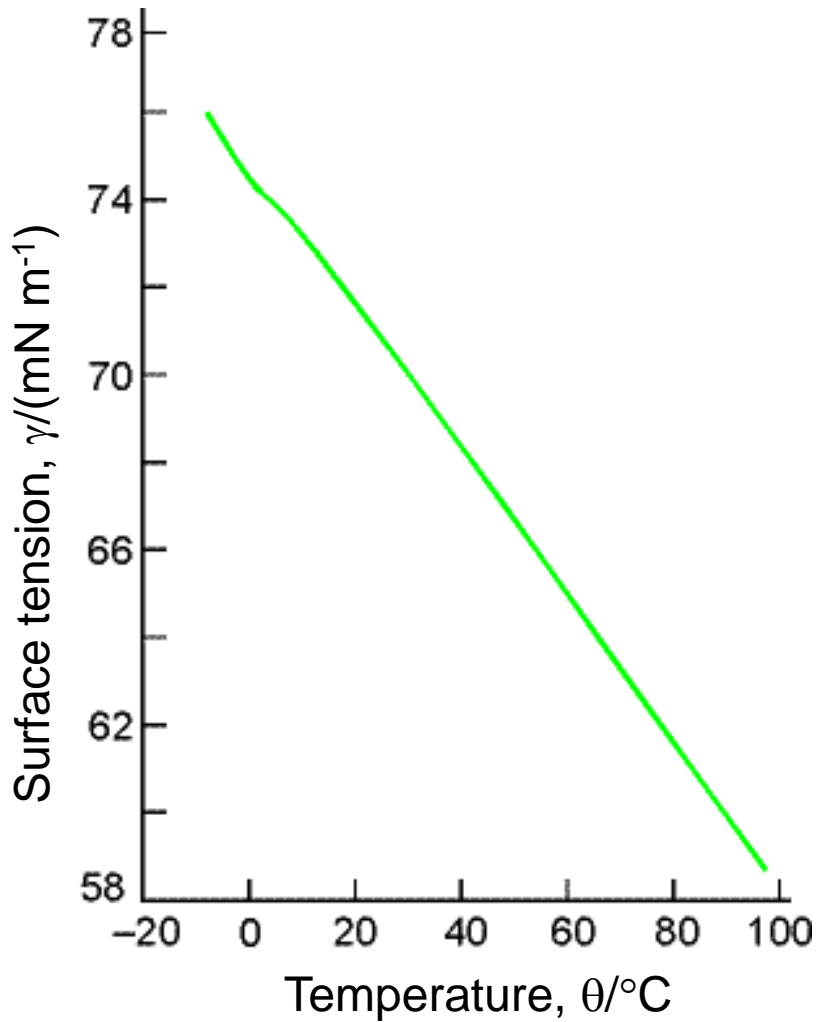
$$p = p - \frac{2\gamma}{r} + \rho gh \Rightarrow \rho gh = \frac{2\gamma}{r}$$

$$h = \frac{2\gamma}{\rho gr}, \quad \gamma = \frac{1}{2} \rho ghr$$



**Figure 4.23**

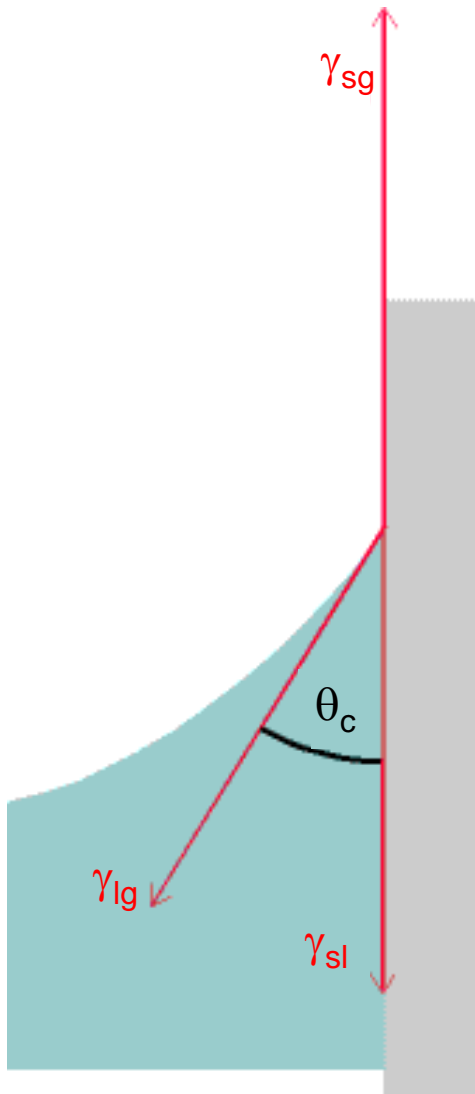
When a capillary tube is first stood in a liquid, the latter climbs up the walls, so curving the surface. The pressure just under the meniscus is less than that arising from the atmosphere by  $2\gamma/r$ . The pressure is equal at equal heights throughout the liquid provided the hydrostatic pressure (which is equal to  $\rho gh$ ) cancels the pressure difference arising from the curvature.



**Figure 4.24**

The variation of the surface tension of water with temperature.





$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta_c$$

$$\cos \theta_c = \frac{\gamma_{sg} + \gamma_{sl}}{\gamma_{lg}}$$

$0 < \theta_c < 90^\circ$       $\gamma_{sg} > \gamma_{sl}$   
 the liquid wets  
 (spread over)

$90^\circ > \theta_c$       $\gamma_{sg} < \gamma_{sl}$

**Figure 4.25**

The balance of forces that results in a contact angle,  $\theta_c$ .

## Thermodynamic work of adhesion

The thermodynamic work of adhesion,  $w_{ad}$ , required to separate a unit area of a solid and a liquid phase forming an interface across which secondary forces are acting may be related to the surface and the interfacial free energies by the Dupre equation. The reversible work of adhesion,  $w_{ad}$ , in an inert medium may be expressed by:

$w_{ad}$  = (sum of the surface free energies of the solid and liquid phase – the interfacial free energy)

$$\text{i.e., } w_{ad} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl} \quad (1)$$

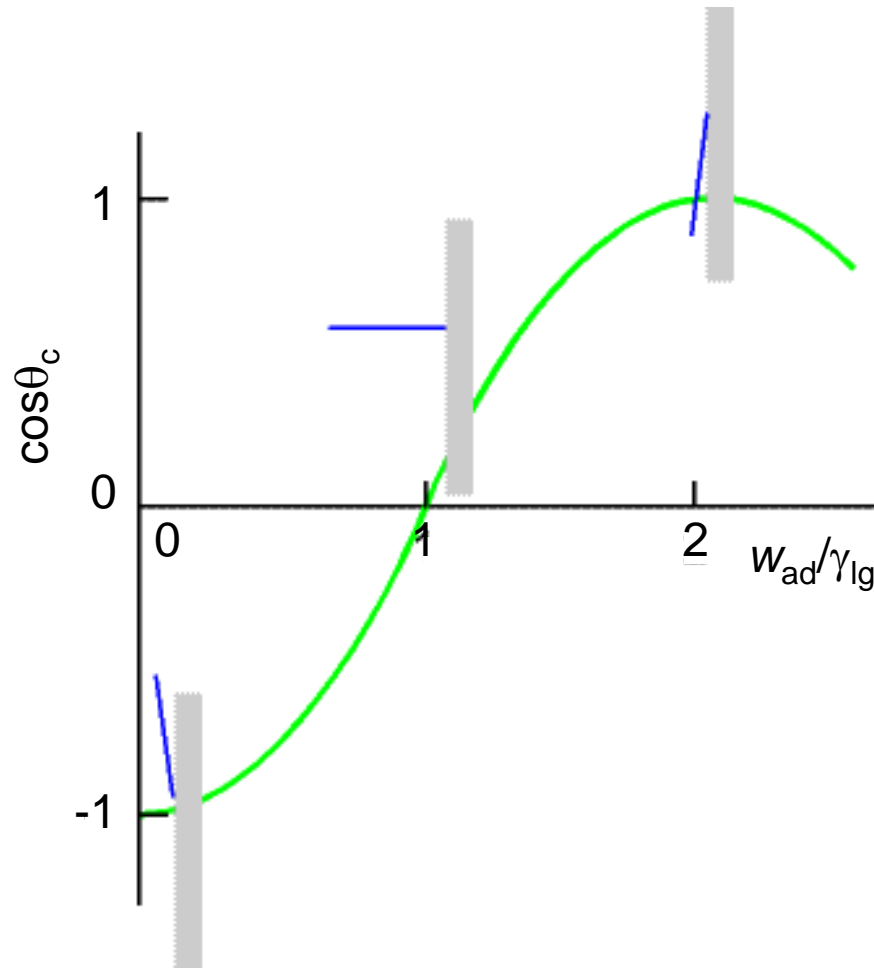
$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta_c \quad (2)$$

$$\cos \theta_c = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \quad (3)$$

Combining eq (1) and eq (3) gives

$$\cos \theta_c = \frac{W_{ad}}{\gamma_{lg}} - 1 \quad (4)$$

We now see that the liquid completely “wets” (spreads over) the surface fully, corresponding to  $\theta_c \approx 0$ , when  $W_{ad} \geq 2\gamma_{lg}$ . The liquid does not wet the surface (corresponding to  $\theta_c > 90^\circ$  when  $W_{ad} < \gamma_{lg}$ ).



**Figure 4.26**

The variation of contact angle (shown by the semaphore-like object) as the ratio  $w_{ad}/\gamma_{lg}$  changes.