FIG. 1: Surface energy and the work, force to move a fluid across a surface.

Surface energy and consequences.

1. Surface Tension. In a simple approximation the particles on the surface of a fluid have approximately half of the energy of a particle within the fluid. The latter have approximate energy

$$-\epsilon_0 = -\frac{1}{2}zV(0),\tag{1}$$

where $V(0)$ is the potential of a particle at the most favorable distance from a neighbor and z is the coordination number (number of near neighbors), about 12, Fig. 1. The energy of a liquid is written in the form

$$E = Vn_B(-\epsilon_0) + An_A\frac{\epsilon_0}{2},\tag{2}$$

where V and A are the area and volume respectively and n_B and n_A are the bulk and areal

particle density respectively. The *surface tension*, the analogue of pressure is

$$\gamma = \frac{\partial E}{\partial A} = n_A \frac{\epsilon_0}{2}. \tag{3}$$

It is the amount of energy necessary to have a unit area of surface, $[\gamma] = [E]/L^2$.

2. Surface Tension, numerical estimate. For a typical liquid the number ϵ_0 is about 0.1 eV; e.g., evaporation of water takes 540 cal/mole. The particles on the surface of a fluid are spaced, as in the bulk, by about 3 A^o. Thus

$$\gamma \approx 50 \; ergs/(cm)^2. \tag{4}$$

The surface tensions for helium, water, mercury are 1, 72 and 470 ergs/(cm)^2 respectively. Fluids in which the binding of particles to one another is strong have large values of the surface tension.

3. Interfacial energy and contact angle. The energy, which is the surface tension, is the energy of a molecule on the surface of a liquid where it *sees* a vapor outside of the liquid. There are many (most) circumstances in which the boundary of a liquid is a solid, another liquid, a vapor, etc. Molecules on the surface of a liquid that is bounded by X have an interfacial energy denoted γ_{LX}. [This is a slightly delicate subject. The class act is *Intermolecular and Surface Forces, Second Edition: With Applications to Colloidal and Biological Systems*, by Jacob N. Israelachvili.] Assuming we have the interfacial energies in hand a situation like that in Fig. 1, bottom can arise. A fluid/vapor interface is pulled along the surface of a solid. Each advance δx of the interface involves energy change $\Delta E = (\gamma_{VS} - \gamma_{LS})b\delta x$. Thus there is a force

$$F = \frac{\partial \Delta E}{\partial x} = (\gamma_{VS} - \gamma_{LS})b \tag{5}$$

tending to pull the interface further onto the solid $(\gamma_{VS} - \gamma_{LS}) > 0$, tending to push the interface off of the solid $(\gamma_{VS} - \gamma_{LS}) < 0$. The important physical point is that an interfaial energy causes forces that work along the line of the interface. A mechanical balance is achieved, if possible, by the orientation of the liquid/vapor interface. As in Fig. 2 (top). Considering the forces due to interfacial energy to work along the line of the relevant surface find

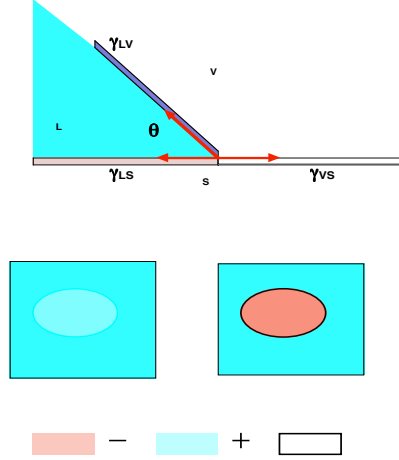$$\gamma_{VS} - \gamma_{LS} - \gamma_{LV} \cos\theta = 0. \tag{6}$$

FIG. 2: Fluid rise in a capillary tube.

The angle θ is called the contact angle. These forces are seen at work in capillary rise.

4. Wetting. [See *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves*, by Pierre-Gilles de Gennes, Francoise Brochard-Wyart, and David Quere; Pierre-Gilles de Gennes: The Nobel Prize in Physics 1991.]

A. Wetting refer qualitatively to your sense of whether or not a liquid wants to lie on a surface. When a car is waxed water drops *bead up* and do not wet. The quantitative measure of this is the contact angle defined in Fig. 2 (top). A contact angle less than $\pi/2$ is taken to mean the liquid wets the substrate (solid) a contact angle greater than $\pi/2$ means that the liquid does not want to wet the solid.

B. While the term wetting is not used, the sense of wetting is involved in the interaction between hydrophilic (water seeking) and hydrophobic (water adverse) ends of a polymer and the solution in which it resides. This interaction can lead to micelles, certain colloids, etc. These systems arise in part because of the interfacial energy of parts of their conformation. For example a micelle may form as a collection of polymers arrange themselves to protect the hydrophobic parts from contact with the water solution in which they reside.

C. A further example of the presence of surface energy occurs as a system undergoes a phase transition (usually first order). Suppose the thermodynamic variables are changed so that a system, in equilibrium in phase 1, should make a transition to phase 2. The transition to
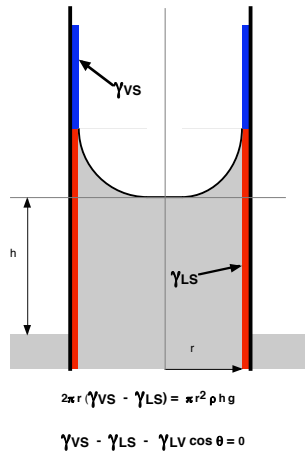
$$2\pi r\,(\gamma_{VS} - \gamma_{LS}) = \pi r^2 \rho h g$$

$$\gamma_{VS} - \gamma_{LS} - \gamma_{LV}\cos\theta = 0$$

FIG. 3: Contact angle (top). Nucleation (bottom).

Randwinkel ß=45,01 °

FIG. 4: Examples of wetting/non-wetting.

phase 2 occurs with little pieces of 1 making the transition to 2 and subsequently growing in size. The energy advantage to a volume $V \sim R^3$, upon making the transition is

$$E_V \approx R^3 \; n(-\Delta e), \tag{7}$$

where $\Delta e = e_2 - e_1 < 0$ and n is the particle number density. If there is an interfacial energy for phase 2 in phase 1 there is an energy cost (if $\gamma_{12} > 0$)

$$E_S \approx R^2 \gamma_{12}, \tag{8}$$

or

$$E = E_V + E_S \approx (-|\Delta e|)R^3 \; n + R^2 \gamma_{12}. \tag{9}$$

This energy is positive for small R. Thus there is a barrier to *nucleation* of the desired phase that is overcome if a piece of 1 can turn into a piece of 2 of size R_c, where R_c is found from

$$\frac{\partial E}{\partial R} \approx -3|\Delta e|R^2 \; n + 2R\gamma_{12} = 0. \tag{10}$$

5. Laplace Formula.

A. The Laplace formula describes the condition for mechanical equilibrium across an interface. Pressures p_1 and p_2 are above and below the interface. If a differential piece of area A, at the interface, is displaced by dz the work done is

$$dW_1 = (p_2 - p_1)Adz. \tag{11}$$

Additional work is done if the interface, with interfacial tension γ_{12}, changes area.

$$dW_2 = \gamma_{12} \; dA. \tag{12}$$

Take the area A to be the product $dl_1 \times dl_2$, where dl_1 and dl_2 are differential elements of length found from swinging radii R_1 and R_2 through angles $d\theta_1$ and $d\theta_2$ respectively. The displacement dz changes these radii to $R_1 + dz$ and $R_2 + dz$ resulting in a change in area given by

$$dA = A\left(\frac{1}{R_1} + \frac{1}{R_2}\right)dz. \tag{13}$$

Thus

$$F_z = \frac{dW_1 + dW_2}{dz} = A\left[(p_2 - p_1) + \gamma_{12}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\right] = 0, \tag{14}$$

where the zero on the RHS comes from the requirement of mechanical equilibrium.
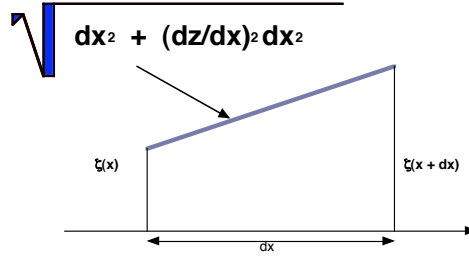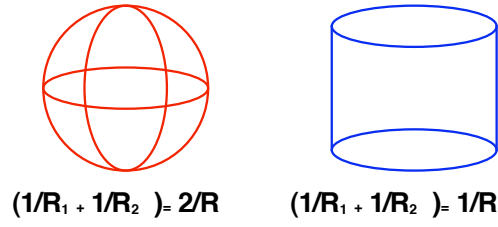
FIG. 5: Curvature in special cases. Curvature of a surface.

B. For simple objects like a soap bubble that is spherical or cylindrical the Laplace equation reduces to $\Delta p = 2\gamma/R$ and $\Delta p = \gamma/R$ respectively. As it costs energy to create surface the direction of the force due to surface tension is toward the center of the figure, in the same direction as the external pressure.

C. For the surface of a fluid with displacement away from equilibrium given by $\zeta(x)$ the additional amount of surface at X is given by

$$\delta A = b\sqrt{dx^2 + \left(\frac{d\zeta}{dx}\right)^2 dx^2} - b\ dx = b\ dx\ \frac{1}{2}\left(\frac{d\zeta}{dx}\right)^2. \tag{15}$$

In an equation describing the energy at the surface we would write (just as above)

$$\int b\ dx \left[(p_2 - p_1)d\zeta\ +\ \gamma_{12}\frac{1}{2}\left(\frac{d\zeta}{dx}\right)^2\right]. \tag{16}$$

The second term can be integrated by parts to yield

$$\int b\ dx\ d\zeta\ \left[(p_2 - p_1)\ -\ \gamma_{12}\ \frac{1}{2}\ \frac{d^2\zeta}{dx^2}\right]. \tag{17}$$

So in mechanical equilibrium

$$p_2 - p_1\ =\ \gamma_{12}\ \frac{1}{2}\ \frac{d^2\zeta}{dx^2}. \tag{18}$$

The direction of these pressures is set by the argument above, p_1 is the pressure in the fluid and p_2, the ambient pressure, is set to zero. Thus

$$p_1 = p = -\gamma_{12}\,\frac{1}{2}\,\frac{d^2\zeta}{dx^2}.\tag{19}$$

Capillary Waves. Go way back to the discussion of surface waves. LL Section 12, Note 11. On the surface of the fluid the velocity potential, pressure and potential energy are related by [i.e., the Bernoulli equation]

$$\frac{\partial\phi}{\partial t} + \frac{p}{\rho_0} + g\zeta = 0.\tag{20}$$

Use Eq. (19) for p

$$\frac{\partial\phi}{\partial t} - \frac{\gamma_{12}}{\rho_0}\,\frac{1}{2}\,\frac{d^2\zeta}{dx^2} + g\zeta = 0.\tag{21}$$

Now $\partial\zeta/\partial t = v_z = \partial\phi/\partial z$ so this equation takes the form

$$\frac{\partial^2\phi}{\partial t^2} - \frac{\gamma_{12}}{\rho_0}\,\frac{1}{2}\,\frac{\partial}{\partial z}\frac{\partial^2\phi}{\partial x^2} + g\frac{\partial\phi}{\partial z} = 0.\tag{22}$$

This is a modification of the boundary condition used in the deep water wave problem. For $\phi \propto cos(kx - \omega t)exp(kz)$

$$\omega^2 = gk + \frac{\gamma_{12}}{\rho_0}k^3.\tag{23}$$