Surface Tension

1. *Capillary forces:*

(a) *i:* The work done by a water droplet on the outside world, needed to increase the radius from R to $R+\Delta R$ is

$$\Delta W = (P - P_o) \cdot 4\pi R^2 \cdot \Delta R,$$

where P is the pressure inside the drop and P_o is the atmospheric pressure. In equilibrium, this should be equal to the increase in the surface energy $\mathcal{S}\Delta A = \mathcal{S} \cdot 8\pi R \cdot \Delta R$, where $\mathcal{S}$ is the surface tension, and

$$\Delta W_{\text{total}} = 0, \quad \Longrightarrow \quad \Delta W_{\text{pressure}} = -\Delta W_{\text{surface}}\,,$$

resulting in

$$(P - P_o) \cdot 4\pi R^2 \cdot \Delta R = \mathcal{S} \cdot 8\pi R \cdot \Delta R, \quad \Longrightarrow \quad (P - P_o) = \frac{2\mathcal{S}}{R}.$$

(a) *ii:* In a soap bubble, there are two air-soap surfaces with almost equal radii of curvatures, and

$$P_{\text{film}} - P_o = P_{\text{interior}} - P_{\text{film}} = \frac{2\mathcal{S}}{R},$$

leading to

$$P_{\text{interior}} - P_o = \frac{4\mathcal{S}}{R}.$$

Hence, the air pressure inside the bubble is larger than atmospheric pressure by $4\mathcal{S}/R$.

(b) *ii:* When steam condenses on a solid surface, water either forms a droplet, or spreads on the surface. There are two ways to consider this problem:

Method 1: Energy associated with the interfaces

In equilibrium, the total energy associated with the three interfaces should be minimum, and therefore

$$dE = S_{aw}dA_{aw} + S_{as}dA_{as} + S_{ws}dA_{ws} = 0.$$

Since the total surface area of the solid is constant,

$$dA_{as} + dA_{ws} = 0.$$

From geometrical considerations (see proof below), we obtain

$$dA_{ws}\cos\theta = dA_{aw}.$$

From these equations, we obtain

$$dE = \left(S_{aw}\cos\theta - S_{as} + S_{ws}\right) dA_{ws} = 0, \quad \Longrightarrow \quad \cos\theta = \frac{S_{as} - S_{ws}}{S_{aw}}.$$

Proof of $dA_{ws}\cos\theta = dA_{aw}$:

Consider a droplet which is part of a sphere of radius R, which is cut by the substrate at an angle θ. The areas of the involved surfaces are

$$A_{ws} = \pi(R\sin\theta)^2, \qquad \text{and} \qquad A_{aw} = 2\pi R^2(1-\cos\theta).$$

Let us consider a small change in shape, accompanied by changes in R and θ. These variations should preserve the volume of water, i.e. constrained by

$$V = \frac{\pi R^3}{3}\left(\cos^3\theta - 3\cos\theta + 2\right).$$

Introducing $x = \cos\theta$, we can re-write the above results as

$$\begin{cases} A_{ws} = \pi R^2\left(1-x^2\right), \\ A_{aw} = 2\pi R^2\left(1-x\right), \\ \quad V = \dfrac{\pi R^3}{3}\left(x^3 - 3x + 2\right). \end{cases}$$

The variations of these quantities are then obtained from

$$\begin{cases} dA_{ws} = 2\pi R\left[\dfrac{dR}{dx}(1-x^2) - Rx\right] dx, \\ dA_{aw} = 2\pi R\left[2\dfrac{dR}{dx}(1-x) - R\right] dx, \\ \quad dV = \pi R^2\left[\dfrac{dR}{dx}(x^3-3x+2) + R(x^2-x)\right] dx = 0. \end{cases}$$

From the last equation, we conclude

$$\frac{1}{R}\frac{dR}{dx} = -\frac{x^2-x}{x^3-3x+2} = -\frac{x+1}{(x-1)(x+2)}.$$

Substituting for dR/dx gives,

$$dA_{ws} = 2\pi R^2\frac{dx}{x+2}, \qquad \text{and} \qquad dA_{aw} = 2\pi R^2\frac{x\cdot dx}{x+2},$$

resulting in the required result of

$$dA_{aw} = x \cdot dA_{ws} = dA_{ws}\cos\theta.$$

Method 2: Balancing forces on the contact line

Another way to interpret the result is to consider the force balance of the equilibrium surface tension on the contact line. There are four forces acting on the line: *(1)* the surface tension at the water–gas interface, *(2)* the surface tension at the solid–water interface, *(3)* the surface tension at the gas–solid interface, and *(4)* the force downward by solid–contact line interaction. The last force ensures that the contact line stays on the solid surface, and is downward since the contact line is allowed to move only horizontally without friction.

These forces should cancel along both the y–direction x–directions. The latter gives the condition for the contact angle known as *Young's equation*,

$$\mathcal{S}_{as} = \mathcal{S}_{aw} \cdot \cos\theta + \mathcal{S}_{ws}\,, \quad \Longrightarrow \quad \cos\theta = \frac{\mathcal{S}_{as} - \mathcal{S}_{ws}}{\mathcal{S}_{aw}}.$$

The critical condition for the complete wetting occurs when $\theta = 0$, or $\cos\theta = 1$, i.e. for

$$\cos\theta_C = \frac{\mathcal{S}_{as} - \mathcal{S}_{ws}}{\mathcal{S}_{aw}} = 1.$$

Complete wetting of the substrate thus occurs whenever

$$\mathcal{S}_{aw} \leq \mathcal{S}_{as} - \mathcal{S}_{ws}.$$

(c) Typical length scales at which the surface tension effects become significant are given by the condition that the forces exerted by surface tension and relevant pressures become comparable, or by the condition that the surface energy is comparable to the other energy changes of interest.

Example 1: Size of water drops not much deformed on a non-wetting surface.

This is given by equalizing the surface energy and the gravitational energy,

$$S \cdot 4\pi R^2 \approx mgR = \rho V g R = \frac{4\pi}{3} R^4 g,$$

leading to

$$R \approx \sqrt{\frac{3S}{\rho g}} \approx \sqrt{\frac{3 \cdot 7 \times 10^{-2} N/m}{10^3 kg/m^3 \times 10 m/s^2}} \approx 1.5 \times 10^{-3} m = 1.5mm.$$

Example 2: Swelling of spherical gels in a saturated vapor:

Osmotic pressure of the gel (about 1 atm) = surface tension of water, gives

$$\pi_{gel} \approx \frac{N}{V} k_B T \approx \frac{2S}{R},$$

where N is the number of counter ions within the gel. Thus,

$$R \approx \left(\frac{2 \times 7 \times 10^{-2} N/m}{10^5 N/m^2} \right) \approx 10^{-6} m.$$

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2. *Surfactants* are molecules having a hydrophilic group and a hydrophobic tail, and prefer to go to the interface between water and air, or water and oil. Some examples are,

$$CH_3 - (CH_2)_{11} - SO_3^- \cdot Na^+,$$

$$CH_3 - (CH_2)_{11} - N^+(CH_3)_3 \cdot Cl^-,$$

$$CH_3 - (CH_2)_{11} - O - (CH_2 - CH_2 - O)_{12} - H.$$

(a) The surfactant molecules are spread over the surface of water and behave as a two dimensional gas. The gas has a pressure proportional to the density and the absolute temperature, which comes from the two dimensional degrees of freedom of the molecules. Thus the surfactants lower the free energy of the surface when the surface area is increased.

$$\Delta F_{\text{surfactant}} = \frac{N}{A} k_B T \cdot \Delta A = (S - S_o) \cdot \Delta A, \quad \Longrightarrow \quad \mathcal{S} = \mathcal{S}_o - \frac{N}{A} k_B T.$$

(Note that surface tension is defined with a sign opposite to that of hydrostatic pressure.)

(b) As shown in Problem 1(b), the contact angle satisfies

$$\cos\theta = \frac{\mathcal{S}_{as} - \mathcal{S}_{ws}}{\mathcal{S}_{aw}}.$$

Touching the surface of the droplet with a small piece of soap reduces $\mathcal{S}_{aw}$, hence $\cos\theta$ increases, or equivalently, the angle θ decreases.

(c) When the surfactant molecules are dense their interaction becomes important, resulting in

$$\left. \frac{\partial \mathcal{S}}{\partial A} \right|_T = \frac{N k_B T}{(A - Nb)^2} - \frac{2a}{A} \left(\frac{N}{A} \right)^2,$$

and

$$\left. \frac{\partial T}{\partial \mathcal{S}} \right|_A = -\frac{A - Nb}{N k_B}.$$

Integrating the first equation, gives

$$\mathcal{S}(A, t) = f(T) - \frac{N k_B T}{A - Nb} + a \left(\frac{N}{A} \right)^2,$$

where $f(T)$ is a function of only T, while integrating the second equation, yields

$$\mathcal{S}(A,T) = g(A) - \frac{Nk_BT}{A-Nb},$$

with $g(A)$ a function of only A. By comparing these two equations we get

$$\mathcal{S}(A,T) = \mathcal{S}_o - \frac{Nk_BT}{A-Nb} + a\left(\frac{N}{A}\right)^2,$$

where $\mathcal{S}_o$ represents the surface tension in the absence of surfactants and is independent of A and T. The equation resembles the van der Waals equation of state for gas-liquid systems. The factor Nb in the second term represents the excluded volume effect due to the finite size of the surfactant molecules. The last term represents the binary interaction between two surfactant molecules. If surfactant molecules attract each other the coefficient a is positive the surface tension increases.

(d) Taking A and T as independent variables, we obtain

$$\delta Q = dE - \mathcal{S}\cdot dA, \quad \Longrightarrow \quad \delta Q = \left.\frac{\partial E}{\partial A}\right|_T dA + \left.\frac{\partial E}{\partial T}\right|_A dT - \mathcal{S}\cdot dA,$$

and

$$\delta Q = \left(\left.\frac{\partial E}{\partial A}\right|_T - \mathcal{S}\right) dA + \left.\frac{\partial E}{\partial T}\right|_A dT.$$

From the above result, the heat capacities are obtained as

$$\begin{cases} C_A \equiv \left.\dfrac{\delta Q}{\delta T}\right|_A = \left.\dfrac{\partial E}{\partial T}\right|_A \\ C_{\mathcal{S}} \equiv \left.\dfrac{\delta Q}{\delta T}\right|_{\mathcal{S}} = \left(\left.\dfrac{\partial E}{\partial A}\right|_T - \mathcal{S}\right) \left.\dfrac{\partial A}{\partial T}\right|_{\mathcal{S}} + \left.\dfrac{\partial E}{\partial T}\right|_{\mathcal{S}} \end{cases},$$

resulting in

$$C_{\mathcal{S}} - C_A = \left(\left.\frac{\partial E}{\partial A}\right|_T - \mathcal{S}\right) \left.\frac{\partial A}{\partial T}\right|_{\mathcal{S}}.$$

Using the chain rule relation

$$\left.\frac{\partial T}{\partial \mathcal{S}}\right|_A \cdot \left.\frac{\partial \mathcal{S}}{\partial A}\right|_T \cdot \left.\frac{\partial A}{\partial T}\right|_{\mathcal{S}} = -1,$$

we obtain

$$C_{\mathcal{S}} - C_A = \left(\left.\frac{\partial E}{\partial A}\right|_T - \mathcal{S}\right) \cdot \left(\frac{-1}{\left.\frac{\partial T}{\partial \mathcal{S}}\right|_A \cdot \left.\frac{\partial \mathcal{S}}{\partial A}\right|_T}\right).$$

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