Surfaces and Interfaces 2023 Fall Semester

Exercise 3-Solutions

1. The microscopic origin of surface tension (σ) for a system in certain conditions (i.e. liquid, solid) lies ultimately in the atomistic nature of matter; in other words, it depends on the type and strength of bonds that hold together the system we are dealing with. (Water, with its peculiar "hydrogen bond network," is a prime example of this). As a consequence surface tension strongly depends on state variables like pressure and temperature; in particular, if the pressure is fixed, the surface tension depends on temperature and concentrations (if our substance is not pure or presents local impurities): σ(T,c).
Mass transfer due to the presence of surface tension gradients represents the important phenomenon called the Gibbs-Marangoni effect (GB). There are numerous manifestations of this effect, although in many cases, other phenomena are preponderant. Here we take as a case study the so-called "tears of wine" that you can see in the snapshot below.

Figure 1 A glass with “tears” of wine caused by the Marangoni effect.

Wine can be regarded as a water-alcohol mixture. If you take a glass of wine like the one in the picture, the Gibbs-Marangoni effect is usually seen when there is a thin film of wine on the internal surface of the glass. This thin film of wine is quickly being depleted of alcohol and since the latter has a lower surface tension than water, a gradient in surface tension appears.

a) Can you explain why the concentration of alcohol in the thin film decreases fast enough to deplete the wine mixture of alcohol? Surface science: what differentiates a bulk quantity of wine from a thin layer of it?

b) What does the presence of a gradient with respect to the concentration give rise to? *Hint: think about the definition of the surface tension. What does a force gradient imply?*

Solution:

a) The large “surface to volume ratio” of the thin film is the responsible for the quick depletion of alcohol ($\frac{S}{V} \propto \frac{1}{D}$ where D is the unit of length (Surface is $\propto D^2$, while volume is $\propto D^3$). The evaporation rate of a substance is directly related to this ratio, since evaporation is a phenomenon occurring on the surface. Then, alcohol (with a higher vapor pressure than water), will tend to evaporate faster.
In general, smaller systems tend to have different properties with respect to their bulk counterpart precisely for this ratio, which increases as the characteristic dimension decreases.

b) Alcohol concentration in the thin film of wine deposited on the glass surface will quickly decrease and the mixture will become water-rich. Because alcohol has a lower surface tension than water, a gradient of surface tension develops pointing upwards and so pulling the mixture up. Wine goes on climbing up the glass surface until gravity becomes equal to the tangential force caused by the surface tension gradient. Eventually, gravity will win because of the increasing mass of substance accumulated, which will fall back into the bulk wine. In theory, this process will continue as long as there is some alcohol left.

2. Several experimental methods can be used to measure surface tensions and liquid-liquid interfacial tensions. Some of the more common ones are based on a microbalance (it measures the force) that holds a probe located at the interface. There are several shapes for this probe, like the Wilhelmy plate and the Du Noüy Ring (Fig. 1 and Fig. 2).

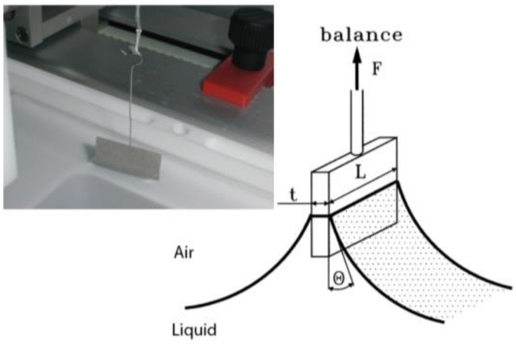


Fig. 1 A schematic of the Wilhelmy plate method.

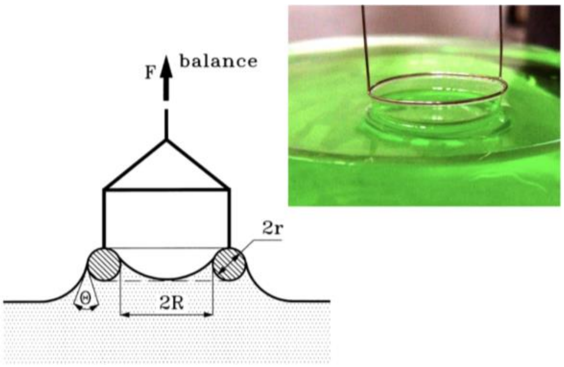


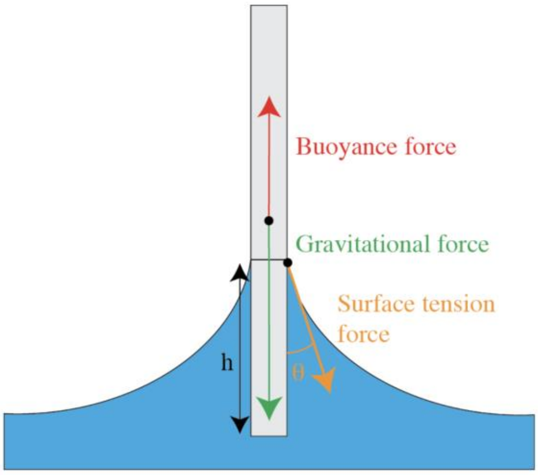
Fig. 2 Illustration of the ring method.

a) For the Wilhemy plate equilibrium situation, deduce the force balancing equations acting on the microbalance.
b) Derive the change in force ΔF due to a change in surface tension $\Delta\gamma$ to maintain equilibrium for the Wilhemy plate and for the Du Noüy ring. Make some geometrical assumptions to simplify the equations.

Solution:

a) The total force acting on the microbalance is the sum of three forces: gravitational, surface tension and buoyancy. If we assume that the wire sustaining the plate is massless, we can obtain the following expression for the vertical balance of forces (compare it with the schematic representation of the forces in the drawing below):

$$F_{balance} = \rho_{plate}V_{plate}g - \rho_{liquid}V_{immersed-plate}g + \gamma_{liquid}\,2(L+t)cos\theta$$



b) Wilhemy plate:

Considering an equilibrium situation all the variables (h, the densities of the solid and the liquid, the dimensions of the plate) that contribute to the vertical component of the total force remain constant. The only force that changes is the one from the microbalance to compensate for the change in surface tension. So the difference (final and initial) in the force is:

$$\Delta F = F^{f} - F^{i} = 2\gamma_f(L+t)cos\theta_f - 2\gamma_i(L+t)cos\theta_i = 2(L+t)(\gamma_f cos\theta_f - \gamma_i cos\theta_i)$$

Typically, the thickness of the plate (t) is much smaller than the side (L) so the term 2(L+t) can be approximated to 2L. Normally the plate is made of a highly hydrophilic material so, for water-based or hydrophilic liquids, both the angles tend to be 0 and the term $\gamma_f cos\theta_f - \gamma_i cos\theta_i$ can be approximated to $\gamma_f - \gamma_i = \Delta\gamma$. Thus we obtain that a change in surface tension leads to the following change in force the microbalance needs to apply to maintain equilibrium :

$$\frac{\Delta F}{\Delta\gamma} = 2L$$

Du Noüy ring:

Equally, in the case of the Du Noüy ring, the only force that change is the one from the microbalance due to the change in surface tension, so we can express it similarly to the previous case:

$$\Delta F = F_{\perp}^{f} - F_{\perp}^{i} = \gamma_f P cos\theta_f - \gamma_i P cos\theta_i = P(\gamma_f cos\theta_f - \gamma_i cos\theta_i)$$

Where P is the total perimeter in contact with the liquid. Here we express θ as half the angle sketched in the drawing to maintain similarity between the equations of the two systems. So, the actual value is:

$$\Delta F = [2\pi R + 2\pi(2r + R)]\big(\gamma_f cos\theta_f - \gamma_i cos\theta_i\big)$$

Like in the former case, the material of the ring is hydrophilic and, typically, the liquids used are water or hydrophilic liquids, so the angle tends to 0. Moreover, the ring is made such that R$\gg r$, so we can rewrite the above expression as:

$$\Delta F = [2\pi R + 2\pi(2r + R)](\gamma_f cos\theta_f - \gamma_i cos\theta_i) \approx 4\pi R(\gamma_f - \gamma_i) = 4\pi R\Delta\gamma$$

$$\frac{\Delta F}{\Delta\gamma} = 4\pi R$$

3. Roughness of a parabolic corrugated solid surface

Consider a liquid droplet on top of a periodic corrugated solid surface: the crest of periodic ripple is parabolic and exists along the x-axis only:
It can be expressed as

$$f(x) = -\frac{x^2}{2} \qquad x \in [\frac{-a_0}{2}, \frac{a_0}{2}]$$

Where a_0 is defined in Fig. 1: the solid surface is flat along the y-axis.
Assuming such system (for simplification of calculation, one may imagine a semi-cylinder: system with semi-circle shape cross section with certain thickness, in contact with a foreign surface), determine the roughness ϕ. *Hint: We would like to recall what is line integral. Line integral is an integral where is function is integrated along a curve C. For the purposes of this exercise, we can write this integral in 2D-space as:*

$$\int_C ds = \int_C \sqrt{(dx)^2 + (dy)^2} = \int_a^b \sqrt{1 + |\frac{dy}{dx}|^2} dx$$

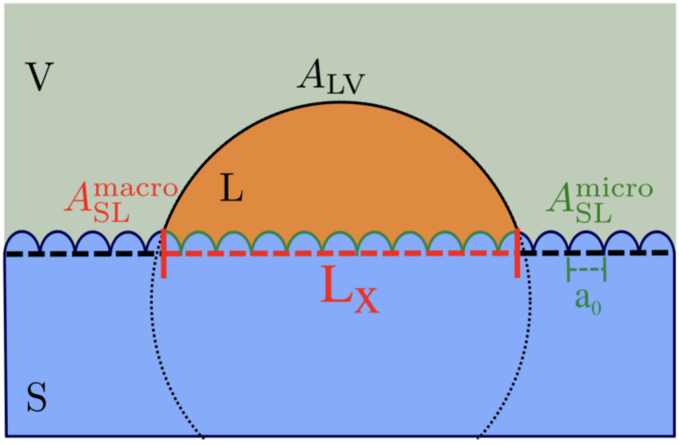
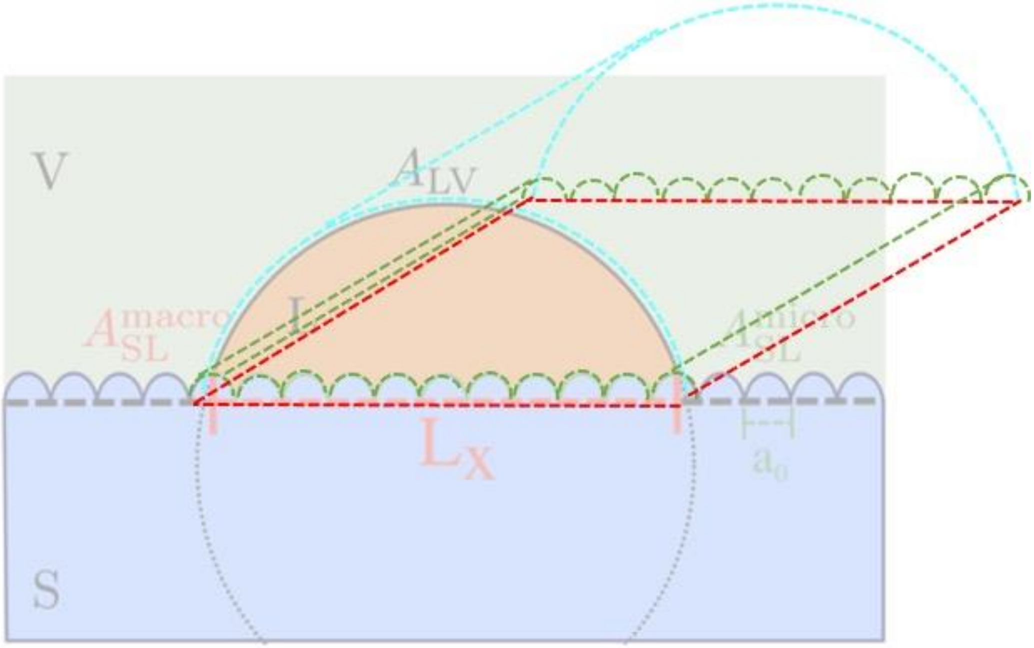


Figure 1: A droplet on top of a parabolic corrugated solid surface. The droplet is bounded by vertices of the parables and a_0 is the projection of the microscopic size along the x-axis.

Solution:



Let’s start form the definition of roughness:

$$\phi = -\frac{A_{SL}^{micro}}{A_{SL}^{macro}} = \frac{L_x^{micro} L_y^{micro}}{L_x^{macro} L_y^{macro}}$$

In this formula, we need only to calculate L_x^{micro} using the definition of the line integral, we can obtain:

$$L_x^{micro} = N \int_0^{a_0} \sqrt{1 + x^2} dx = 2N \int_0^{a_0/2} \sqrt{1 + x^2} dx$$

Where N is the number of crests.
Now, if we write $N = Lx/a_0$ and make this substitution, $x = sinh\theta$, we get:

$$sinh\theta = \frac{e^{\theta} - e^{-\theta}}{2}$$

$$cosh\theta = \frac{e^{\theta} + e^{-\theta}}{2}$$

$$L_x^{micro} = \frac{L_x^{macro}}{a_0} [sinh\theta cosh\theta + \theta]|_0^{sinh^{-1}(a_0/2)}$$

$$= \frac{L_x^{macro}}{a_0} [\frac{a_0}{2} cosh\left(sinh^{-1}\left(\frac{a_0}{2}\right)\right) + sinh^{-1}\left(\frac{a_0}{2}\right)]$$

We can rewrite the above expression as (one may also use other integration ways to derive the following expression):

$$L_x^{micro} = \frac{L_x^{macro}}{a_0} [\frac{a_0}{4} \sqrt{4 + {a_0}^2} + ln\,(\frac{a_0 + \sqrt{4 + {a_0}^2}}{2})]$$

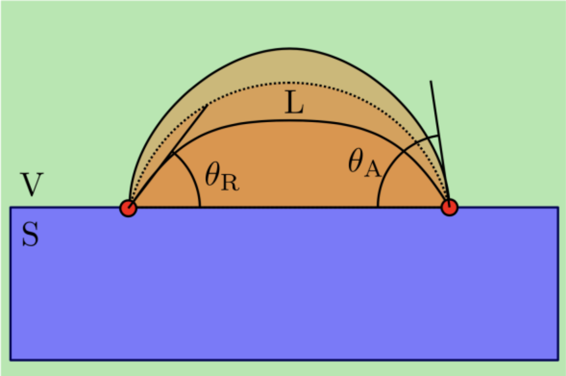
Eventually, we get:

$$\phi = \frac{L_x^{micro}}{L_x^{macro}} = \frac{1}{a_0} [\frac{a_0}{4} \sqrt{4 + {a_0}^2} + ln\,(\frac{a_0 + \sqrt{4 + {a_0}^2}}{2})]$$

4. Spreading equilibrium pressure and work of adhesion of a droplet

In real surfaces, the triple line is ‘‘pinned’’, so in practice there is a range of meta-stable contact angles (‘‘contact angle hysteresis’’). Consider a liquid droplet on top of a flat solid surface and a micro-syringe, which can insert additional liquid, immersed inside the droplet.

In this way we can expand the droplet to its maximum volume allowable for the initial liquid–solid interfacial area: any further addition will increase both volume and the liquid–solid interfacial area. The contact angle for this maximum volume is called “advancing contact angle”, θ_A. Vice versa, if liquid is removed from the droplet by micro-syringe, the volume will decrease keeping the same liquid-solid interfacial area until the latter will be forced to shrink. Just before the shrinking the droplet assumes the smallest contact angle, called “receding contact angle”, θ_R.



In the receding condition (suction phase), there is an internal negative pressure π, also called “spreading equilibrium pressure”, which acts on the surface of the droplet. This pressure changes the Young expression as follows:

$$\gamma_{LV}\, cos\theta_R - \pi = \gamma_{SV} - \gamma_{SL}$$

Since θ_A and θ_R can be easily measured by experiments and γ_{LV} is generally known in literature:

a) Derive the spreading equilibrium pressure as a function of these physical quantities, $\pi(\theta_A, \theta_R, \gamma_{LV})$

b) Derive the work of adhesion in advancing mode as a function of two of these physical quantities, $W^{adv}(\theta_A, \gamma_{LV})$

Solution:

a) If we consider Young’s equation both in receding mode (above expression) and in advancing one,

$$\gamma_{LV}\, cos\theta_A = \gamma_{SV} - \gamma_{SL}$$

We can derive the spreading equilibrium pressure as follows:

$$\pi = \gamma_{LV}(cos\theta_R - cos\theta_A)$$

b) If we use Dupre equation

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - W^{adv}$$

And Young’s equation in advancing mode, we obtain:

$$W^{adv} = \gamma_{LV}(1 + cos\theta_A)$$