Surfaces and Interfaces 2023 Fall Semester

Exercise 3

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). Consequently, 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): $\sigma(T,c)$.

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 other phenomena are preponderant in many cases. 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?*

2. Several experimental methods can be used to measure surface tension and liquid-liquid interfacial tension. 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, but the Wilhelmy plate and the Du Noüy Ring (Fig. 1 and Fig. 2) are the most common ones.

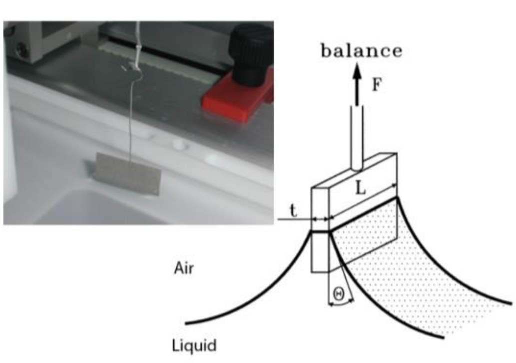


Fig. 1 A schematic of the Wilhelmy plate method.

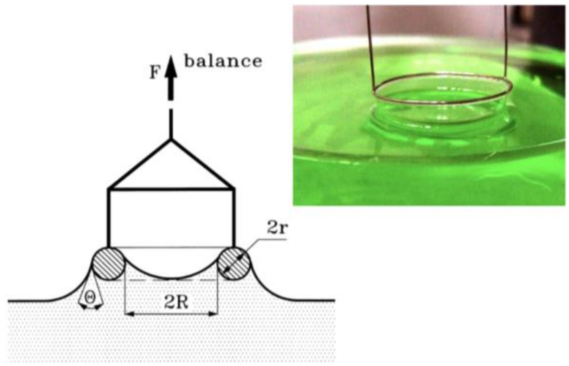


Fig. 2 Illustration of the ring method.

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 $\Delta\gamma$ for the Wilhemy plate and for the Du Noüy ring. Make some geometrical assumptions to simplify the equations.

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:*

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

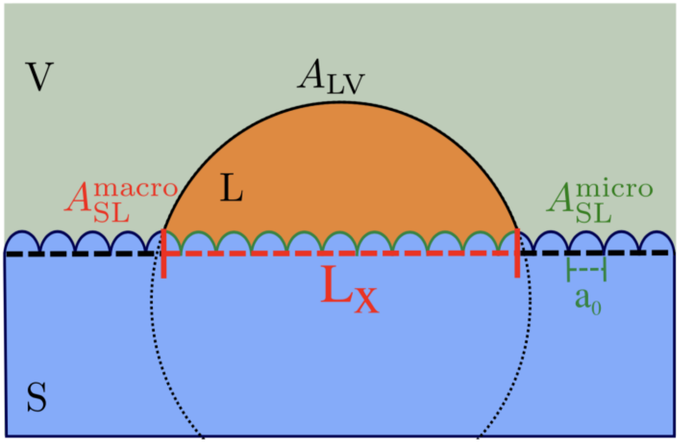
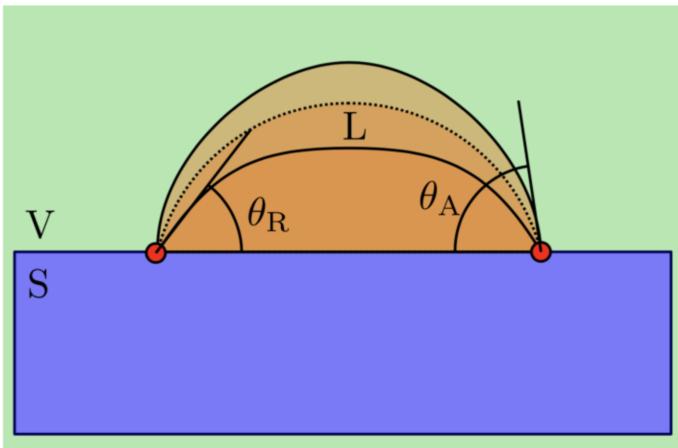


Figure 1: A droplet on top of a parabolic corrugated solid surface. The droplet is bounded by vertices of the parables and a_0 is the projection of the microscopic size along the x-axis.

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, $W^{adv}(\theta_A, \gamma_{LV})$