* Exercise 1 Surface tension gradients

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

Mass transfer due to the presence of surface tension gradients represents the important phenomenon called *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 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 σ with respect to the concentration give rise to? *Hint: think about the definition of surface tension. What does a force gradient imply?*

Solution to Exercise 1

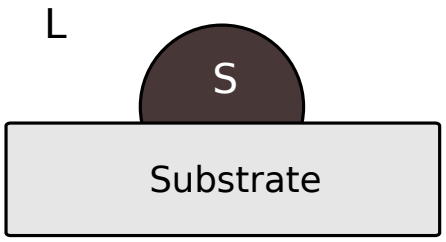
(**a**) The "surface to volume ratio" is responsible of the quick depletion of alcohol. $S/V \propto 1/D$ where D is the unit of length (surface is $\propto D^2$, while the volume $\propto D^3$). In general, smaller systems tend to have different properties with respect to their bulk counterpart precisely for this ratio which increases as the characteristic dimension decreases. The boiling temperature of a substance is a property which is roughly proportional to to S/V. A thin film is a system where surface has a much larger contribution than in bulk. Alcohol, with a higher vapour pressure, will tend to evaporate faster than in the bulk.

(**b**) Alcohol concentration in the thin film of wine deposited on the glass surface will quickly decrease and the mixture will became 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 can go on climbing up the glass surface until the second force into play (gravity) equal 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 until there is some alcohol left.

** Exercise 2 Heterogeneous crystal nucleation on a substrate

Crystallization can also be facilitated by introducing foreign substances. In fact, heterogeneous nucleation, nucleation starting at a surface, is faster and more common than homogeneous nucleation.

(a) Take γ_{SL}, $\gamma_{SS'}$, $\gamma_{S'L}$ to be the interfacial free energy between solid-liquid, solid-substrate, and substrate-liquid, respectively. Can you predict the equilibrium shape of a nucleus formed on the substrate? Assume $\gamma_{S'L} + \gamma_{SL} - \gamma_{SS'} > 0$.



(b) For the nucleus formed on the substrate as in (a), can you write out the expression for the free energy ΔG as a function of volume V and contact angle θ?

(c) Make a plot to illustrate the relationship between ΔG and the volume of the nucleus both in heterogeneous nucleation and in homogeneous nucleation. How do the free energy barriers of the two compare to each other?

(d) Suppose for this system γ_{SL} is constant across all temperatures, and the chemical potential ΔG_{SL} can be expressed as

$$\Delta G_{SL} = H_f \frac{T_m - T}{T_m},$$

where $H_f > 0$ is the constant of latent heat per unit volume, and T_m is the melting point of the system. Based on these assumptions, can you write down the nucleation free energy barrier as a function of the temperature T?

(e) According to (d), will the system solidify at $T = T_m$? Write down the condition between γ_{SL}, $\gamma_{SS'}$ and $\gamma_{S'L}$, under which the system will solidify at $T = T_m$.

Solution to Exercise 2

Question (a).

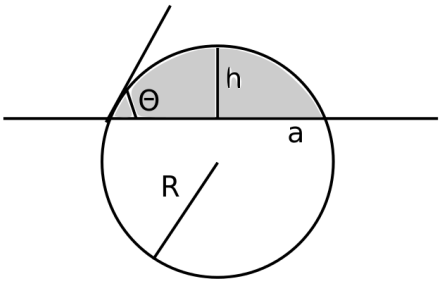
Cont.

The shape of a nucleus formed on the substrate is a truncated sphere with contact angle θ following the Young's equation:

$$\gamma_{S'L} = \cos(\theta)\gamma_{SL} + \gamma_{SS'},$$

so

$$\theta = \arccos(\frac{\gamma_{S'L} - \gamma_{S'S}}{\gamma_{SL}}).$$



Question (b).

Take the height of the cap as $h = R(1 - \cos\theta)$, then the volume V of the truncated sphere is

$$V = \frac{\pi h^2}{3}(3R - h)$$

and the curved surface area A_{SL} of the spherical cap is

$$A_{SL} = 2\pi Rh.$$

The contact area between the nucleus and the substrate is

$$A_{SS'} = \pi a^2.$$

Notice that $h = (1 - \cos\theta)R$ and $a = \sin(\theta)R$, and we have

$$A_{SL} = (72\pi)^{\frac{1}{3}}(1 - \cos\theta)^{-\frac{1}{3}}(2 + \cos\theta)^{-\frac{2}{3}}V^{\frac{2}{3}}$$

and

$$A_{SS'} = (9\pi)^{\frac{1}{3}}(1 + \cos\theta)(1 - \cos\theta)^{-\frac{1}{3}}(2 + \cos\theta)^{-\frac{2}{3}}V^{\frac{2}{3}}.$$

Plug these values into the expression for $\Delta G = -V\Delta G_{SL} + A_{SL}\gamma_{SL} + A_{SS'}(\gamma_{SS'} - \gamma_{S'L})$, and obtain

$$\begin{aligned}\Delta G(V) &= -V\Delta G_{SL} + (72\pi)^{\frac{1}{3}}(1 - \cos\theta)^{-\frac{1}{3}}(2 + \cos\theta)^{-\frac{2}{3}}V^{\frac{2}{3}}\gamma_{SL} + \\ &\qquad (9\pi)^{\frac{1}{3}}(1 + \cos\theta)(1 - \cos\theta)^{-\frac{1}{3}}(2 + \cos\theta)^{-\frac{2}{3}}(\gamma_{SS'} - \gamma_{S'L}) \\ &= -V\Delta G_{SL} + (9\pi)^{\frac{1}{3}}(1 - \cos\theta)^{-\frac{1}{3}}(2 + \cos\theta)^{-\frac{2}{3}}V^{\frac{2}{3}}(2\gamma_{SL} + (1 + \cos\theta)(\gamma_{SS'} - \gamma_{S'L})) \\ &= -V\Delta G_{SL} + (9\pi)^{\frac{1}{3}}(1 - \cos\theta)^{\frac{2}{3}}(2 + \cos\theta)^{\frac{1}{3}}V^{\frac{2}{3}}\gamma_{SL}.\end{aligned}$$

Question (c).

For homogeneous nucleation,

$$\Delta G(V) = -V\Delta G_{SL} + (36\pi)^{\frac{1}{3}}V^{\frac{2}{3}}\gamma_{SL}.$$

Notice that the geometrical constant $(9\pi)^{\frac{1}{3}}(1 - \cos\theta)^{\frac{2}{3}}(2 + \cos\theta)^{\frac{1}{3}}$ for heterogeneous nucleation is smaller than the geometrical constant $(36\pi)^{\frac{1}{3}}$ for homogeneous nucleation. This means the free energy barrier for heterogeneous nucleation is lower.

Cont.

Question (d).

$$\Delta G(V) = -VH_f \frac{T_m - T}{T_m} + (9\pi)^{\frac{1}{3}}(1-\cos\theta)^{\frac{2}{3}}(2+\cos\theta)^{\frac{1}{3}}V^{\frac{2}{3}}\gamma_{SL}$$

Question (e). Only if the contact angle $\theta = 0$, i.e. complete wetting, so when

$$\gamma_{S'L} \geq \gamma_{S'S} + \gamma_{SL}.$$

The End.