* 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.

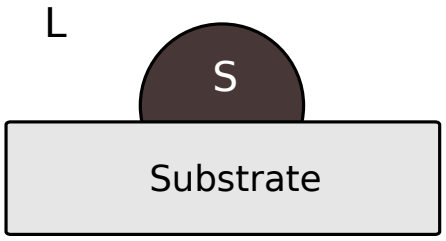
(a) Can you explain why the concentration of alcohol in the thin film decreases fast enough to deplete the wine mixture of alcohol? *Surface science: what differentiates a bulk quantity of wine from a thin layer of it?*

(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?*

** 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 $T = T_m$.

The End.