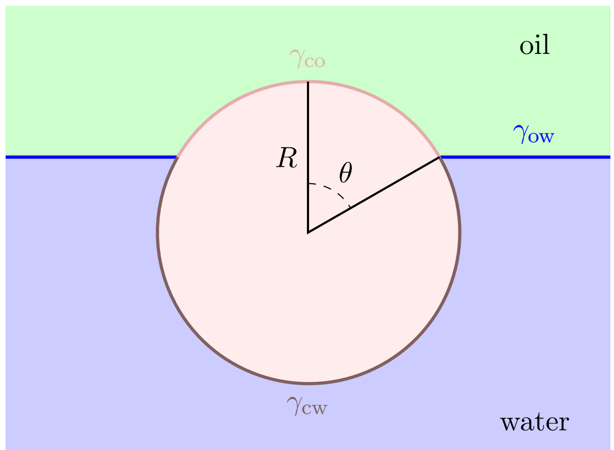
Dynamics of a Colloidal Suspension

A colloid refers to a mesoscopic particle, $\sim 1\ \mu$m across, often charged and placed in some liquid. A colloidal suspension can occur when you place many of these colloids in, say, a mixture of water and oil. If the colloids are placed near the surface between oil and water, thermodynamically we know that they will get stuck.

We begin by studying a simple classical model. Suppose we have a spherical colloid of radius R stuck on the interface between oil and water, with surface tension γ_{ow} between oil/water, γ_{co} between colloid/oil, and γ_{cw} between colloid/water. Note that it is a safe assumption that $\gamma_{\text{ow}} > \gamma_{\text{cw}} + \gamma_{\text{co}}$, almost always.



(a) Determine the free energy change ΔG, due to the changes in surface energies, when the particle is at angle θ as shown in the figure above.

(b) At what angle will the particle come to rest?

(c) Using $R \approx 1\ \mu$m, $k_{\text{B}}T \approx 4 \times 10^{-21}$ J, and $\gamma_{\text{ow}} \approx 4 \times 10^{-2}$ J/m^2, explain why the colloid will get stuck to the interface in an experiment.

Now, let us classically approximate the dynamics of a colloid approaching and getting stuck to the interface. Assume, as is usually reasonable, that the (kinematic) viscosity $\eta \approx 10^{-2}$ kg/s $\cdot$ m of water is much larger than of oil. The density of water is about $\rho \approx 1000$ kg/m^3.

(d) Argue that the flow is at very low Reynolds number, and so it is a reasonable approximation that the viscous damping force balances the force due to the free energy gradient found the previous part.

(e) One can estimate the power loss for viscous dissipation for $\theta \ll 1$ as:

$$P \approx \frac{\eta R^2 \dot{\theta}^2}{\theta}.$$

Equate this to the power dissipated by viscous damping due to the force from the free energy gradient to show that

$$\dot{\theta} \approx \frac{1}{\eta R} \left(\gamma_{\text{ow}} + \gamma_{\text{cw}} - \gamma_{\text{co}}\right) \theta^2$$

for small θ.

(f) Estimate the time scale of the dynamics – how long (order of magnitude speaking) does it take for the colloid to reach equilibrium?

Your answer to the above is off by *orders of magnitude*, compared to experimental data, suggesting that another mechanism is actually responsible for the dynamics of the colloid. It turns out the model which gives the best fit to experimental data is described as follows: there are many small defects on the surface of the colloid, perhaps charges on the surface. These defects get trapped on the boundary, and you need to provide a thermal kick to get over these defects. We can thus justify the following empirical relation:

$$\dot{\theta} = \frac{u}{R} \exp\left[\frac{A}{k_{\mathrm{B}}T}\left(\gamma_{\mathrm{ow}}\cos\theta + \gamma_{\mathrm{cw}} - \gamma_{\mathrm{co}}\right)\right]$$

with u an unknown constant related to the speed of hopping over the defects, and A related to the area of the defects.

(g) If θ_0 is the equilibrium angle found earlier, let

$$\begin{aligned} \alpha &= \frac{u}{R} \\ \beta &= \frac{A\gamma_{\mathrm{ow}}\sin\theta_0}{k_{\mathrm{B}}T}. \end{aligned}$$

By expanding about the equilibrium point: $\phi = \theta_0 - \theta$, show that the equation

$$\phi(t) \approx -\frac{1}{\beta}\log(\alpha\beta(t - t_0))$$

captures the dominant dynamics.

(h) The presence of a logarithm is experimentally observable in the dynamics, which is a good sign for this model. Argue that the value of u is not very important experimentally, but the value of A is, and that for any reasonable guess at A, the dynamics are *extremely slow* and that an estimate that the time required for equilibrium is on the scale of 10^6 seconds is not unreasonable.