

SURFACE TENSION AND CLOUD FORMATION

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.46.

At the boundary between two phases, there are some molecules that are in a sort of “transition phase”, that is, in neither one phase nor the other. To describe the phase boundary more fully, then, we need to add a term to the Gibbs free energy for these boundary molecules. It turns out that the thickness of the boundary layer is more or less constant, independent of the area of the boundary. The extra Gibbs free energy is therefore proportional to the area of the boundary:

$$G_{\text{boundary}} = \sigma A \quad (1)$$

where the proportionality coefficient σ is called the *surface tension*. It represents the minimum work (per unit area) required to reshape a portion of a substance into a form with a larger surface area. For liquid water at 20° C, $\sigma = 0.073 \text{ J m}^{-2}$.

As an example, suppose we have a spherical droplet of water of radius r containing N_l molecules surrounded by $N - N_l$ molecules of water vapour. If we write the Gibbs free energy in terms of the chemical potential, the Gibbs energy of this system, initially neglecting surface tension, is

$$G = N_l \mu_l + (N - N_l) \mu_g \quad (2)$$

where the subscripts l and g stand for 'liquid' and 'gas'.

Given the volume per molecule v_l in the liquid, we can write

$$v_l = \frac{4\pi r^3}{3N_l} \quad (3)$$

$$G = -\frac{4\pi r^3}{3v_l} (\mu_g - \mu_l) + N\mu_g \quad (4)$$

Adding in the energy due to surface tension gives

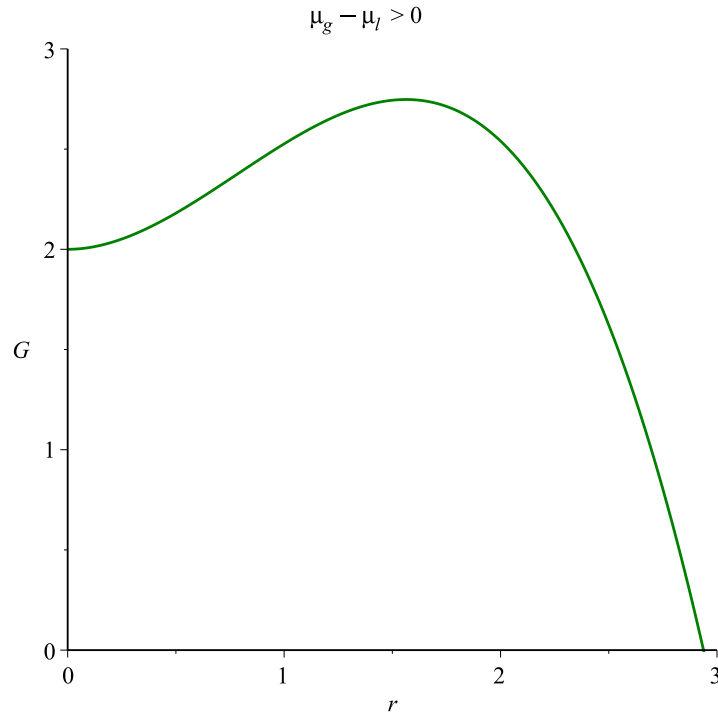
$$G = -\frac{4\pi r^3}{3v_l} (\mu_g - \mu_l) + N\mu_g + 4\pi r^2 \sigma \quad (5)$$

Equilibrium values of the sphere's radius r are obtained when $\partial G/\partial r = 0$, so that there is no change in Gibbs energy when r is changed by an amount dr . This gives

$$\frac{\partial G}{\partial r} = -\frac{4\pi r^2}{v_l}(\mu_g - \mu_l) + 8\pi r\sigma = 0 \quad (6)$$

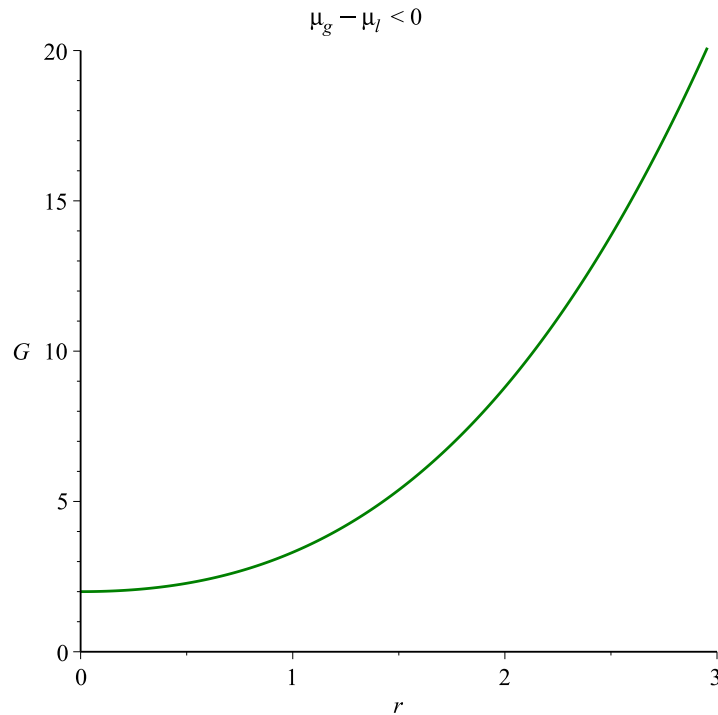
$$r_c = \frac{2\sigma v_l}{\mu_g - \mu_l} \quad (7)$$

In order for $r_c > 0$, we need $\mu_g > \mu_l$. The Gibbs energy for this case looks qualitatively like this [units are arbitrary; it's just the shape of the graph we're interested in]:



Because G is a maximum at the equilibrium point, this is an unstable equilibrium, meaning that if r is nudged slightly lower, the tendency is for the droplet to continue to decrease in size due to evaporation, while if r is nudged slightly higher, the tendency is for the droplet to continue to increase in size.

If $\mu_g < \mu_l$ we get:



There is a minimum at $r = 0$, but this isn't a physical solution.

To convert 7 into a form involving the relative humidity, we can start with the thermodynamic identity for the Gibbs energy:

$$dG = -S dT + V dP + \mu dN \quad (8)$$

At constant temperature and number we have

$$dG = N d\mu = V dP \quad (9)$$

So for the liquid and gas phases, a slight change in the vapour pressure P results in

$$d\mu_g = \frac{V_g}{N_g} dP \quad (10)$$

$$= v_g dP \quad (11)$$

$$d\mu_l = v_l dP \quad (12)$$

Therefore the change in the difference between the chemical potentials is given by

$$d(\mu_g - \mu_l) = (v_g - v_l) dP \quad (13)$$

$$\approx v_g dP \quad (14)$$

$$= \frac{kT}{P} dP \quad (15)$$

where in the second line we used the fact that $v_g \gg v_l$, since the volume per gas molecule is much greater than the volume per liquid molecule. The last line assumes that the vapour is an ideal gas, so $v_g = V_g/N_g = kT/P$.

If the liquid and gas are in diffusive equilibrium, $\mu_g = \mu_l$ and the vapour is saturated so that $P = P_v$, so we can integrate to get

$$\mu_g - \mu_l = \int_0^{\mu_g - \mu_l} d(\mu_g - \mu_l)' \quad (16)$$

$$= kT \int_{P_v}^P \frac{dP'}{P'} \quad (17)$$

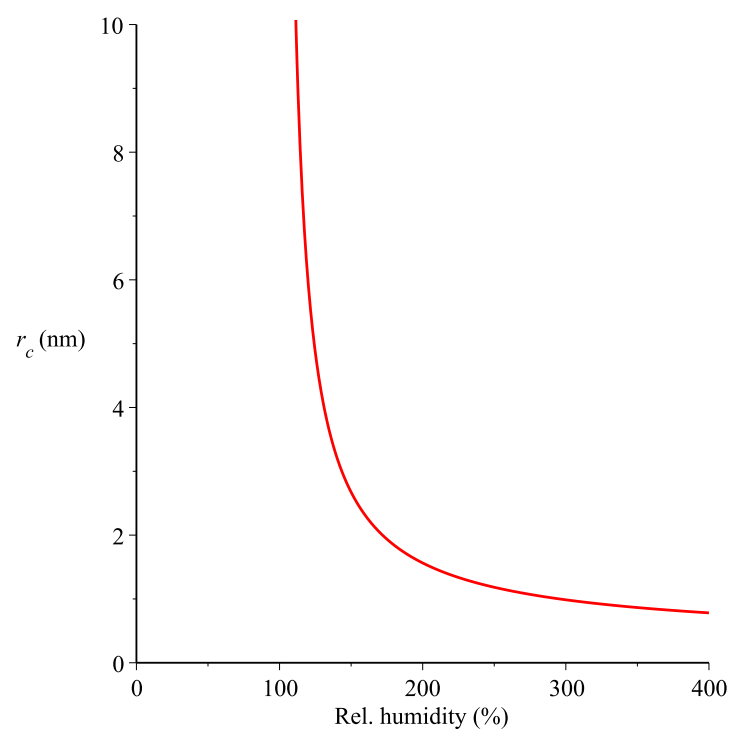
$$= kT \ln \frac{P}{P_v} \quad (18)$$

$$= kT \ln h \quad (19)$$

where h is the relative humidity. Plugging this into 7 we get

$$r_c = \frac{2\sigma v_l}{kT \ln h} \quad (20)$$

The snag with this equation is that the relative humidity is usually between 0 and 1, so $\ln h < 0$ and $r_c < 0$, which is clearly nonsense. In order for this equation to give a physical radius, we need $h > 1$, so the air is 'supersaturated'. In this case, a plot of r_c versus h looks like this:



In order for droplets to form, the initial droplet size has to be very large (relatively speaking; a radius of a few nanometres still contains a very large number of water molecules) so it would seem unlikely that such droplets would form spontaneously.