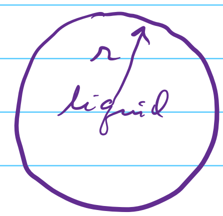
Phys 335: Problem 5.46: Nucleation

$$G = U - TS + pV + \underbrace{G_{boundary}}$$

Vapor



$G_{boundary} = \sigma A$

σ = surface tension
A = area

All other things being equal, minimizing $G \Rightarrow$ minimizing A; i.e. drops tend to be spherical.

Consider N molecules:

N_ℓ liquid
$N_v = (N - N_\ell)$ vapor

pure system: (Eq. 5.35)

$G = N\mu$ (neglecting boundary for now)

$\therefore$

$$G_v = N_v \mu_v = (N - N_\ell)\mu_v$$

$$G_\ell = N_\ell \mu_\ell = \left(\frac{\frac{4}{3}\pi r^3}{v_\ell}\right)\mu_\ell$$

where r = radius of the droplet and
v_ℓ = volume per molecule.

$$\therefore \; G = \left(N - \frac{\frac{4}{3}\pi r^3}{v_\ell}\right)\mu_v + \frac{\frac{4}{3}\pi r^3}{v_\ell}\mu_\ell$$

$$G = N\mu_v + \left(\frac{\frac{4}{3}\pi r^3}{v_\ell}\right)(\mu_\ell - \mu_v)$$

Now add in boundary:

$$G = N\mu_v + \frac{4\pi r^3}{3v_\ell}(\mu_\ell - \mu_v) + \sigma(4\pi r^2)$$

(a) if $\mu_\ell > \mu_v$, all terms are positive

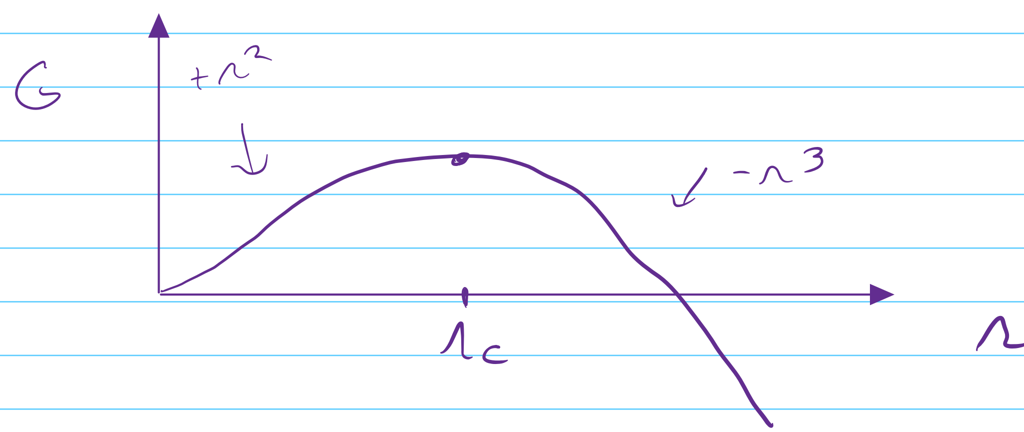
Minimizing $G \Rightarrow r \to 0$. Droplet evaporates.

(b) if $\mu_\ell < \mu_v$, our expectation without the boundary would be

$$G = N_v \mu_v + N_\ell \mu_\ell$$

make G minimum by converting entirely to liquid.
With the boundary:

$$G = N\mu_v + \frac{4\pi r^3}{3N_\ell}\underbrace{\left(\mu_\ell - \mu_v\right)}_{\text{negative}} + \sigma\left(4\pi r^2\right)$$



r_c = critical radius

If $r > r_c$, minimize G by growing further.
If $r < r_c$, " " " shrinking further.

$\therefore$ $r = r_c$ is unstable!

What is r_c?
Solve $\left.\frac{\partial G}{\partial r}\right) = 0$

$$G = N\mu_v + \frac{4\pi r^3}{3 v_\ell}\underbrace{(\mu_\ell - \mu_v)}_{\text{negative}} + \sigma(4\pi r^2)$$

$$\left.\frac{\partial G}{\partial r}\right|_{r=r_c} = 0 + \frac{4\pi r_c^2}{v_\ell}(\mu_\ell - \mu_v) + 8\pi r_c \sigma = 0$$

$$-\frac{r_c}{v_\ell}(\mu_\ell - \mu_v) = 2\sigma$$

$$r_c = \frac{2\sigma v_\ell}{\mu_v - \mu_\ell}$$

You can rewrite μ in terms of the relative humidity (RH) (Problem 5.42)

$$\mu_v = \mu_v^\circ + kT\ln(P/P^\circ) \qquad (P = \text{vapor pressure})$$

$^\circ \Rightarrow$ reference state
e.g. in equilibrium with a flat interface
$(r \to \infty)$
$\mu_v^\circ = \mu_\ell$, P/P° = relative humidity = RH

$\therefore$

$$\mu_v - \mu_\ell = kT\ln(RH)$$

$$r_c = \frac{2\sigma v_\ell}{kT \ln(RH)}$$

#'s: $\sigma = 0.073\ J/m^2$ at $T = 293\ K$

Units trick:

v_ℓ = volume of one molecule

V_ℓ = volume of 1 mole = $N_A v_\ell$

$$V_\ell = 18\ cm^3 \times \left(\frac{1\ m}{100\ cm}\right)^3 = 18 \times 10^{-6}\ m^3$$

$$r_c = \frac{2\sigma V_\ell / N_A}{kT \ln(RH)} = \frac{2\sigma V_\ell}{(N_A k) T \ln(RH)} = \frac{2\sigma V_\ell}{RT \ln(RH)}$$

$$r_c = \frac{2(0.073\ J/m^2)\cdot(18 \times 10^{-6}\ m^3)}{(8.314\ J/K)(293\ K)\ \ln(RH)}$$

$$r_c = \frac{1.08\ nm}{\ln(RH)}$$

Tiny, but .... each water molecule is much smaller. How many molecules is this

$$N_c = \frac{\frac{4}{3}\pi r_c^3}{v_\ell} = \frac{\frac{4}{3}\pi r_c^3}{V_\ell / N_A} = \frac{4}{3}\pi r_c^3 \cdot \frac{N_A}{V_\ell}$$

Suppose RH = 120% (i.e. supersaturated)

$$r_c = \frac{1.08\ nm}{\ln(1.2)} = 5.9\ nm$$

$$N_c = \frac{4}{3}\pi(5.9 \times 10^{-9} m)^3 \cdot \frac{6.02 \times 10^{23}}{18 \times 10^{-6}\ m^3} = 29{,}000 \text{ molecules.}$$

Groupings smaller than this will dissolve.

To get spontaneous growth, we need $N > N_c$ molecules to randomly cluster together. That is highly unlikely!

Getting such nucleation in a pure system is known as homogeneous nucleation. Getting nucleation on a pre-existing "seed" (e.g. a dust particle) is <u>much</u> easier, and is known as

heterogeneous nucleation.