

Nucleation Thermodynamics

- Fundamental question:
How (why?) do cloud droplets form in the atmosphere?
 - Water vapor can supersaturate as “closed” air parcels rise and cool (or cool some other way, e.g. radiatively)
 - Will drops form as soon as relative humidity exceeds 100%?
 - What do the first condensed drops look like (i.e., how large are they)?
 - And a related question, how do they keep growing into precipitation-sized drops?
- The process of forming a pure water droplet by condensation from the vapor phase, in the absence of a foreign particle or nucleating surface, is known as **homogeneous nucleation**.
- We ask the question: what is the energy cost of forming a water droplet from the vapor phase, and how does it depend on conditions (temperature, vapor pressure, size of droplet, ...)?


Before and after!

Same total water molecules, same T

Vapor only

N_T molecules

Each has chemical potential (partial molar Gibbs free energy), μ_v

 We used n molecules to make the drop

Vapor plus a droplet

$(N_T - n)$ vapor molecules
Each has chemical potential (partial molar Gibbs free energy), μ_v

n liquid molecules
Each has chemical potential (partial molar Gibbs free energy), μ_v

Plus, we had to make an interface

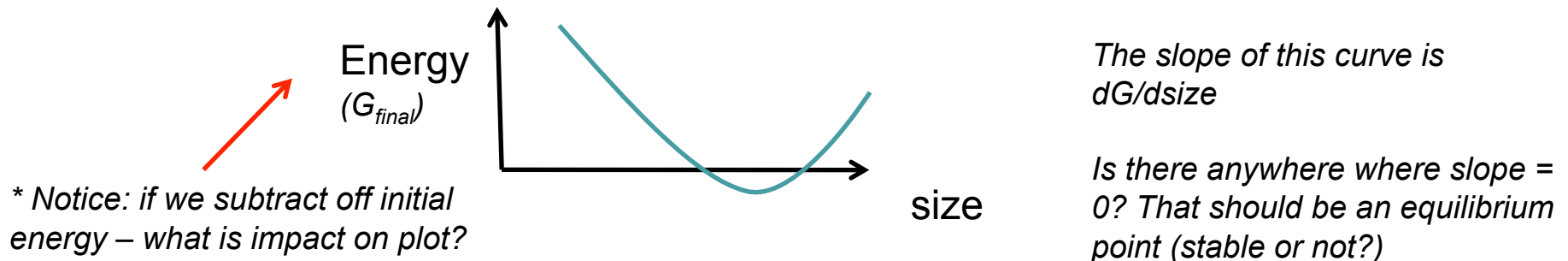
Calculating G

- Start with the “after” energy calculation:

$$G_{final} = (N_T - n)\mu_v + n\mu_l + 4\pi R^2\sigma$$

$$= N_T\mu_v + n(\mu_l - \mu_v) + 4\pi R^2\sigma$$

- The “before” calculation is straightforward: $G_{final} = N_T\mu_v$
- I think it’s easier to think about just the “final” energy calculation and see if we can find an equilibrium somewhere*. We don’t vary T as it’s already in equilibrium. The one thing that we *can* vary is the *size* of the droplet (called an “embryo” in nucleation theory).
- Notice that R and n both refer to the “size” of the embryo or droplet formed. We’ll need to get those into the same basis so we can vary only one “size” variable.
- We also need some guidance on how to compute μ_v and μ_l .
- Assuming we can do those things, then the general idea will be:



Energy calculations, continued

- Here's the equation that expresses the difference between the initial and final states:

$$\Delta G = n(\mu_l - \mu_v) + 4\pi R^2 \sigma$$

- First we need to eliminate either n or R . Let's keep R .
- The volume of a drop with radius R , containing n molecules:

$$\frac{4}{3}\pi R^3 = nV_l$$

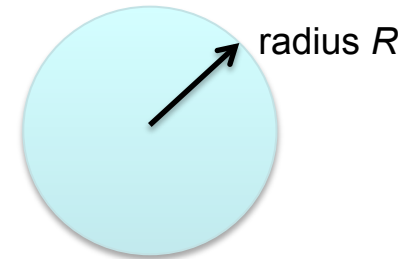
if V_l is the volume occupied by one molecule of water in the liquid phase. Define (plays the role of a density-type variable, molecules per unit volume):

$$n_l = \frac{1}{V_l}$$

- So now, $\Delta G = (n_l \frac{4}{3}\pi R^3)(\mu_l - \mu_v) + 4\pi R^2 \sigma$

Notice we should be writing this as σ_{LV} , the surface tension between the liquid and the vapor (but we can look this up for whatever T we are doing the calcs for)

Now we need to know how to deal with these terms!



Deriving expressions for chemical potentials

- We go back to the definition of the chemical potential that we can apply to each phase. Remember $dG = -SdT + pdV$
- If we have just a single component, we can put this on a per-mole or per- molecule basis. Then we end up with, for each of the phases,

$$dg^v = -s^v dT + v^v dp = d\mu^v$$

$$dg^l = -s^l dT + v^l dp = d\mu^l$$

- That is close to what we are looking for:

$$d\mu^l - d\mu^v = d(\mu^l - \mu^v) = -s^l dT + v^l dp + s^v dT - v^v dp$$

- We restrict the phase change to a constant- T process, so the dT terms disappear. So now we have

$$d(\mu^l - \mu^v) = (v^l - v^v) dp$$

- Remember our arguments about the relative magnitudes of the specific volumes (inverse of densities) of the liquid and the vapor. Based on that, we note $v^v \gg v^l$,

$$d(\mu^l - \mu^v) \approx -v^v dp = -v^v de^v$$

- The Ideal Gas Law on a molecule basis is $e^v v^v = kT$

$$(\mu^l - \mu^v) = -\int_{e_s}^e kT d \ln e^v$$

Integration limits:

Vapor pressure for saturated liquid (same as saturated vapor), to arbitrary vapor pressure e

Note the limits of integration

When $e = e_s$ equilibrium is established and $\mu_v = \mu_l$

When $e \neq e_s$, non-equilibrium exists, $\mu_v \neq \mu_l$

Integration yields, $\mu_l - \mu_v = -kT \ln \frac{e}{e_s}$

$$\mu_v - \mu_l = kT \ln \frac{e}{e_s} = kT \ln S$$

S is the “saturation ratio”



So now our equation for the energy change becomes,

$$\begin{aligned} \Delta G &= \left(n_l \frac{4}{3} \pi R^3\right) (\mu_l - \mu_v) + 4\pi R^2 \sigma_{LV} \\ &= -\left(n_l \frac{4}{3} \pi R^3\right) kT \ln \left(\frac{e}{e_s}\right) + 4\pi R^2 \sigma_{LV} \end{aligned}$$

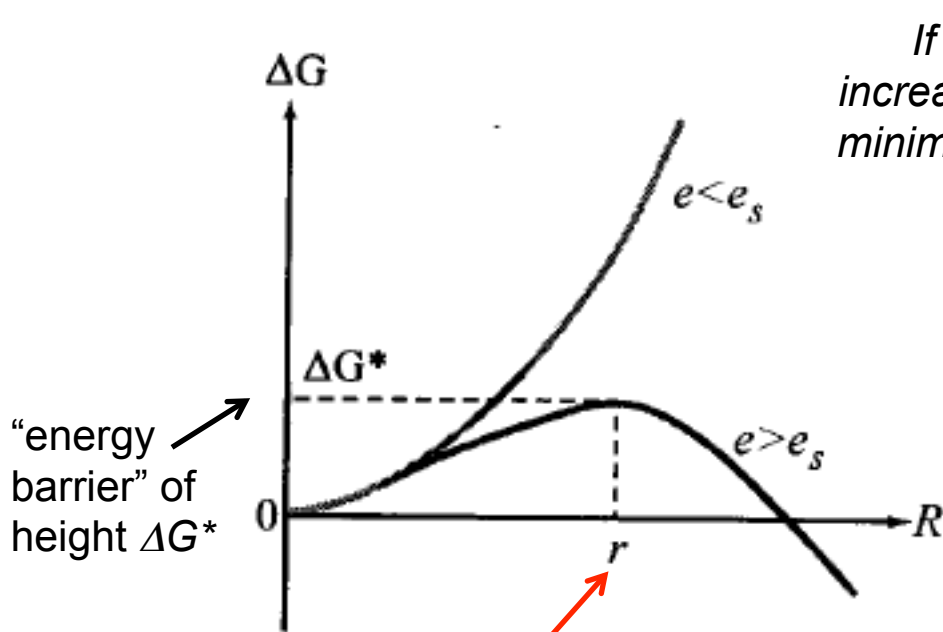
***We have to specify S too!
(phase rule)***



Let's construct the plot we envisioned,
G (or more properly, ΔG) as a function of R

Characteristics of the energy plot

$$\Delta G = -\left(n_l \frac{4}{3} \pi R^3\right) kT \ln\left(\frac{e}{e_s}\right) + 4\pi R^2 \sigma_{LV}$$



“energy barrier” of height ΔG^*

call this r^*
or r_{crit}

This looks like an equilibrium condition!
But is it a stable equilibrium?

If $S < 1$, then ΔG keeps increasing as we increase $R \rightarrow$ minimum energy is if there's no phase change!

$$\frac{d\Delta G}{dR} > 0 \text{ for all } R$$

If $S > 1$, then we can find a region where ΔG **decreases** as we increase $R \rightarrow$ if we can get into this region, can keep growing drop

$$\frac{d\Delta G}{dR} < 0 \text{ for } R > r^*$$

$$\frac{d\Delta G}{dR} = 0 \text{ for } R = r^*$$

Take the derivative of the ΔG equation above, and set it to zero, and solve for r_{crit} .

$$\left. \frac{\partial \Delta G}{\partial r} \right|_{r=r_{crit}} = 0 \quad \text{leads to} \quad r_{crit} = \frac{2\sigma_{LV}}{n_l kT \ln\left(\frac{e}{e_s}\right)}$$

$$\Delta G^* = \Delta G \Big|_{r=r_{crit}} \quad \Delta G^* = \frac{16\pi\sigma_{LV}^3}{3 \left[n_l kT \ln\left(\frac{e}{e_s}\right) \right]^2}$$

$$r_{crit} = \frac{2\sigma_{LV}v_l}{kT \ln S}$$

Kelvin's Equation

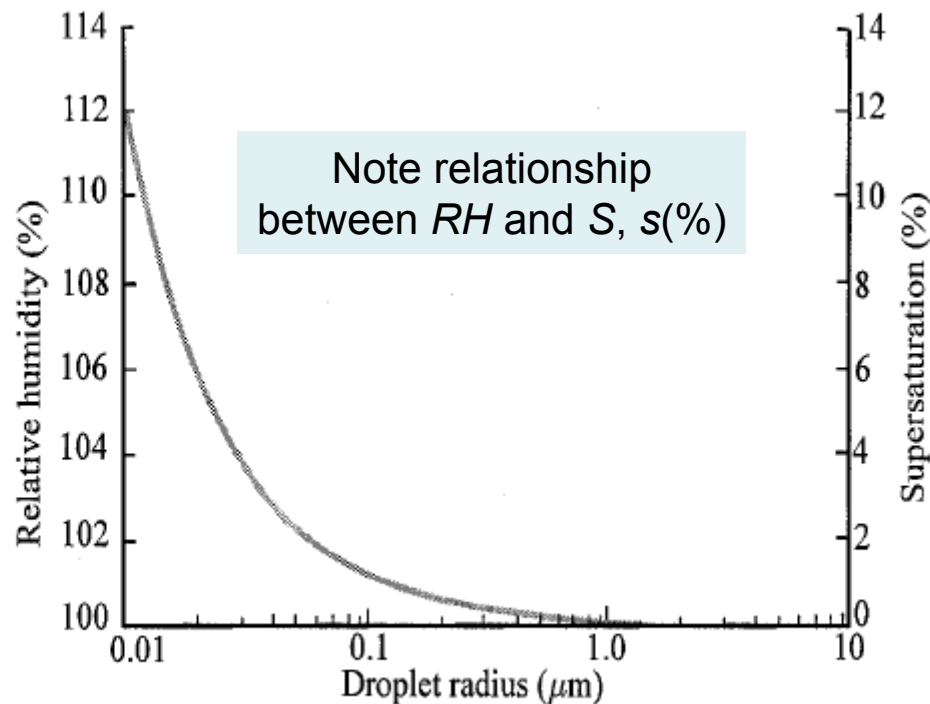
What happens to r_{crit} and ΔG^* as S increases?

r_{crit} is the critical size that must form by spontaneous collisions of vapor molecules. This size is **unstable** w.r.t. vapor, such that if a single molecule attaches to the embryo, it will decrease in free energy while increasing in R . If the embryo evaporates somewhat, free energy will also decrease, but for decreasing R , and evaporation (complete) is therefore favored.

Clearly, for an embryo to grow into a cloud droplet, it must have a **radius** $\geq r_{crit}$.

Plot of Kelvin equation

- The Kelvin equation (applied to water) tells us the radius of a pure water drop in unstable equilibrium with a saturation ratio S
- Or, equivalently, given S , what size pure water drop is just in unstable equilibrium with the environment?



Calculated at 5 °C (Cotton course notes)

$$r_{crit} = \frac{2\sigma_{LV}v_l}{kT \ln S}$$

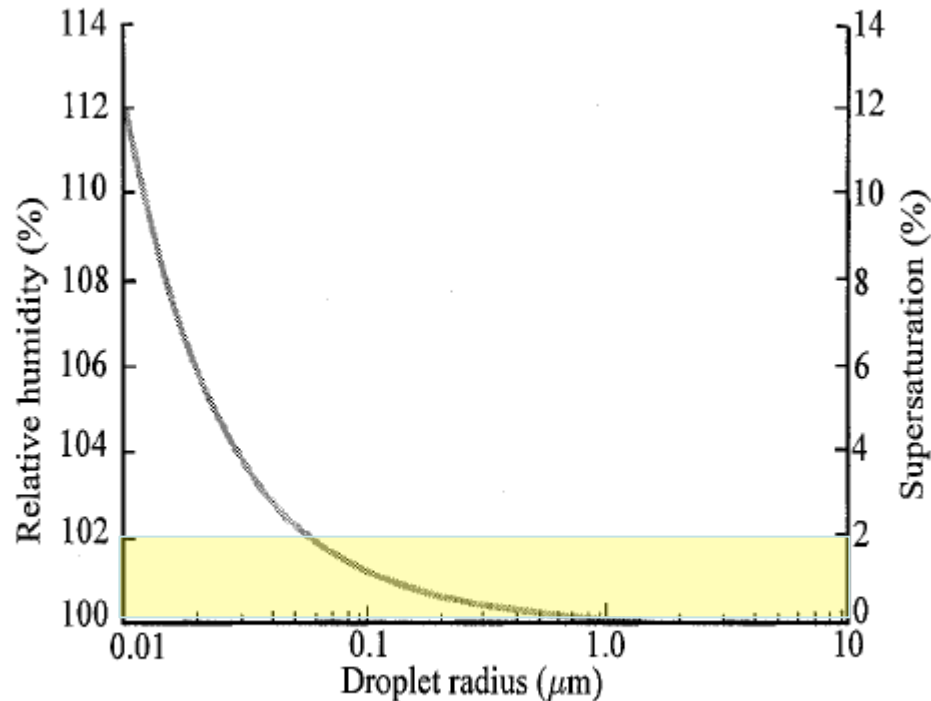
$$S = \frac{p_A}{p_A^0} = \exp\left(\frac{2\sigma M}{RT\rho_l r}\right)$$

Molecular weight

Molar units; see density of the liquid shows up here (we assumed bulk properties extrapolate down to these small droplets)

Does this explain atmospheric cloud formation?

- If we can make drops bigger than ~ 1 micron, $RH \sim 100\%$ (drop is large enough to “look like” a plane surface)
- Supersaturations in clouds rarely exceed $\sim 1 - 2\%$ (see shaded area below). We’d need to spontaneously cluster together enough molecules to form a droplet of radius ~ 0.1 micron
- As the size of the “embryo” increases, the likelihood of chance collisions forming a drop of that size decreases. We don’t expect this to happen for any embryo sizes greater than $\sim 0.01 \mu\text{m}$.
- An embryo of that size requires $s \sim 12\% \rightarrow$ much greater than available in clouds



Something else must lead to nucleation of drops in the atmosphere!

Let's examine homogeneous nucleation in a bit more detail by considering the following experiment. Suppose we have a cloud chamber containing just water vapor. Through cooling, we can control the supersaturation and can easily produce supersaturations of several hundred %. At some value of supersaturation, a fog would be observed to instantaneously form in the vessel when some critical supersaturation was achieved.

(Even smallest of embryos are activated)

Here critically-sized embryos are 'nucleated'- they quickly grow into visible cloud droplets as they are bombarded by vapor molecules.

R increases and ΔG (free energy) decreases.

To explore how this occurs we need to consider the **rate** that critically-sized embryos are nucleated by bombardment from vapor molecules.

First, we need to know **concentration of critically-sized embryos** (embryo size corresponding to max embryo size allowed by chance collision.)

Assume a **Boltzmann distribution** $\Delta G \uparrow$ with $\downarrow R$ for given e/e_s

$$n(r^*) = n(I) \exp(-\Delta G^* / kT) \quad (1)$$

$n(I)$ = concentration of unassociated (free) vapor molecules

The flux of embryos growing past size r^* (r_{crit}) is $\# \text{cm}^{-3} \text{s}^{-1}$

$$J = Bn(I) \exp(-\Delta G^* / kT) \quad (2)$$

J is the nucleation rate; # of critically-sized embryos nucleated per cm^3 per second.

B is the rate at which embryos of an area $4\pi r^{*2}$ intercept vapor molecules and thus nucleate.

B =bombardment rate (s^{-1})

B can be shown to be given by

$$B = \frac{P}{\sqrt{2\pi mkT}} 4\pi r^{*2} \quad (3)$$

m =molecular mass

p =vapor pressure

r^* = radius of critically-sized embryos

Think about this on a linear scale ... what would we observe in lab?

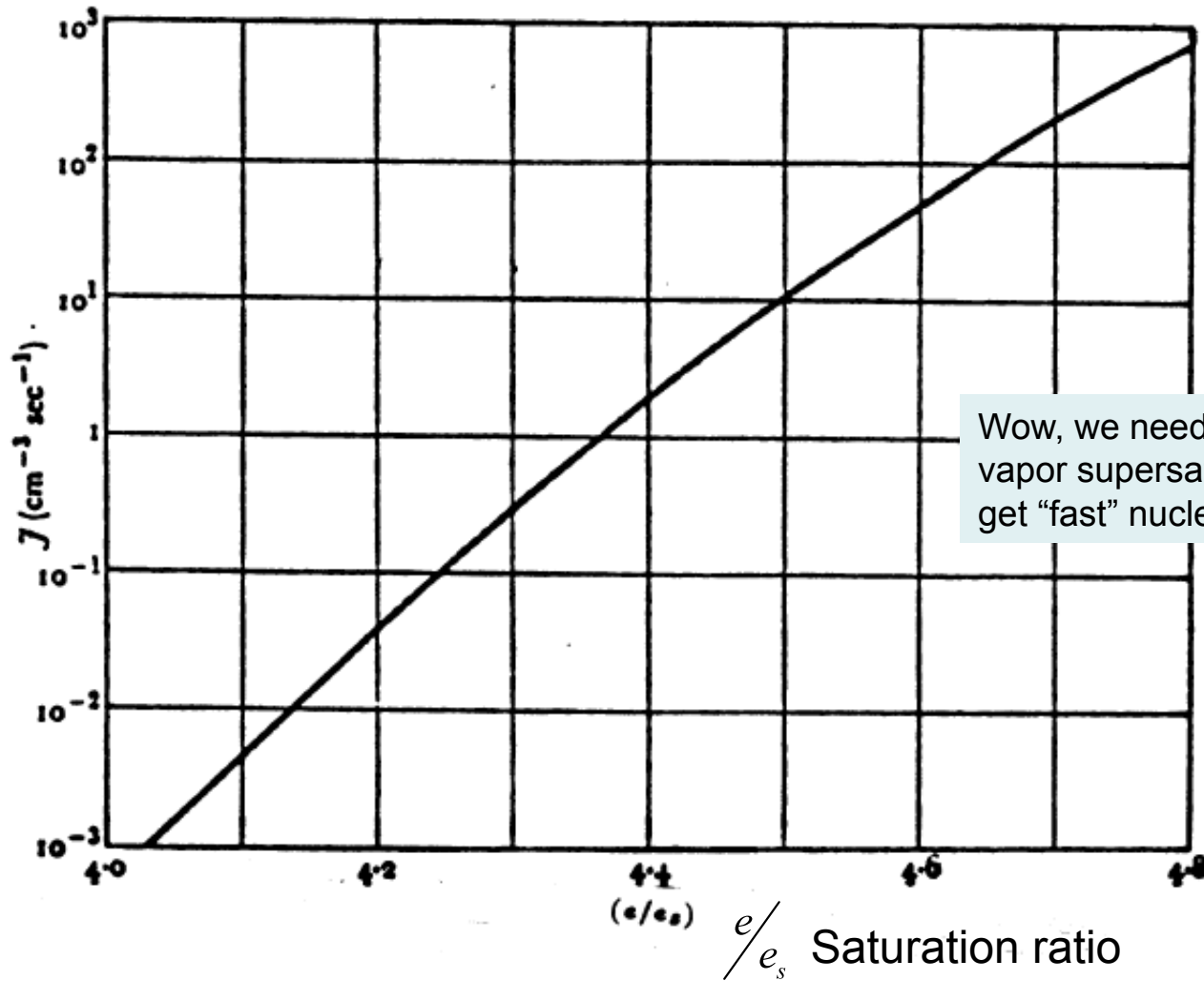


Figure 3.3: The nucleation rate J as a function of saturation ratio near the critical value. [From Fletcher (1969).]

$$\text{At } 0^\circ\text{C} \quad \sigma = .076 \text{ J m}^{-2}$$

$$n_l = 3.3 \times 10^{22} \text{ cm}^{-3}$$

$$\text{So, } Bn(I) \approx 10^{25} \text{ cm}^{-3} \text{ s}^{-1} \quad \text{for } r^* \approx 0.01 \mu\text{m}$$

Assume “appreciable” nucleation rate is

$$J = 1 \text{ cm}^{-3} \text{ s}^{-1}$$

With J and Bn(I) given, solve for ΔG^* using equation (2) above. Then use ΔG^* expression to solve for corresponding $\frac{e}{e_s}$ associated with this nucleation rate. For this calculation $\frac{e}{e_s}$ assumes a value of 4.4.

Examining Fig. 3.3 implies that as the supersaturation is increased, the nucleation rate remains essentially zero (or small) until the critical supersaturation is achieved, at which point it becomes very large over extremely short ranges of supersaturation.

Homogeneous Nucleation Rate and Critical Cluster Size for Water at T=293 K

S	i^*	J (cm⁻³ s⁻¹)
2	525	2×10^{-54}
3	132	1.2×10^{-6}
4	66	0.84×10^6
5	42	1.33×10^{11}
6	30	1.08×10^{14}
7	24	0.8×10^{16}
8	19	1.6×10^{17}
9	16	1.5×10^{18}
10	14	8.5×10^{18}

(Seinfeld and Pandis, Table 10.4)

Extension: homogeneous nucleation of atmospheric particles??

- Notice that if surface tension is lowered, r_{crit} and S can be lowered
- There is sensitivity to density as well
- If vapor pressure is very low, then large values of S can be achieved even for very trace amounts of a species

$$r_{crit} = \frac{2\sigma_{LV}v_l}{kT \ln S}$$

$$S = \frac{p_A}{p_A^0} = \exp\left(\frac{2\sigma M}{RT\rho_l r}\right)$$

- Candidates: organic species that arise from photochemical reactions (emissions from pine trees and other vegetation)
- Sulfuric acid and water (a classic!)
 - Probably affected by both ammonia and organic species