OUTLINE

1. Nucleation of water droplets (6.1)

    Homogeneous and Heterogeneous nucleation

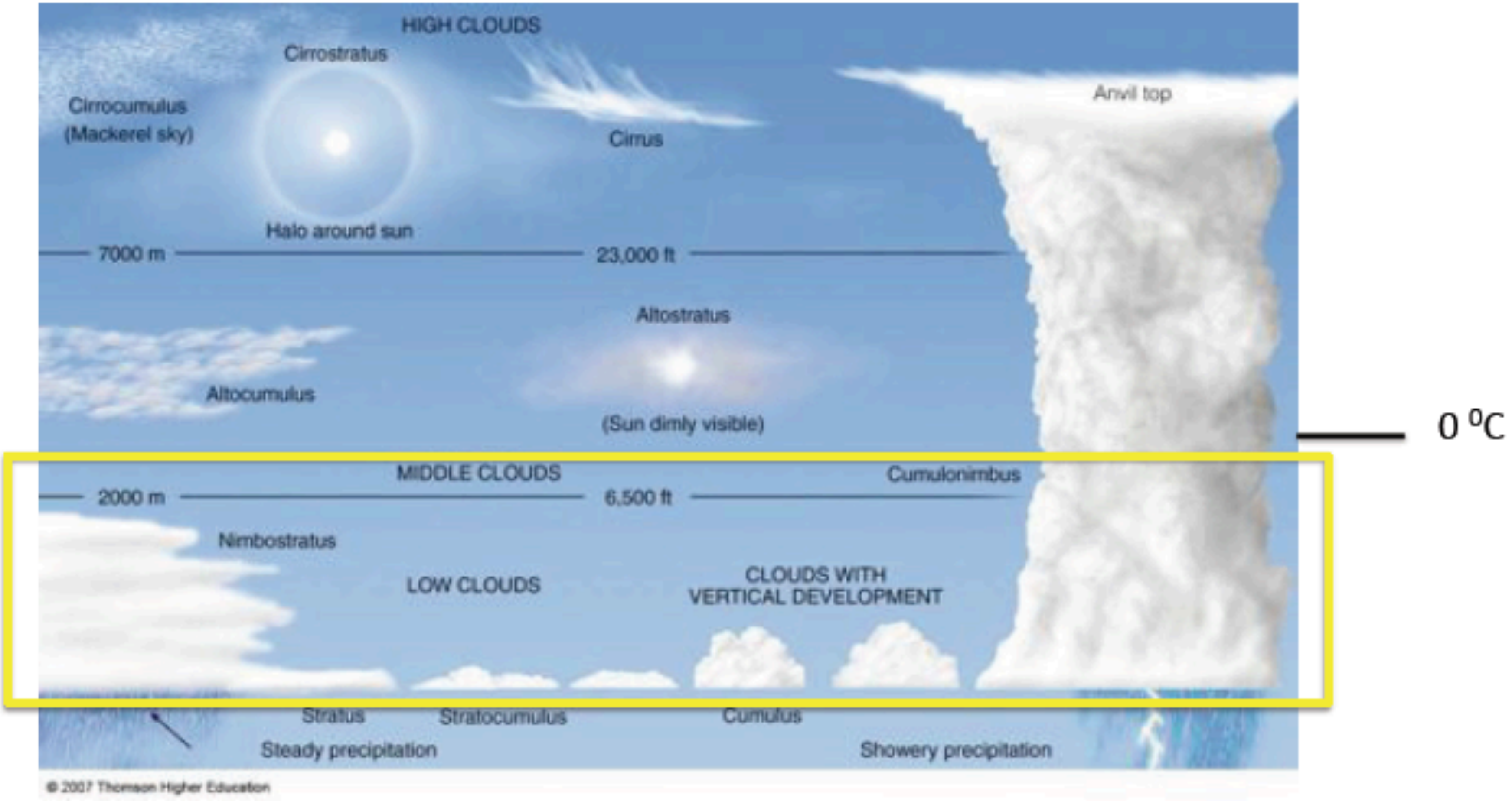
2. Microstructures of warm clouds (6.2)

3. Cloud Liquid Water Content and Entrainment (6.3)

4. Growth of Water Droplets and Formation of Rain (6.4)

5. Microphysics of Ice Clouds (6.5)

6. Lightning and cloud chemistry (6.7)



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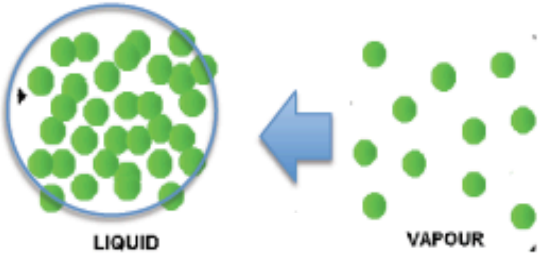
Warm Clouds: Clouds below 0˚ C isotherm
Cold Clouds –
    Mixed Phase – contain ice and liquid
    Ice Clouds – only contain ice

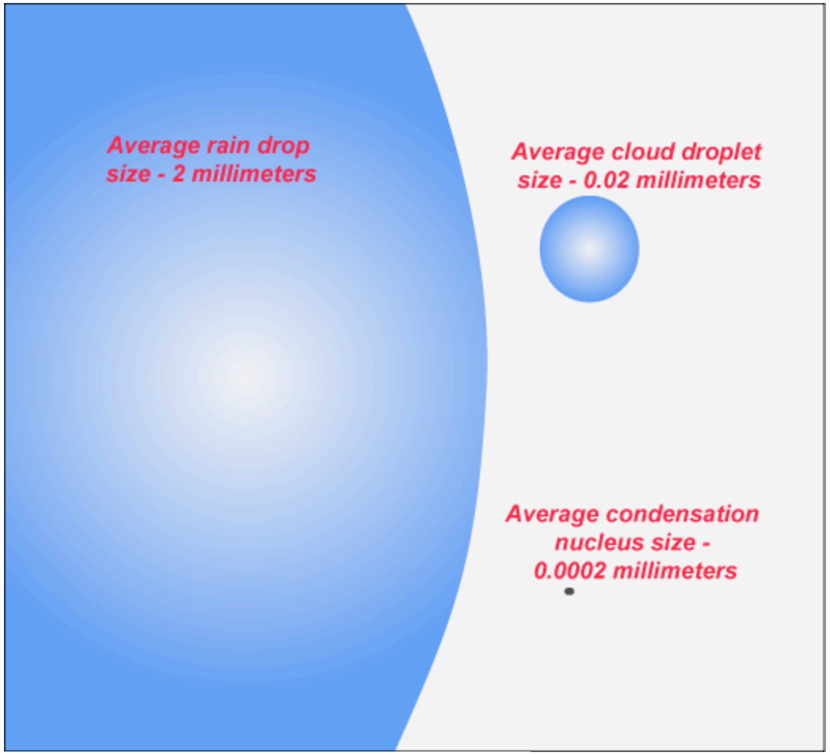
MOTIVATION

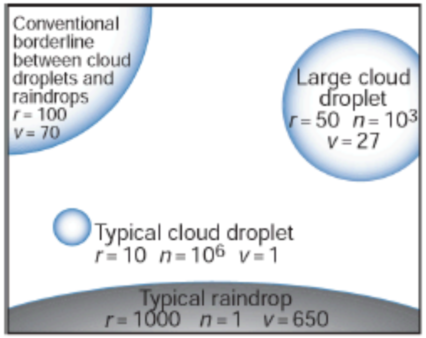
- How do we get from tiny water vapor to cloud droplets?



Cloud droplet size: ~ 10^{-5} m

molecule size: ~ 10^{-10} m





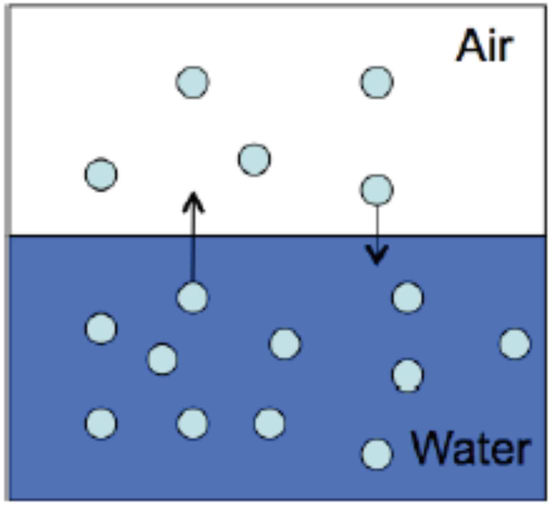
<u>Vapor molecules</u>: ~ 10^{-10} m

<u>Cloud droplets</u>: ~ 10^{-5} m (or 10 μm)

<u>Rain drops</u>: ~ 10^{-3} m (or 1000 μm)

How fast will these transitions happen and what are the primary pathways?

MOTIVATION



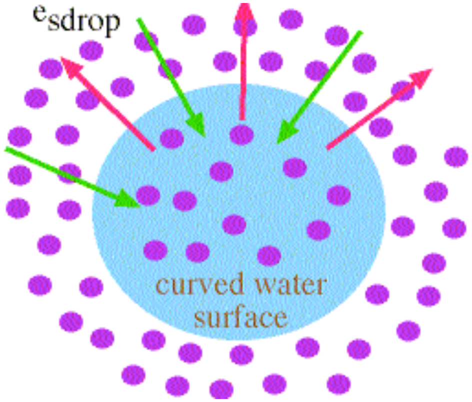
$$RH \equiv 100\frac{r}{r_s} = 100\frac{e}{e_s}$$

Saturation (RH=100%) is defined with respect to a plane water surface. But here we deal with water droplet (spheres).

It takes more energy to organize vapor molecules in a spherical form than to push them to a plane surface because of surface tension.

Saturation vapor pressure

- Can also refer to equilibrium ***e*** *over cloud particle surface* (e.g., e_i, e')



- Supersaturation refers to

  $e > e_s$

  (as when rising parcel cools, e_s decreases)

- $e > e_s$ does NOT guarantee net condensation onto cloud particles!

- But, e_s useful as *reference point* when describing (super-) saturation level of air relative to cloud droplet or ice particle.

Homogeneous nucleation

- Cloud formation in supersaturated air with *no* aerosols, i.e., pristine air
  - What are aerosols: tiny particles, suspended in air.
- Are chance collisions of vapor molecules likely to produce droplets large enough to survive?
- Take droplet with volume *V*, surface area *A*, and *n* molecules per unit volume of liquid, μ: Gibbs free energy. σ: work to create vapor-liquid interface.
- Consider surface energy of droplet and energy spent during phase change:

Work to create unit area of droplet surface

EQUATION #1

$$\Delta E = \boxed{A\sigma} - \boxed{nV(\mu_v - \mu_l)} = \boxed{4\pi R^2 \sigma} - \boxed{\frac{4}{3}\pi R^3 nkT \ln\frac{e}{e_s}}$$

Net increase in system energy due to formation of the droplet

Energy spent during phase change.

Key: a system approaches an equilibrium state by reducing its energy, i.e., atmospheric processes act to minimize ΔE

Kelvin’s equation & curvature effect

- Solve $d(\Delta E)/dR = 0$ to relate r, e, e_s:

$$r = \frac{2\sigma}{nkT \ln \frac{e}{e_s}}$$

Critical radius for given ambient vapor pressure

$$\frac{e}{e_s} = \exp\left(\frac{2\sigma}{nkTr} \right)$$

Vapor pressure required for droplet of radius *r* to be in unstable equilibrium

- Top equation can be used to calculate the radius r of a droplet that is in unstable equilibrium.

- <u>“Kelvin” or “curvature” effect</u>: $e > e_s$ required for equilibrium *since less energy needed for molecules to escape curved surface*

(see previous graph)

- Smaller droplet → larger <u>*supersaturation*</u> *required.*

(see next graph)

Critical radius *r*

- If condensation occurs, R increases
- As R increases, ΔE changes.
- If ΔE increases the liquid produced by condensation will evaporate. No growth

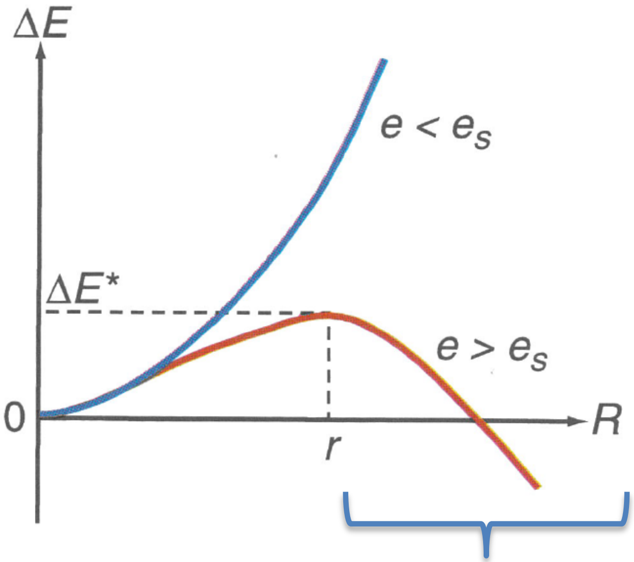


Fig 6.1

Blue: unsaturated
Red: saturated

Radius large enough for cloud to stay.

- Subsaturation ($e < e_s$) → $d\Delta E/dR > 0$ → embryonic droplets evaporate (all sizes)

- Supersaturation ($e > e_s$)
- If $d\Delta E/dR > 0$ then $R < r$ → embryonic droplets evaporate.
- If $d\Delta E/dR < 0$ then $R > r$ → sufficiently large droplets tend to grow (energy loss from phase change > energy gain from droplet surface)

Kelvin’s equation

Droplet Critical Radius (r)

$$r = \frac{2\sigma}{nkT\ln\frac{e}{e_s}} = \frac{2\sigma}{nkT\ln RH}$$

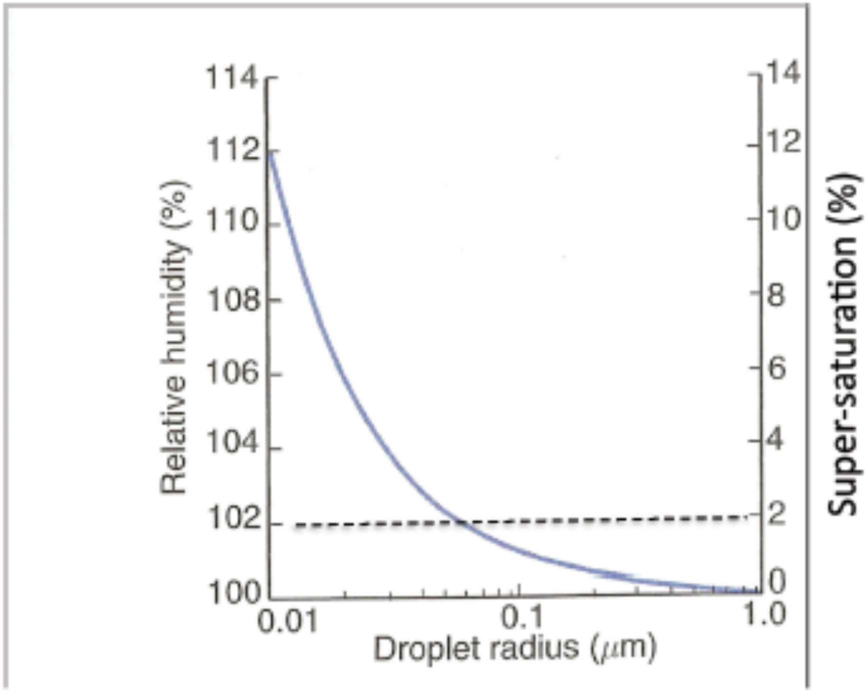


Fig 6.2

Supersaturation: RH-100

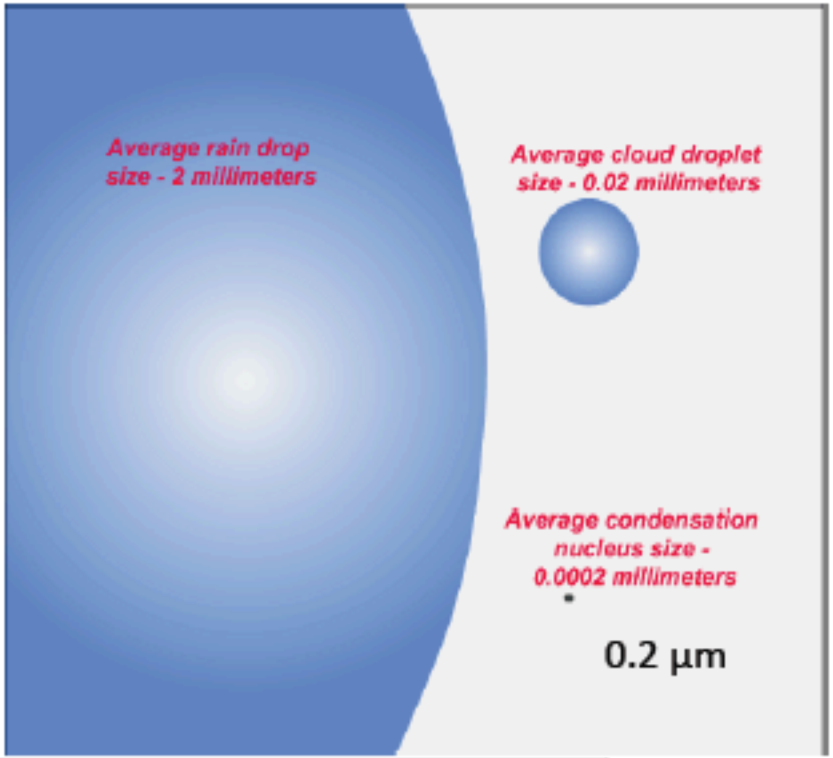
In nature, super-saturation (w.r.t. water) rarely exceeds a few percent, which translates to critical radius ~ 0.1 µm.

But it’s impossible for chance collision of water molecules (0.0001 µm) to pass this critical size.

So, cloud droplets cannot grow through the aforementioned process, which we call ***homogeneous nucleation.*** We need the help from small aerosols suspended in the air for ***heterogeneous nucleation***.

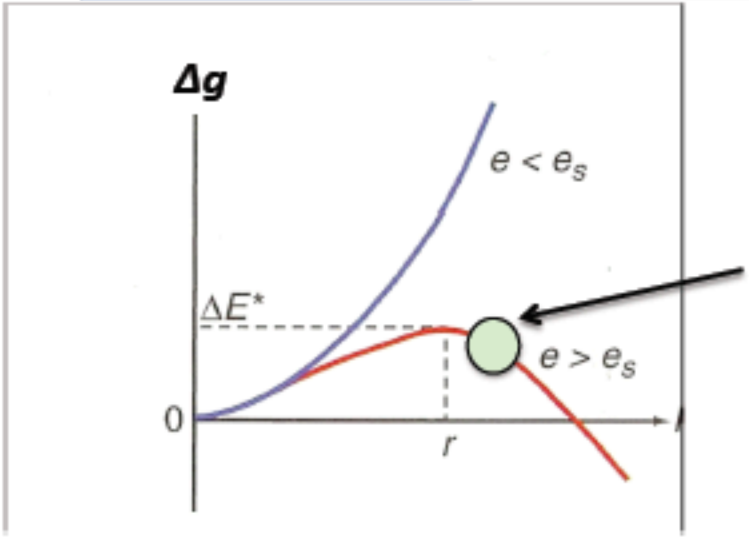
This figure illustrates the curvature effect

Cloud Condensation Nuclei (CCN)



Water molecules condense onto existing atmospheric aerosols (CCN). Heterogeneous nucleation can occurs at much lower super-saturation.

Only a small fraction of aerosols in the air can serve as CCN. To be CCN, aerosols will have to be 1) big enough (> ~ 0.1 µm) and 2) wettable.



If the starting point is here (thanks to CCN), droplet will grow spontaneously (Δg < 0)

Heterogeneous nucleation

- Aerosols : tiny particles, e.g., sea salt, dust, volcanic ash, car exhaust, any burnt stuff that rises.

- Some aerosols dissolve when water condenses on them - cloud condensation nuclei (CCN)

- Due to relatively low water vapor pressure of solute molecules in droplet surface, *solution droplet saturation vapor pressure* $e'_{DROPSAT} < e_{DROPSAT}$

$e'_{DROPSAT}$ = *saturation vapor pressure of water adjacent to* ***a solution droplet*** *containing a mole fraction f of pure water.*

$e_{DROPSAT}$ = saturation vapor pressure of water adjacent to a pure water droplet of the same size at the same temperature.

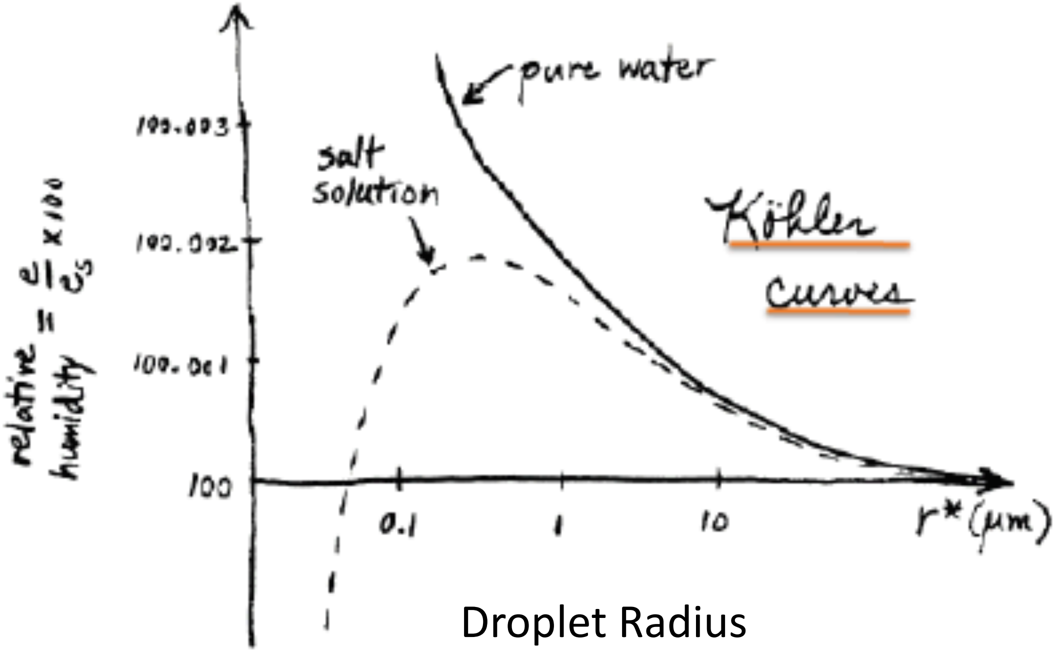
f is mole faction of pure water in the solution.

- Raoult's law: $e'_{DROPSAT} = fe_{DROPSAT}$ Equation 6.6

Heterogeneous nucleation

Heterogeneous nucleation can occur in two ways:

1. Onto insoluble but "wettable" aerosols (already discussed)
2. On soluble aerosols (e.g., salts)



Heterogeneous nucleation on *hygroscopic* particles is very effective: NaCl solution may have a saturation vapor pressure below that of pure water.

But as it grows larger, it approaches pure water (because the original NaCl particle, which serves as CCN, is diluted)

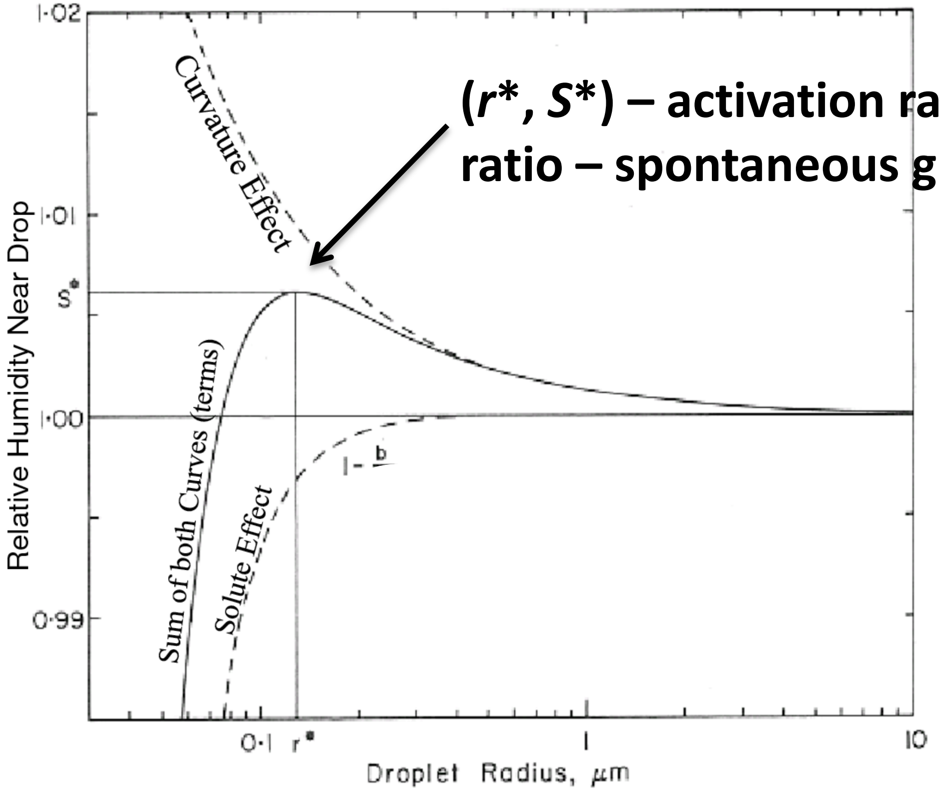
Kohler curves

- Combining curvature and solute effects, we can model equilibrium conditions for range of droplet sizes:

Saturation ratio for solution droplet

$$S \equiv \frac{e'}{e_s} = \frac{e'}{e}\frac{e}{e_s} = f \exp\left(\frac{2\sigma'}{n' kTr}\right)$$

e' is $e'_{DROPSAT}$



(r^*, S^*) – activation radius, critical saturation ratio – spontaneous growth occurs for $r > r^*$

Rogers & Yau

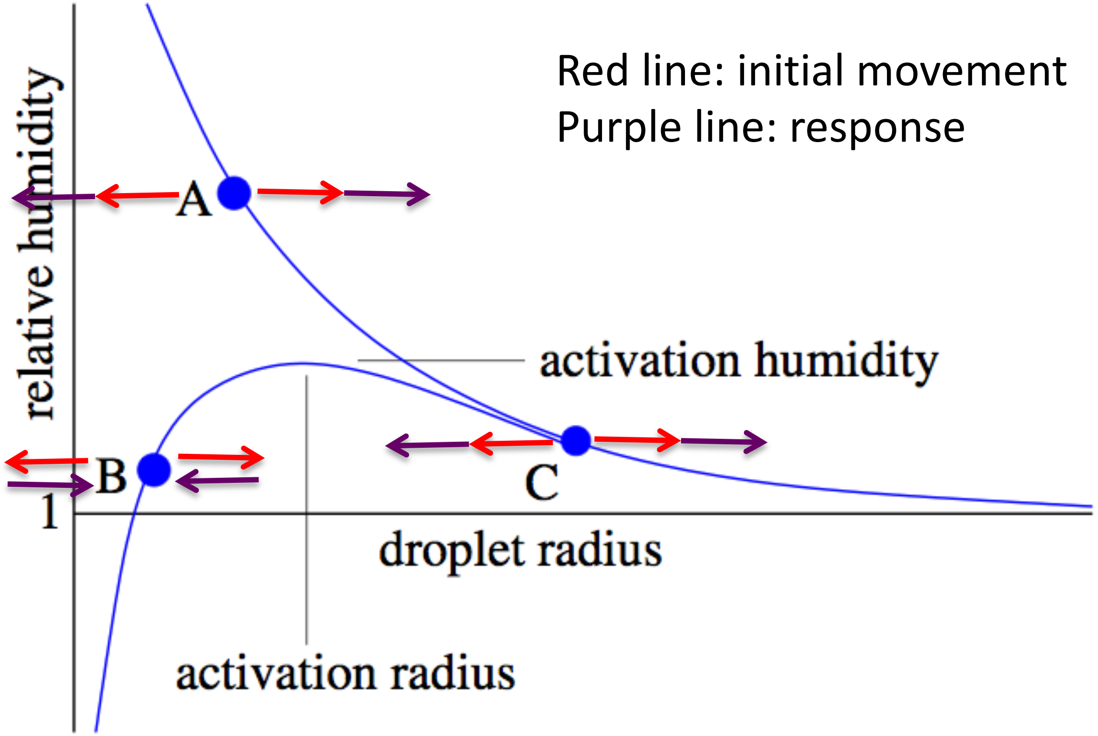
Kohler curves

Assume RH is fixed at blue DOT values.
“Equilibrium RH” refers to values based on blue curve for new r values

- **A**: *r* increase →
  RH > equilibrium RH
  → *r* increases further;
  similarly for *r* decrease
  (unstable equilibrium)

- **B**: *r* increase →
  RH < equilibrium RH
  → *r* decreases
  similarly for *r* increase
  (stable equilibrium)

- **C**: as in A, but droplet activated (grows spontaneously, i.e., without further *RH* increases)

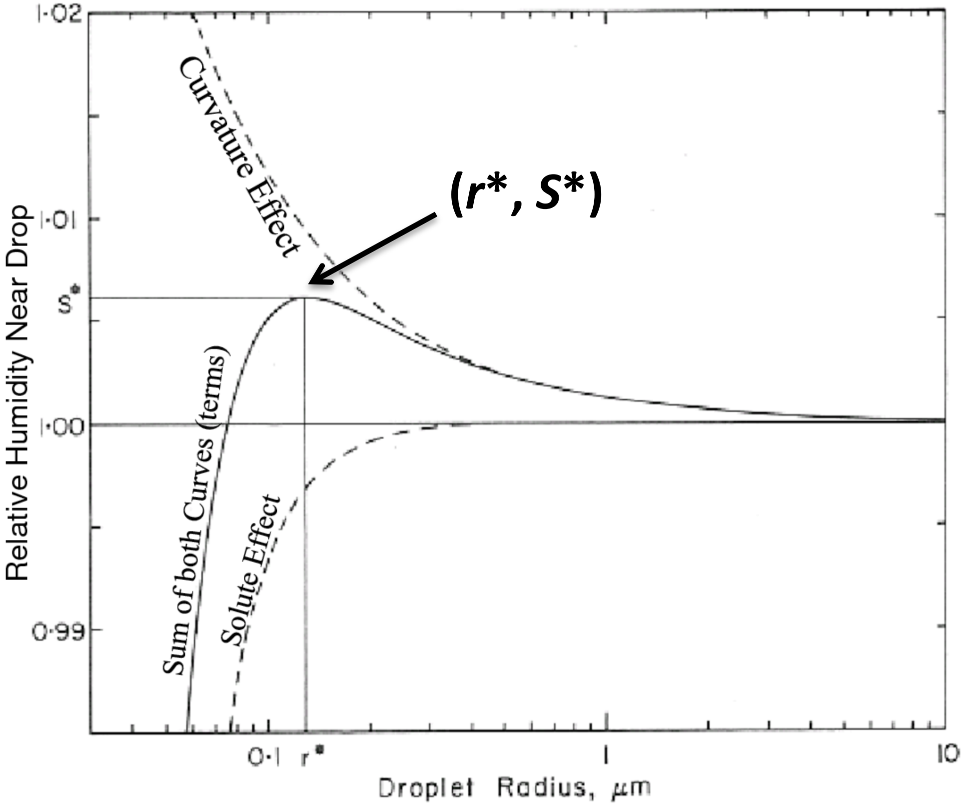


Red line: initial movement
Purple line: response

Adapted from www.physics.nmt.edu/~raymond/classes/ph536/notes/microphys.pdf

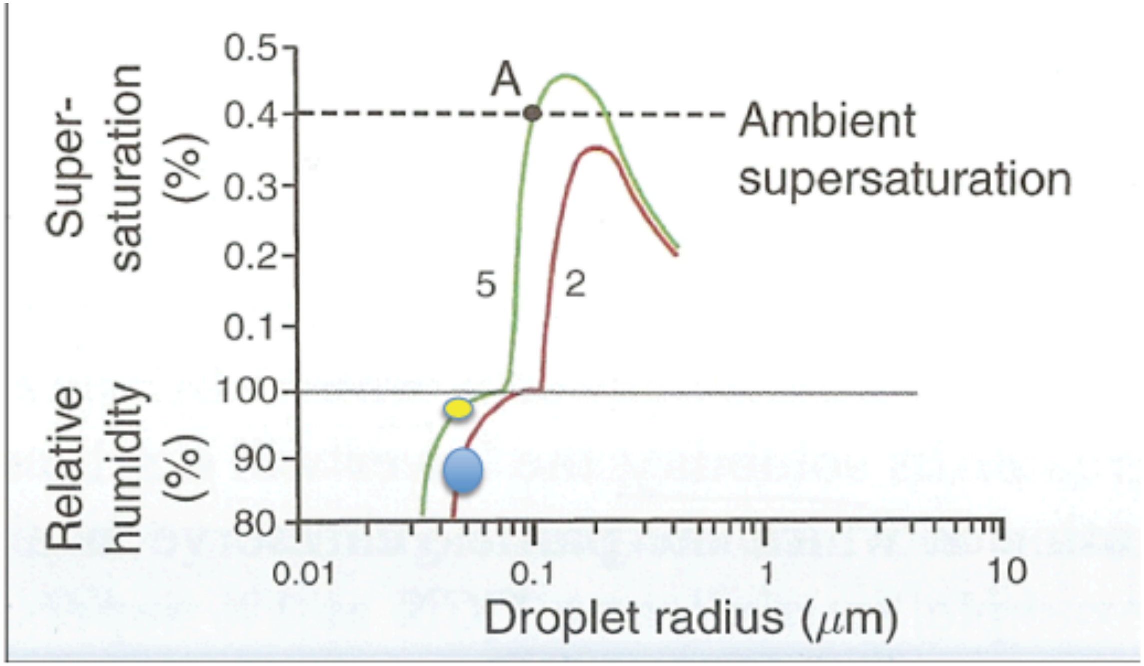
Kohler curves

	Left of peak	Right of peak
Equilibrium	Stable	Unstable
Dominant effect	Solute	Curvature
Droplet type	Haze particles	Activated CCN



Kohler curves

Ambient supersaturation: i.e., the actual RH is measured to be 100.4



Curve 2: Solution droplet containing 10^{-19} kg of NaCl

Curve 5: Solution droplet containing 10^{-19} kg of $(NH_4)_2SO_4$

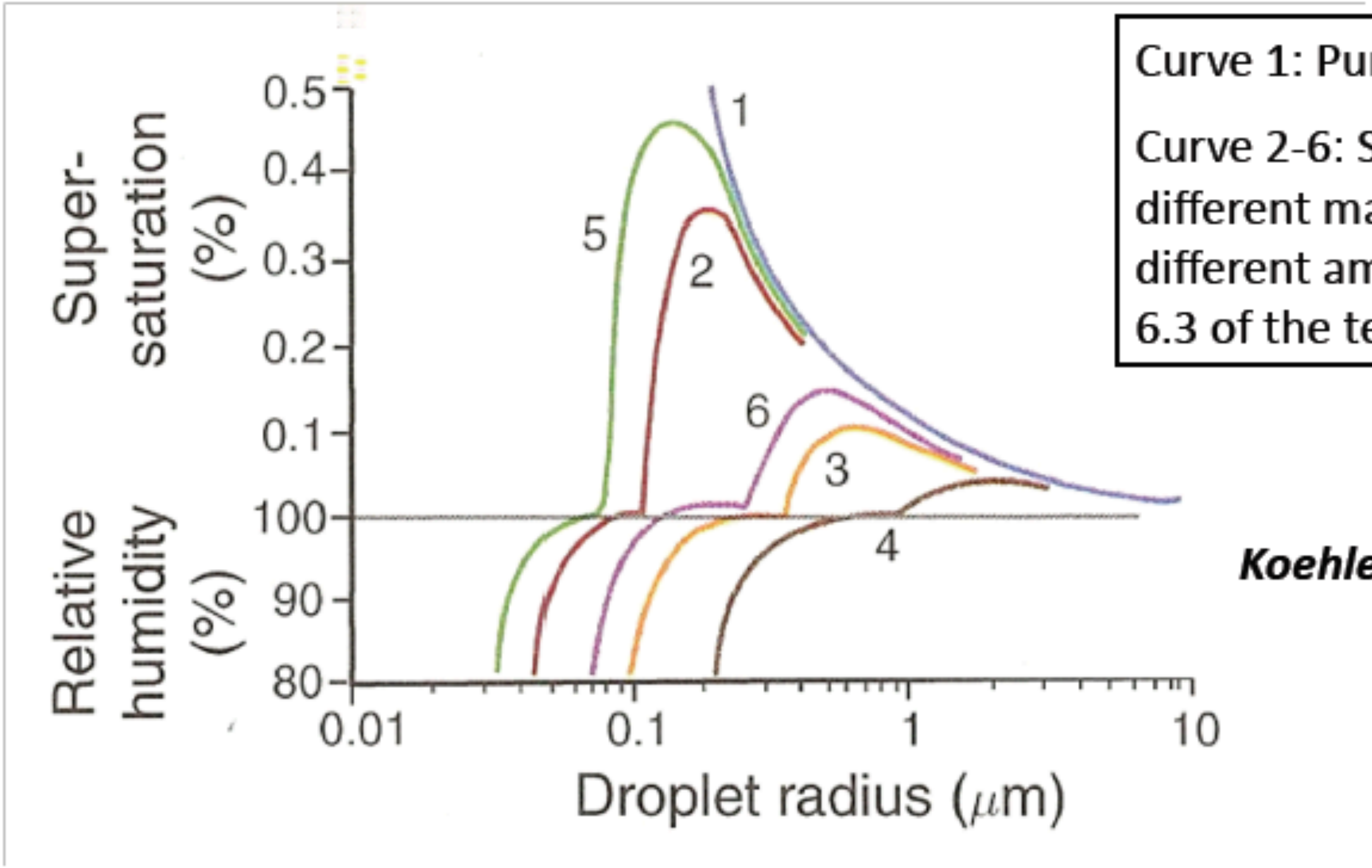
T-P-S:

1. Starting from the blue dot on curve 2 (NaCl solution), what the final fate of this droplet?
2. What about starting from the yellow dot ($(NH_4)_2SO_4$ solution)?

Curve 2: Activated droplet

Curve 5: unactivated droplets (haze)

Kohler curves



Curve 1: Pure water

Curve 2-6: Solution of different materials of different amounts (see Fig. 6.3 of the text; p 213)

Koehler Curve