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)
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: $\sim 10^{-5}$ m

molecule size: $\sim 10^{-10}$ m

Vapor molecules: $\sim 10^{-10}$ m

Cloud droplets: $\sim 10^{-5}$ m (or 10 $\mu$m)

Rain drops: $\sim 10^{-3}$ m (or 1000 $\mu$m)

Average rain drop size - 2 millimeters

Average cloud droplet size - 0.02 millimeters

Average condensation nucleus size - 0.0002 millimeters

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

\[ RH = 100 \frac{r}{r_s} = 100 \frac{e}{e_s} \]

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 $e \text{ over cloud particle surface}$ (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, $\mu$: Gibbs free energy. $\sigma$: work to create vapor-liquid interface.
- Consider **surface energy of droplet** and **energy spent during phase change**:

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

**Key**: a system approaches an equilibrium state by reducing its energy, i.e., atmospheric processes act to minimize $\Delta E$
Kelvin’s equation & curvature effect

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

\[
r = \frac{2\sigma}{nkT \ln \left(\frac{e}{es}\right)}
\]

Critical radius for given ambient vapor pressure

\[
e = \exp\left(\frac{2\sigma}{nkTr}\right)
\]

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.

- “Kelvin” or “curvature” effect: \( e > es \) required for equilibrium since less energy needed for molecules to escape curved surface (see previous graph)

- Smaller droplet \( \rightarrow \) larger supersaturation required. (see next graph)
Critical radius $r$

- If condensation occurs, $R$ increases.
- As $R$ increases, $\Delta E$ changes.
- If $\Delta E$ increases the liquid produced by condensation will evaporate. No growth.

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

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

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

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

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

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

Supersaturation: RH-100

This figure illustrates the curvature effect.
**Cloud Condensation Nuclei (CCN)**

Water molecules condense onto existing atmospheric aerosols (CCN). Heterogeneous nucleation can occur at much lower supersaturation.

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

If the starting point is here (thanks to CCN), droplet will grow spontaneously (\(\Delta g < 0\))
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* $e'_{\text{DROPSAT}} < e_{\text{DROPSAT}}$

\[ e'_{\text{DROPSAT}} = \text{saturation vapor pressure of water adjacent to a solution droplet containing a mole fraction} \, f \, \text{of pure water.} \]

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

- Raoult’s law: $e'_{\text{DROPSAT}} = fe_{\text{DROPSAT}}$
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)
Combining curvature and solute effects, we can model equilibrium conditions for range of droplet sizes:

\[ S \equiv \frac{e'}{e_s} = \frac{e'}{e} \frac{e}{e_s} = f \exp \left( \frac{2\sigma'}{n' k T r^*} \right) \]

Saturation ratio for solution droplet

\( e' \) is \( e'_{\text{DROPSAT}} \)

\((r^*, S^*)\) – 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)

Adapted from [www.physics.nmt.edu/~raymond/classes/ph536/notes/microphys.pdf](www.physics.nmt.edu/~raymond/classes/ph536/notes/microphys.pdf)
## Kohler curves

<table>
<thead>
<tr>
<th></th>
<th>Left of peak</th>
<th>Right of peak</th>
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<tbody>
<tr>
<td><strong>Equilibrium</strong></td>
<td>Stable</td>
<td>Unstable</td>
</tr>
<tr>
<td><strong>Dominant effect</strong></td>
<td>Solute</td>
<td>Curvature</td>
</tr>
<tr>
<td><strong>Droplet type</strong></td>
<td>Haze particles</td>
<td>Activated CCN</td>
</tr>
</tbody>
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![Kohler curve diagram](image)

$(r^*, S^*)$
Ambient supersaturation: i.e., the actual RH is measured to be 100.4

T-P-S:
1. Starting from the blue dot on curve 2 (NaCl solution), what is the final fate of this droplet?
2. What about starting from the yellow dot ((NH₄)₂SO₄ 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)