



Atmospheric Physics

Lecture 15

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CLOUD FORMATION

U

The Gibbs free energy

$$G = U - TS + pV$$

$$H = U + pV$$

$$F = U - TS$$

$$\delta G = \delta U - T\delta S - S\delta T + p\delta V + V\delta p$$

$$G = H - TS$$

Using

$$dU = dQ + dW,$$

$$\delta G = -S \delta T + V \delta p$$

Consider a water droplet immersed in water vapour, at partial pressure e and temperature T (the remaining 'dry air' plays no role and can be ignored).

Suppose that the liquid and vapour are not in equilibrium,

so that

$$e \neq e_s(T)$$

Suppose that the Gibbs free energy per unit mass of the vapour is

$$G_v(T, e)$$

and that of the liquid is

$$G_l(T, e)$$

Now let the partial pressure be varied slightly from

$$e \text{ to } e + de,$$

while the temperature is held constant

$$\delta G = -S \delta T + V \delta p$$

$$\delta G_v = V_v \delta e$$

$$\delta G_l = V_l \delta e$$

where V_v and V_l are the specific volumes of the vapour and liquid, respectively.

$$V_v \gg V_l$$

$$\delta(G_v - G_l) = (V_v - V_l) \delta e \approx V_v \delta e$$

The vapour satisfies the ideal gas law $V_v = R_v T / e$

$$\delta(G_v - G_l) = R_v T \delta e / e = R_v T \delta(\ln e)$$

Integrating at fixed T gives

$$G_v(T, e) - G_l(T, e) = R_v T \ln e + F(T)$$

where $F(T)$ is a function of integration

However, at equilibrium, on the vapour pressure curve where

$$e = e_s(T) \quad \Rightarrow \quad G_v = G_l$$

(This result is used in the standard derivation of the Clausius-Clapeyron equation.) Using this condition to fix $F(T)$,

$$0 = R_v T \ln e_s + F(T)$$

$$G_v(T, e) - G_l(T, e) = R_v T \ln\left(\frac{e}{e_s(T)}\right)$$

Now suppose that at some initial time we have a

at	mass of water vapour,	m
and	partial pressure	e
	temperature	T
	with no droplet present	

The total Gibbs free energy at this time is

$$G_0 = G_v(T, e) m_0 \quad *$$

A droplet then starts to condense, at fixed temperature and pressure; suppose that at some later instant its radius is a , so that its surface area is

$$A = 4 \pi a^2$$

and its mass is

$$m_l = 4 \pi a^3 \rho_l / 3$$

(where ρ_l is the density of the liquid) and the mass of the surrounding vapour is m_v

The total Gibbs free energy of the system is now the sum of the Gibbs free energies of the liquid and vapour, plus a contribution due to surface tension:

$$G = G_v(T, e) m_v + G_l(T, e) m_l + \gamma A \quad **$$

where γ is the surface tension (or the surface energy per unit area)

By conservation of mass $m_v = m_0 - m_l$

using equations * and **, we get

$$G - G_0 = (G_l - G_v) m_l + \gamma A$$

using $G_v(T, e) - G_l(T, e) = R_v T \ln\left(\frac{e}{e_s(T)}\right)$

$$G - G_0 = -\frac{4}{3} \pi a^3 \rho_l R_v T \ln\left(\frac{e}{e_s(T)}\right) + 4\pi a^2 \gamma$$

The variation with radius a of the total Gibbs free energy of the system therefore takes the form

$$G(a) = G_0 - \beta a^3 + \alpha a^2$$

Figure plots this function for two values of the relative humidity e/e_s

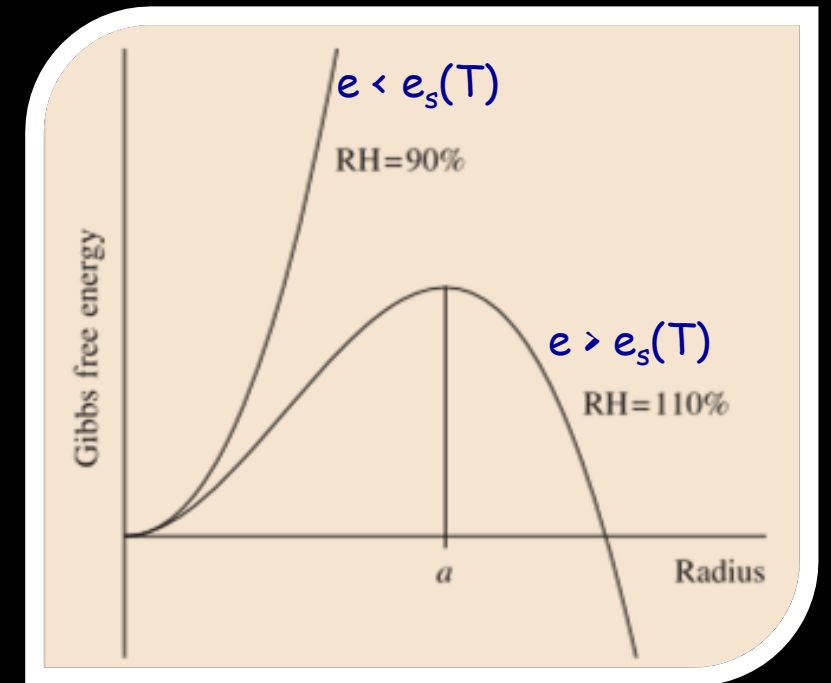
Several useful facts can be learned from this figure

Note first that, if $e \leq e_s(T)$

(indicating subsaturated or exactly saturated conditions), then the logarithm in equation is negative or zero, so that $\beta \leq 0$ and the curve of $G(r)$ has no turning point other than $a = 0$.

If $e > e_s(T)$ (indicating supersaturated conditions), then the logarithm is positive, $\beta > 0$, and there is a maximum of G at a radius a given by

$$a = 2\alpha / 3\beta = \frac{2\gamma}{\rho_l R_v T \ln\left(\frac{e}{e_s(T)}\right)}$$

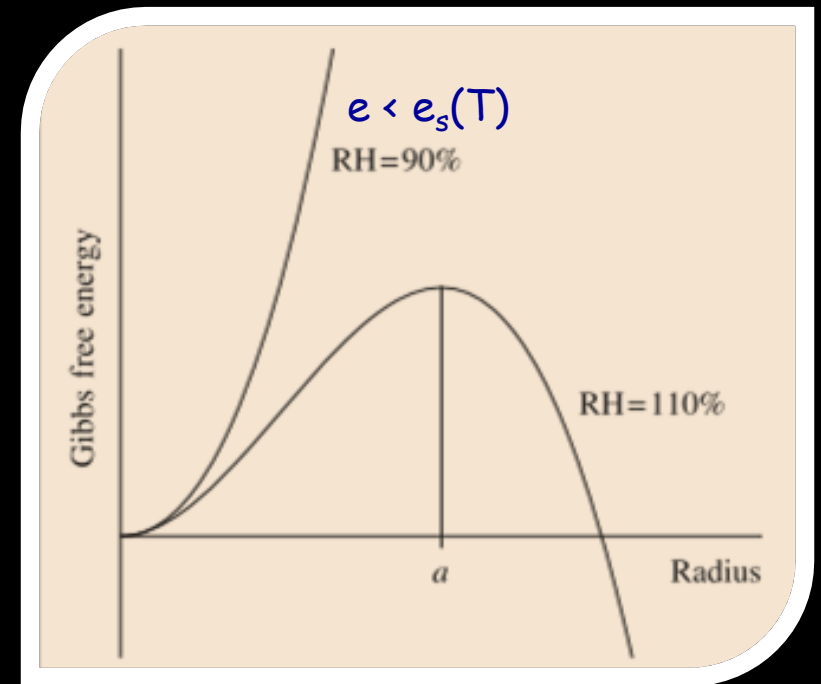


Subsaturated conditions ($e < e_s$)

$$\Delta G = \underbrace{-\frac{4}{3}\pi a^3 \rho_l R_v T \ln(e / e_s(T))}_{>0} + \underbrace{4\pi a^2 \gamma}_{>0}$$

Formation of droplets is not favored Random collisions of water molecules do occur, forming very small embryonic droplets (that evaporate)

These droplets never grow large enough to become visible



If droplet grows (a increases), then $\Delta G > 0$, this won't happen spontaneously

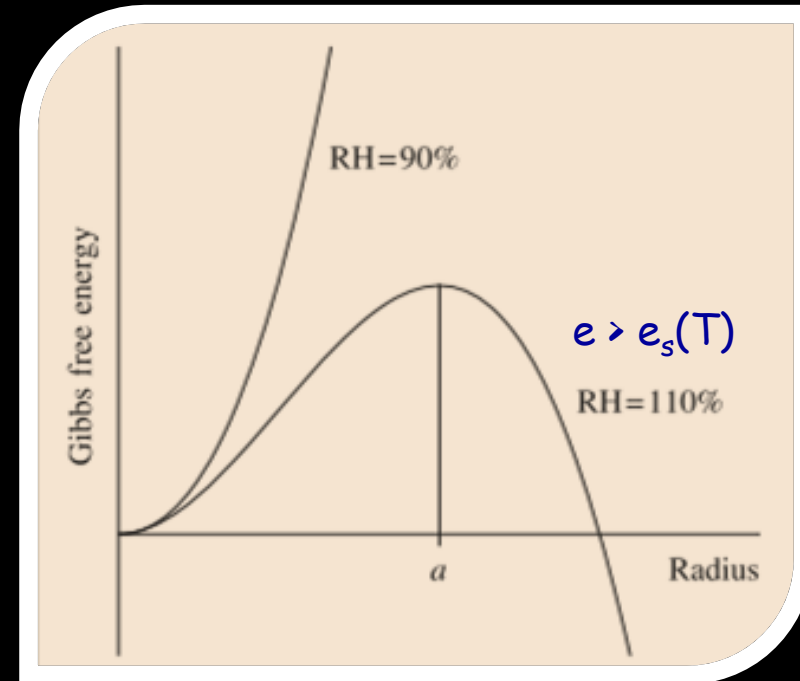
Supersaturated conditions ($e > e_s$)

$$\Delta G = \underbrace{-\frac{4}{3}\pi a^3 \rho_l R_v T \ln(e / e_s(T))}_{<0} + \underbrace{4\pi a^2 \gamma}_{>0}$$

ΔG initially increases with increasing a

ΔG is a maximum where radius = a

ΔG decreases with increasing Radius beyond a



If droplet grows (R increases), then ΔG can be positive or negative

Supersaturated conditions ($e > e_s$)

Embryonic droplets with $R < a$ tend to evaporate

Droplets which grow by chance (collisions) with $R > a$ will continue to grow spontaneously by condensation

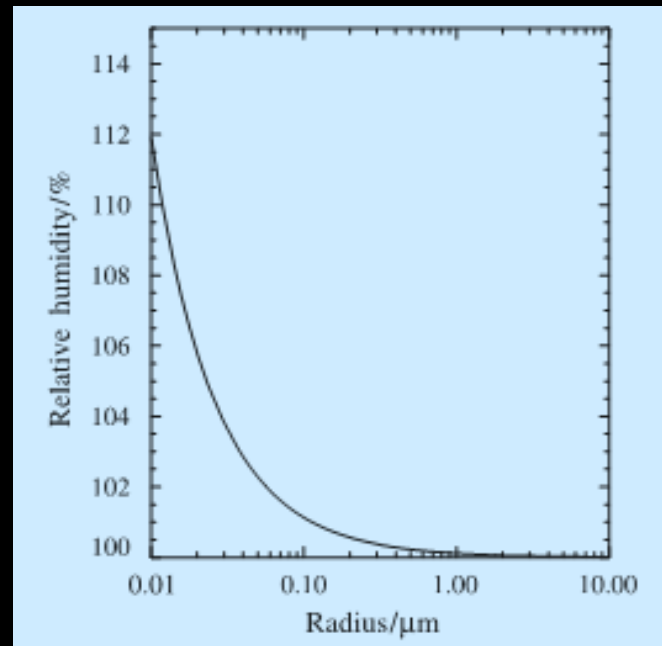
They will cause a decrease in the Gibbs free energy (total energy) of the system

This is known as **Kelvin's formula**; it may also be written in the form

$$a = \frac{2\alpha}{3\beta} = \frac{2\gamma}{\rho_l R_v T \ln\left(\frac{e}{e_s(T)}\right)}$$

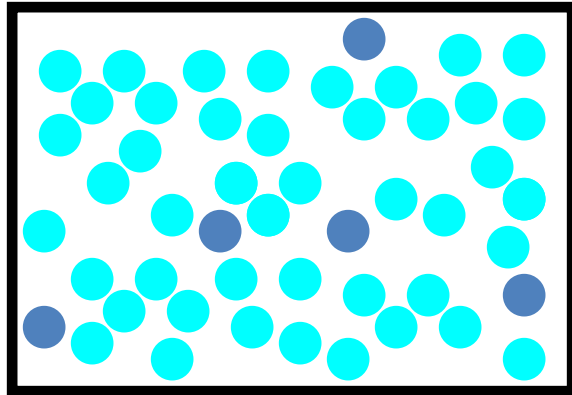
$$e = e_s(T) \exp \frac{A}{a}$$

$$A = \frac{2\gamma}{\rho_l R_v T}$$



Clouds- homogeneous nucleation

Consider a clean atmosphere with water vapor in it.



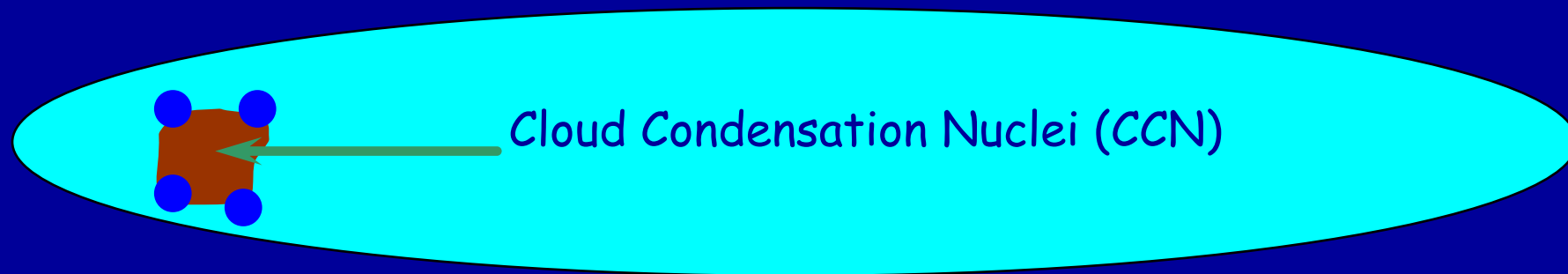
- Dry Atmosphere
- Water Vapor

Given a long enough time, some water vapor molecules will run in to one another.

Typically they won't stay together. Even if the atmosphere was saturated, the likelihood that water vapor molecules will form a droplet is small.

If more water is added such that the atmosphere is supersaturated ($RH \sim 300-400\%$), then water molecules can form a stable droplet.

This process is called homogeneous nucleation.



These serve as centers for condensation

Clouds- Heterogeneous Nucleation

With CCN, we need much smaller supersaturations.

In nature we find supersaturations on the order of 1.5%.

The atmosphere has plenty of CCN

Dust

Volcanoes

Forest Fires

Anthropogenic Origins

Salt Spray from Oceans

Sulfate Particles from Phytoplankton

Trees

CCN are more plentiful near the surface of the earth.

CCN are more plentiful over land rather than the ocean.

The formation of cloud droplets using CCN is called:

Heterogeneous Nucleation.

The Precipitation Process

How can a very small droplet grow to the size of a rain drop?

Typical Sizes (Radius)

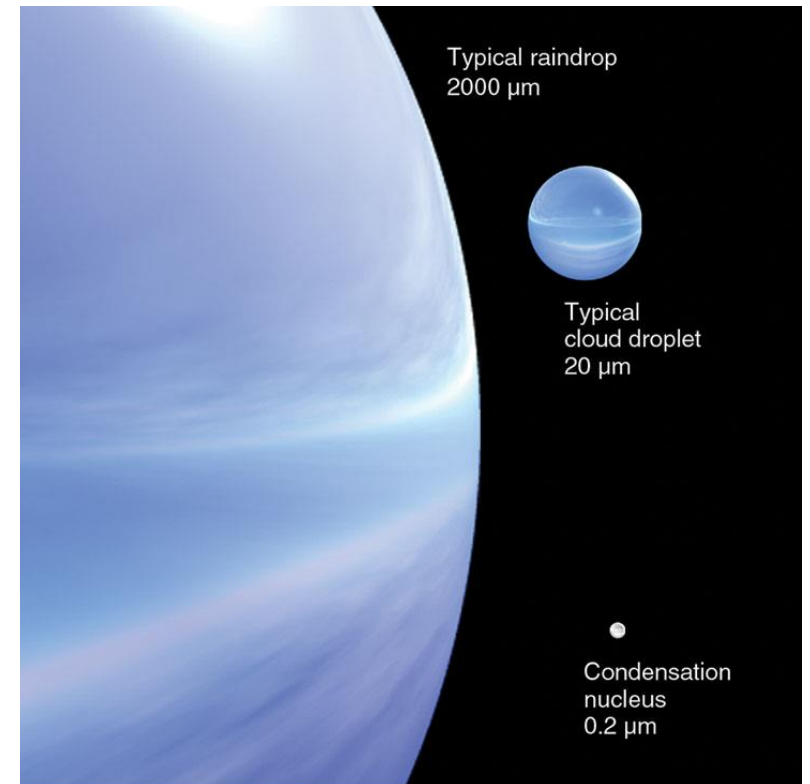
CCN - $0.2 \mu\text{m}$

Typical Cloud Droplet - $20 \mu\text{m}$

Typical Rain Drop - $2000 \mu\text{m}$

How fast can this process occur?

In the tropics, a cloud can form, grow, and produce rain in as little as 30 minutes.



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Droplet Growth by Condensation

A droplet can grow only if the number of water molecules entering the drop exceeds the number of water molecules leaving the drop.

Supersaturation!

