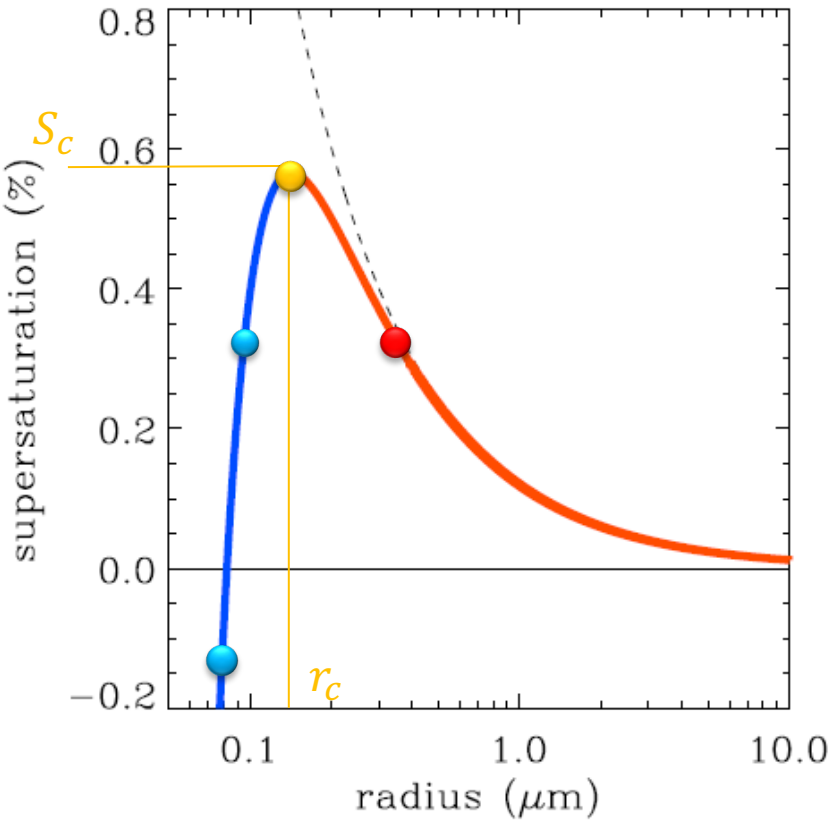
CONDENSATIONAL GROWTH OF CLOUD DROPLETS



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Equilibrium conditions

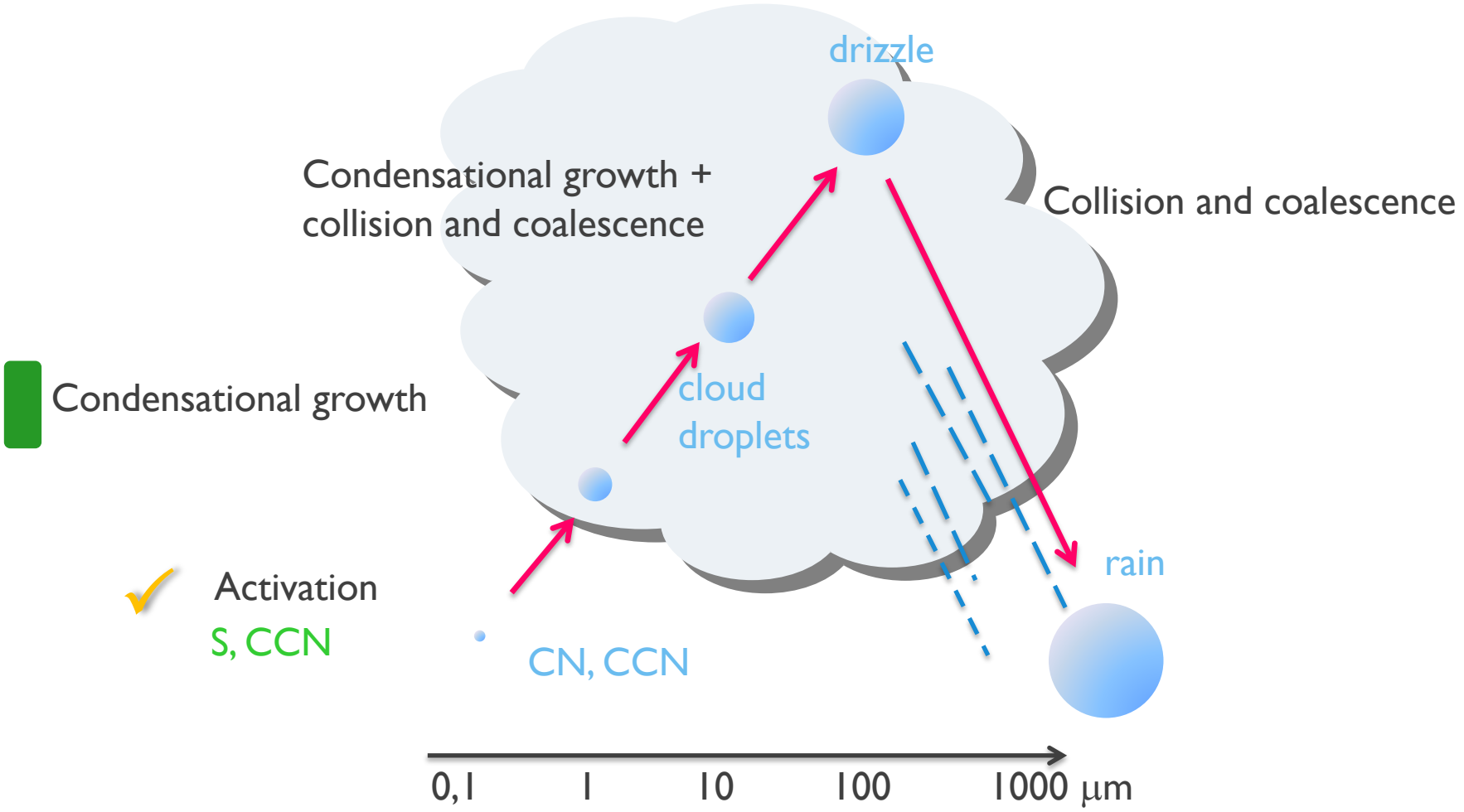


Stable equilibrium ($r < r_c$):

- An increase or decrease in ambient supersaturation causes unactivated haze particles to expand or evaporate until a new equilibrium radius is established.
- For these droplets to continue growing toward activation, ambient supersaturation must rise until reaching the critical threshold values: the critical supersaturation (S_c) and critical radius (r_c).

Unstable equilibrium ($r > r_c$):

- Once relative humidity exceeds the critical supersaturation threshold (S_c), the droplet transitions into the unstable regime.
- In this state, droplet growth lowers the droplet's required equilibrium saturation ratio below ambient levels.
- Water vapor diffuses continuously toward the droplet, fueling spontaneous growth without requiring further increases in ambient supersaturation.


drizzle
Condensational growth +
collision and coalescence
Collision and coalescence
Condensational growth
cloud
droplets
Activation
S, CCN
rain
CN, CCN
0,1
1
10
100
1000 μm

Droplet Growth by Water Vapor Diffusion

- Droplets must reach critical radius (r_c) and critical supersaturation (S_c) to activate into cloud droplets.
- Water vapor diffusion toward the droplet surface governs growth both prior to activation (stable haze regime) and after activation (unstable growth regime).
- We will formulate the condensational growth rate of an isolated droplet driven by vapor diffusion.

Condensational growth



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An isolated spherical droplet of radius r suspended in a vapor field;

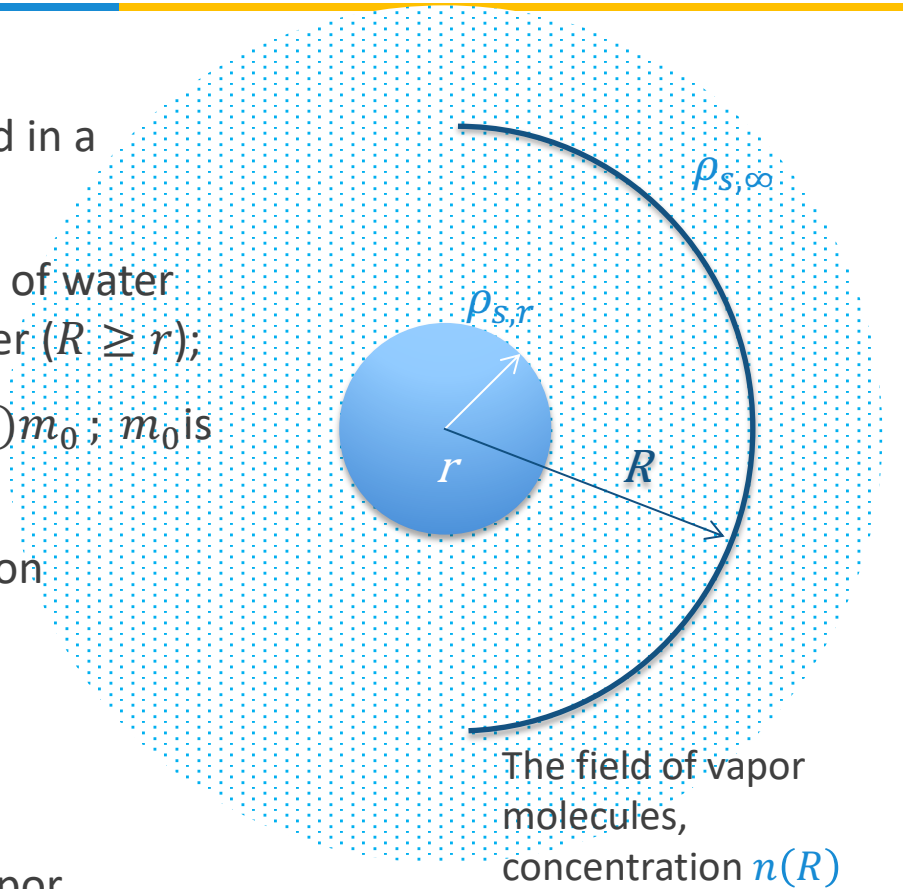
Let $n(R)$ represent the molecular number density of water vapor at a radial distance R from the droplet center ($R \geq r$);

Vapor density or absolute humidity: $\rho_v(R) = n(R)m_0$; m_0 is the mass of a single water molecule;

The vapor density is assumed to satisfy the diffusion equation:

$$\frac{\partial \rho_v}{\partial t} = D\nabla^2 \rho_v$$

D $[m^2 s^{-1}]$ is the molecular diffusivity of water vapor.



The field of vapor molecules, concentration $n(R)$

The diffusion equation can be trivially derived from the continuity equation, which states that a change in density in any part of the system is due to inflow and outflow of material into and out of that part of the system. Effectively, no material is created or destroyed:

$$\frac{\partial n}{\partial t} + \nabla \cdot \vec{j} = 0$$

where $\vec{j}$ is the flux of the diffusing material. The flux of the diffusing material in any part of the system is proportional to the local density gradient (Fick's first law of diffusion):

$$\vec{j} = -D\nabla n$$

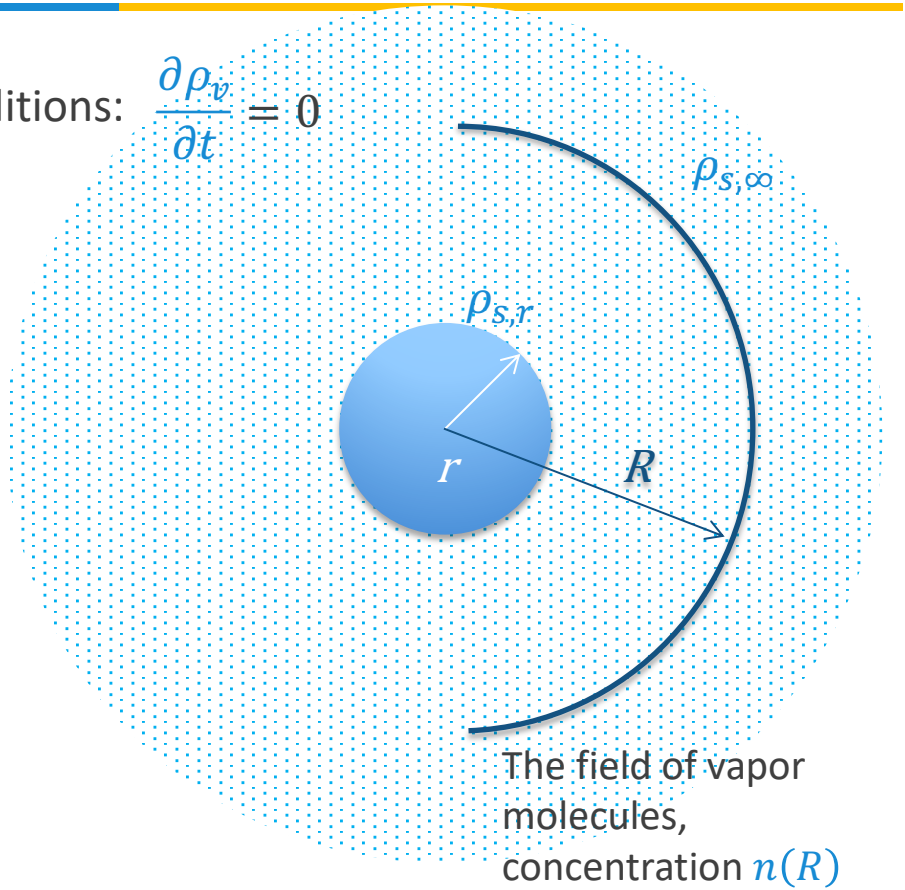
We assume the steady-state or ‘stationary’ conditions: $\frac{\partial \rho_v}{\partial t} = 0$

$$\rho_v(R) = n(R) m_0$$

$$\frac{\partial n}{\partial t} = D\nabla^2 n \qquad \longrightarrow \qquad D\nabla^2 n = 0$$

$$D\nabla^2(R) = 0 = \frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2 \frac{\partial n}{\partial R}\right)$$

$$n(R) = C_1 - \frac{C_2}{R}$$



The field of vapor molecules, concentration $n(R)$

Boundary conditions

$R \to \infty, \quad n \to n_\infty$ The ‘ambient’ or undisturbed value of vapor concentration.

$R \to r, \quad n \to n_r$ The vapor concentration at the droplet’s surface.

$$n(R) = n_\infty - \frac{r}{R}(n_\infty - n_r)$$ Vapor concentration around the droplet.

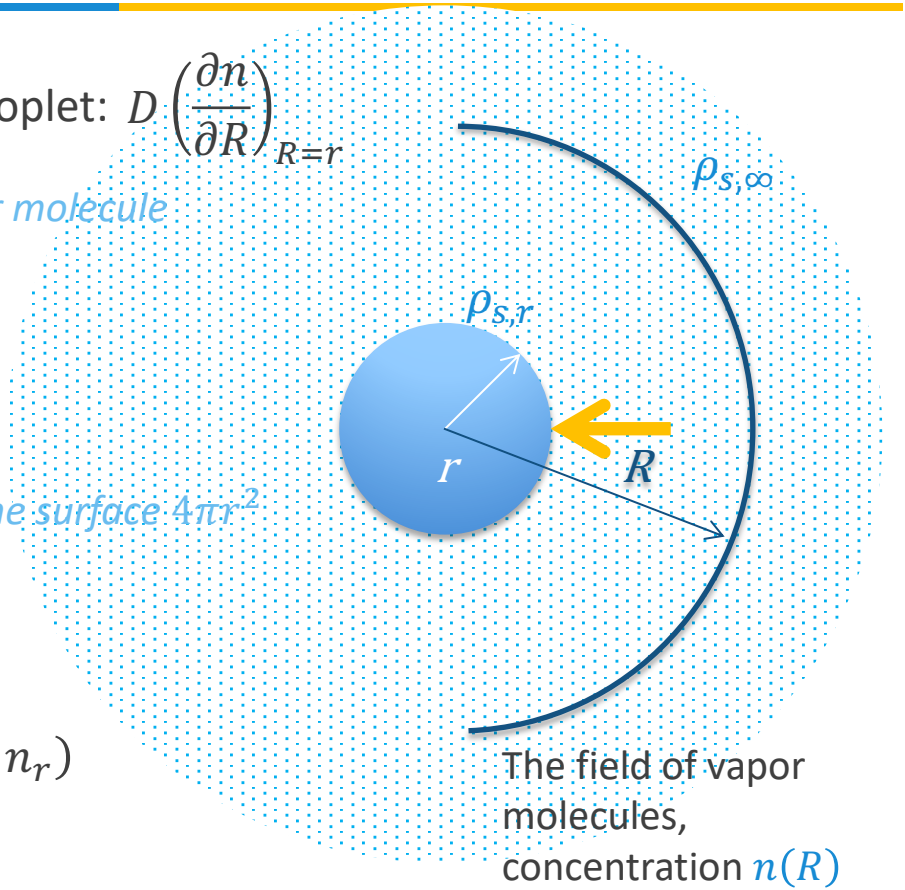
The flux of molecules onto the surface of the droplet: $D\left(\frac{\partial n}{\partial R}\right)_{R=r}$

$$\frac{dm}{dt} = 4\pi r^2 D\left(\frac{\partial n}{\partial R}\right)_{R=r} m_0$$

the mass of one water molecule

the rate of mass increase

the flux of mass over the surface $4\pi r^2$



The field of vapor molecules, concentration $n(R)$

$$n(R) = n_\infty - \frac{r}{R}(n_\infty - n_r)$$

$$\left(\frac{\partial n}{\partial R}\right)_{R=r} = \frac{r}{R^2}(n_\infty - n_r)\Big|_{R=r} = \frac{1}{r}(n_\infty - n_r)$$

The diffusional growth equation for an isolated droplet at rest in a vapor field:

$$\frac{dm}{dt} = 4\pi r D(n_\infty - n_r)m_0$$

$$\rho_v = nm_0$$

$$\frac{dm}{dt} = 4\pi r D(\rho_v - \rho_{vr})$$

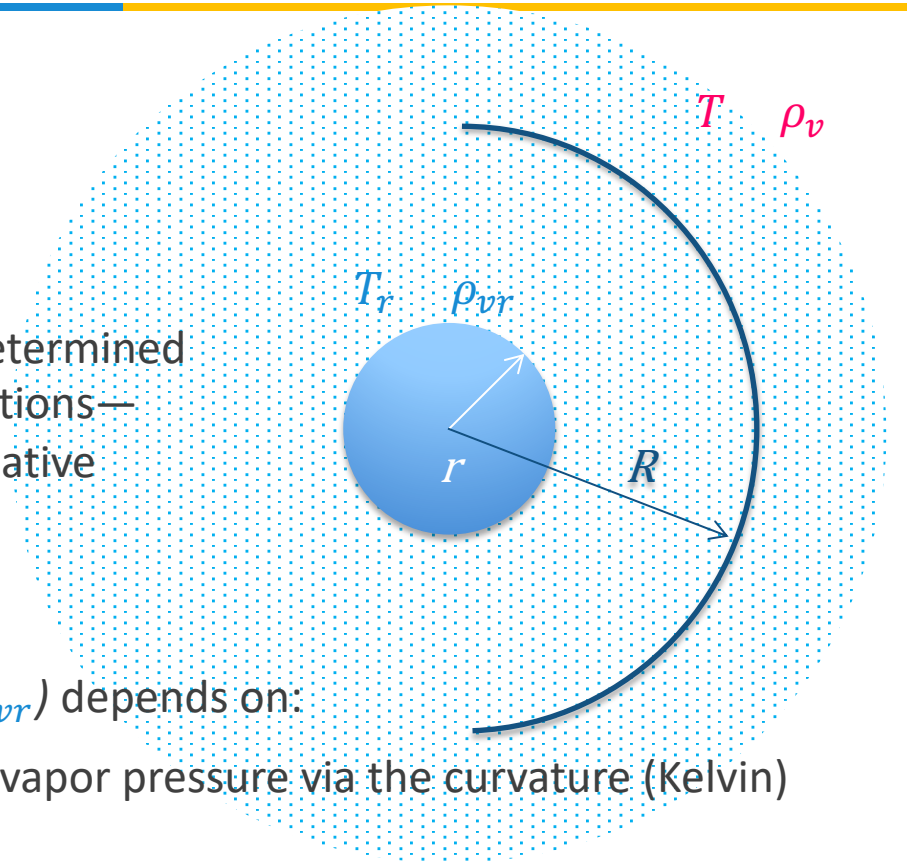
the ambient vapor density

the vapor density at the droplet's surface

The droplet grows if $\rho_v > \rho_{vr}$

The droplet evaporates if $\rho_v < \rho_{vr}$

$$\frac{dm}{dt} = 4\pi r D(\rho_v - \rho_{vr})$$



- The far-field ambient vapor density (ρ_v) is determined directly from prevailing environmental conditions—specifically, ambient temperature (T) and relative humidity (RH)

- The vapor density at the droplet's surface (ρ_{vr}) depends on:
  - Dropet radius (r): Increases equilibrium vapor pressure via the curvature (Kelvin) effect.
  - Chemical composition: Decreases equilibrium vapor pressure via the solute (Raoult) effect.
  - Surface temperature (T_r): Alters the saturation por density (ρ_{vr}).

The droplet surface temperature T_r generally differs from the ambient temperature (T) due to the release or absorption of latent heat during condensation or evaporation. T_r cannot be treated as a free parameter; it must be determined by solving the coupled heat and mass transfer equations between the droplet and its surrounding environment.

Condensation is accompanied by the release of latent heat, which elevates the droplet surface temperature above that of the surrounding ambient air ($T_r > T$).

Heat transfer away from the droplet surface is governed by Fourier's law, which takes a mathematical form directly analogous to steady-state vapor diffusion:

$$\frac{dQ}{dt} = 4\pi r K (T_r - T)$$

Q is the thermal energy

coefficient of thermal conductivity of air [J m^{-1} s^{-1} K^{-1}]

temperature at the surface of the droplet

ambient temparature

On the right hand side the signs are reversed comparing to the mass diffusion equation beacuse the positive heat flux is 'outside' the droplet, and the positive mass flux is 'towards' the droplet.

Equations of mass and heat fluxes were first derived by James Clerk Maxwell in 1877, in slightly different form, in an article in *Encyclopaedia Britannica* on the theory of the wet-bulb thermometer (Maxwell, 1890).

The theory of the steady-state growth of a spherical drop in rest in a vapor field regarded as a continuum is therefore often called the Maxwellian growth theory**.**

During condensational growth, the net change in a cloud droplet's surface temperature (T_r) is governed by the thermal energy balance between two competing heat transfer processes:

- Latent heat release.
- Sensible heat dissipation.

$$mcdT_r = Ldm - dQ$$

$$\frac{4}{3}\pi r^3 \rho_l c \frac{dT_r}{dt} = L\frac{dm}{dt} - \frac{dQ}{dt}$$

water density *specific heat capacity of water*

Assuming a steady state: $\frac{dT_r}{dt} = 0$

$$L\frac{dm}{dt} = \frac{dQ}{dt} \quad \rightarrow \quad 4\pi r D L(\rho_v - \rho_{vr}) = 4\pi r K(T_r - T)$$

$$\begin{cases} \frac{dm}{dt} = 4\pi r D(\rho_v - \rho_{vr}) \\ \frac{dQ}{dt} = 4\pi r K(T_r - T) \end{cases}$$

$$\frac{\rho_v - \rho_{vr}}{T_r - T} = \frac{K}{LD}$$

Weak sensitivity to temperature and pressure; Table 7.1 R&Y

Neither the droplet surface temperature (T_r) nor the surface vapor density (ρ_{vr}) is known a priori.

However, the surface temperature (T_r) and surface vapor density (ρ_{vr}) are uniquely linked through the Clausius-Clapeyron equation and Köhler theory. :

$$\rho_{vr} = \frac{e_s(r)}{R_v T_r} = \frac{\left(1 + \frac{A}{r} - \frac{\kappa r_d^3}{r^3}\right) e_s(T_r)}{R_v T_r}$$

the equilibrium vapor pressure over a plane surface at temperature T_r is given by the Clausius-Clapeyron equation

Equations:

$$\rho_{vr} = \frac{\left(1 + \frac{A}{r} - \frac{\kappa r_d^3}{r^3}\right) e_s(T_r)}{R_v T_r} \qquad \frac{\rho_v - \rho_{vr}}{T_r - T} = \frac{K}{LD}$$

constitutes a system of simultaneous equations which can be solved numerically for ρ_{vr} and T_r to permit evaluation of the rate of drop growth by condensation

$$\frac{dm}{dt} = 4\pi r D(\rho_v - \rho_{vr})$$

Condensational growth
Mason's solution



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Analytical approximation (Mason, 1971)

As an alternative to the iterative numerical solutions, Mason (1971) introduced an analytical approximation fthat provides an explicit closed-form expression for the condensational growth rate of a droplet.

Assuming a saturated environment, variations in saturation vapor density (ρ_{vs}) with respect to temperature are linked via the Clausius-Clapeyron relation:

$$\rho_{vs} = \frac{e_s}{R_v T} \quad \rightarrow \quad \frac{d\rho_{vs}}{\rho_{vs}} = \frac{de_s}{e_s} - \frac{dT}{T}$$

$$\frac{de_s}{e_s} = \frac{L dT}{R_v T^2}$$

Clausius-Clapeyron equation

$$\frac{d\rho_{vs}}{\rho_{vs}} = \frac{L}{R_v}\frac{dT}{T^2} - \frac{dT}{T}$$

We will integrate this equation between the droplet surface temperature T_r and the ambient temperature T, assuming $T/T_r \sim 1$.

Mason, B. J., 1971. The Physics of Clouds. Clarendon Press, Oxford, 671 pp.

$$\int_{T_r}^{T} \frac{d\rho_{vs}}{\rho_{vs}} = \int_{T_r}^{T} \left(\frac{L}{R_v} \frac{dT}{T^2} - \frac{dT}{T} \right)$$

$$\ln \frac{\rho_{vs}}{\rho_{vsr}} = -\frac{L}{R_v} \frac{1}{T} \Big|_{T_r}^{T} - \ln T \Big|_{T_r}^{T}$$

$$\ln \frac{\rho_{vs}}{\rho_{vsr}} = -\frac{L}{R_v} \left(\frac{1}{T} - \frac{1}{T_r} \right) - \ln \frac{T}{T_r}$$

$$\frac{T}{T_r} \approx 1 \; ; \quad \frac{T}{T_r} = 1 + \varepsilon$$

$$\ln(1+\varepsilon) \approx \varepsilon \; ; \; \ln \frac{T}{T_r} = \frac{T}{T_r} - 1$$

$$\ln \frac{\rho_{vs}}{\rho_{vsr}} = -\frac{L}{R_v} \frac{T_r - T}{T T_r} - \left(\frac{T}{T_r} - 1 \right) = (T_r - T) \left[\frac{L}{R_v T T_r} - \frac{T_r - T}{T_r (T_r - T)} \right]$$

$$\ln \frac{\rho_{vs}}{\rho_{vsr}} = (T_r - T) \left[\frac{L}{R_v T T_r} - \frac{1}{T_r} \right]$$

$$\ln\frac{\rho_{vs}}{\rho_{vsr}} = (T_r - T)\left[\frac{L}{R_v T T_r} - \frac{1}{T_r}\right]$$

$$\frac{\rho_{vs}}{\rho_{vsr}} \approx 1\,; \quad \ln\frac{\rho_{vs}}{\rho_{vsr}} \approx \frac{\rho_{vs}}{\rho_{vsr}} - 1 = \frac{\rho_{vs} - \rho_{vsr}}{\rho_{vsr}} \qquad T \cdot T_r \approx T^2$$

$$\frac{\rho_{vs} - \rho_{vsr}}{\rho_{vsr}} = \left(\frac{T - T_r}{T}\right)\left(\frac{L}{R_v T} - 1\right)$$

$T - T_r$ can be replaced from the equation of the heat diffusion

$$\frac{dQ}{dt} = 4\pi r K (T_r - T) \longrightarrow (T_r - T) = \frac{1}{4\pi r K}\frac{dQ}{dt}$$

for a steady-state $\frac{dQ}{dt} = L\frac{dm}{dt}$

$$(T_r - T) = \frac{L}{4\pi r K}\frac{dm}{dt}$$

$$\frac{\rho_{vs} - \rho_{vsr}}{\rho_{vsr}} = \left(1 - \frac{L}{R_v T}\right)\frac{L}{4\pi r K T}\frac{dm}{dt}$$

$$\frac{dm}{dt} = 4\pi r D(\rho_v - \rho_{vr}) \longrightarrow (1)\quad \frac{\rho_v - \rho_{vr}}{\rho_{vr}} = (4\pi r D \rho_{vr})^{-1}\frac{dm}{dt}$$

$$(2)\quad \frac{\rho_{vs} - \rho_{vsr}}{\rho_{vsr}} = \left(1 - \frac{L}{R_v T}\right)\frac{L}{4\pi r K T}\frac{dm}{dt}$$

Subtracting (2) from (1), assuming $\rho_{vr}=\rho_{vsr}$ and neglecting the effect of curvature

$$\frac{\rho_v - \rho_{vr}}{\rho_{vr}} - \frac{\rho_{vs} - \rho_{vsr}}{\rho_{vsr}} \approx \frac{\rho_v - \rho_{vs}}{\rho_{vsr}} \approx \frac{\rho_v}{\rho_{vs}} - 1 \approx S - 1$$

saturation over plane water surface

(1)-(2)

$$S - 1 = \frac{dm}{dt}\left[\frac{1}{4\pi r D \rho_{vr}} + \left(\frac{L}{R_v T} - 1\right)\frac{L}{4\pi r K T}\right]$$

$$\frac{dm}{dt} = \frac{S - 1}{\left[\frac{1}{4\pi r D \rho_{vr}} + \left(\frac{L}{R_v T} - 1\right)\frac{L}{4\pi r K T}\right]}$$

$$\frac{dm}{dt} = \frac{S-1}{\left[\frac{1}{4\pi r D \rho_{vr}} + \left(\frac{L}{R_v T} - 1\right)\frac{L}{4\pi r K T}\right]}$$

$$\frac{dm}{dt} = \frac{d\left(\frac{4}{3}\pi\rho_l r^3\right)}{dt} = 4\pi\rho_l r^2 \frac{dr}{dt} = (4\pi\rho_l r) r \frac{dr}{dt}$$

$$r\frac{dr}{dt} = \frac{S-1}{\left[\frac{4\pi\rho_l r}{4\pi r D \rho_{vr}} + \left(\frac{L}{R_v T} - 1\right)\frac{4\pi\rho_l r L}{4\pi r K T}\right]}$$

$$\rho_{vr} \approx \frac{e_s(T)}{R_v T}$$

$$r\frac{dr}{dt} = \frac{S-1}{\left[\frac{\rho_l R_v T}{D e_s(T)} + \left(\frac{L}{R_v T} - 1\right)\frac{\rho_l L}{K T}\right]}$$

$$r\frac{dr}{dt} = \frac{S-1}{[F_d + F_k]} \qquad F_d = \frac{\rho_l R_v T}{D e_s(T)} \qquad F_k = \left(\frac{L}{R_v T} - 1\right)\frac{\rho_l L}{K T}$$

the term associated with vapor diffusion

the term associated with heat conduction

F_d+F_k depends on both ambient temperature and pressure. Its sensitivity to temperature is substantially more pronounced.

$$r\frac{dr}{dt} = \frac{S-1}{[F_d + F_k]}$$

saturation over a flat, pure water surface

To account for microphysical boundary corrections at the droplet surface, the saturation over a flat, pure water surface (1) is replaced by the equilibrium saturation over a curved solution droplet (S_{eq}).

$$r\frac{dr}{dt} = \frac{S - S_{eq}}{[F_d + F_k]}$$

$$S_{eq} = 1 + \frac{A}{r} - \frac{\kappa r_d^3}{r^3}$$

$$S_{eq} = \frac{r^3 - r_d^3}{r^3 - (1-\kappa)r_d^3}\exp\left(\frac{A(T)}{r}\right)$$

This closed-form analytical equation provides a highly accurate approximation to the exact solution obtained by numerically solving the coupled mass diffusion and thermal conduction equations for ρ_{vr} and T_r.

In the term represented by F_k, it may be shown that $L/R_vT >> 1$, and we can neglect 1 in brackets

$$F_d = \frac{\rho_l R_v T}{D e_s(T)} \qquad F_k = \left(\frac{L}{R_v T} - 1\right)\frac{\rho_l L}{KT} \approx \frac{\rho_l L^2}{K R_v T^2}$$

$$F_d = \frac{\rho_l R_v T}{D e_s(T)} \qquad F_k = \left(\frac{L}{R_v T} - 1\right)\frac{\rho_l L}{KT} \approx \frac{\rho_l L^2}{K R_v T^2}$$

K depends on *T, D depends on T and p*

$K \propto \mu$, μ *Dynamic viscosity of the air*

$D \propto {}^{\mu}/_{\rho}$, ${}^{\mu}/_{\rho} = \nu$ *Kinematic viscosity of the air*

$$\mu(T) = 1.72 \cdot 10^{-5} \frac{393}{T + 120}\left(\frac{T}{273}\right)^{3/2}$$

$$K = 4.1868 \cdot 10^{-3}[5.69 + 0.017(T - T_0)] \; Wm^{-1}K^{-1}$$

$$D = 2.11 \cdot 10^{-5}\left(\frac{T}{T_0}\right)^{1.94}\left(\frac{p_0}{p}\right) \; m^2 s^{-1}$$

$$T_0 = 273.15\,K; \quad p_0 = 1013.25\,hPa$$

For small solution droplets, where curvature (Kelvin) and solute (Raoult) effects significantly alter the equilibrium surface supersaturation, the non-linear differential equation governing condensational growth cannot be solved analytically in closed form and requires numerical integration.

$$r\frac{dr}{dt} = \frac{(S-1) - \frac{A(T)}{r} + \frac{\kappa r_d^3}{r^3}}{[F_d + F_k]}$$

$$r\frac{dr}{dt} = \frac{S - \frac{r^3 - r_d^3}{r^3 - (1-\kappa)r_d^3}\exp\left(\frac{A(T)}{r}\right)}{[F_d + F_k]}$$

Numerical solution

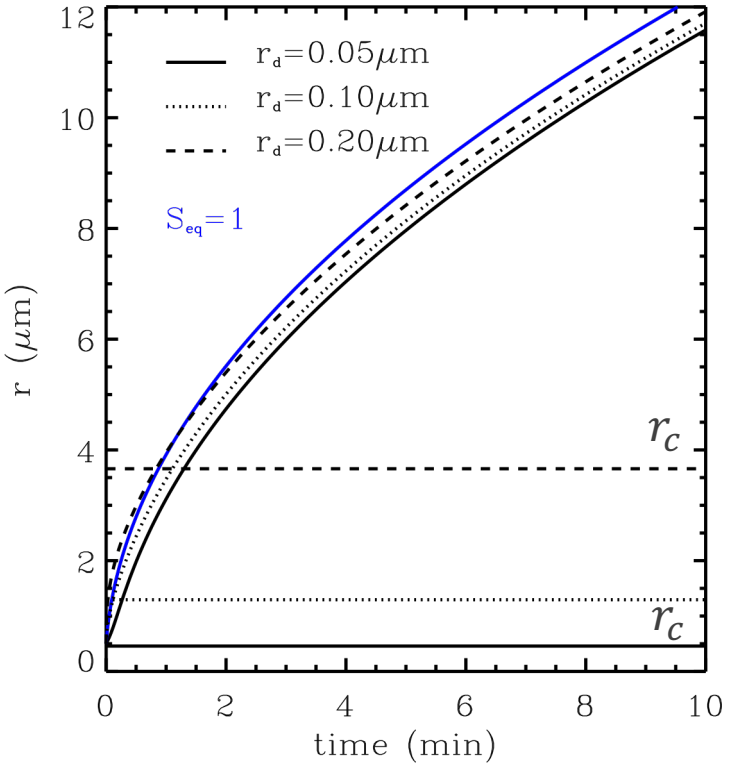
The figure shows the time necessary for a droplet to grow from the initial radius *0,5μm*, for different initial dry radii of the condensation nucleus ($\kappa = 0.67$).

Supersaturation 0,2%, p=900hPa, T=273 K

Droplets formed on big CCN grow initially faster (shorter time) than droplets formed an small CCN.

From a certain drop's diameter (~10 μm) the rate of growth is similar.

r_d (μm)	Time (s) to grow from $r = 0.5$ μm to 2 μm	Time (s) to grow from $r = 10$ μm to 12 μm
0.05	32.7	186.78
0.1	22.9	186.74
0.2	10.8	186.39



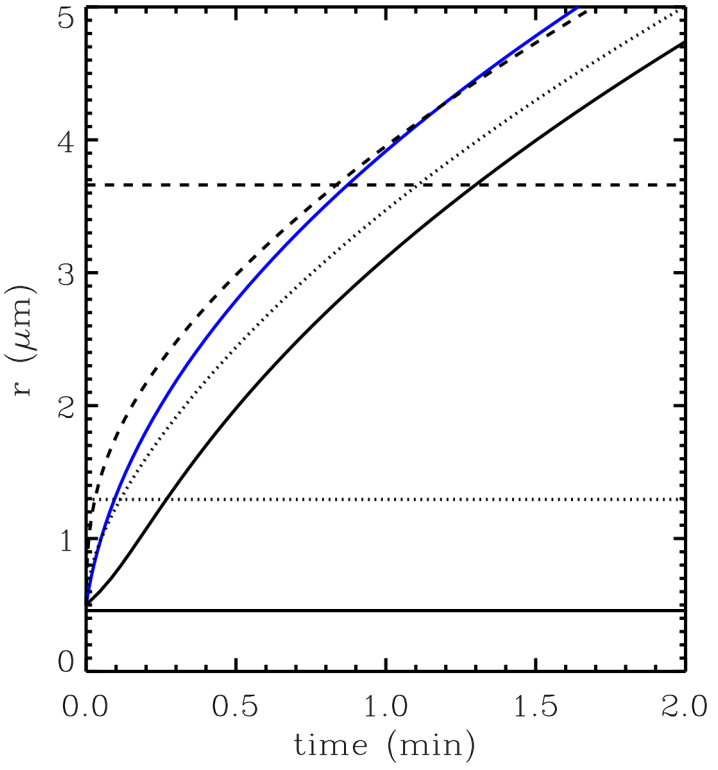
$$r\frac{dr}{dt} = \frac{(S-1) - \frac{A}{r} + \frac{\kappa r_d^3}{r^3}}{[F_d + F_k]}$$

$$r\frac{dr}{dt} = \frac{S - \frac{r^3 - r_d^3}{r^3 - (1-\kappa)r_d^3}\exp\left(\frac{A(T)}{r}\right)}{[F_d + F_k]}$$

Numerical solution

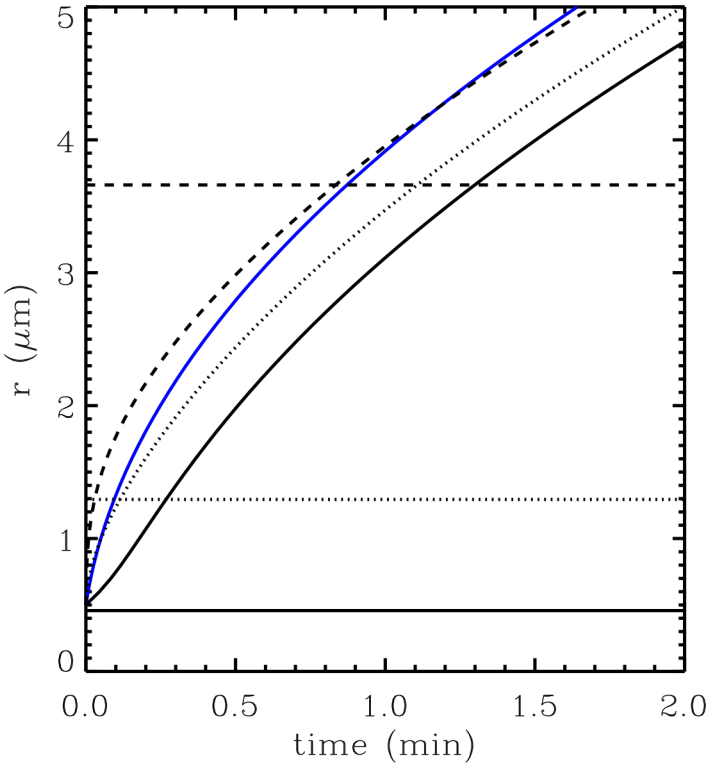
Droplets formed on big CCN grow initially faster (shorter time) than droplets formed an small CCN.

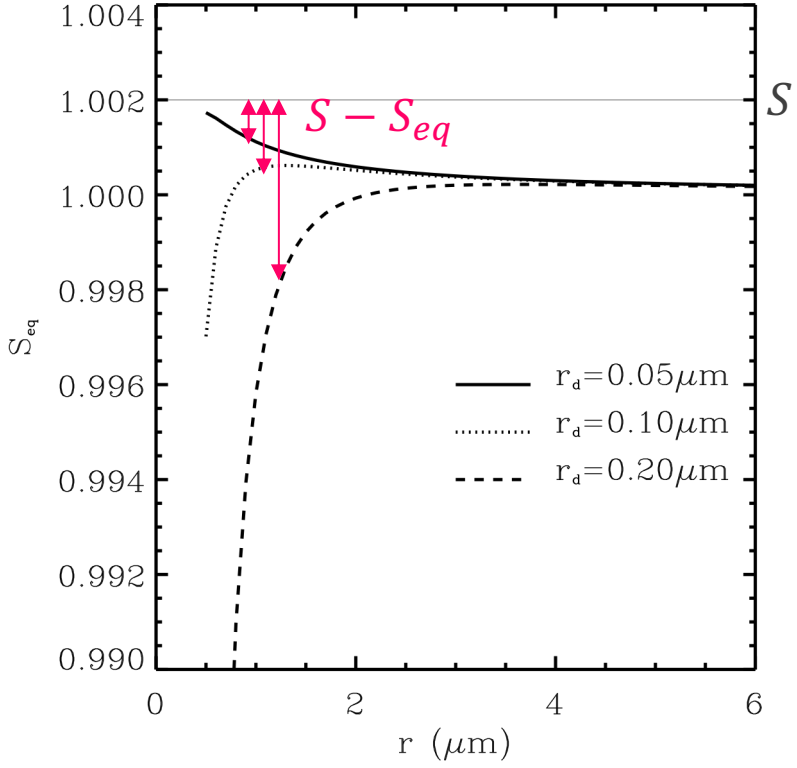
$r_d\ (\mu m)$	Time (s) to grow from $r = 0.5\ \mu m$ to $2\ \mu m$	Time (s) to grow from $r = 10\ \mu m$ to $12\ \mu m$
0.05	32.7	186.78
0.1	22.9	186.74
0.2	10.8	186.39



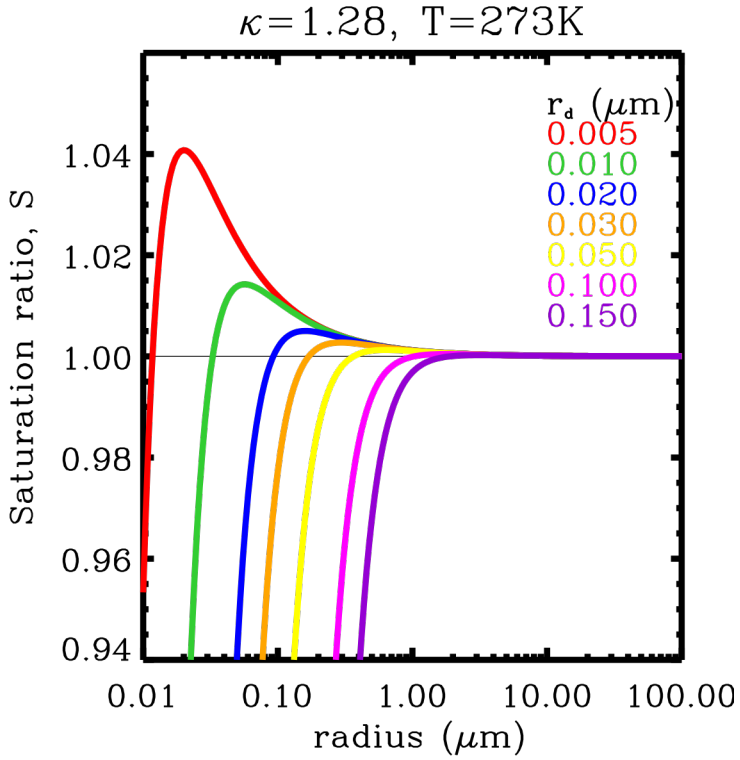
$$r\frac{dr}{dt} = \frac{(S - S_{eq})}{[F_d + F_k]}$$

$$S_{eq} = 1 + \frac{A}{r} - \frac{\kappa r_d^3}{r^3}$$





When a droplet becomes larger (approx. *10 μm*) the curvature and solution effects (A/r and $\kappa r_d^3/r^3$) become negligible compared to *(S-1)*, or in other words $S_{eq} \approx 1$.



When a droplet becomes larger (approx. *10 μm*) the curvature and solution effects (A/r and $\kappa r_d^3/r^3$) become negligible compared to *(S-1)*, or in other words $S_{eq} \approx 1$.

The equation for condensational growth can be solved analiticay.

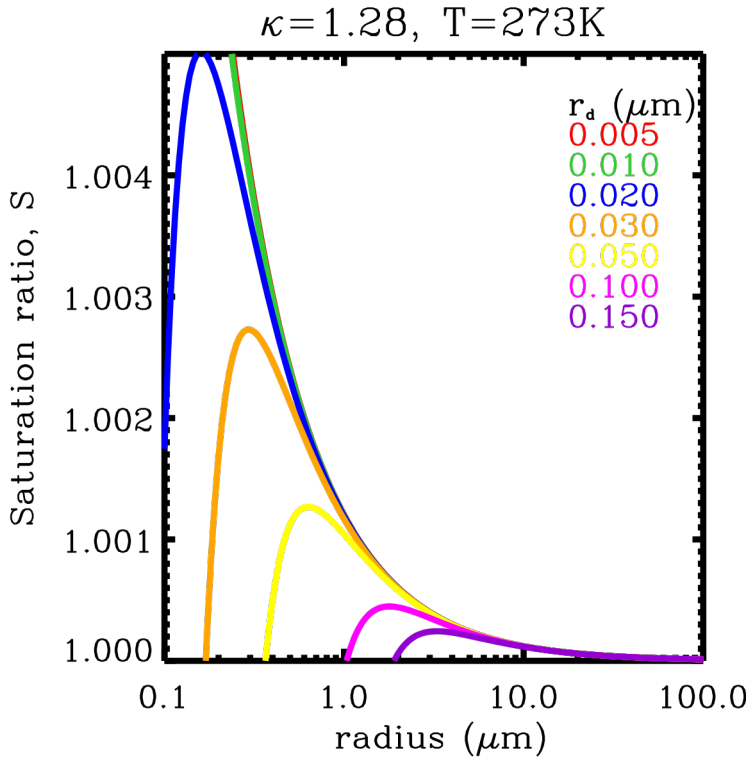
$$r\frac{dr}{dt} = \frac{S-1}{[F_d + F_k]}$$

$$\frac{dr^2}{dt} = 2\xi(S-1)\,, \qquad \xi = \frac{1}{F_d + F_k}$$

The growth rate of a droplet's surface area is independent of its radius.

$$r^2(t) - r^2(t_0) = 2\xi(S-1)\cdot(t-t_0)$$

$$r(t) = \sqrt{r^2(t_0) + 2\xi(S-1)\cdot(t-t_0)}$$

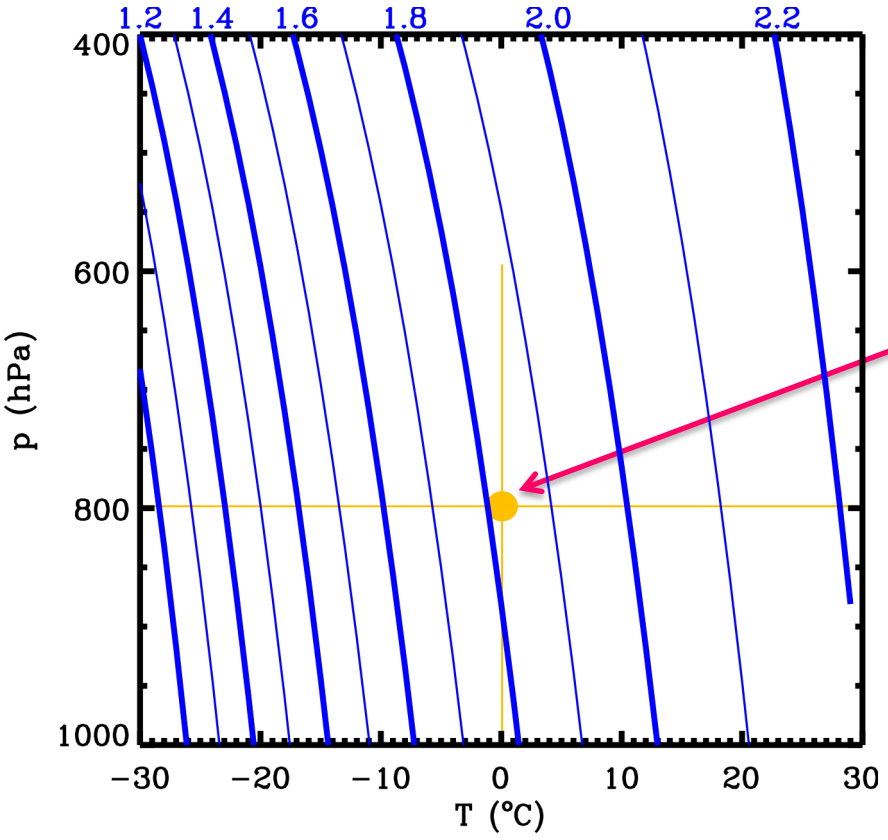


Smaller droplets grow faster, causing the droplet spectrum to narrow during condensational growth.

$$\xi = \frac{1}{F_d + F_k}$$

ξ is a function of temperature and pressure

Solid lines represent $log_{10}\,\xi$



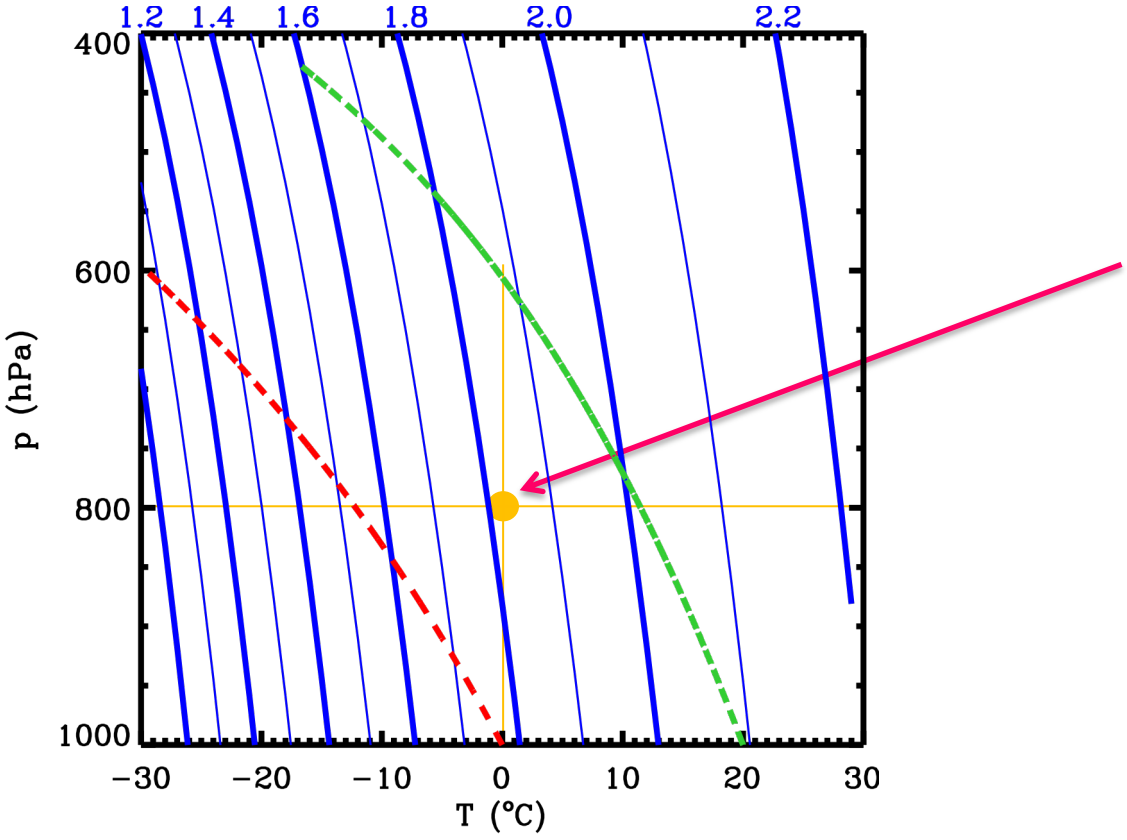
$$\xi = 10^{1.834} = 68.2\ \mu m^2 s^{-1}$$

$$\xi = \frac{1}{F_d + F_k}$$

ξ is a function of temperature and pressure

Solid lines represent $log_{10}\,\xi$

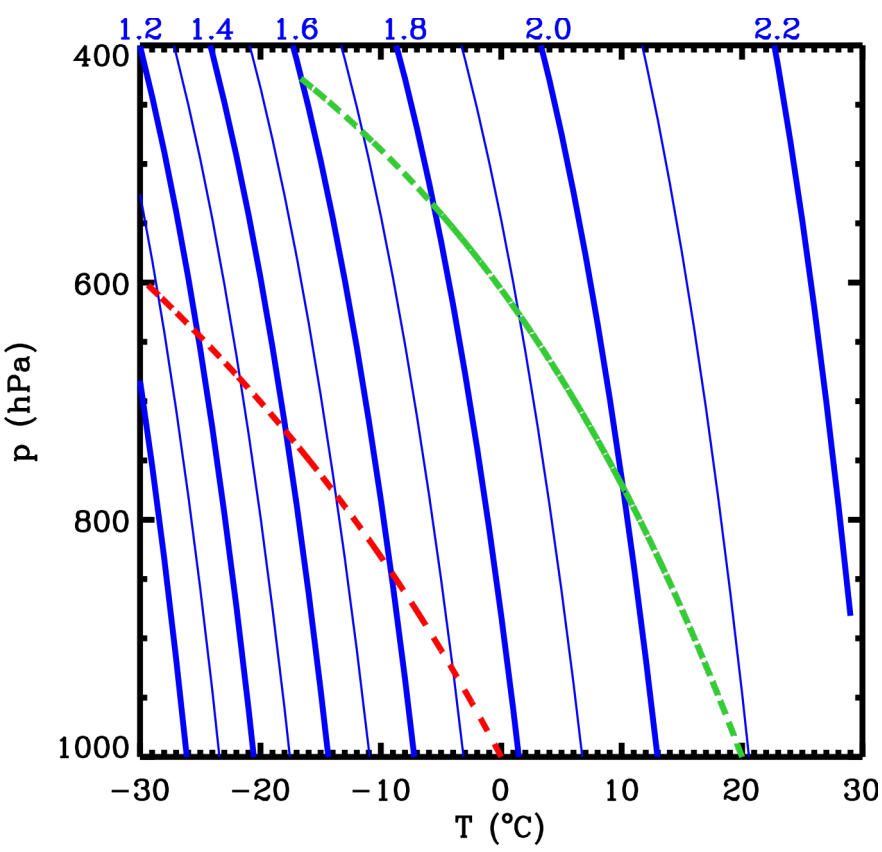
Dashed lines represent pseudoadiabats corresponding to *T= 0 ℃ and 20 ℃*

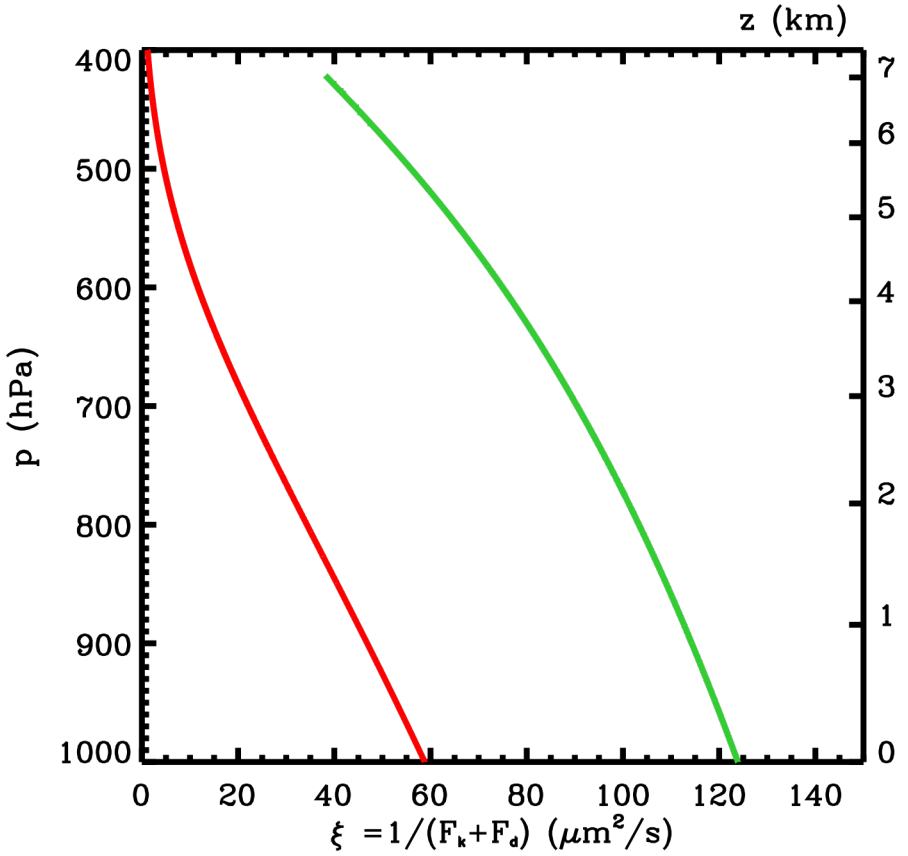


$p = 800\ hPa\,,\qquad T = 0℃$

$\xi = 10^{1.834} = 68.2\ \mu m^2 s^{-1}$

$$\xi = \frac{1}{F_d + F_k}$$

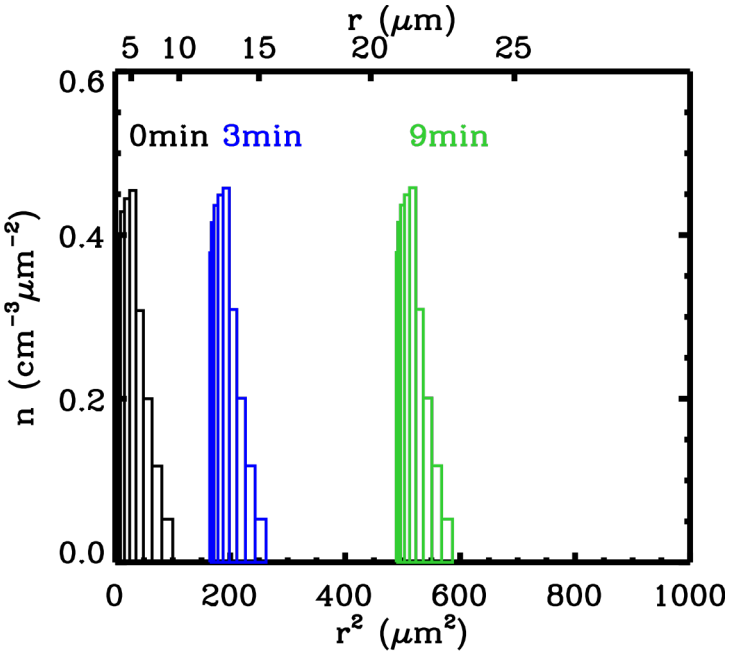




$$\frac{dr}{dt} = \xi \frac{S-1}{r}, \qquad \xi = \frac{1}{F_d + F_k}$$

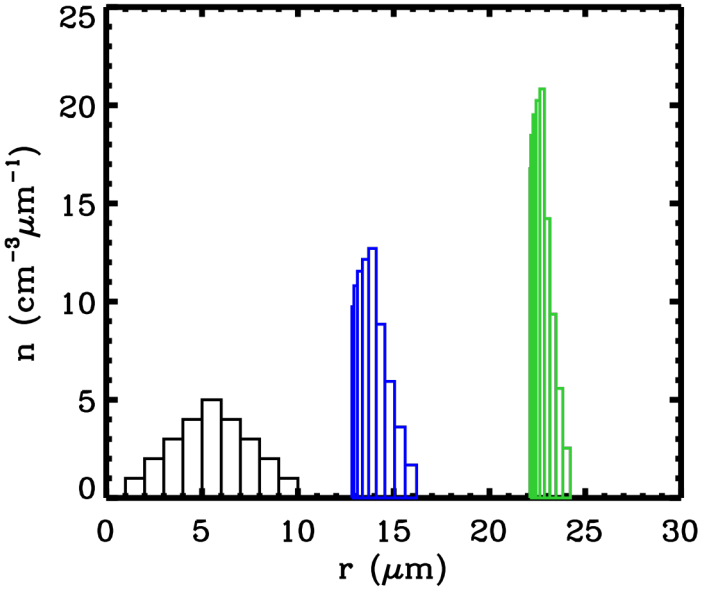
$$\rightarrow \quad \frac{dr^2}{dt} = 2\xi(S-1)$$

For a given thermodynamic conditions the growth rate of droplet surface area (~r^2) is constant and depends only on supersaturation .

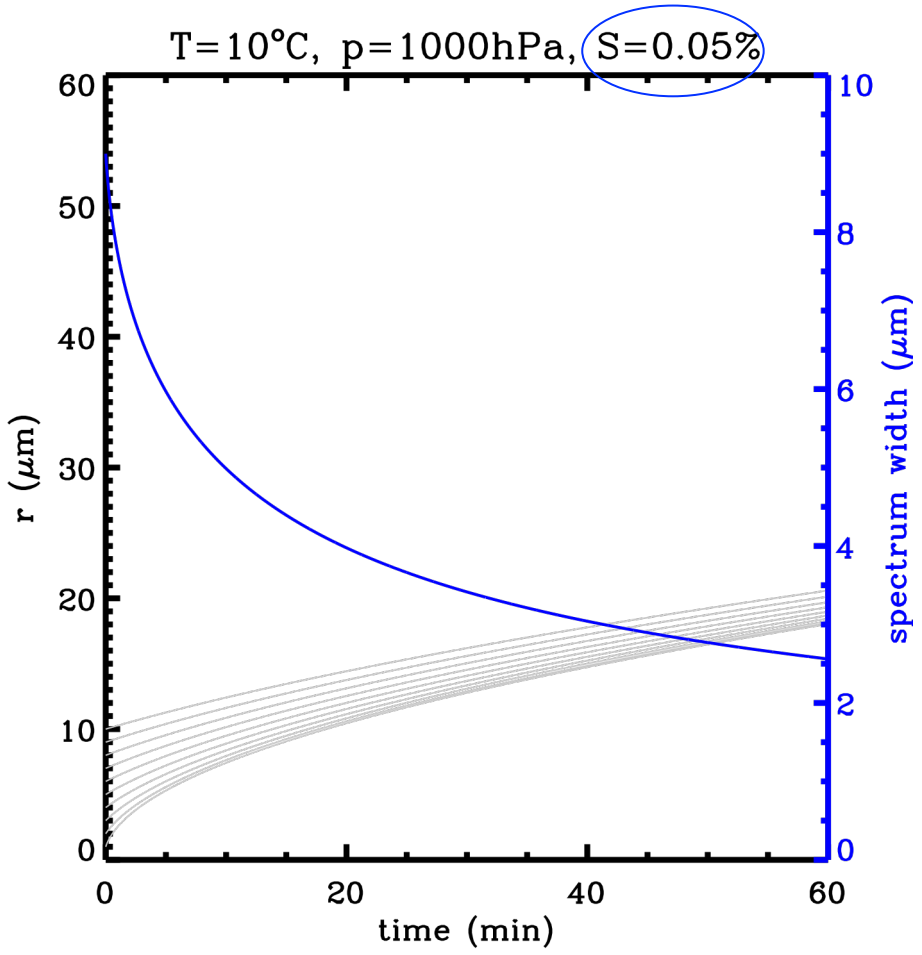


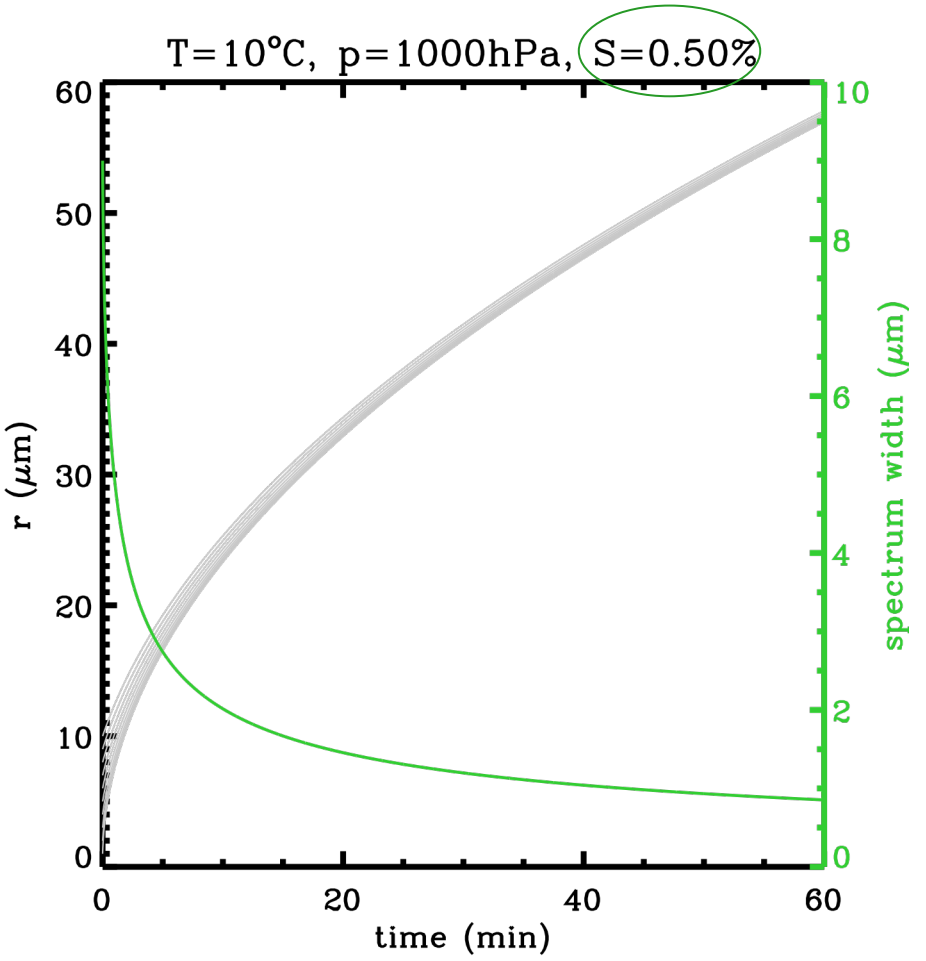
At the same supersaturation level, smaller droplets grow faster (experiencing a more rapid increase in radius) than larger droplets.

Condensational growth leads to a narrowing of the droplet size distribution.

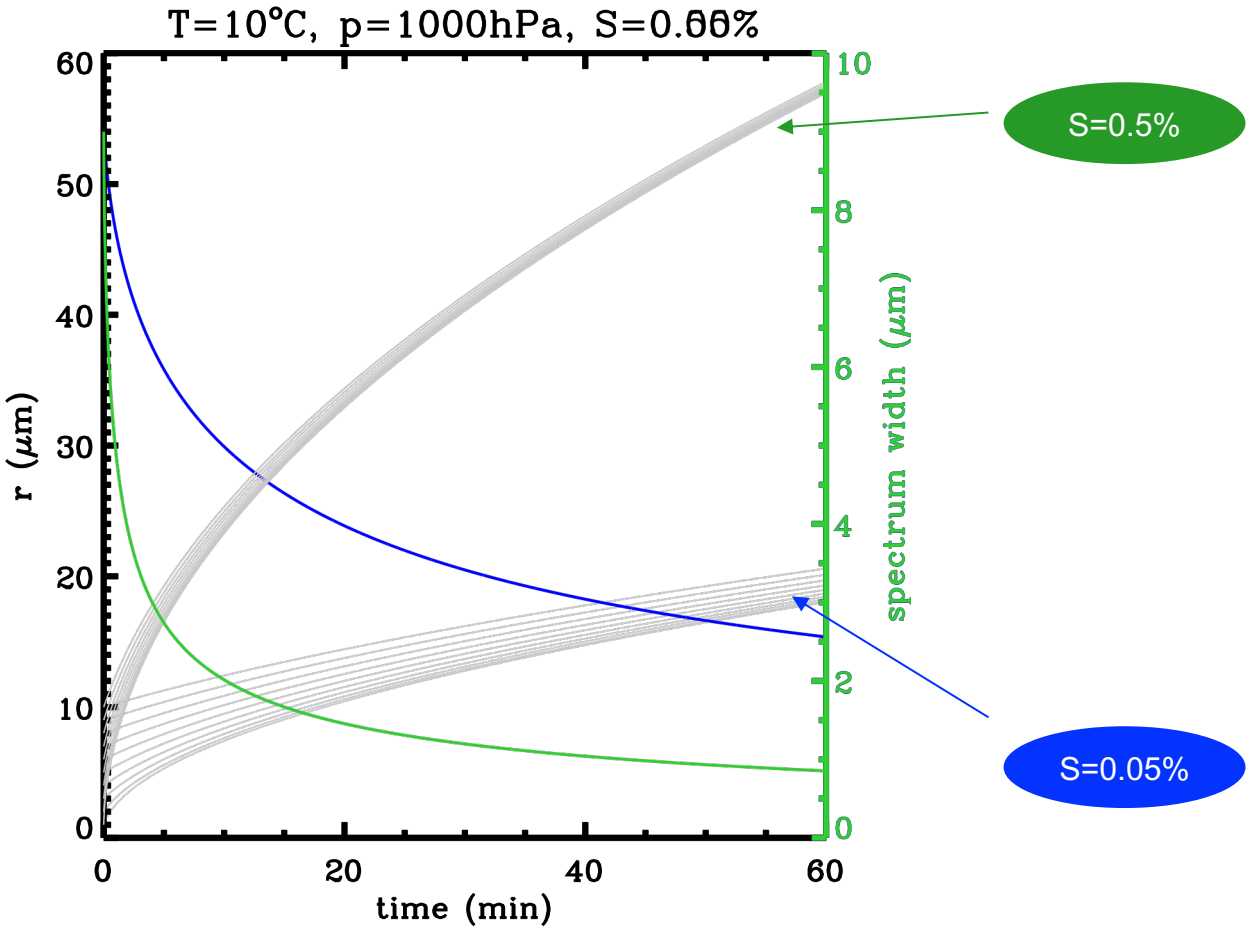


T=10°C, p=1000 hPa, S=0.5%





In realistic cloud conditions, growth by water vapor diffusion seldom produces droplets with radii close to 20 μm because of the low magnitude of the supersaturation field and the time available for growth (~20 min).


T=10°C, p=1000hPa, S=0.66%
r (μm)
spectrum width (μm)
time (min)
0
20
40
60
0
10
20
30
40
50
60
0
2
4
6
8
10
S=0.5%
S=0.05%