CONDENSATIONAL GROWTH OF CLOUD DROPLETS

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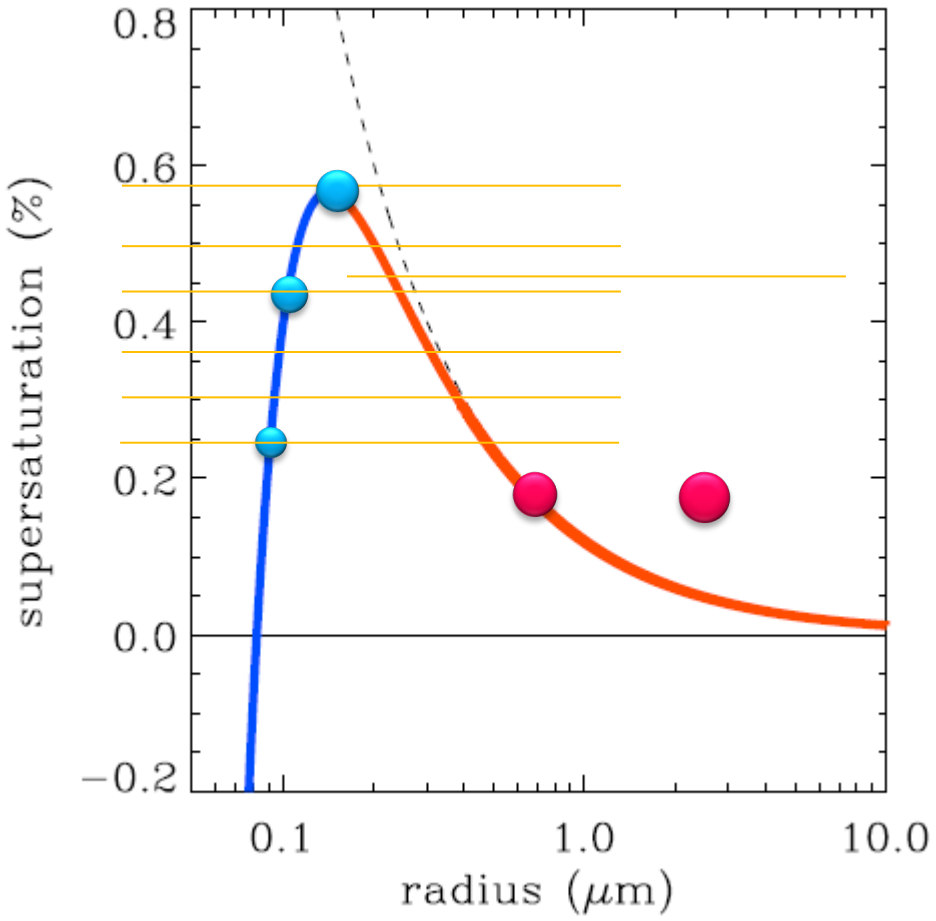
Equilibrium conditions

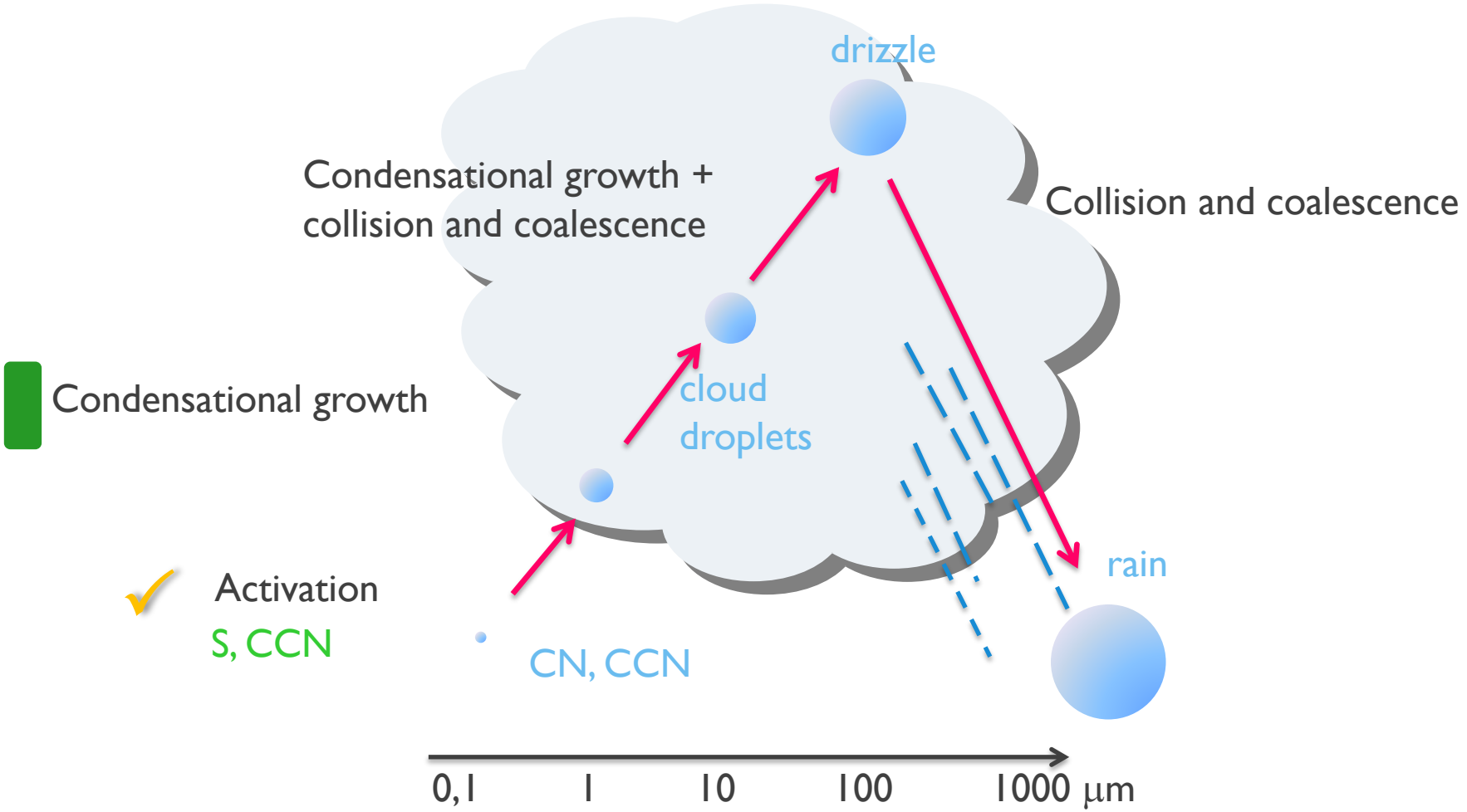


Stable equilibrium:

- increase of the relative humidity (supersaturation) leads to a growth of cloud droplet until the new equilibrium is reached
- for the droplets to grow the supersaturation has to rise until critical values (supersaturation, radius) are reached

Unstable equilibrium:

- increase of the realtive humidity (supersaturation) above the critical value leads to a growth of the droplet and a decrease of the saturation equiibrium value
- water vapor diffuses toward the droplet causing its growth without an increase of suparsaturation


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

Growth by diffusion of water vapor

- For a droplet to become a cloud droplet critical values of radius and supersaturation should be reached
- Before and after the critical values are reached a droplet grows by diffusion of water vapor towards the droplet surface
- We will describe a growth of a single droplet by diffusion of water vapor

Condensational growth

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A droplet of radius *r* in a field of water vapor;

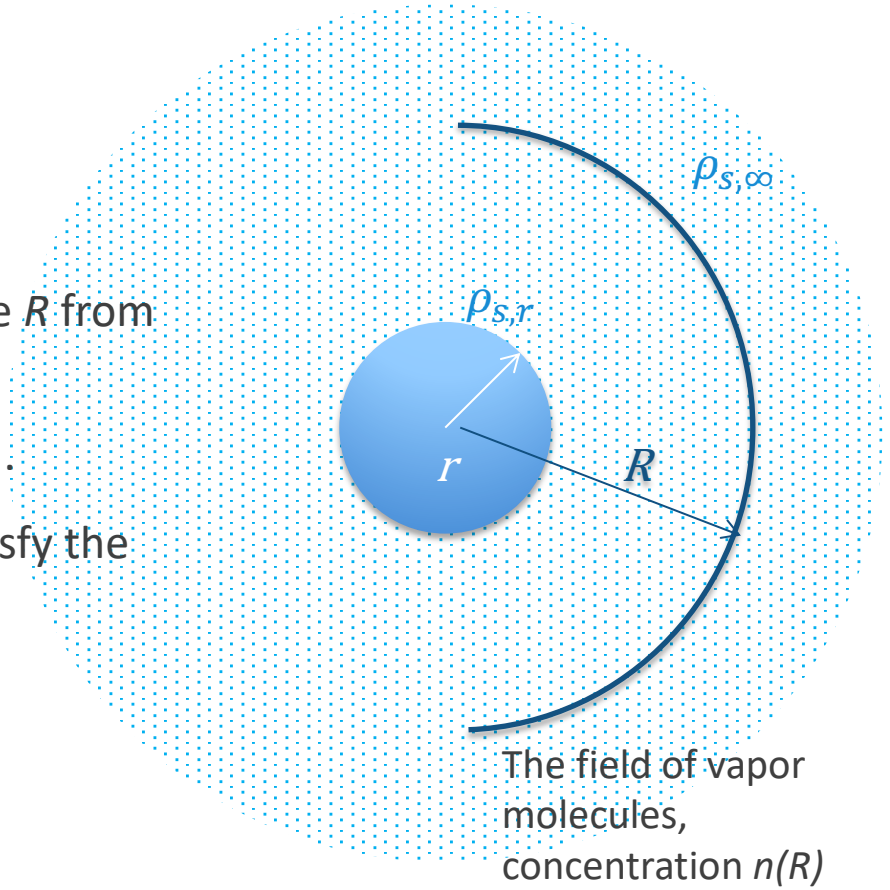
Concentration of vapor molecules, *n(R)* at distance *R* from the droplet center;

Vapor density or absolute humidity $\rho_v(R) = nm_0$.

The concentration of molecules is assumed to satisfy the diffusion equation:

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

D [m^2s^{-1}] is the molecular diffusion coefficient.



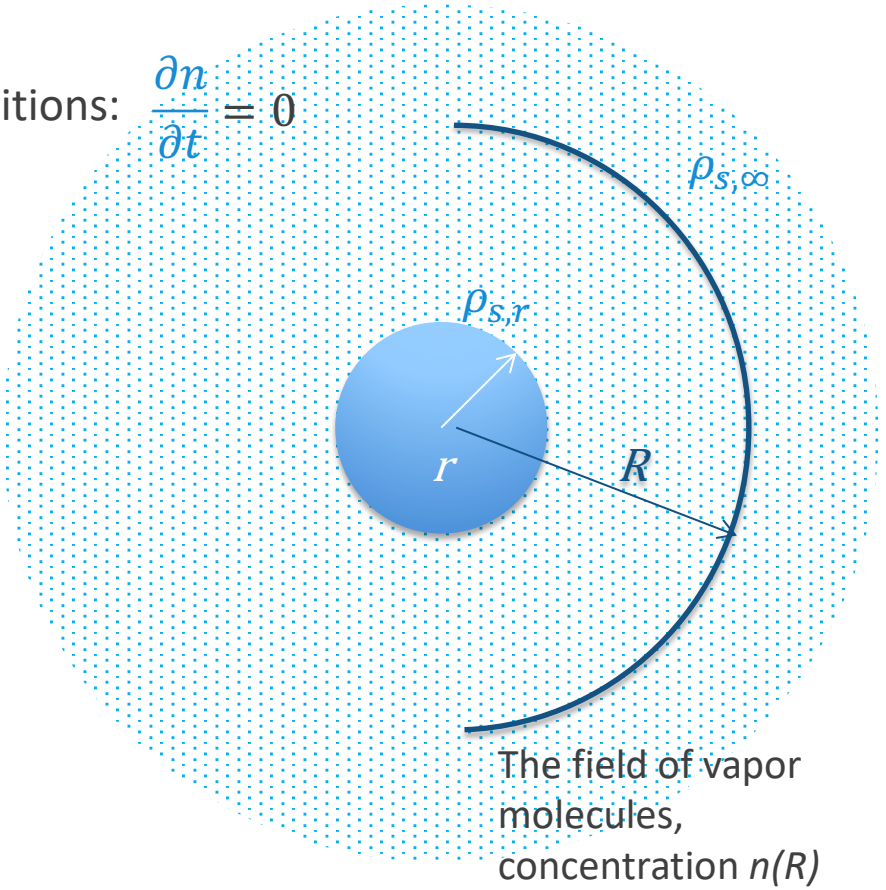
The field of vapor molecules, concentration *n(R)*

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

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

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

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



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

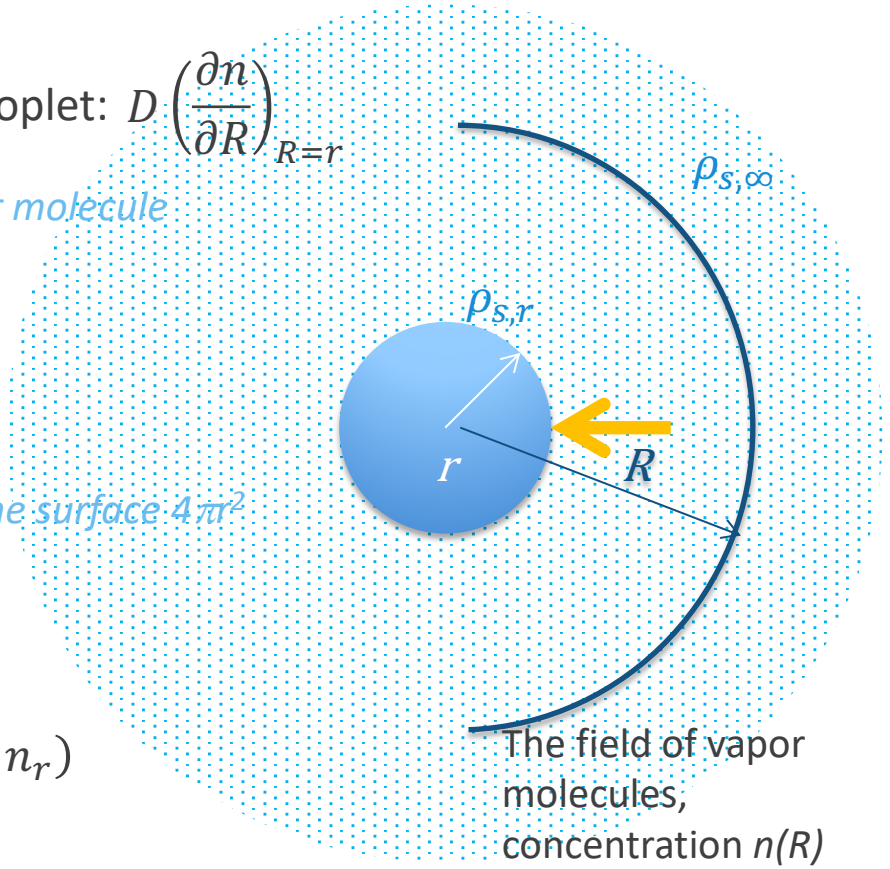
The flux of molecules onto the surface of the droplet: $D\left(\frac{\partial n}{\partial R}\right)_{R=r}$

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

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:

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

$$\rho_v = nm_0 \qquad \frac{dm}{dt} = 4\pi r D(\rho_v - \rho_{vr})$$

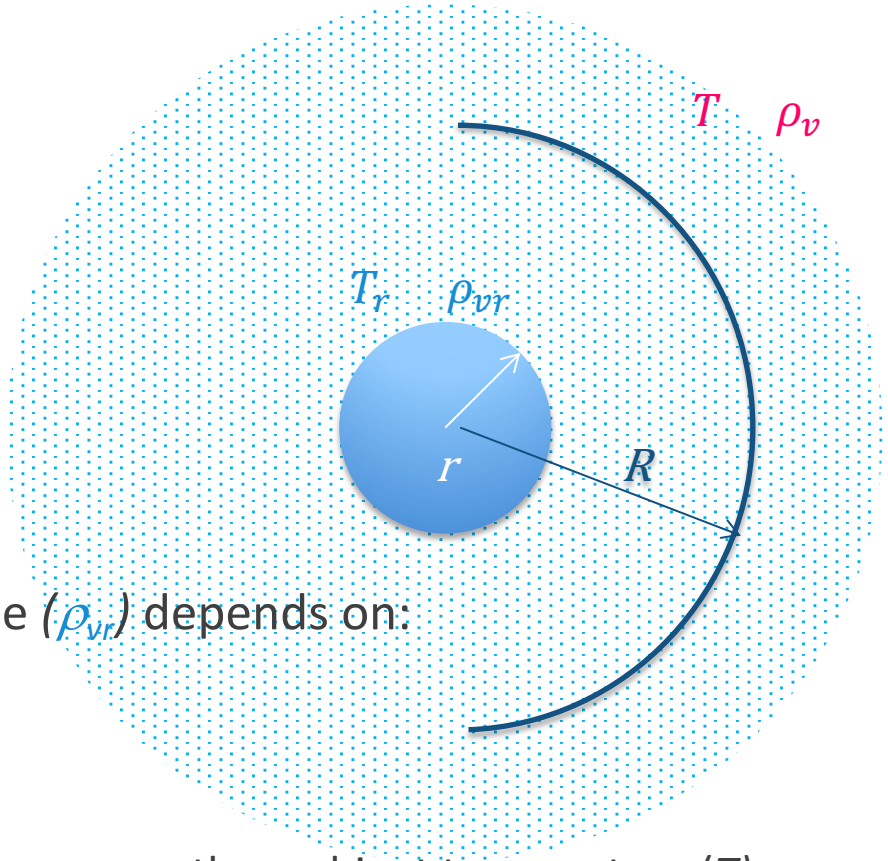
the ambient vapor density

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 ambient vapor density (ρ_v) may be determined from given environmental conditions

- The vapor density at the droplet's surface (ρ_{vr}) depends on:
  - the dropet size
  - the chemical composition
  - temperature (T_r), which is usually not the same as the ambient temperature (T), and must be determined by considering the heat transfer between the droplet and its surrounding.

Associated with condensation is the release of latent heat, which tends to raise the droplet temperature above the ambient value.

The diffusion of heat away from the droplet (*Q)* is given by an equation analogous to the mass diffusion:

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

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 Clerc 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 Maxwell theory**.**

The change of cloud droplet's temperature (T_r) in the condensation process is due to:

- the release of the latent heat of condensation
- the heat release to the environment:

$$mcdT_r = Ldm - dQ$$

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

density of water *specific heat capacity of water*

For stationary 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 dependence on temperature and pressure; Tabele 7.1 R&Y

Ordinarily the drop temperature (T_r) and the water vapor density at its surface (ρ_{vr}) are unknown.

However we know the relation between T_r and ρ_{vr} :

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

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

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

comprise a simultaneous systems 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 numerical method of solution, Masson (1971) introduced a useful analytical approximation for calculating the rate of growth of a drop by condensation.

In a field of saturated vapor, changes in vapor density are related to changes in tempearture by:

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

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

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 from temperature T_r to temperature T, assuming $T/T_r \sim 1$

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

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

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

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

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

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

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

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

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

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

$T\text{-}T_r$ 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 $\quad \frac{dQ}{dt} = L\frac{dm}{dt}$

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

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

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

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

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)

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

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

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

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

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

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

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

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

the term associated with vapor diffusion

the term associated with heat conduction

F_d+F_k depends on temperature and pressure (the dependence on temperature is stronger)

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

saturation over plane water surface

Saturation over plane water surface will be replaced by the equilibrium saturation over droplet solution

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

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

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

The equation is an excellent approximation to that obtained by simultaneous solution of equations for ρ_{vr} i 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

$$F_d = \frac{\rho_l R_v T}{D e_s(T)}$$

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

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

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

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*

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

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

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

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

For very small drops, for which the Kelvin and Raoult effects are important the equation of condensational growth cannot be solved analiticaly.

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

Numerical solution

The table gives the time necessary for a droplet to grow from the initial radius *0,75 μm*, for different initial mass of NaCl in the condensation nucleus.

Supersaturation 0,05%, p=900hPa, T=273 K

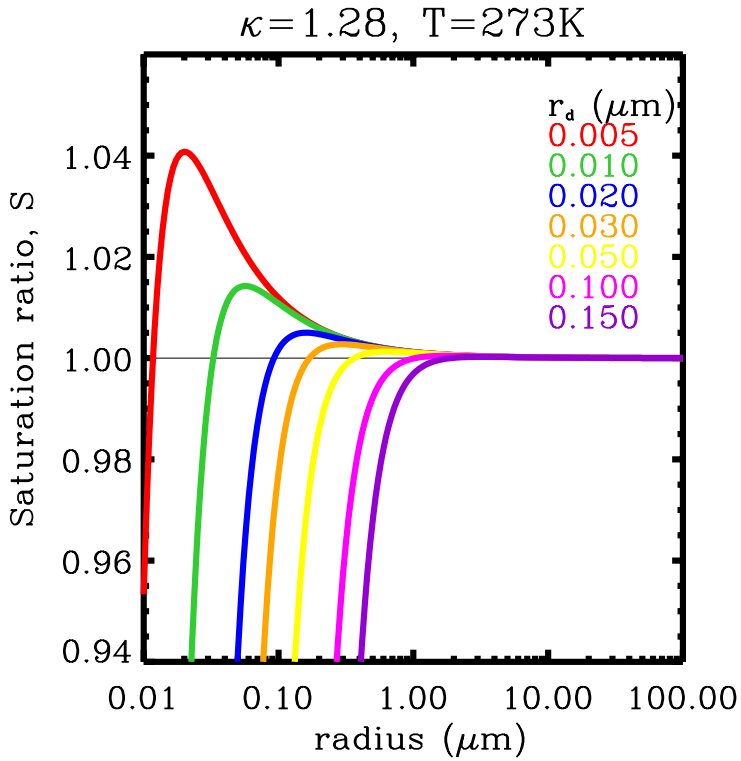
Droplets formed on big CCN grow initially faster (shorter time) than droplets formed an small CCN.

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

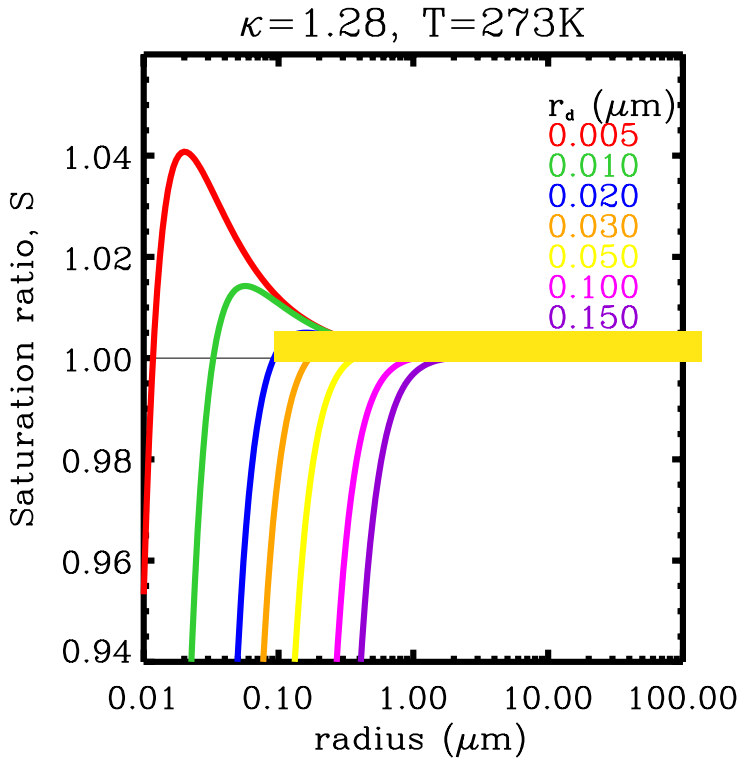
TABLE 7.2. *Rate of Growth of Droplets by Condensation (initial radius 0.75 μm). (From Mason, 1971)*

Nuclear mass (g)	10^{-14}	10^{-13}	10^{-12}
Radius (μm)	Time (sec) to grow from initial radius 0.75 μm		
1	2.4	0.15	0.013
2	130	7.0	0.61
4	1,000	320	62
10	2,700	1,800	870
20	8,500	7,400	5,900
30	17,500	16,000	14,500
50	44,500	43,500	41,500

When a droplet becomes larger (approx. *10 μm*) the curvature and solution effects (A/r i B_s/r^3) become negligible compared to *(S-1)*.



When a droplet becomes larger (approx. *10 μm*) the curvature and solution effects (A/r i B_s/r^3) become negligible compared to *(S-1)*.



When a droplet becomes larger (approx. *10 μm*) the curvature and solution effects (A/r i B_s/r^3) become negligible compared to *(S-1)*.

The equation for condensational growth can be solved analiticaly.

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

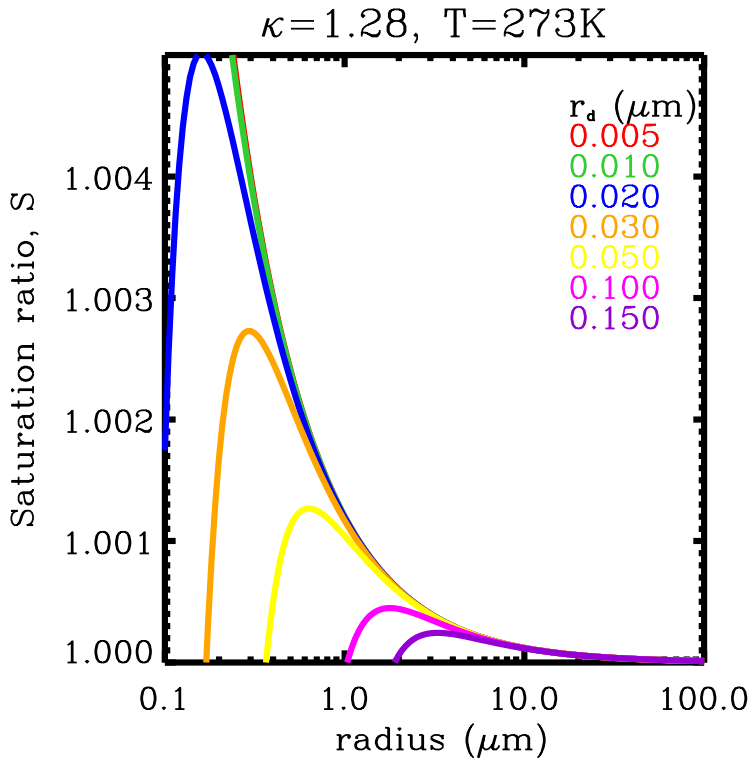
$$\frac{dr^2}{dt} = 2\xi(S-1)\,, \qquad \xi = \frac{1}{F_d + F_k}$$

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

The rate of growth of a droplet's surface does not depend on radius

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

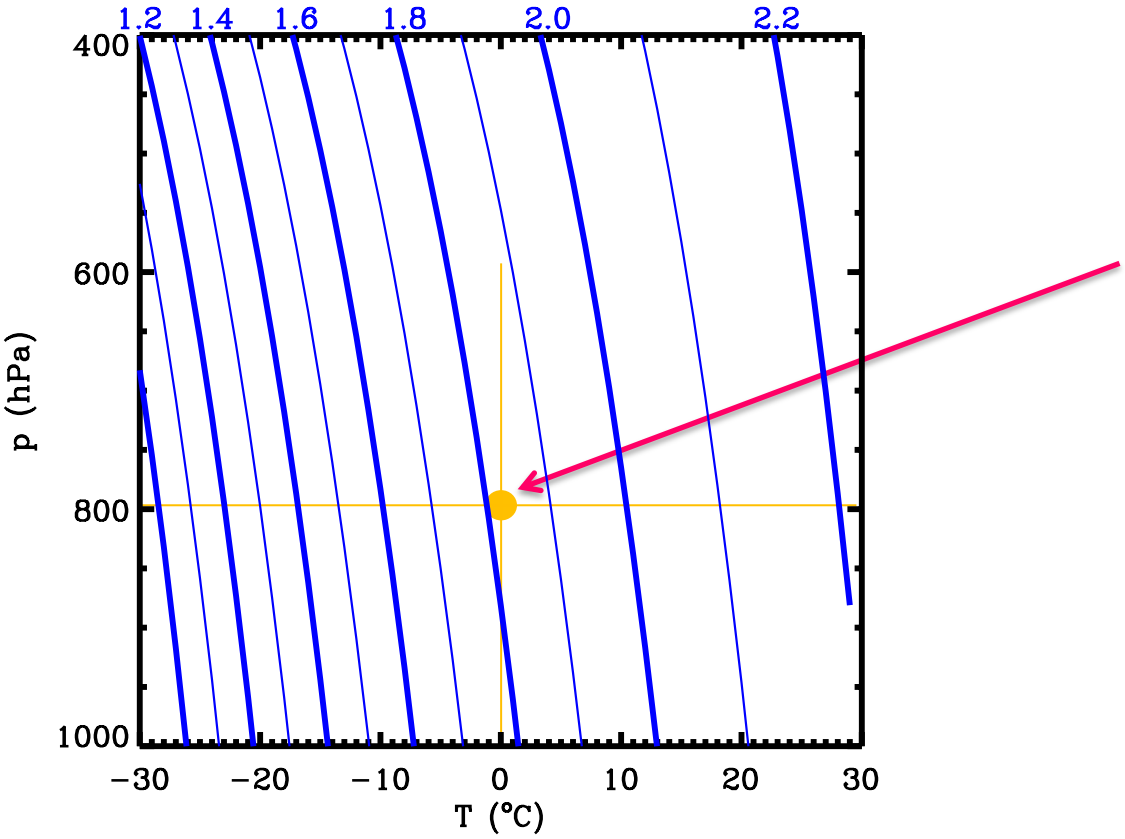
Smaller droplets grow faster. The droplet spectrum becomes narrower due to the condensational growth.



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

ξ is a function of temperature and pressure

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



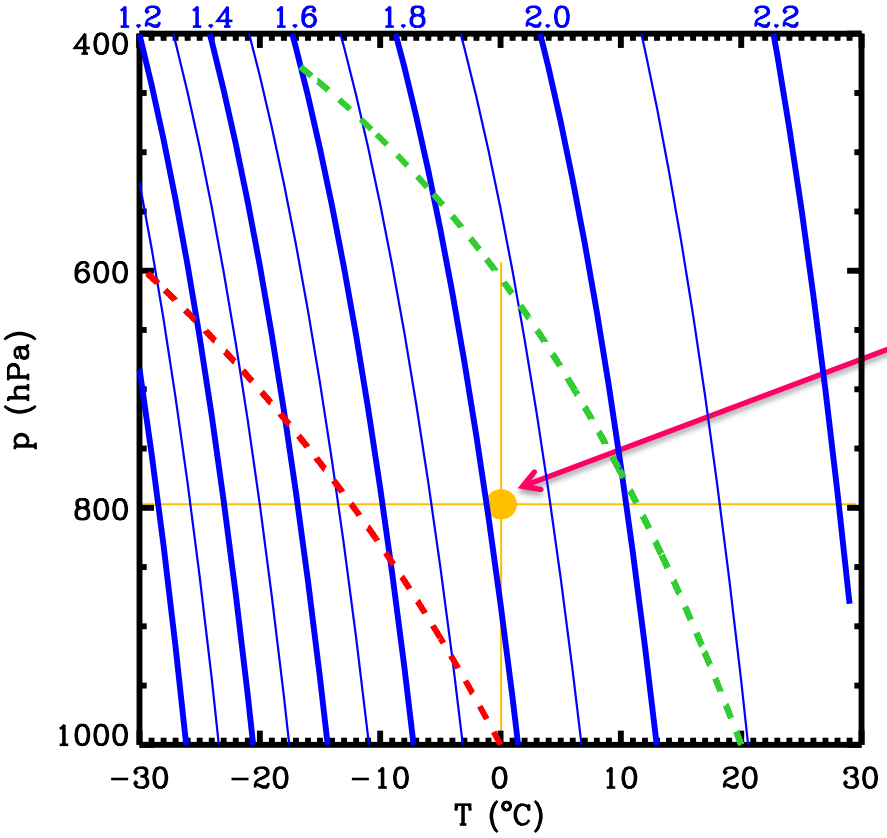
$$\xi = 10^{1.834} = 68.2\ \mu m^2 s^{-1}$$

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

ξ is a function of temperature and pressure

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

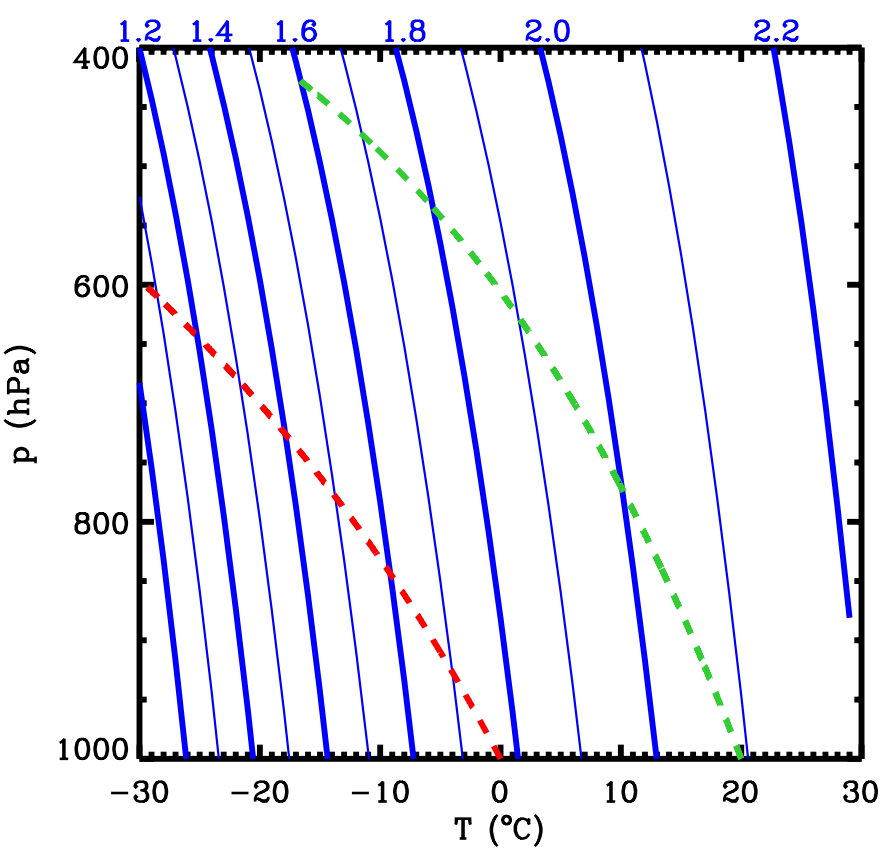
Dashed lines represent pseudoadiabats corresponding *T= 0 ℃ and 20 ℃*

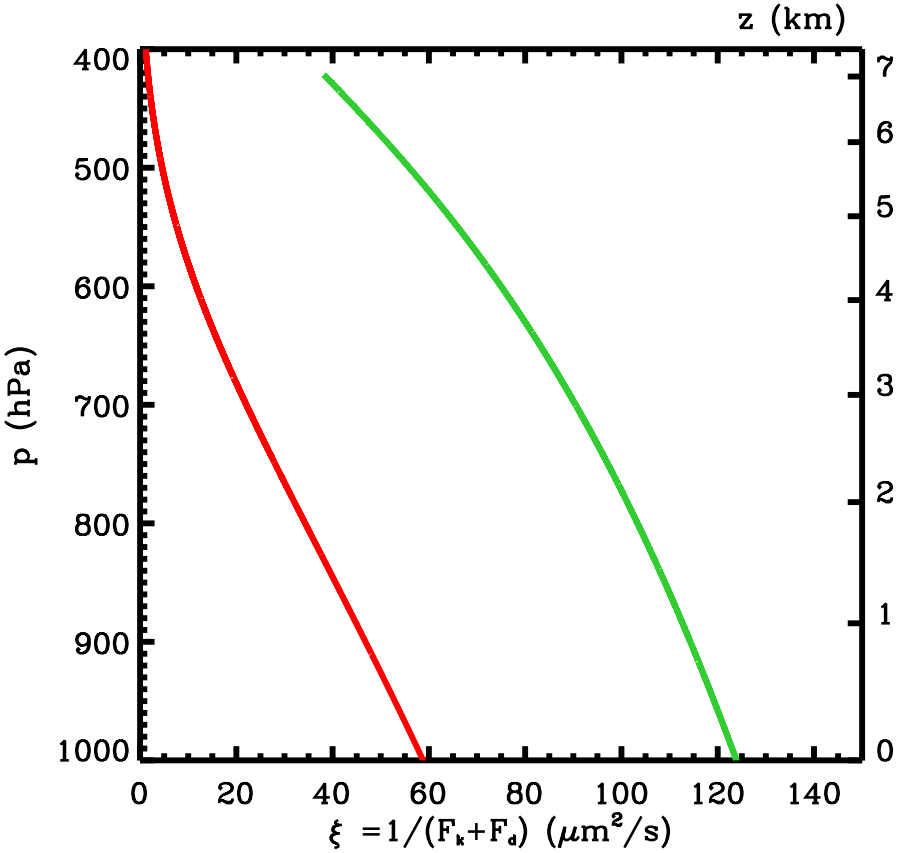


$p = 800\ hPa\,,\qquad T = 0℃$

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

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

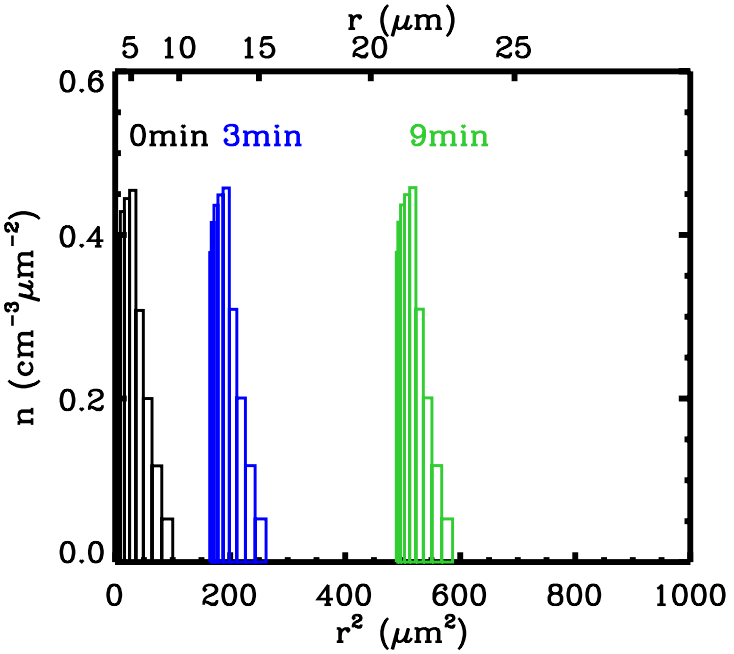




$$\frac{dr}{dt} = \xi \frac{S-1}{r}, \qquad \xi = \frac{1}{F_d + F_k}$$

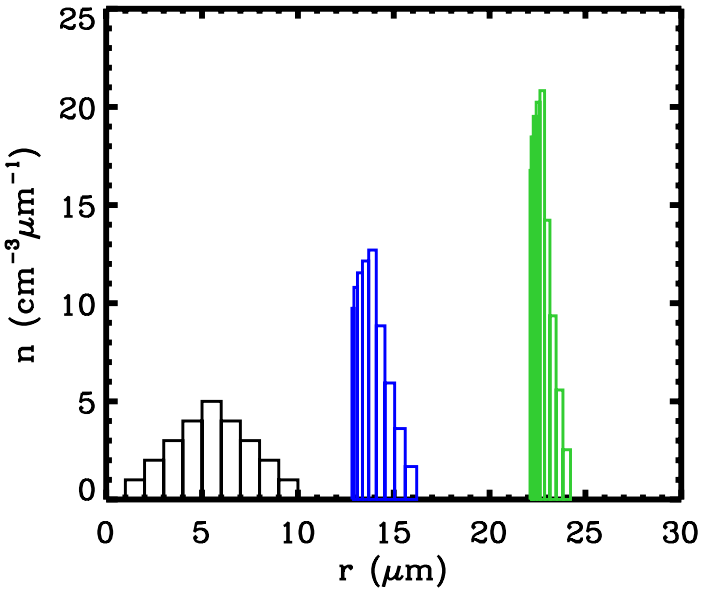
$$\rightarrow \quad \frac{dr^2}{dt} = 2\xi(S-1)$$

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

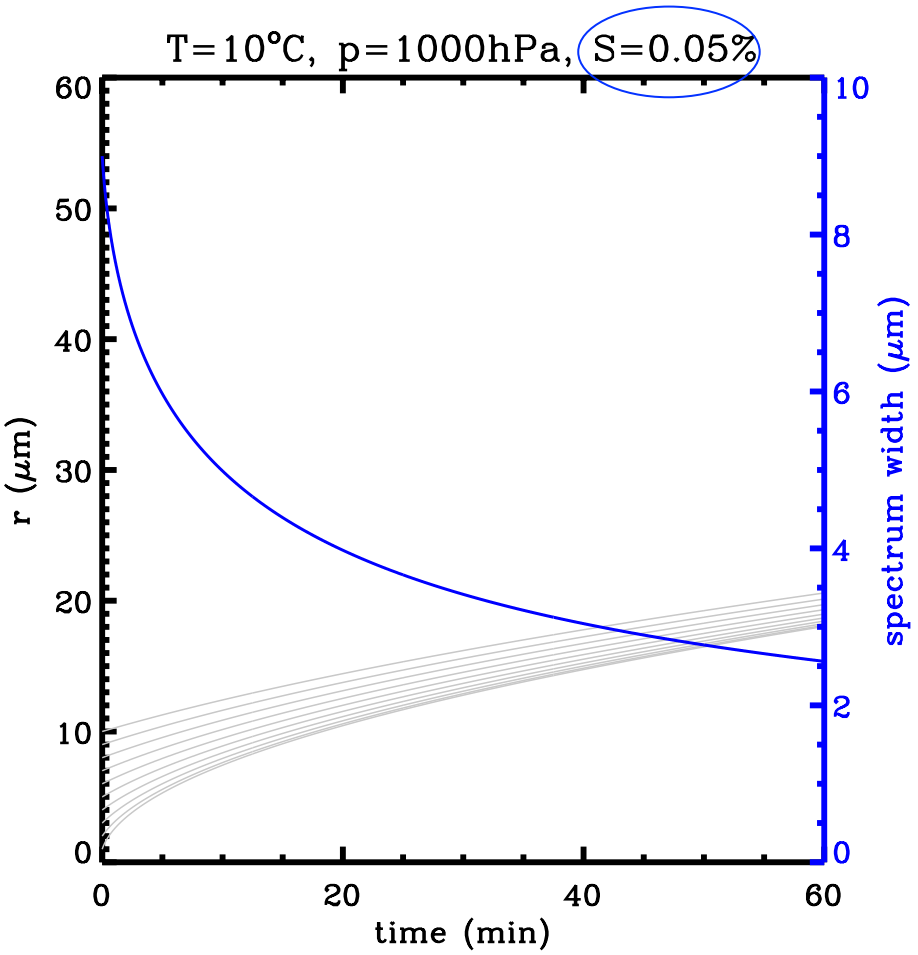


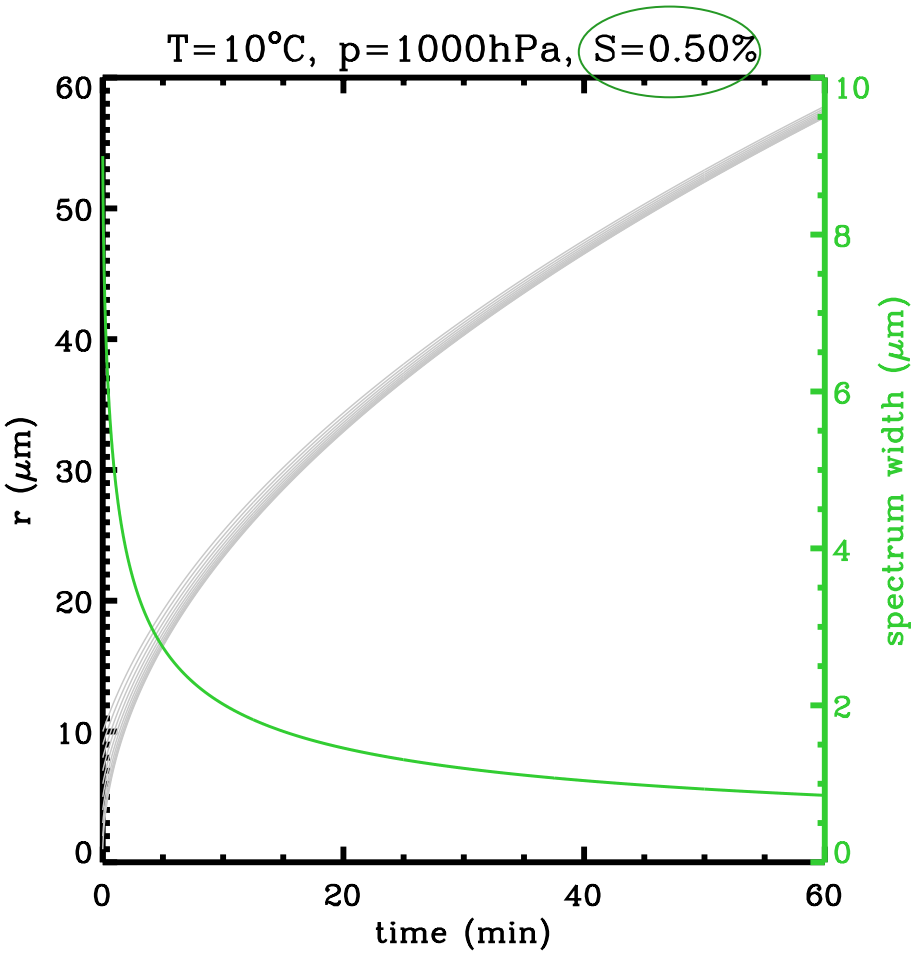
For the same supersaturation values smaller droplets grow faster (faster increase of their radius) than bigger droplets.

Condensational growth leads to a narrowing of the drop-size distribution.

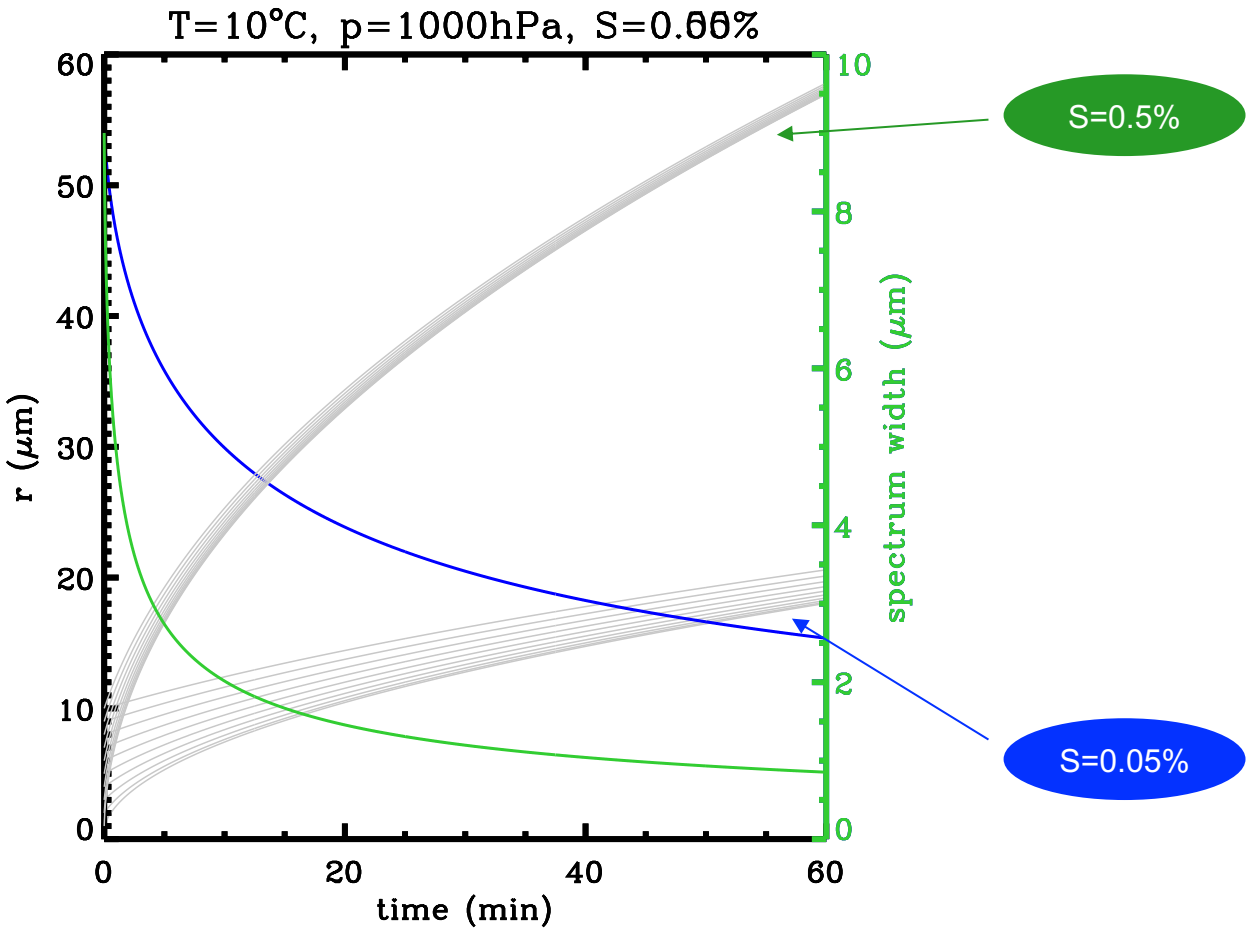


T=10°C, p=1000 hPa, S=0.5%





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 the growth (~20 min).


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