# Modeling of aerosol processes in the atmosphere

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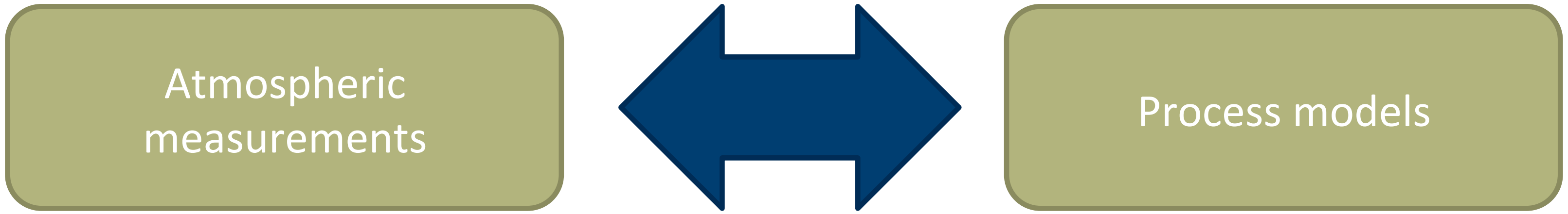
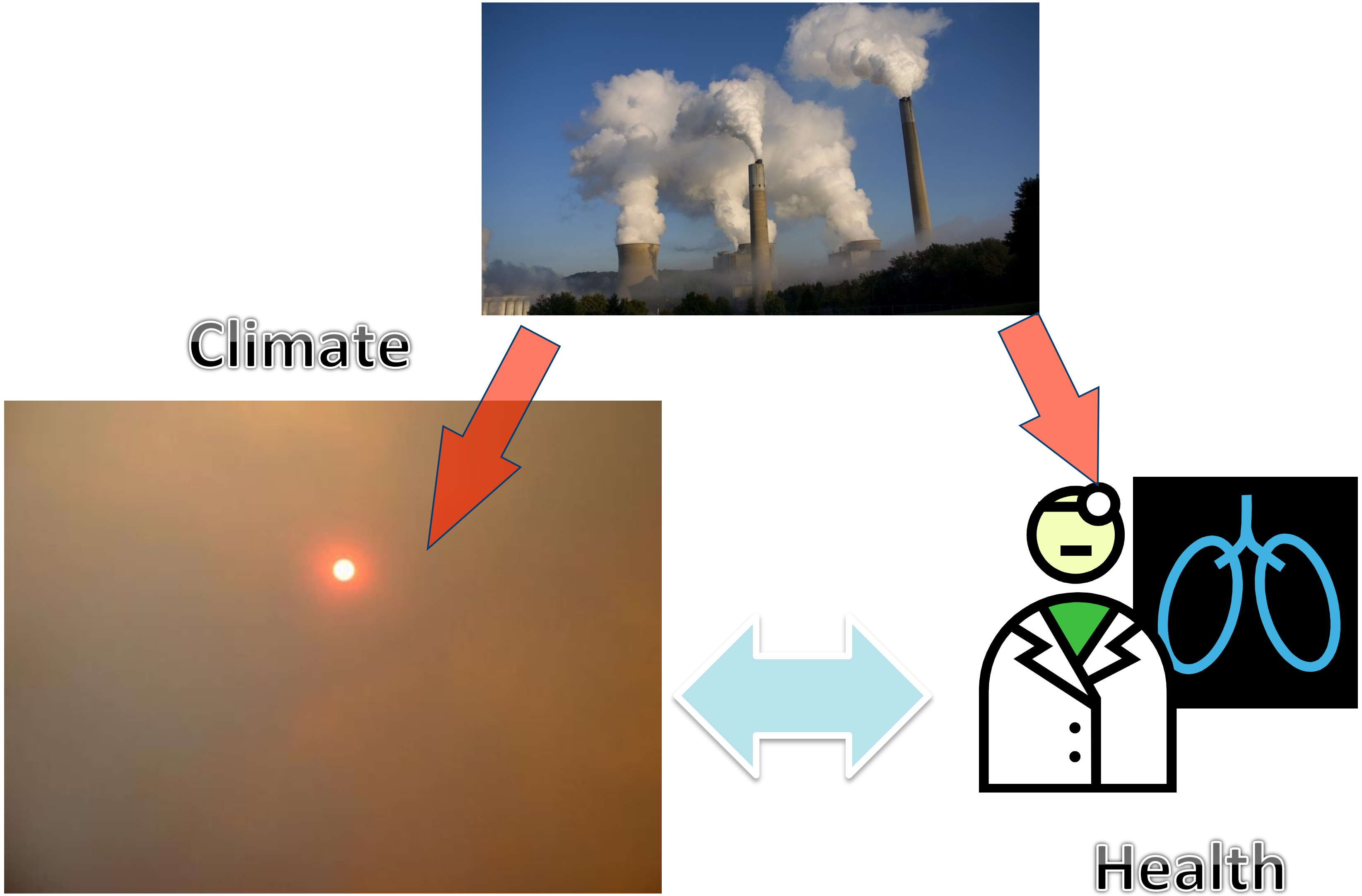
# Scope of lecture

- Provide a fundamental overview of processes affecting aerosols in the atmosphere under cloud-free conditions
- Familiarize with basic functions to be used in exercises
- Apply process understanding to atmospheric data collected during the GoAmazon campaign.



# Why interested in aerosols?



Climate

Health

# Aerosols and health

- Urban outdoor air pollution responsible for **1.3 million deaths annualy**
- Indoor air pollution responsible for **~2 million premature deaths** annualy (mainly in developing countries)

*WHO, 2011*

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# Aerosols and climate

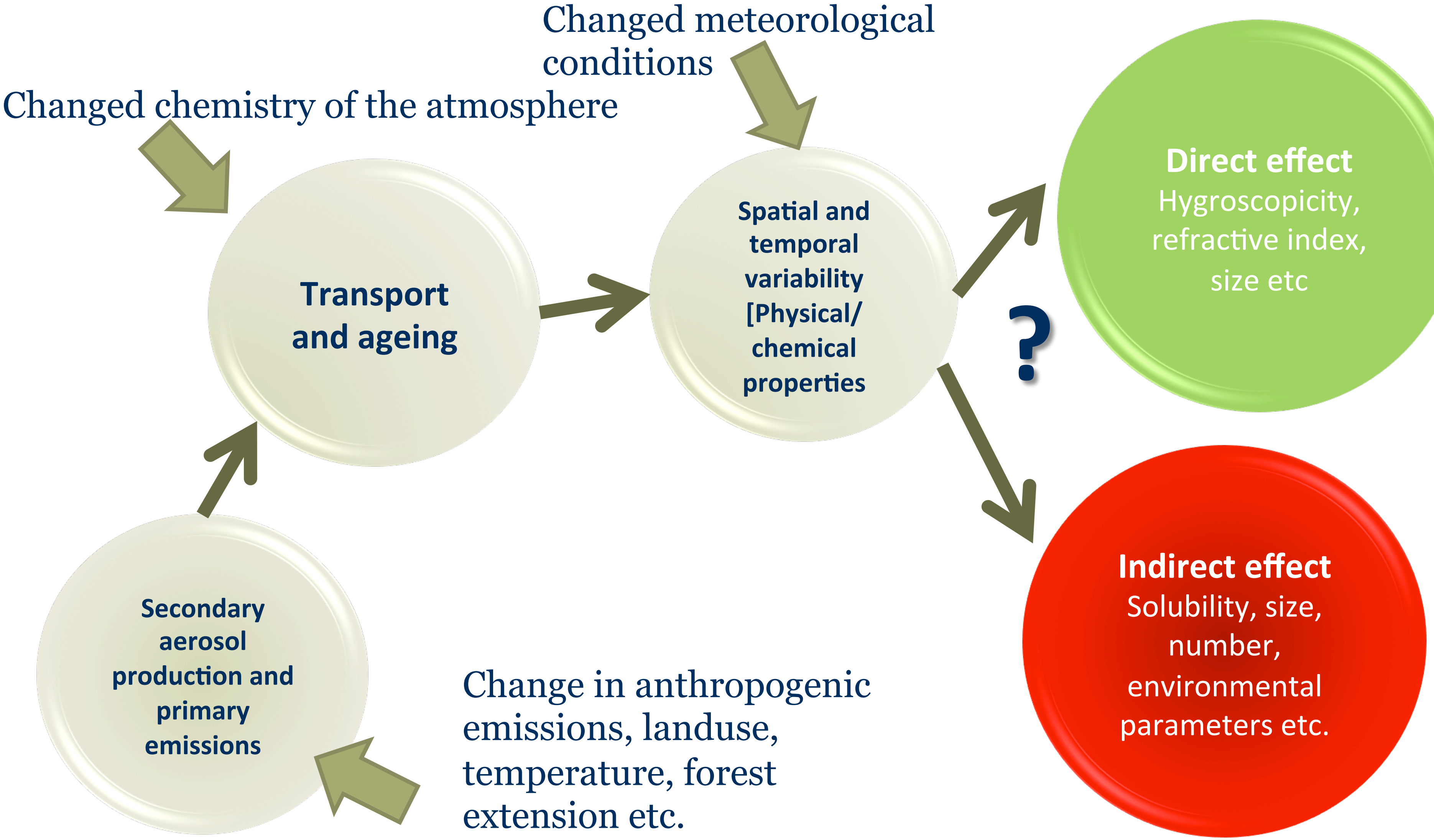
**" The RF of the total aerosol effect in the atmosphere, which includes cloud adjustments due to aerosols, is −0.9 [−1.9 to −0.1] W $m^{-2}$ (medium confidence), and results from a negative forcing from most aerosols and a positive contribution from black carbon absorption of solar radiation.**

**There is high confidence that aerosols and their interactions with clouds have offset a substantial portion of global mean forcing from well-mixed greenhouse gases.**

**They continue to contribute the largest uncertainty to the total RF estimate. "**

Apparently important….

# Aerosols and climate in a changing atmosphere: “need-to-knows”



Changed meteorological conditions

Changed chemistry of the atmosphere

**Transport and ageing**

**Spatial and temporal variability [Physical/ chemical properties**

**Direct effect**
Hygroscopicity, refractive index, size etc

?

**Indirect effect**
Solubility, size, number, environmental parameters etc.

**Secondary aerosol production and primary emissions**

Change in anthropogenic emissions, landuse, temperature, forest extension etc.

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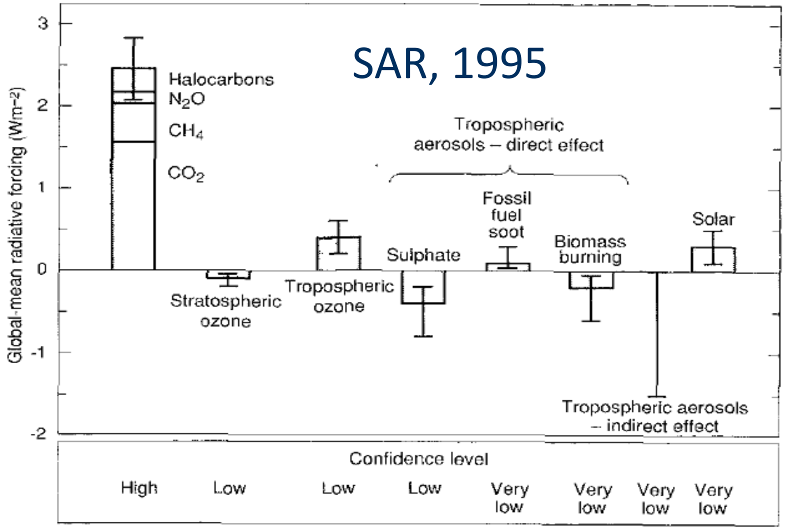
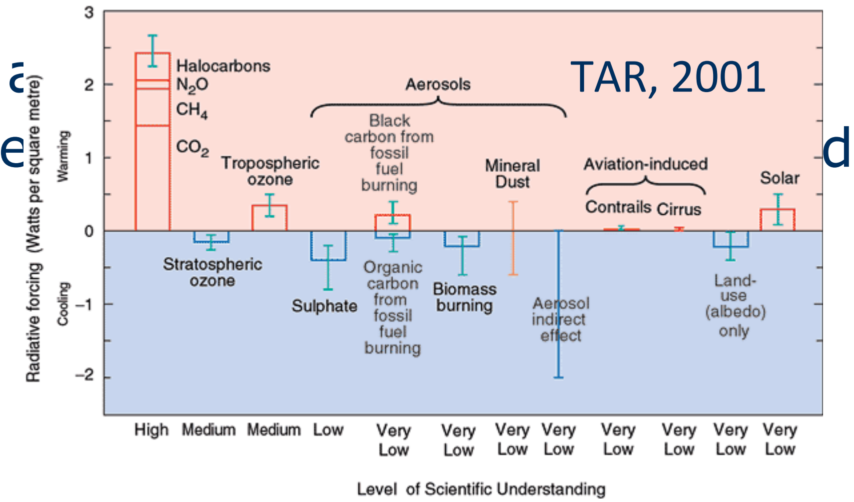
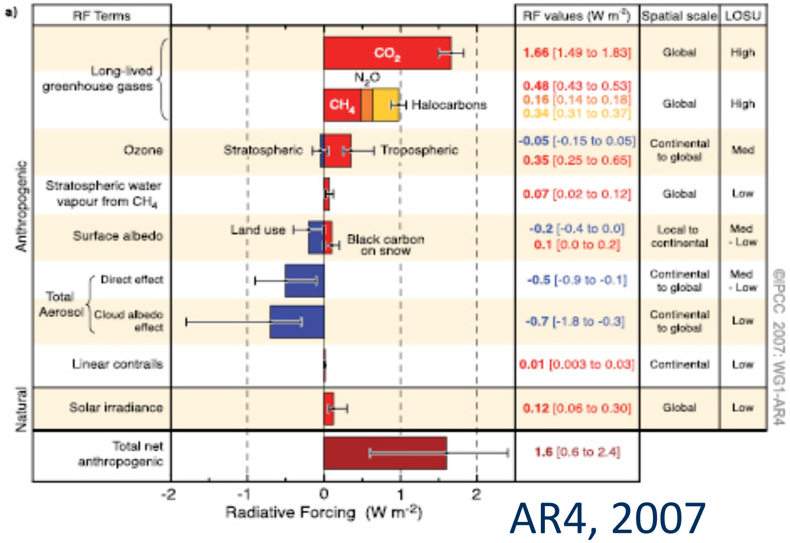
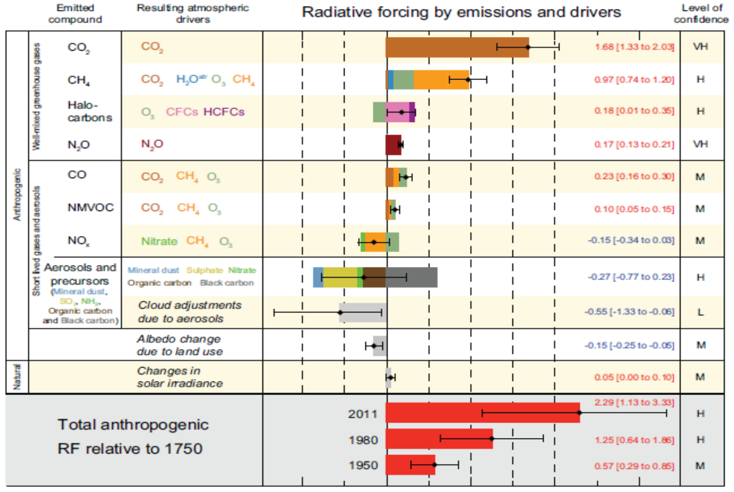
# Constraining the aerosol effects







AR4, 2007



AR5, 2013

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# Why so difficult to get the indirect effect right?

- Aerosol-cloud-interactions are inherently difficult to describe – both qualitatively and quantitatively
- Even though progress has been made, further progress is hindered by limited model resolution and observation capabilities (e.g. Rosenfeld et al., 2014)
- This substantially hampers our ability to assess the role of these interaction in the climate system

# Why important to describe aerosol dynamics?

The aerosol is continously changed via a number of dynamical (both physical and chemical) processes, altering the properties of the size distribution

Knowledge of these processes is necessary in order to accurately assess both **smaller scale interactions** (e.g. aerosol cloud interactions) as well as **large scale transport and processing**

**Thus, aerosol processes are relevant on both micro and synoptic scale**

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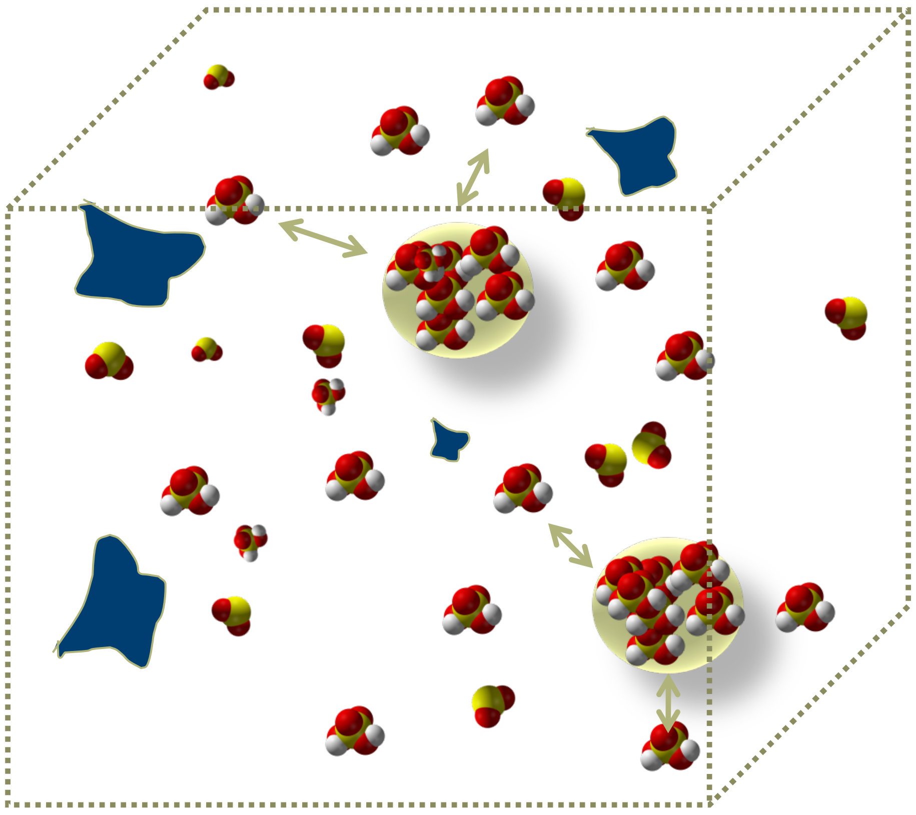
# Definition of aerosol



**Aerosol**
**(particles+gases)**

**Solid particles or liquid droplets suspended in gasphase**

**$H_2SO_{4(l)} \leftrightarrow H_2SO_{4(g)}$, $SO_2$, sot, (air)**

# Aerosol definition, cont.

A solid or liquid particle suspenden in a gas phase

The aerosol in the atmosphere is polydisperse and appear over a size range from a few nm up to 100µm

Always observed in the atmosphere; from a few 10’s of particles in clean environments up to $10^6$ in polluted enviornments

Mass varies between few tenths of µg * $m^{-3}$ up to mg*$m^{-3}$ under extreme conditions

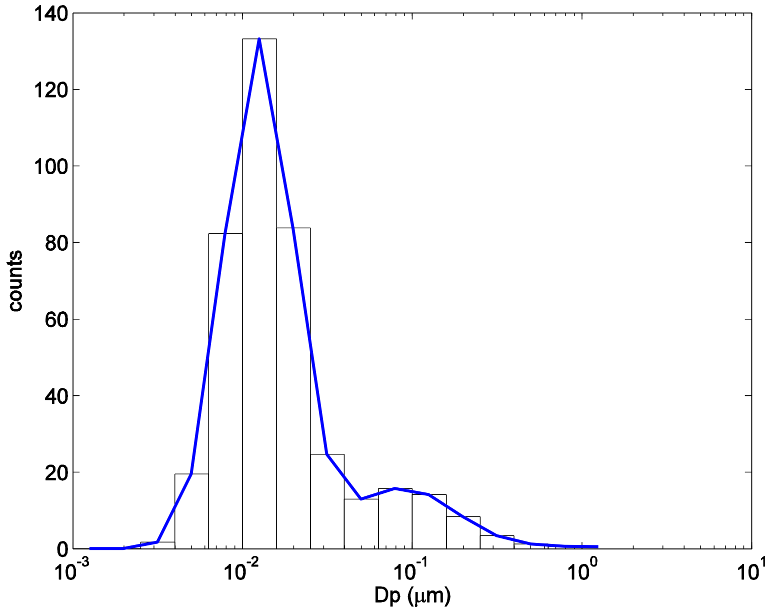
Typical tropospheric liftimes: days-weeks

# Observing the aerosol

**Mass, number, optical properties, chemical composition**

**Either as bulk or size distributed**

540 $cm^{-3}$ or…



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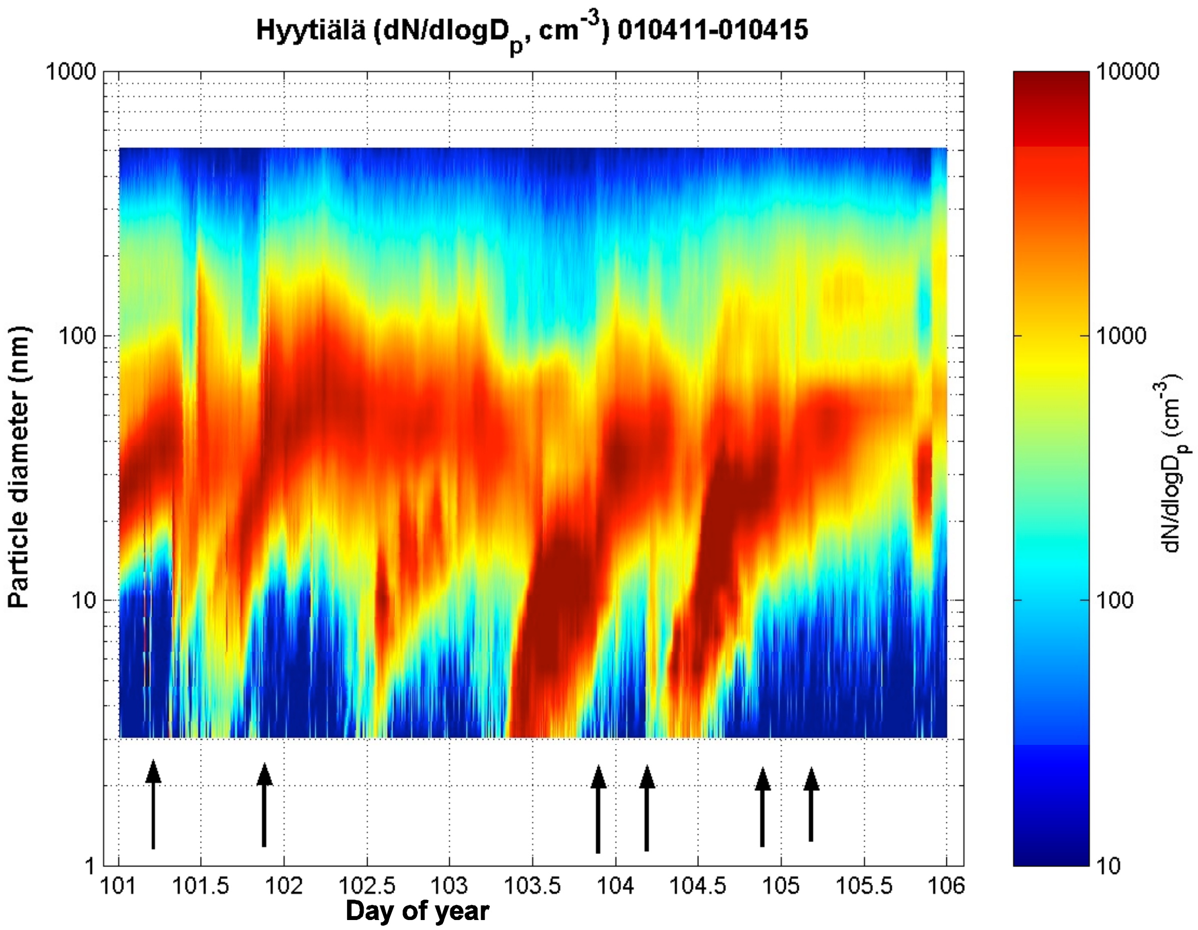
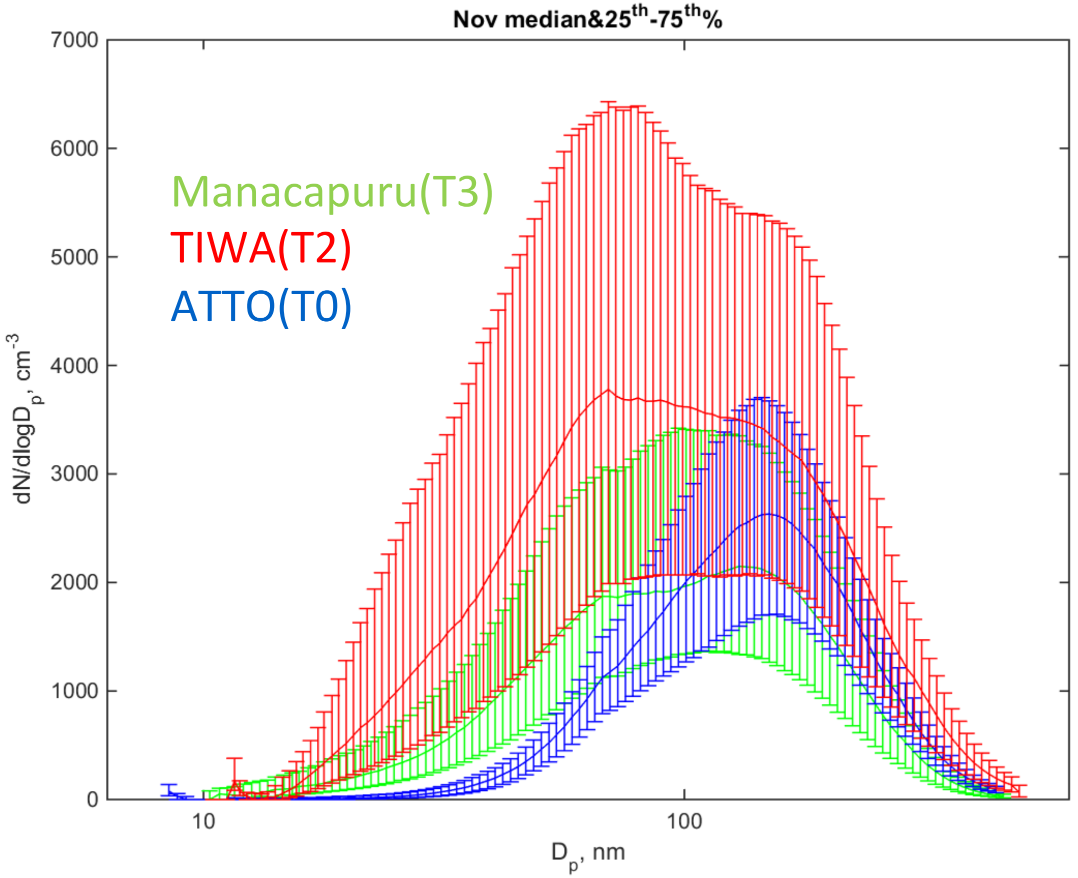
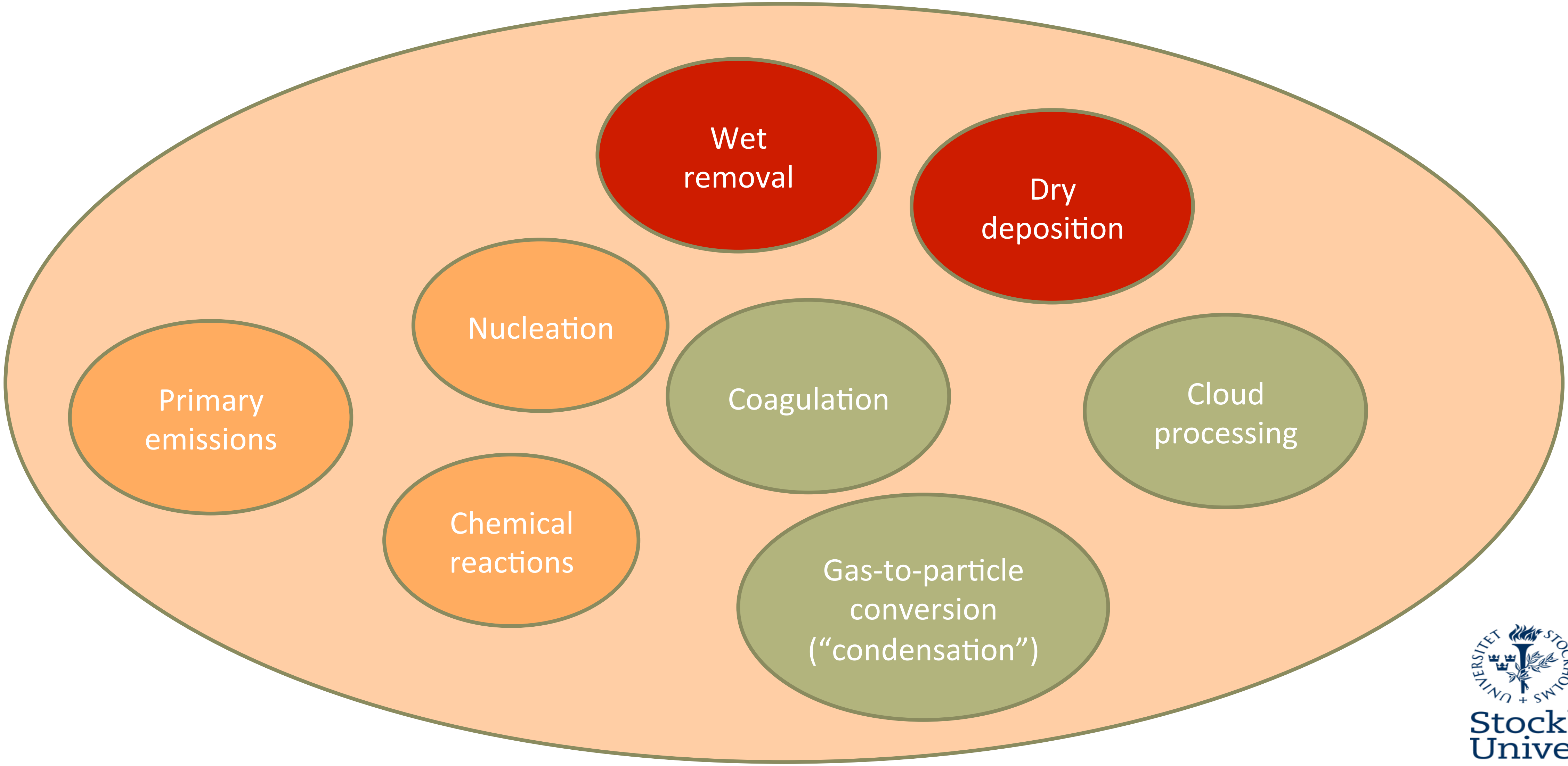
# The aerosol is highly variable in space and time





# Modeling the atmospheric aerosols



Wet removal

Dry deposition

Nucleation

Primary emissions

Coagulation

Cloud processing

Chemical reactions

Gas-to-particle conversion (“condensation”)

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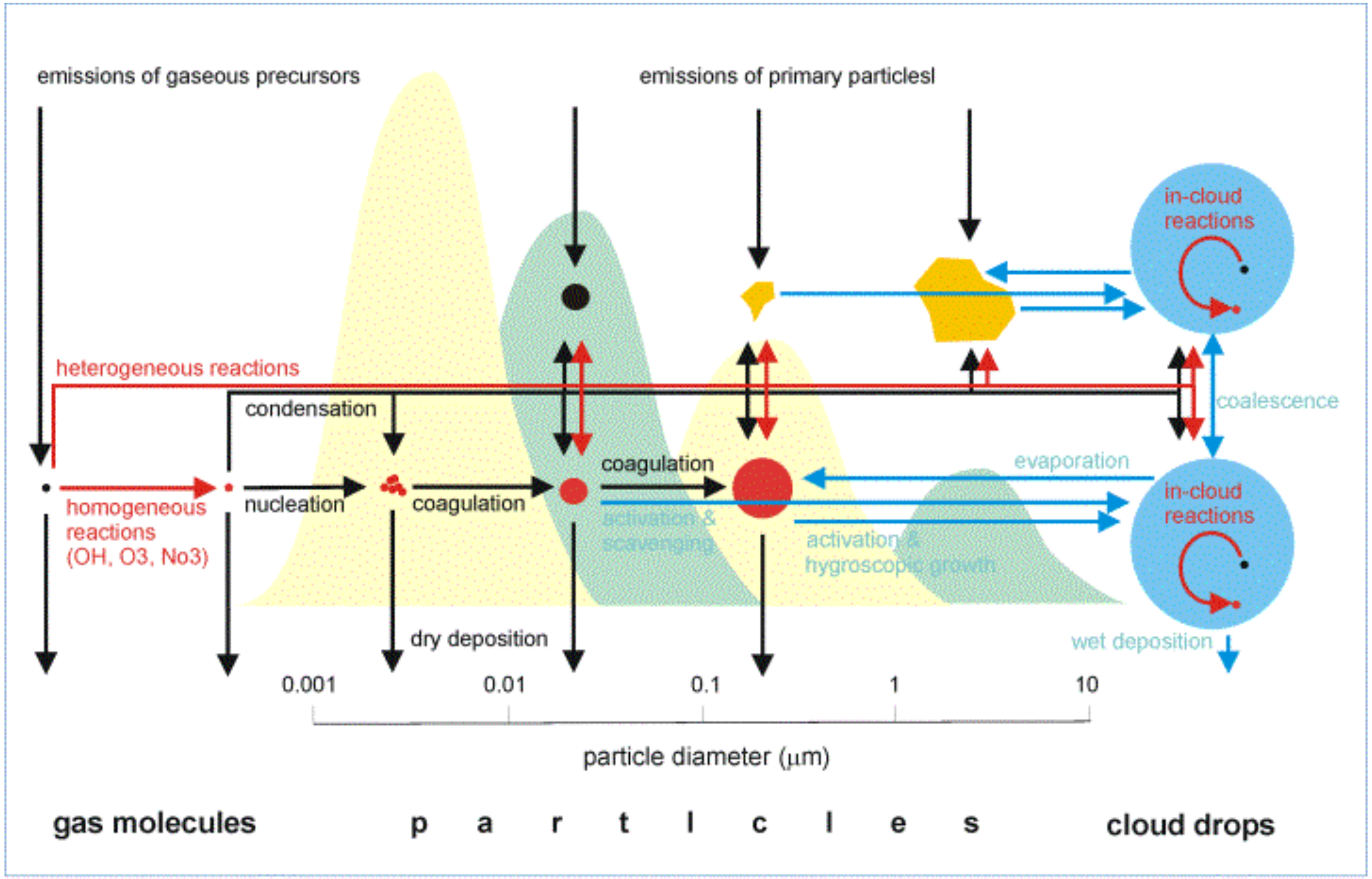
# Aerosol processes



*Raes et al., Atm. Env., 2000*

# Sources of atmospheric aerosols

# Sources of secondary and primary aerosols

## Inorganic

$SO_2$ (DMS,COS, $CS_2$)→$H_2SO_4$

$NO_x$, $NH_3$ → $HNO_3$, $NH_4NO_3$

## Organic

Biogenic VOC (BVOC’s; eg Monoterpenes)

Anthropogenic VOC’s (generally high Mw)

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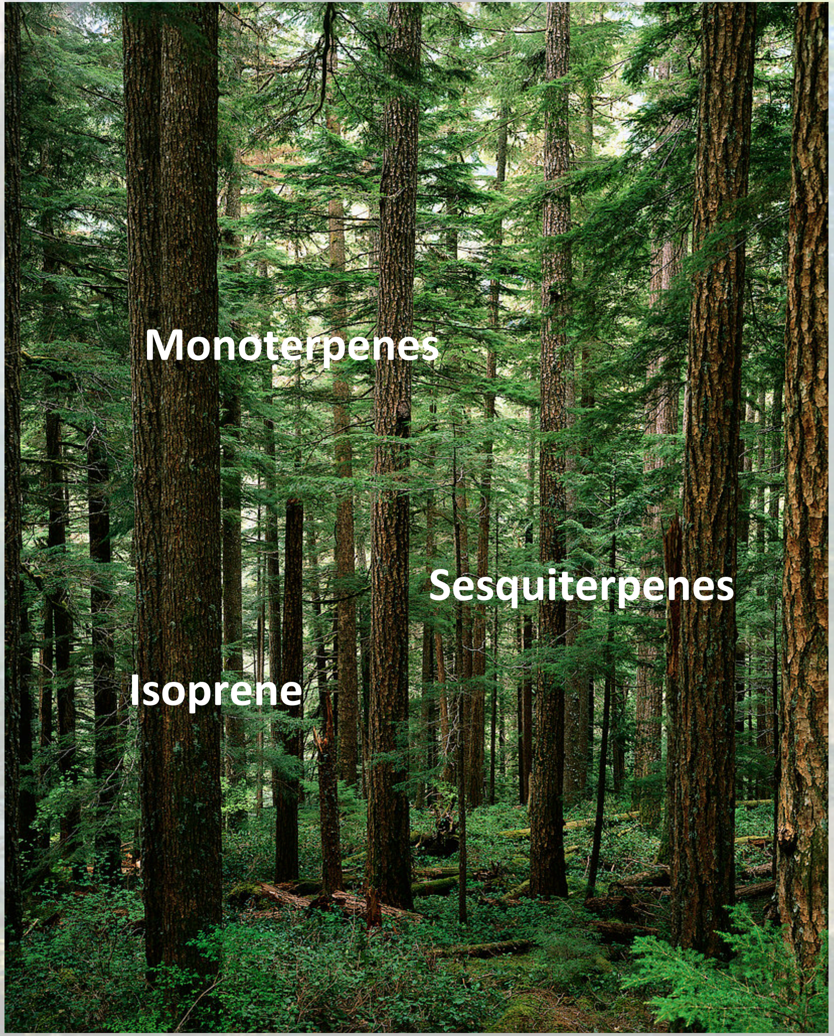
# Terpenoids: globally a very important source of secondary aerosols



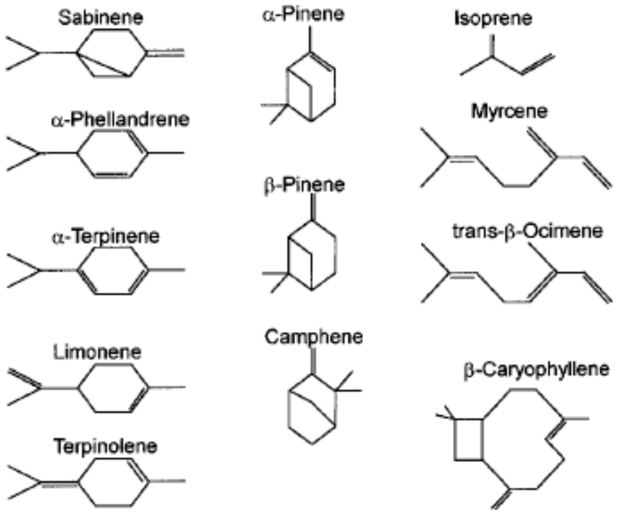
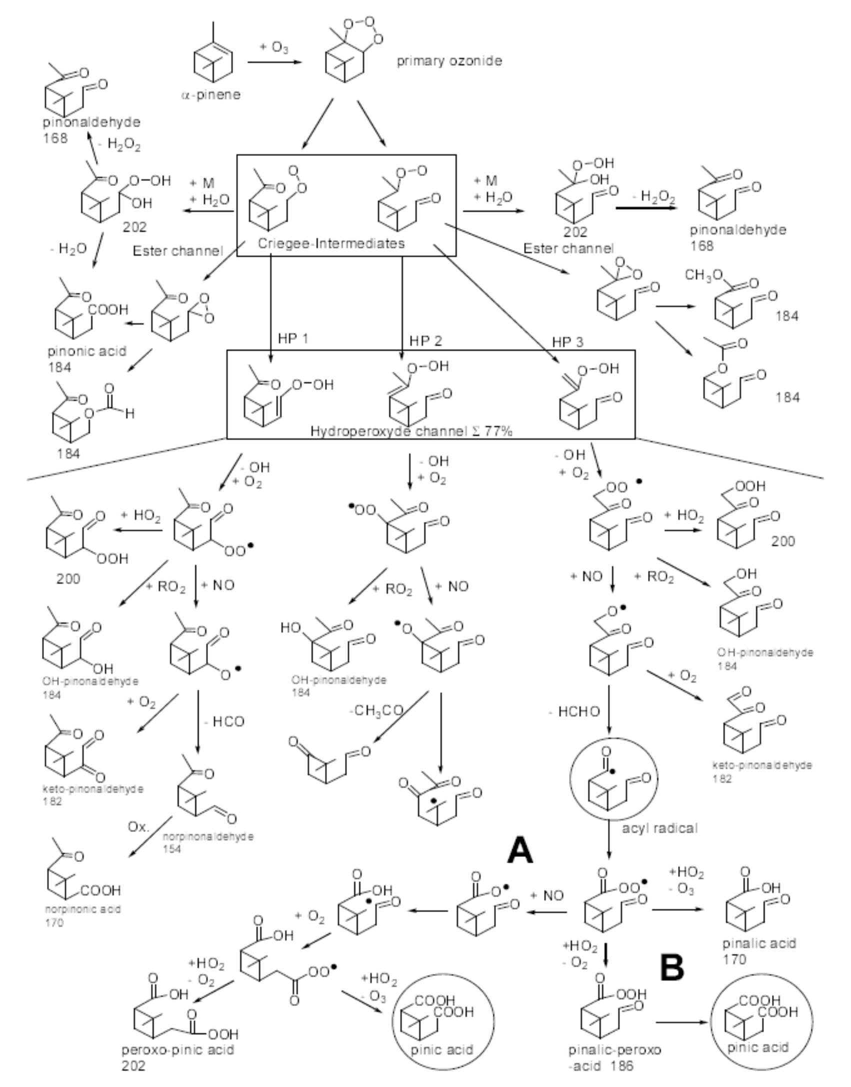


*Figure 1.* Molecular structures of the volatile hydrocarbons isoprene ($C_5$), some monoterpenes ($C_{10}$) and the semivolatile sesquiterpene *β*-Caryophyllene ($C_{15}$).

*Kesselmeier and Staudt, 1999.*

# Terpene chemistry: α-pinene



*Kanakidou et al., 2005*

**Very complex chemistry!**

**Most well studied for α-pinene and β-pinene**

**For most compounds, secondary oxidation steps are largely unknow**

**α-pinene most commonly abundant monoterpene**

**The ozone reaction believed to dominate SOA production**

# Sinks

**Dry deposition**

Transport through air to a surface: Turbulent transport, transport over the laminar surface layer, surface properties

**Wet deposition**

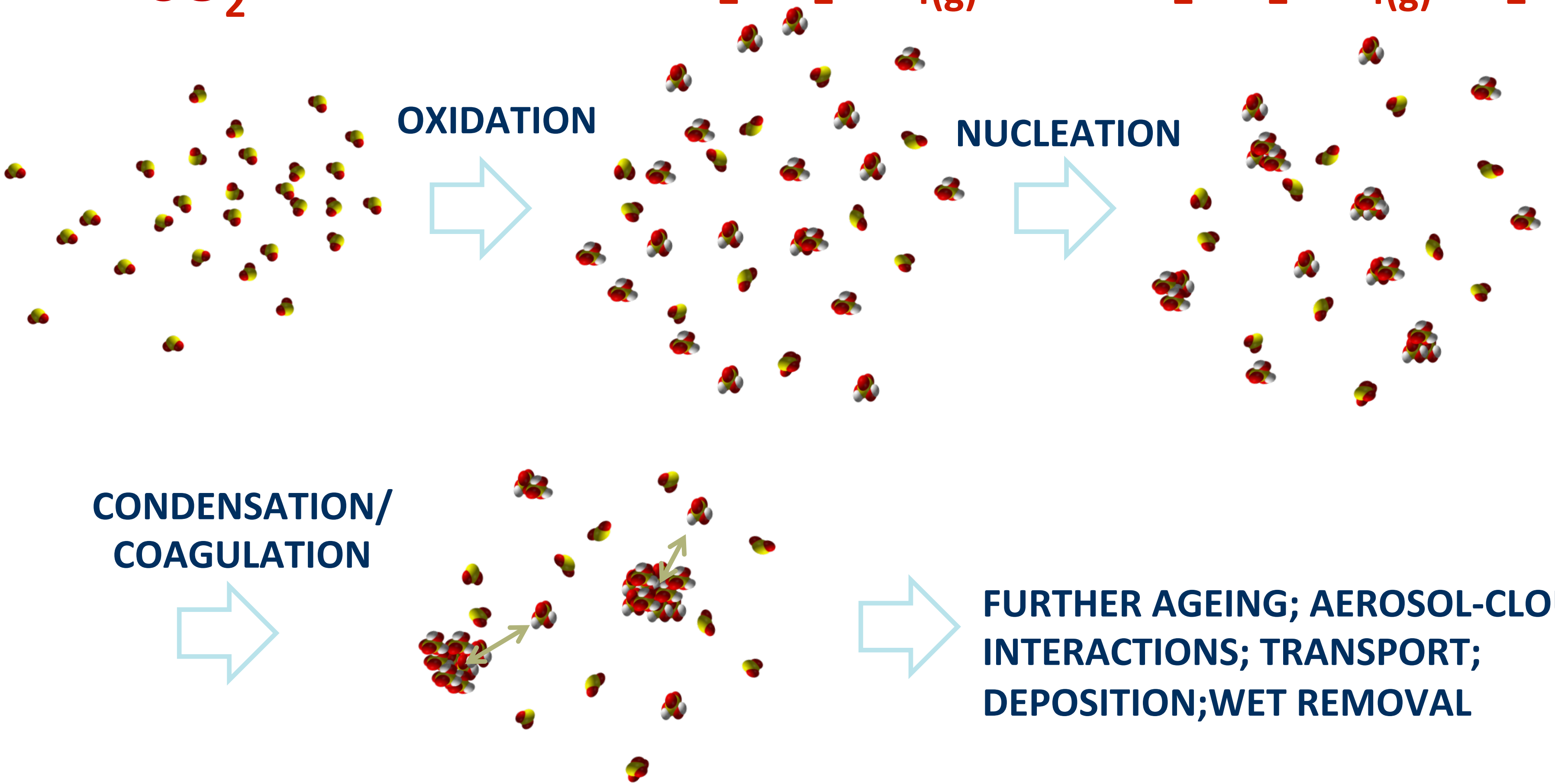
Up-take in cloud droplets (”in-cloud scavenging”), up-take in falling rain droplets (”below-cloud scavenging”)

**Chemical reactions in the atmosphere**

Reactions of different compounds with OH, ozone och $NO_3$

$C_2H_6 \rightarrow CO_2+H_2O$

# Aerosol dynamics



$SO_2$

OXIDATION

$SO_2 + H_2SO_{4(g)}$

NUCLEATION

$SO_2 + H_2SO_{4(g)} + H_2SO_{4(l)}$

CONDENSATION/
COAGULATION

FURTHER AGEING; AEROSOL-CLOUD INTERACTIONS; TRANSPORT; DEPOSITION;WET REMOVAL

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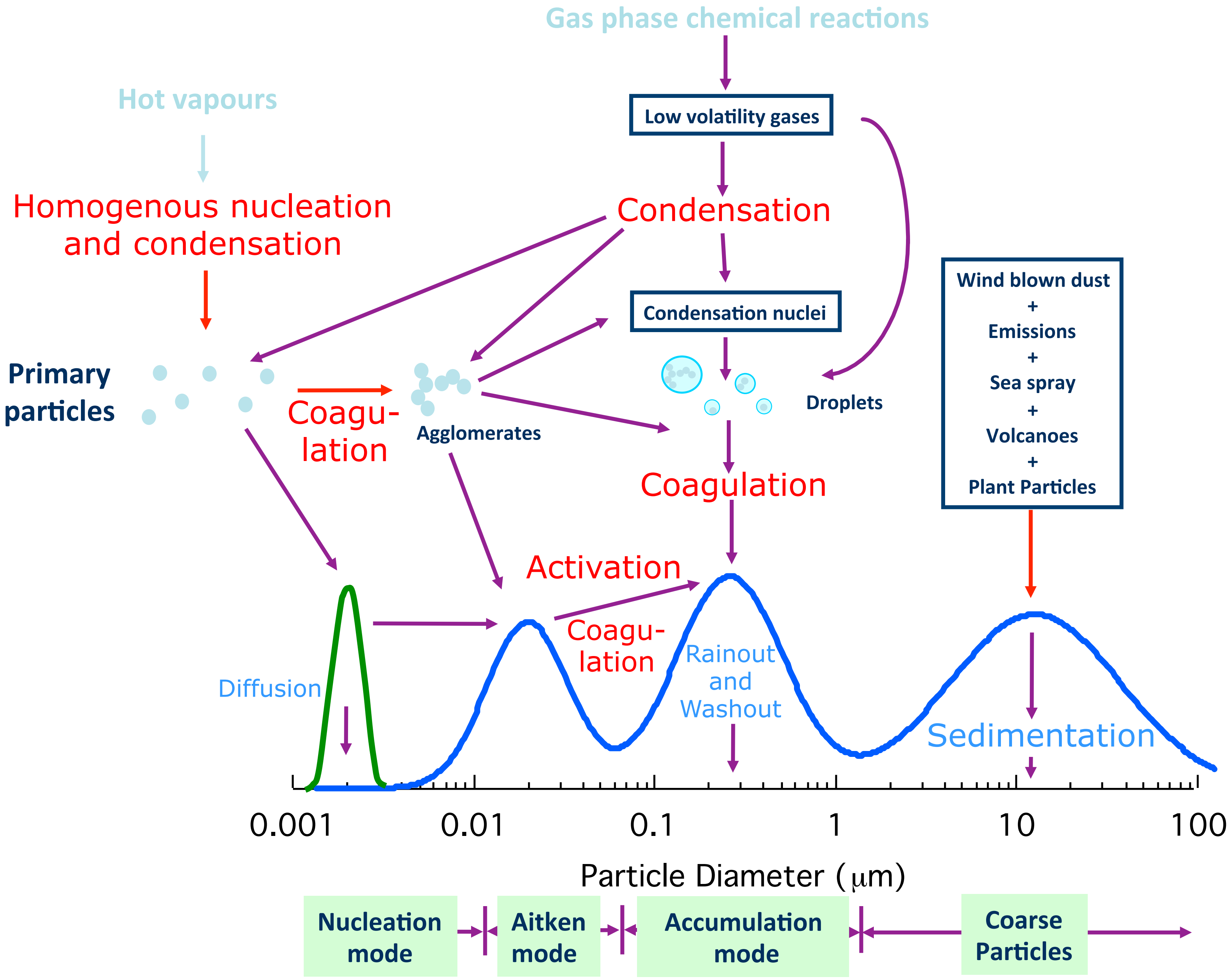

Gas phase chemical reactions

Low volatility gases

Condensation

Condensation nuclei

Droplets

Coagulation

Hot vapours

Homogenous nucleation and condensation

Primary particles

Coagulation

Agglomerates

Wind blown dust
+
Emissions
+
Sea spray
+
Volcanoes
+
Plant Particles

Activation

Coagulation

Diffusion

Rainout and Washout

Sedimentation

Nucleation mode

Aitken mode

Accumulation mode

Coarse Particles

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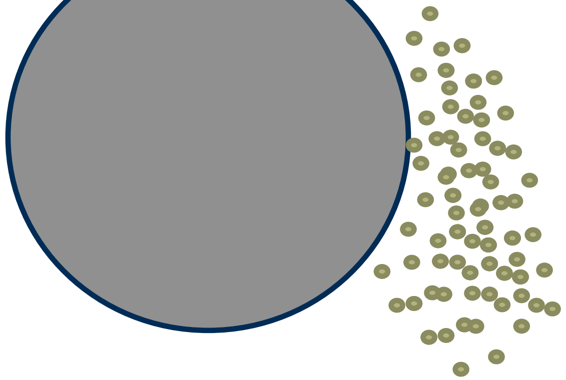
# Basic processes acting on single aerosol particles

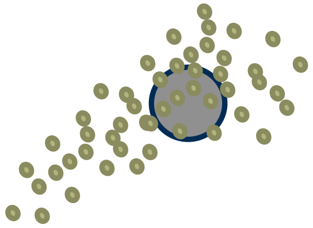
- Gravitational settling
- Drag force
- Brownian motion

# Single particle dynamics and Knudsen number



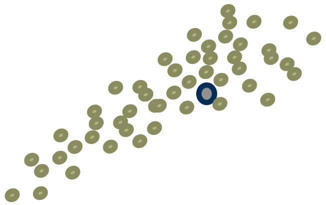
Continuum regime

$$Kn \to 0$$



transition regime

$$Kn \approx 1$$



Free molecular regime

$$Kn \to \infty$$

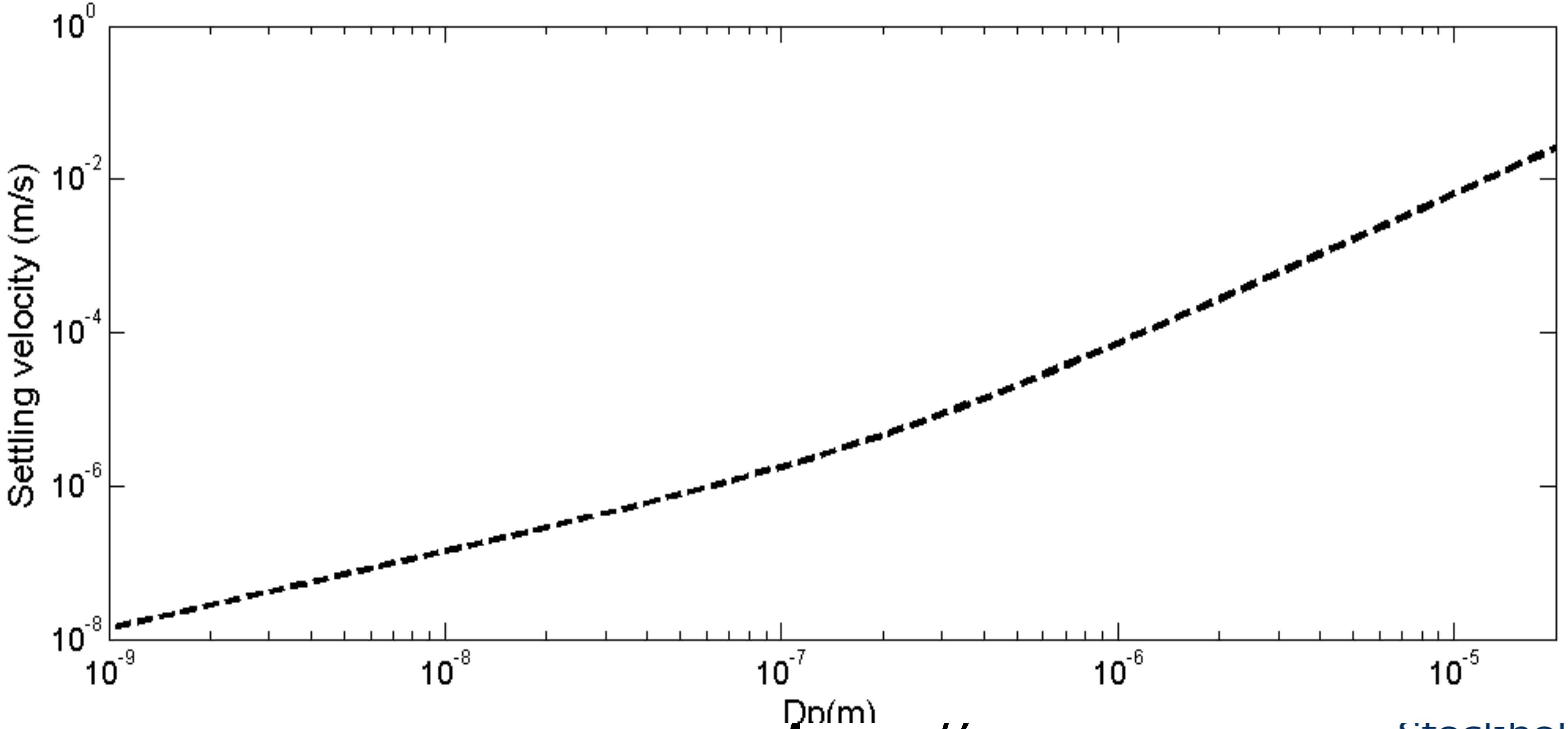
$$Kn = \frac{2\lambda}{D_p}$$

*Knudsen number*

*Where $\lambda$ is mean free path of air (66nm@293K) and Dp is diameter of particle*

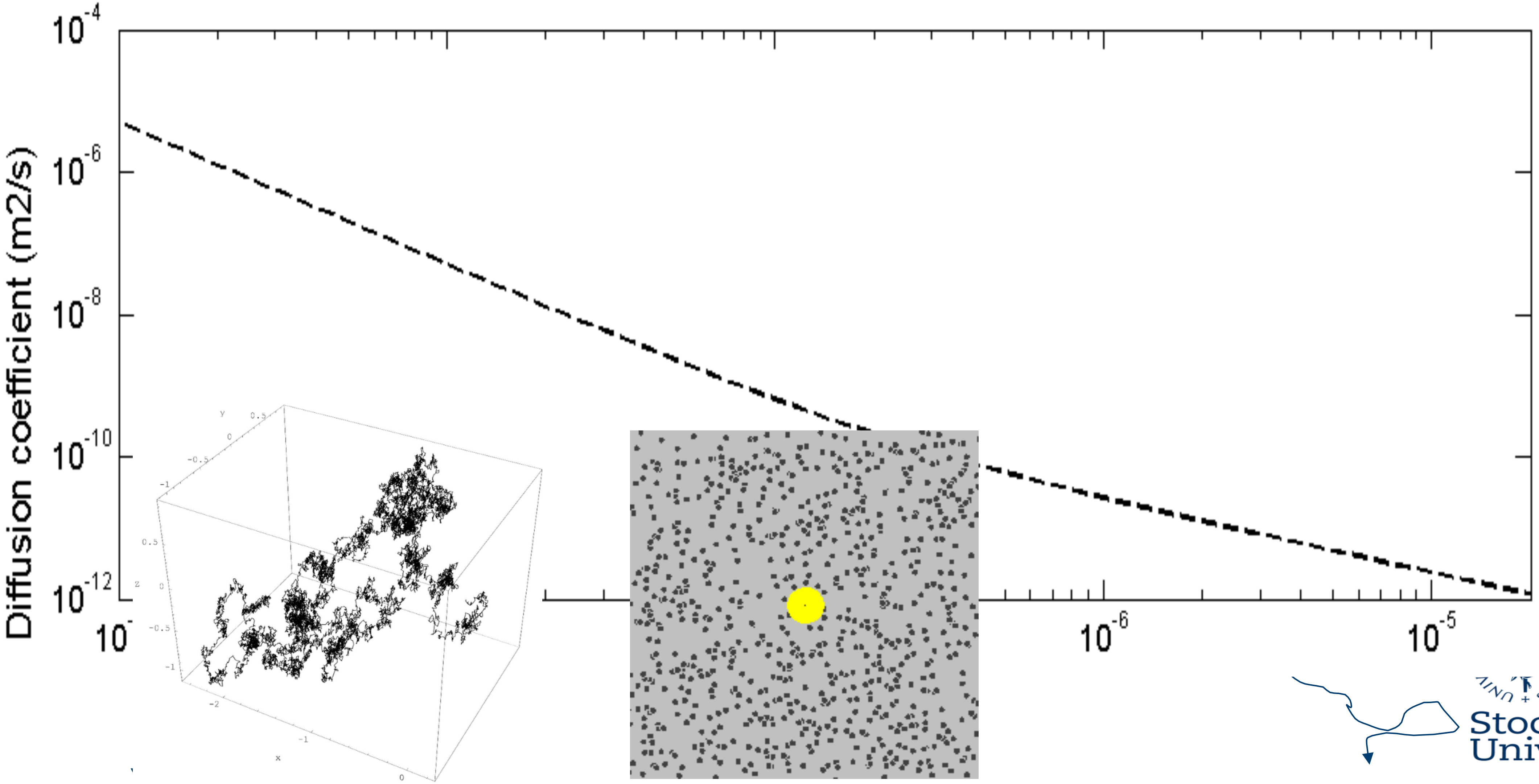
# Gravitational settling

$$F_{drag} = F_{grav}$$

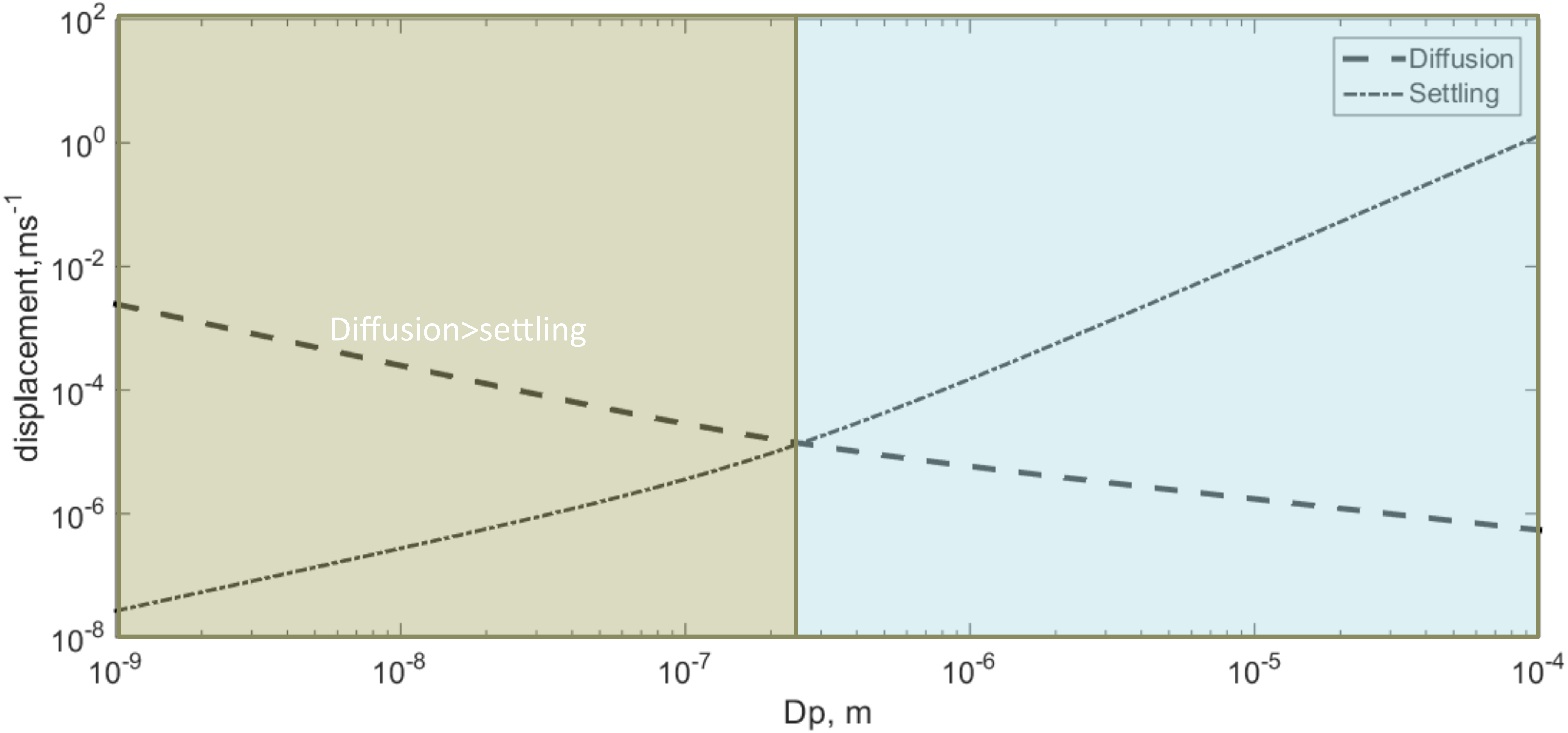


$\rho$

# Brownian diffusion



# Estimating displacement as function of size; Brownian diffusion vs gravitational settling



# Dry depsoition

**$F=-v_d*C$**

**where:**

F=flux to surface $m^{-2}s^{-1}$

$v_d$=deposition velocity (m/s)

C=concentration of particles

$$F = -V_d C$$

$$F = -{}^{m}\!/_{s} * {}^{\#}\!/_{cm^3} \Longrightarrow {}^{\#}\!/_{m^2 s}$$

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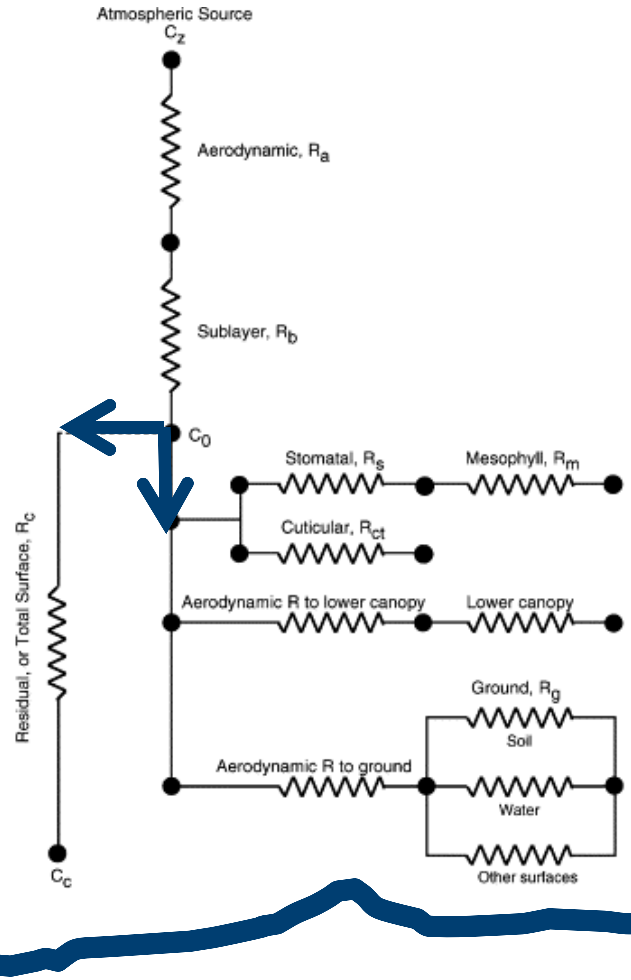
# Dry Deposition

**Only removal path in the dry atmosphere**

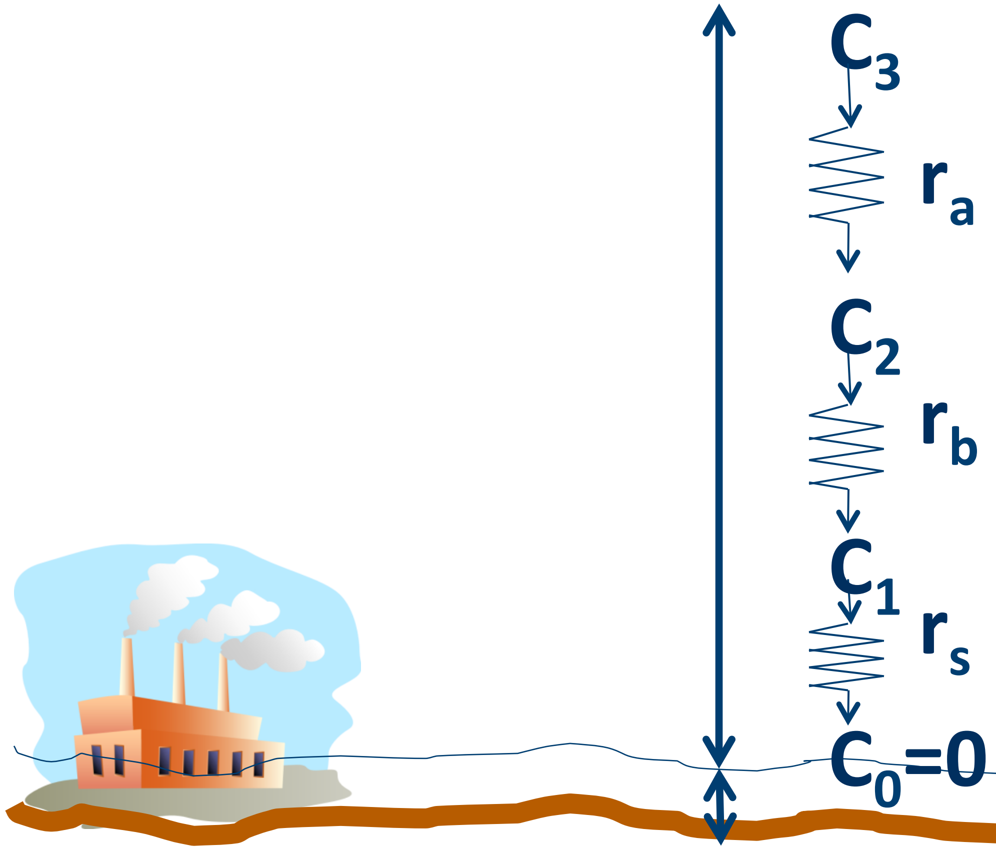
**Depends on:**

- Atmospheric turbulence
- Phase of species (gas or particle)
- Physio-chemical properties of depositing species
  - Particles: size, density
  - Gases: water solubility, reactivity
- Surface properties (Reactive? Sticky? Irregular?(eg vegetation)

# Resistance analogy cont’d



# Resistance analogy



**Aerodynamic resistance; surface layer: ~f(temperature; windspeed; surface roughness)**

**Laminar resistance; laminar surface layer: ~f(molecular or brownian diffusivity)**

**Surface resistance; surface properties: ~f(reactivitiy, solubility, pH etc.)**

$$v_d = \frac{1}{r_t} = \frac{1}{r_a + r_b + r_s}$$

# Dry deposition velocity

$$v_d = \frac{1}{r_t} + v_s = \frac{1}{r_a + r_b + r_a r_b v_s} + v_s$$

SEDIMENTATION VELOCITY

$$V_s = \frac{C_c m_p g}{3\pi\mu D_p}$$

Sedimentation

AERODYNAMIC RESISTANCE

$$r_a = U \big/ u^{*2}$$

QUASI-LAMINAR RESISTANCE

$$r_b = \frac{1}{u^{*}\left(Sc^{-2/3} + 10^{-3/St}\right)}$$

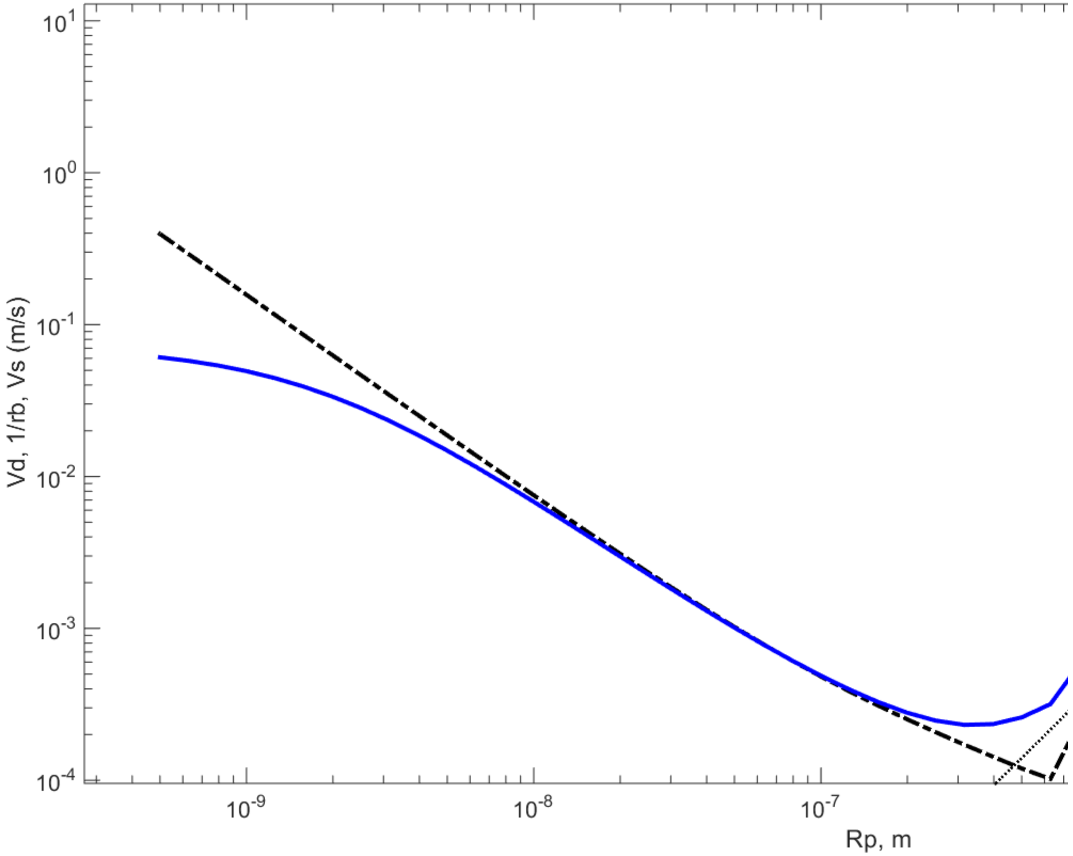
Turbulent transport

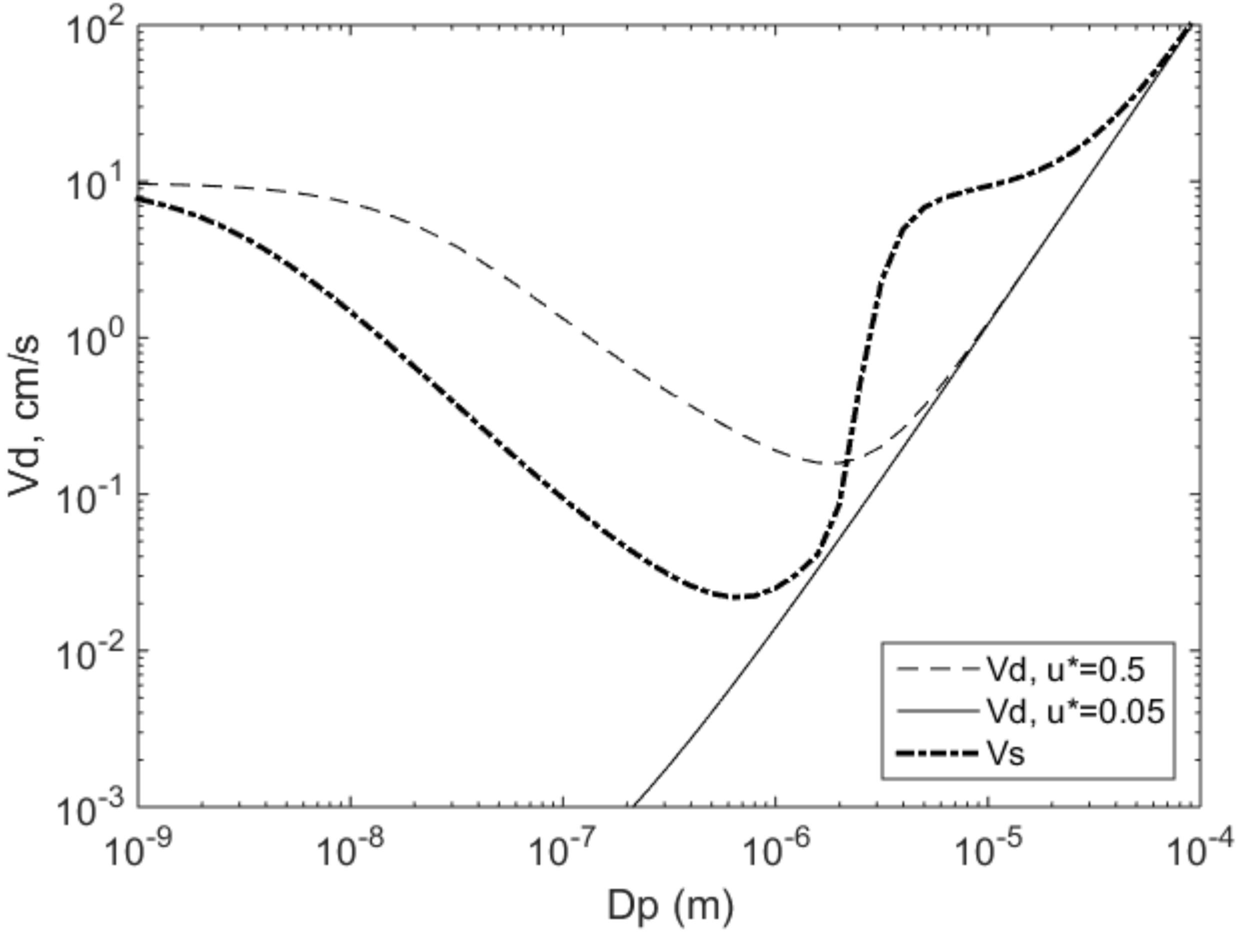
Diffusion

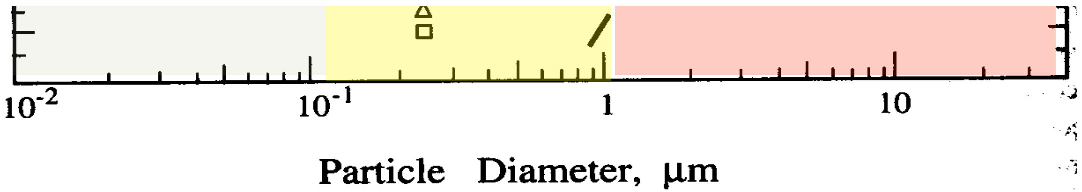
Impaction

$u^{*}$ = *friction velocity*

# Dry deposition-strongly de







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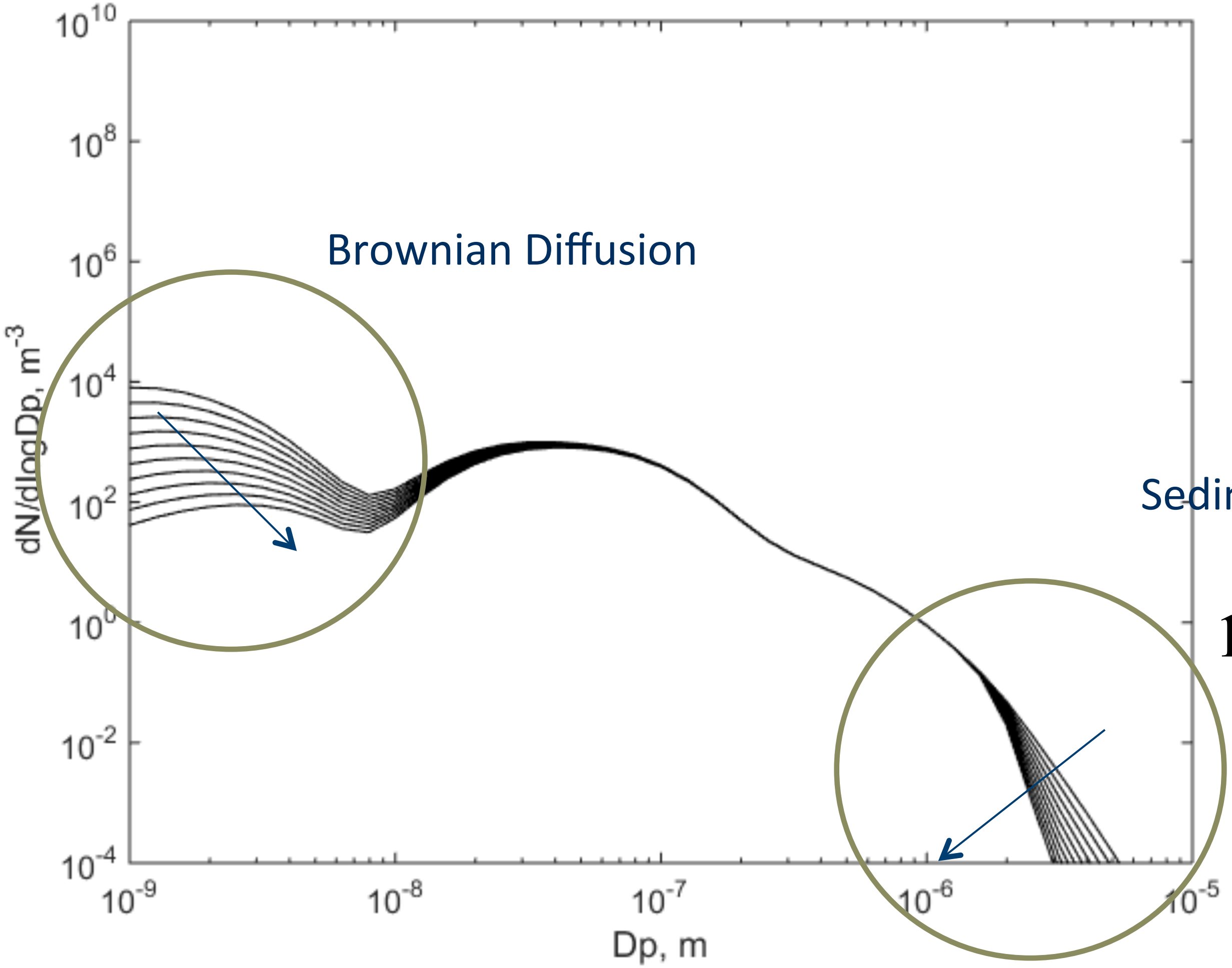
# Ageing due to dry deposition

$$Sc^{-2/3}$$

$$Sc = \mu_{air} / Diff_p$$



Brownian Diffusion

$$\frac{dM}{dt} < 0,$$

$$\frac{dN}{dt} < 0$$

Sedimentation, impaction

$$10^{-3/St}, St = \frac{u*^2 V_s}{g\mu} \text{ and } \mathrm{V_s}$$

# Coagulation

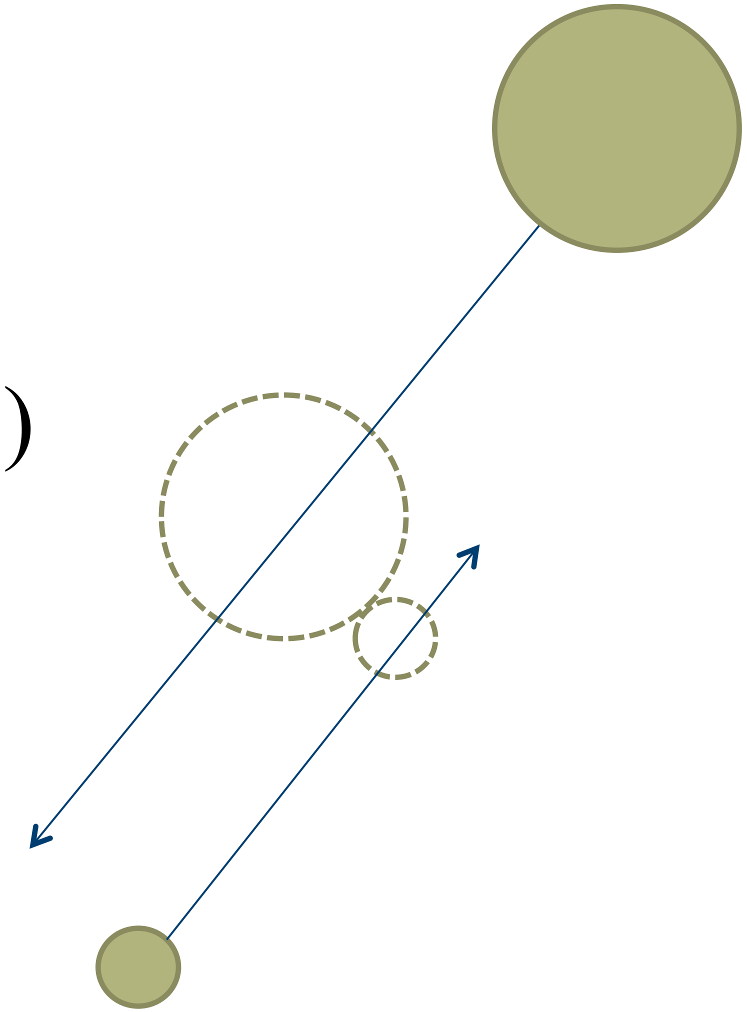
- Mainly the result of Brownian motion, although other forces may come into play (electrical, gravitational etc)
- *Two particles* collide, aggregate and form *one new particle*
- Coagulation does not affect mass, but reduce number
- Most efficient for small particles

# Coagulation

- Free molecular regime

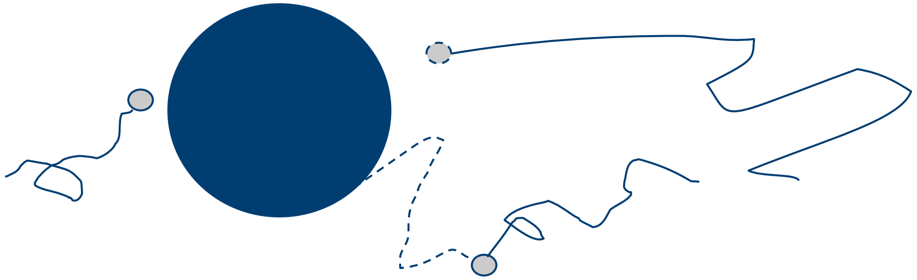
$$RMS = \sqrt{(v_i^{\,2} + v_j^2)}$$

$$CC = \pi(r_i^{\,2} + r_j^{\,2})$$



# Coagulation

- Continuum regime
  - the kernel in this regime is found by solving the time-dependent diffusion equation around a stationary spherical absorber in an infinite medium with suspended particles. ***Transport and collision through "random walk"***



- Transition regime (~1<Kn<50)
  - Semi-empirical solution to the collision kernels (Fuchs 1964, "Flux matching")

# **Coagulation;** ***Fuchs form of the coagulation coefficient***

$$\frac{dN}{dt} = -K_{12} N_1 N_2$$

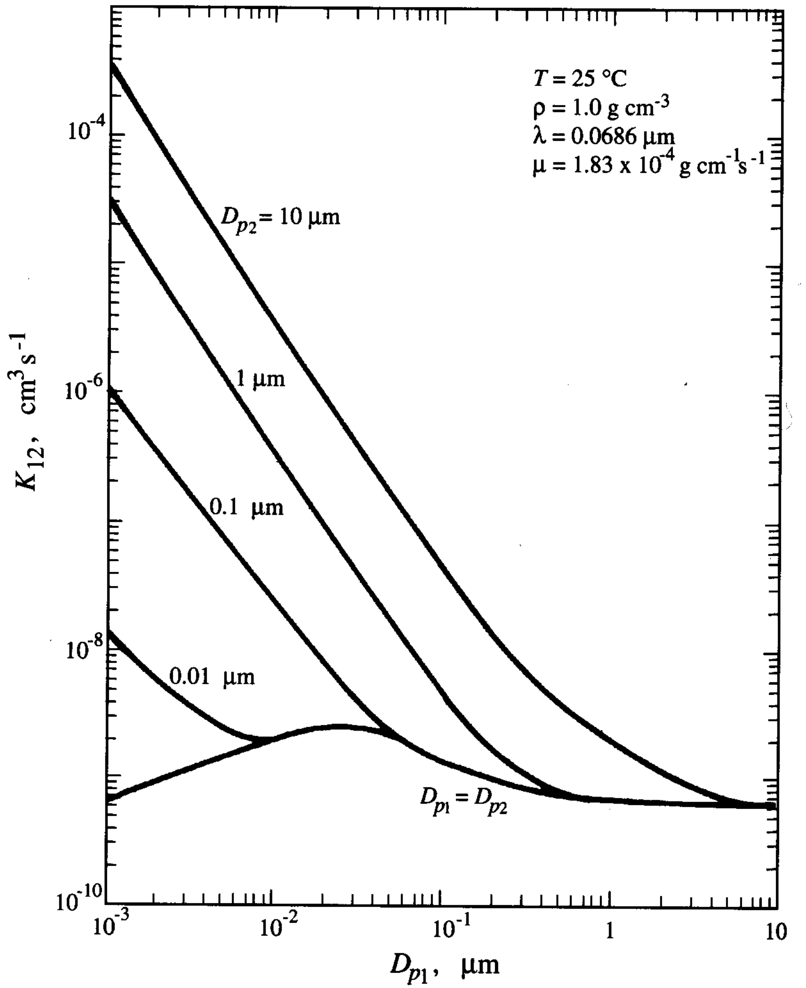
$$K_{12} = 2\pi D_1 D_2 (Dp_1 + Dp_2) \left( \frac{Dp_1 + Dp_2}{Dp_1 + Dp_2 + 2\left(g_1^2 + g_2^2\right)^{1/2}} + \frac{8(D_1 + D_2)}{\left(c_1 + c_2\right)^{1/2} (Dp_1 + Dp_2)} \right)^{-1}$$

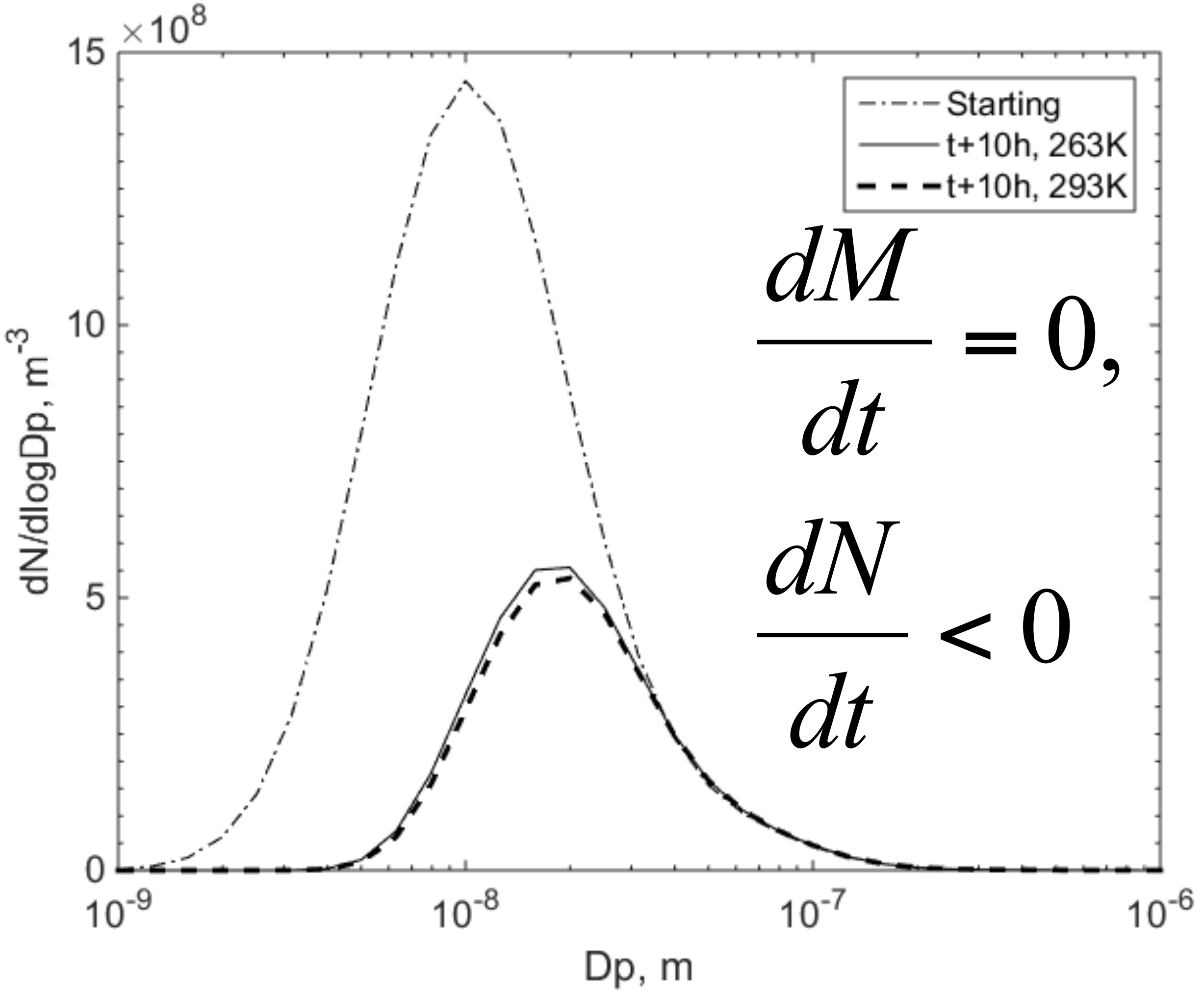
$$D_{1,2} = f\left(T, \frac{1}{Dp}\right)$$

$$C = f\left(T, \frac{1}{Dp^3}\right)$$

K12=COAG_COEFF(Dp$_{1,}$ Dp$_2$, T, P)

# Aerosol dynamics: coagulation

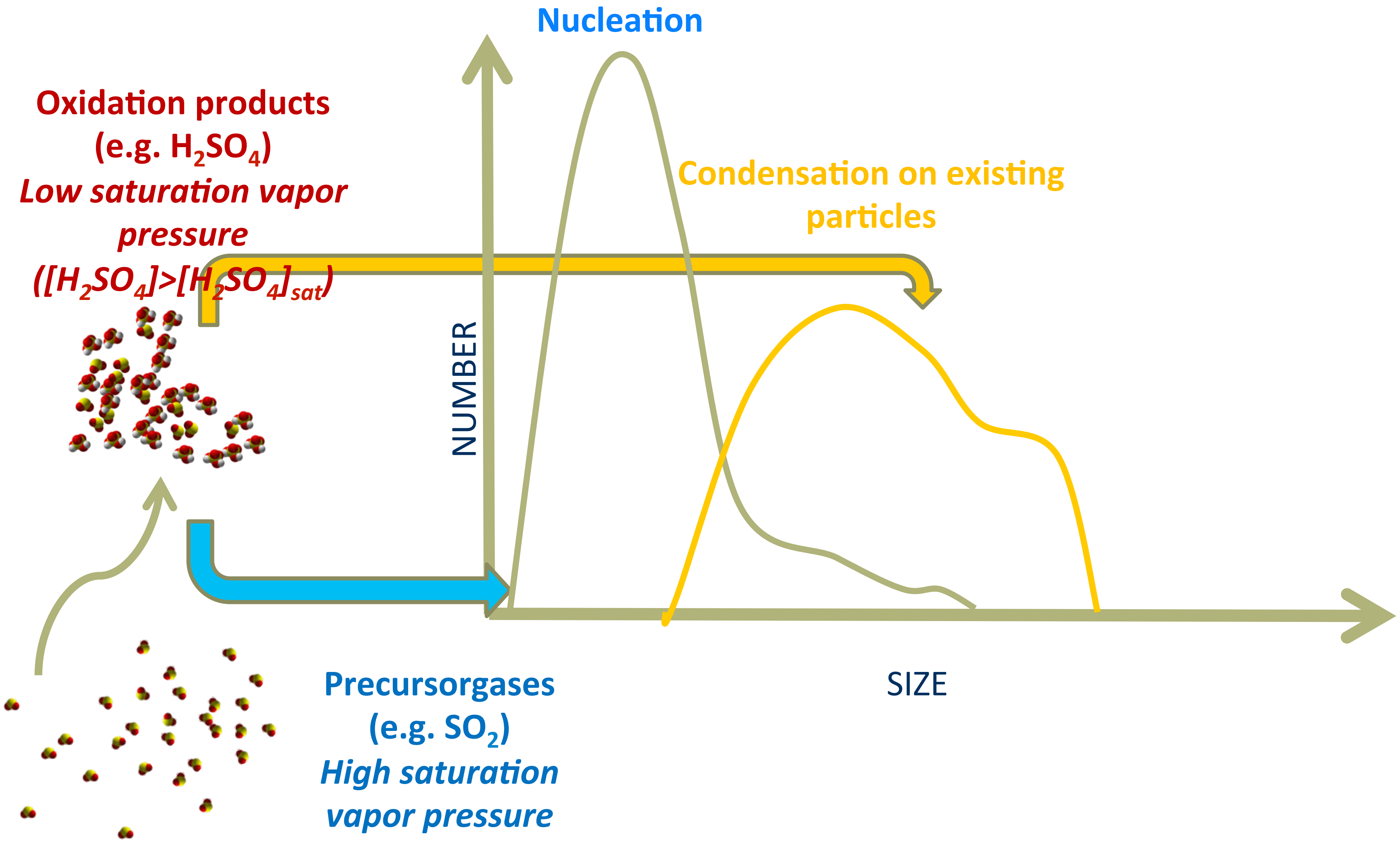




$$\frac{dM}{dt} = 0,$$

$$\frac{dN}{dt} < 0$$

# Gas-to-particle production



**Oxidation products**
**(e.g. $H_2SO_4$)**
***Low saturation vapor pressure***
***($[H_2SO_4]>[H_2SO_4]_{sat}$)***

**Nucleation**

**Condensation on existing particles**

NUMBER

SIZE

**Precursorgases**
**(e.g. $SO_2$)**
***High saturation vapor pressure***

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# Secondary particle production: Saturation ratio

$$S = \frac{p_a}{p^s{}_a(T)}$$

$$S < 1, Subsaturation$$

$$S > 1, Supersaturation$$

$$S = 1, Saturation$$

S=saturation ratio

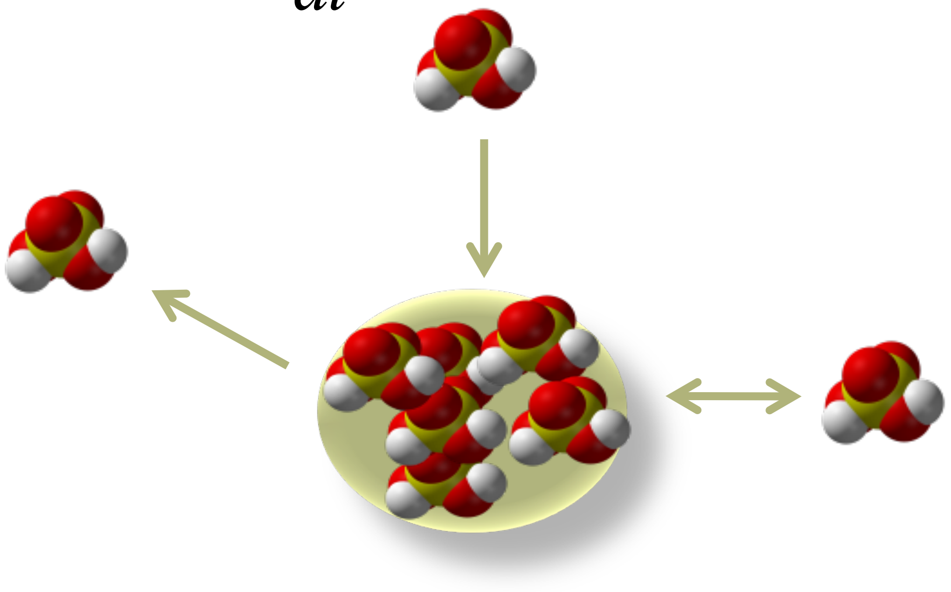
$p_{a=}$partial pressure of a

$p_a^s$=saturation vapor pressure of a at temperature T

$$\ln\left(\frac{p^s{}_{a,1}}{p^s{}_{a,2}}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

**Clausius-Clapeyron relation**

# Concepts of gas-to-particle conversion



$$\frac{dr}{dt} > 0 \; at \; S > 1$$

$$\frac{dr}{dt} < 0 \; at \; S < 1$$

$$\frac{dr}{dt} = 0 \; at \; S = 1$$

# Kelvin effect

$$p_A = p_A^0 \exp\left(\frac{2\sigma v_m}{kTr_d}\right)$$

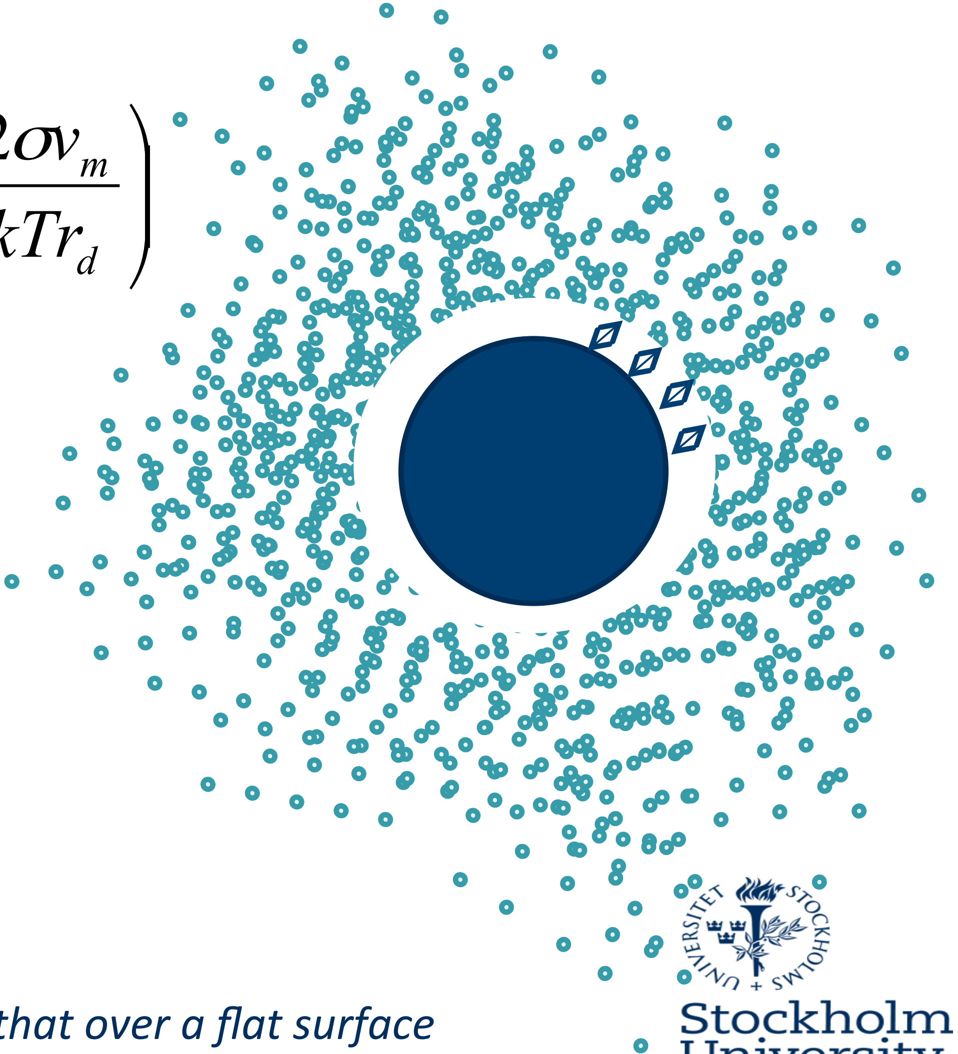
$\sigma$ = *surface tension*

$v_m$ =*molecular* volume

k=Boltzmanns constant

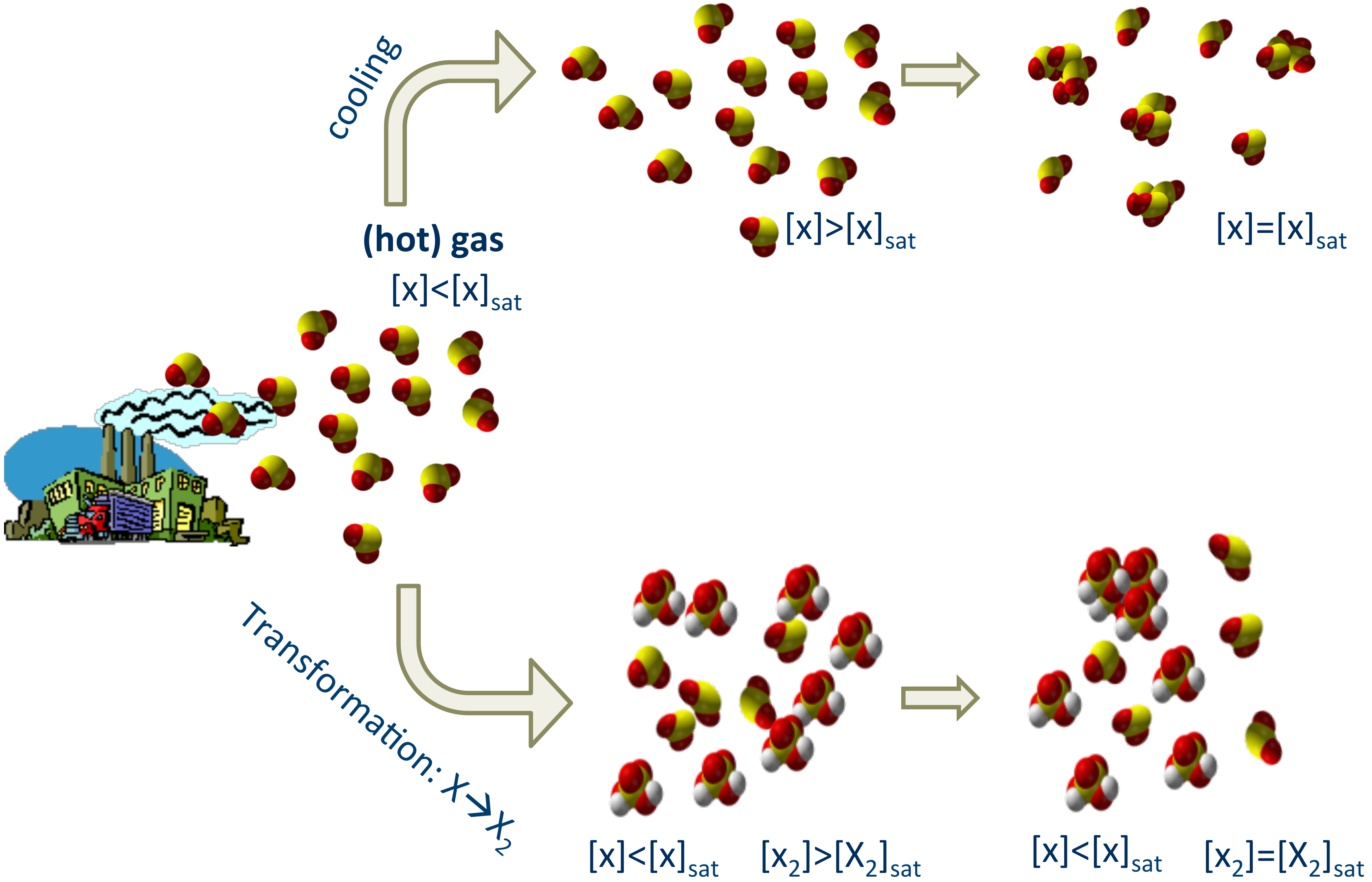
T=Temp

$r_d$ = *droplet radius*



*Vapor pressure of compound A over a curved surface always exceed that over a flat surface*

# Gas-to-particle conversion: How is supersaturation reached



cooling

**(hot) gas**

$[x]<[x]_{sat}$

$[x]>[x]_{sat}$

$[x]=[x]_{sat}$

Transformation: $X \rightarrow X_2$

$[x]<[x]_{sat}$ $[x_2]>[X_2]_{sat}$

$[x]<[x]_{sat}$ $[x_2]=[X_2]_{sat}$

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# Nucelation

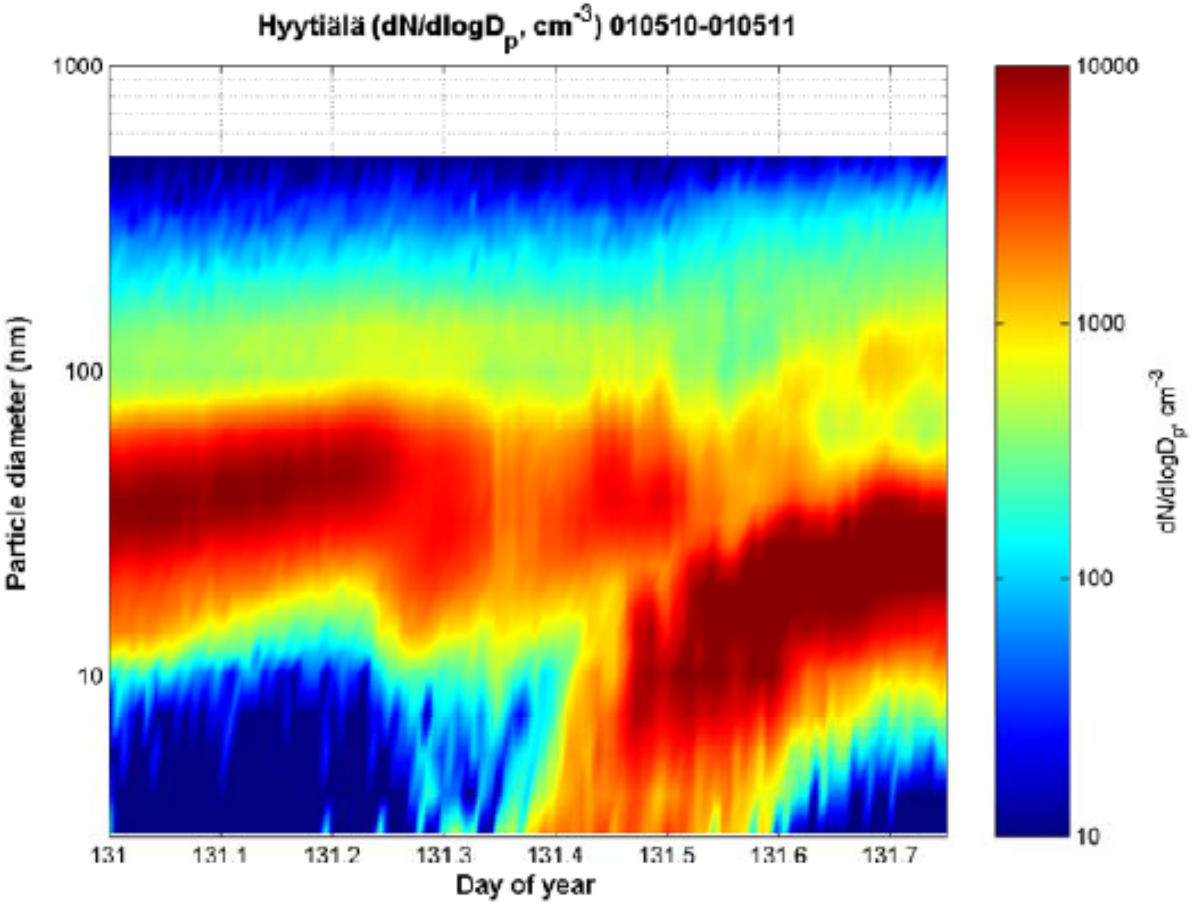

Figure 2: Example of nucleation event observed on 11th May 2001, Hyytiälä (61.51°N, 24.17°E).

# Particle number or particle mass? Role of condensation sink

- Amount of pre-existing aerosol surface crucial
  - Generation of supersaturated conditions + low surface area of pre-existing particles favours formation of particle number via nucleation
  - Generation of supersaturated conditions + High concentration of pre-existing particles favours formation of particle mass via condensation
  - This is often referred to as **”condensation sink”**

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# Condensation

$c_s$ = *saturation* vapor pressure/concentration over surface

$c_s = kc_0, \quad k$ = Kelvin effect

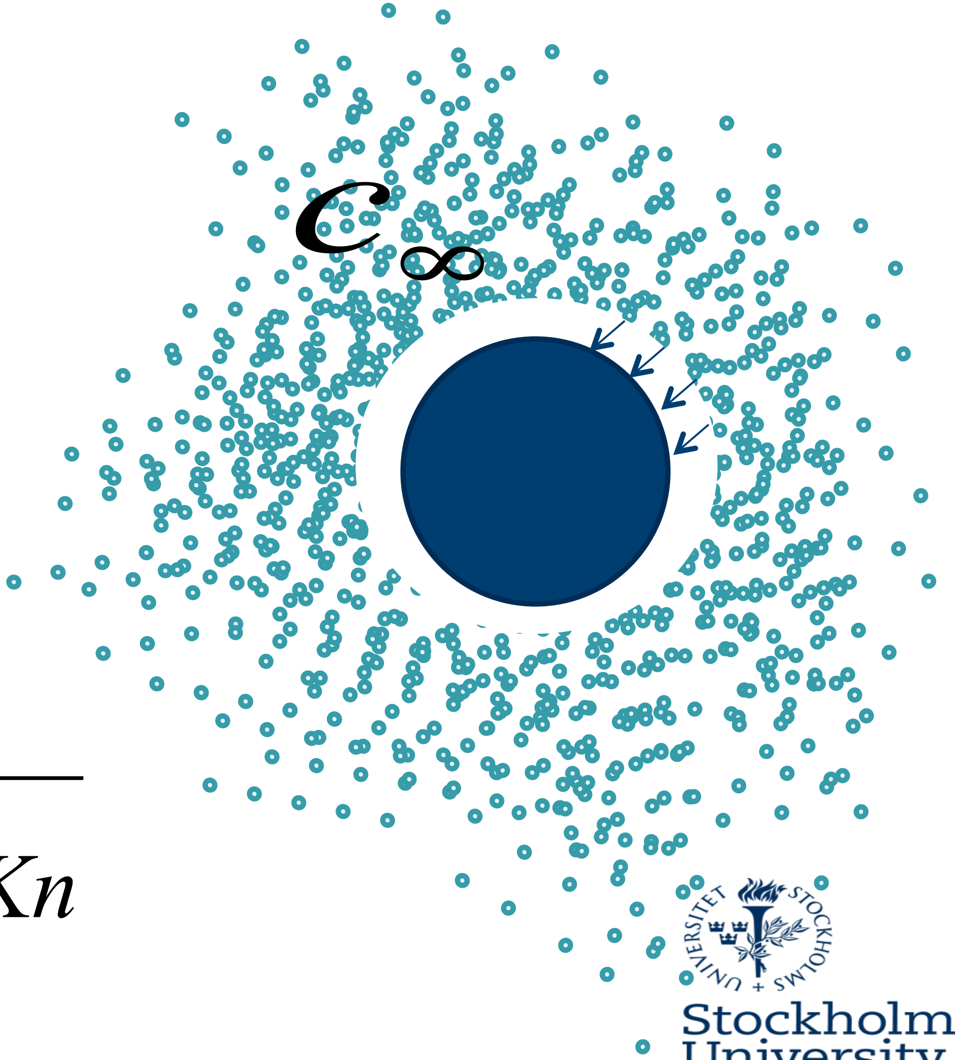
$$\frac{dM}{dt} = 4\pi r_p D_g (c_\infty - c_s)$$

$$\frac{dM}{dt} = \beta 4\pi (r_p + r_g)(D_p + D_g)(c_\infty - c_s)$$

*where*

$$\beta_M = \frac{Kn + 1}{0.377Kn + 1 + \frac{4}{3}\alpha^{-1}Kn^2 + \frac{4}{3}\alpha^{-1}Kn}$$

β=Fuchs  and Sutugin non-contnuum correction factor



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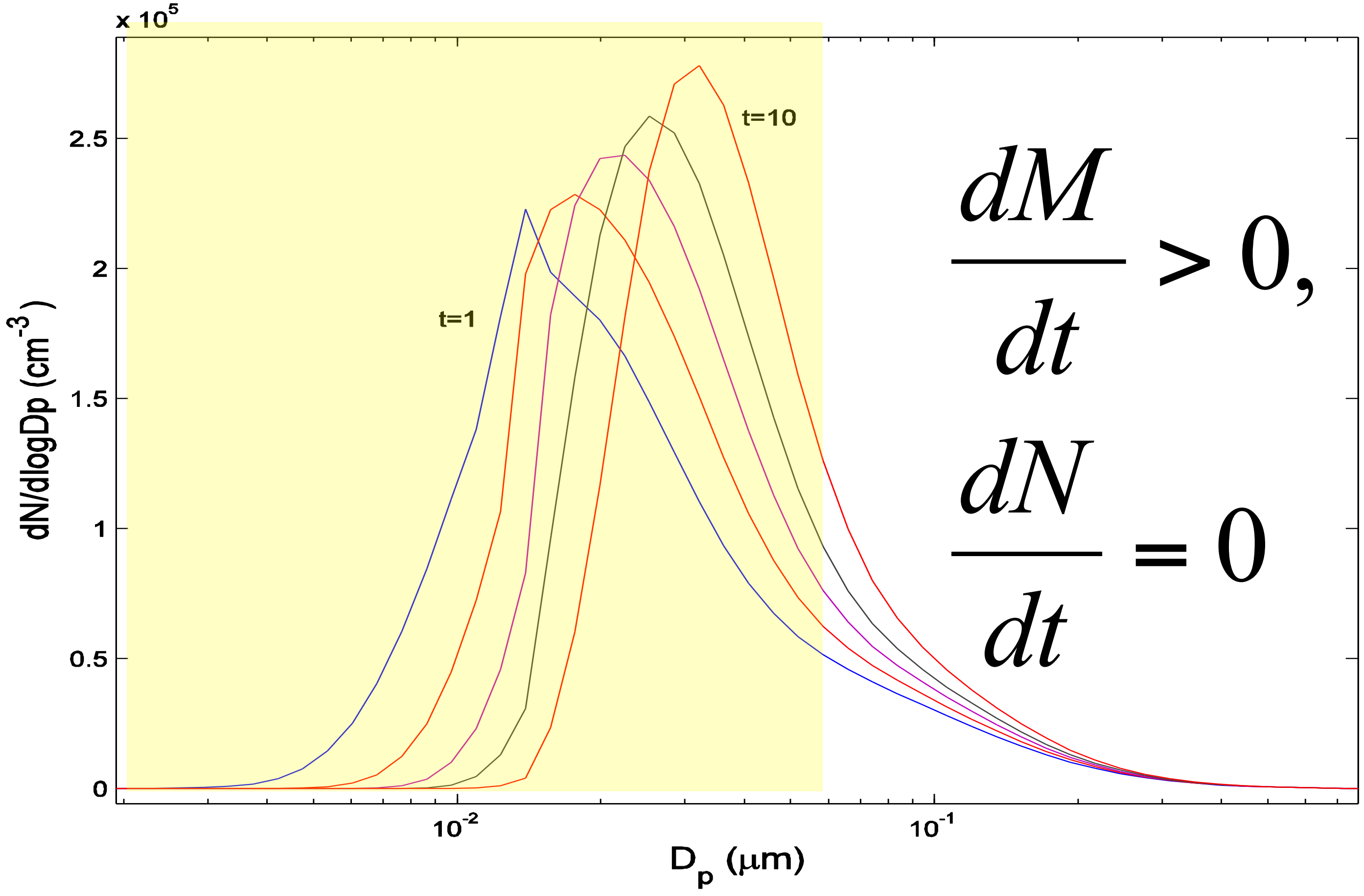
# Aerosol dynamics: condensation



$$\frac{dM}{dt} > 0,$$

$$\frac{dN}{dt} = 0$$

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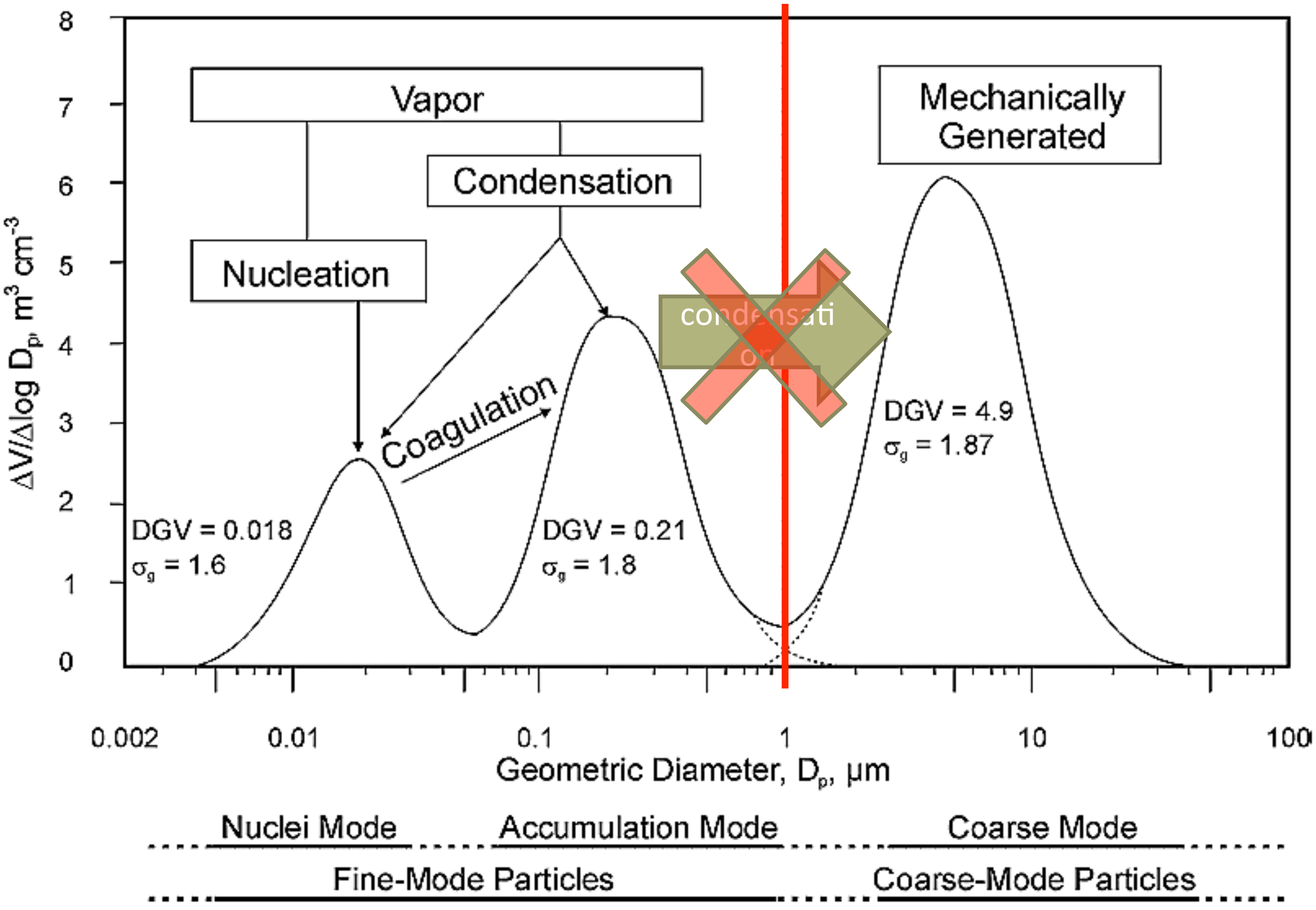
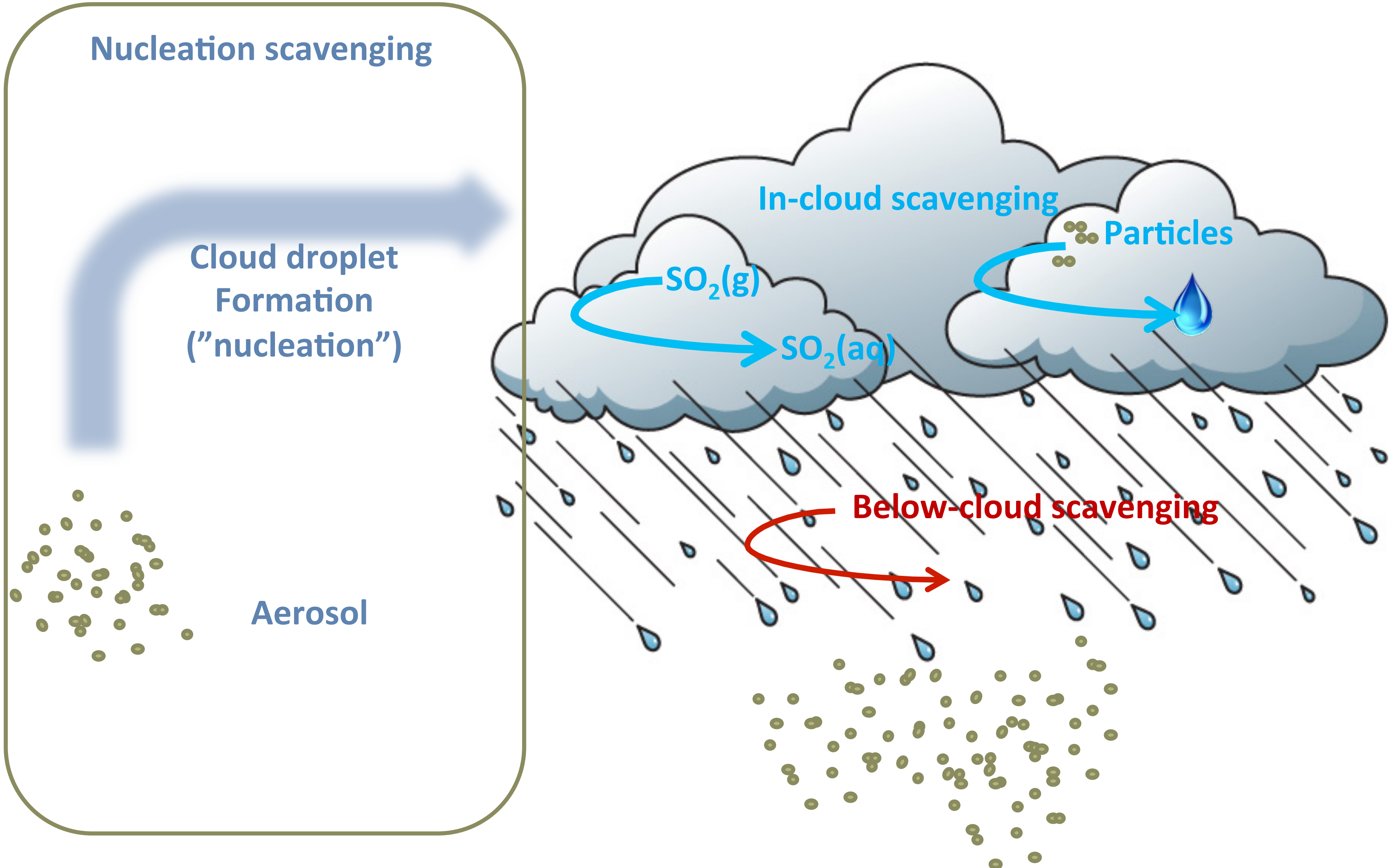

Vapor
Condensation
Nucleation
Coagulation
Mechanically Generated
~~condensati~~
~~on~~
DGV = 0.018
σg = 1.6
DGV = 0.21
σg = 1.8
DGV = 4.9
σg = 1.87
ΔV/Δlog Dp, m3 cm-3
0
1
2
3
4
5
6
7
8
0.002
0.01
0.1
1
10
100
Geometric Diameter, Dp, µm
Nuclei Mode
Accumulation Mode
Coarse Mode
Fine-Mode Particles
Coarse-Mode Particles

# Wet depositon



Nucleation scavenging

Cloud droplet
Formation
(”nucleation”)

Aerosol

In-cloud scavenging

$SO_2(g)$

$SO_2(aq)$

Particles

Below-cloud scavenging

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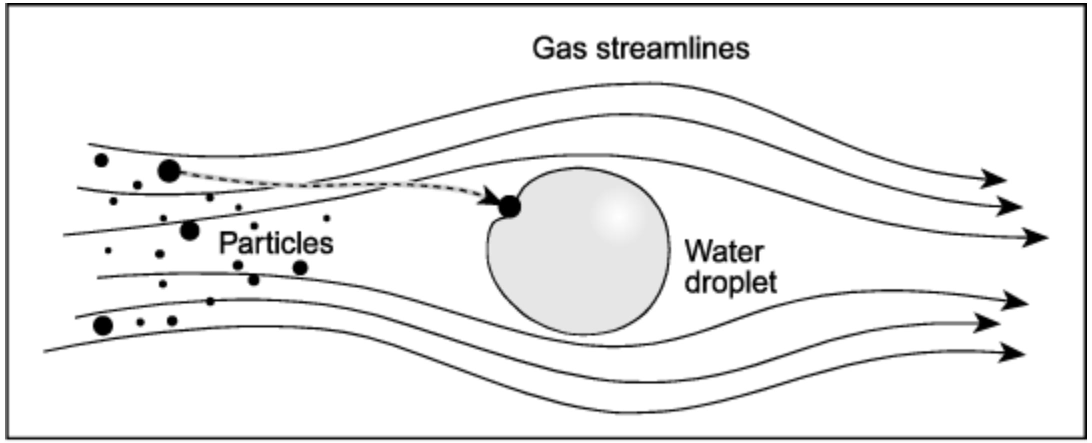
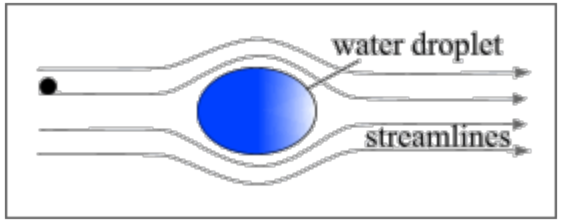
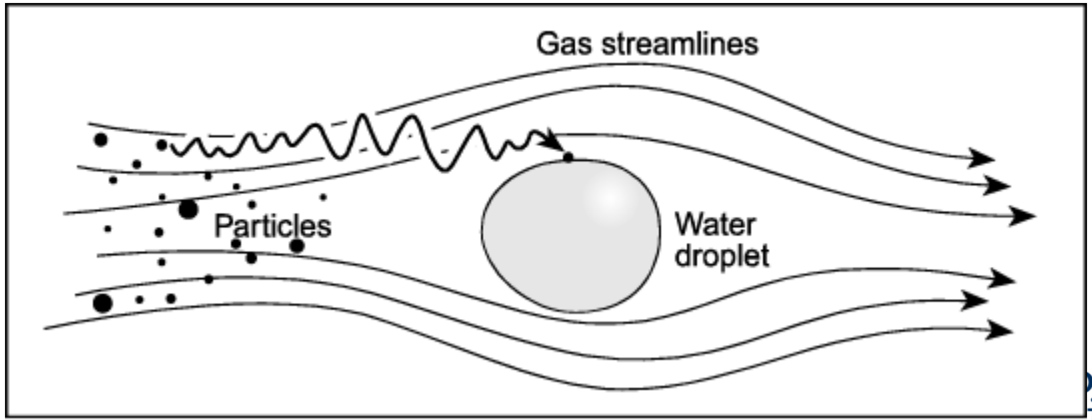
# Scavenging of aerosols: Impaction, diffusion and interception







# Below cloud scavengning of particles

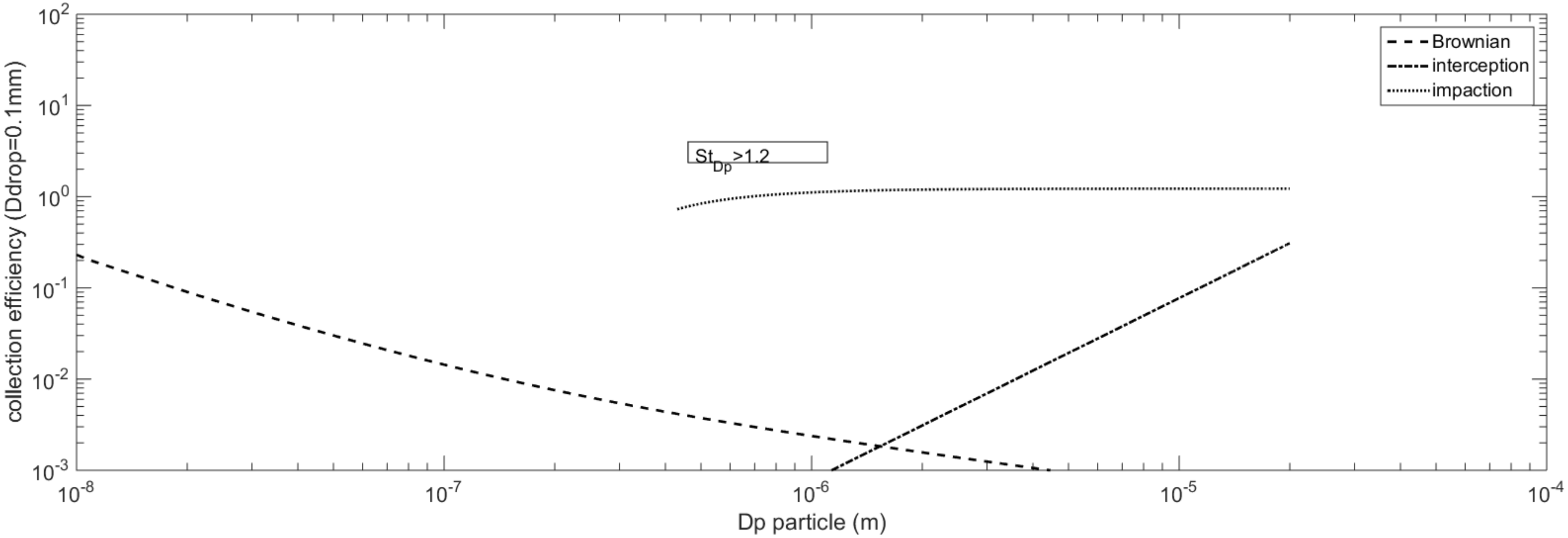
$$\Lambda(d_p) = \int_0^\infty \frac{\pi}{4} D_p^2 U(D_p) E(D_p, d_d) N_{D_p} dD_p$$

$Dp$ = rain droplet diameter

$d_d$ = *particle* diameter

$E(Dp, d_d)$ = *scavenging* efficiency

# Collection efficiency



# Scavengning

- Thus, we need a droplet distribution
- Marshal Palmer droplet distribution

$$\frac{N(Dp)}{dDp} = n_0 \exp\left(4.1\mathrm{p}_0^{-0.21} D_p\right)$$

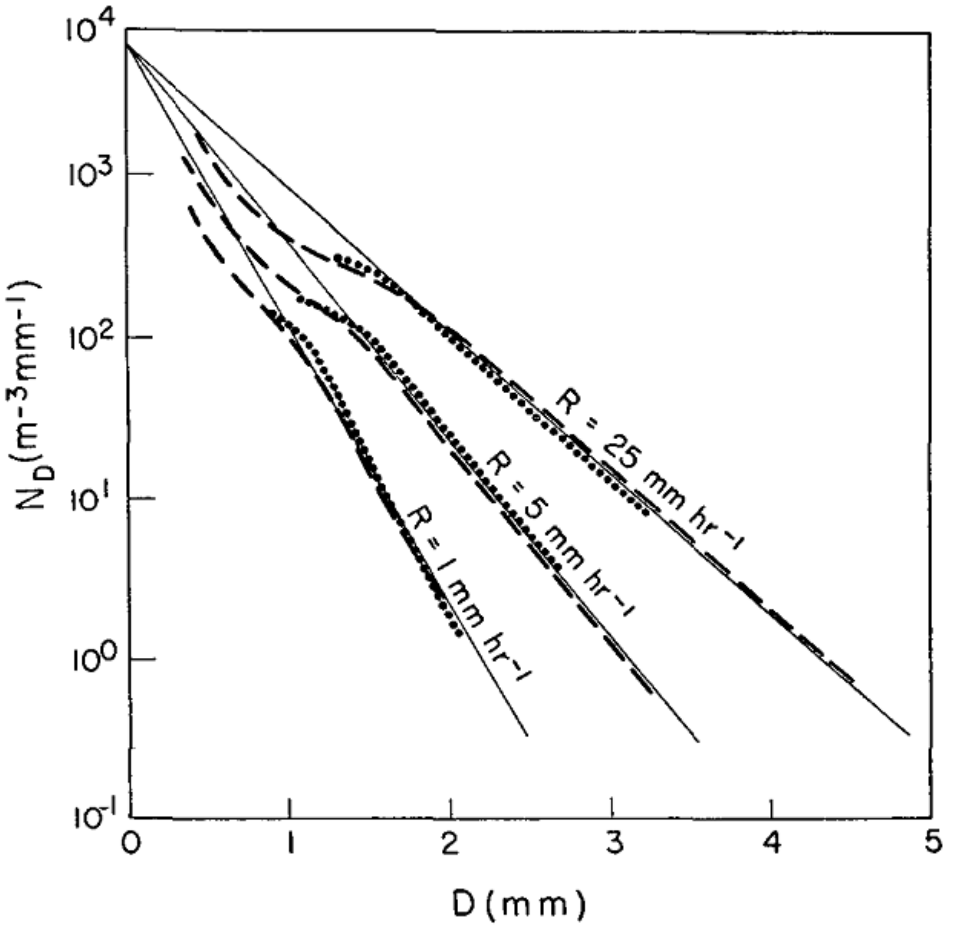
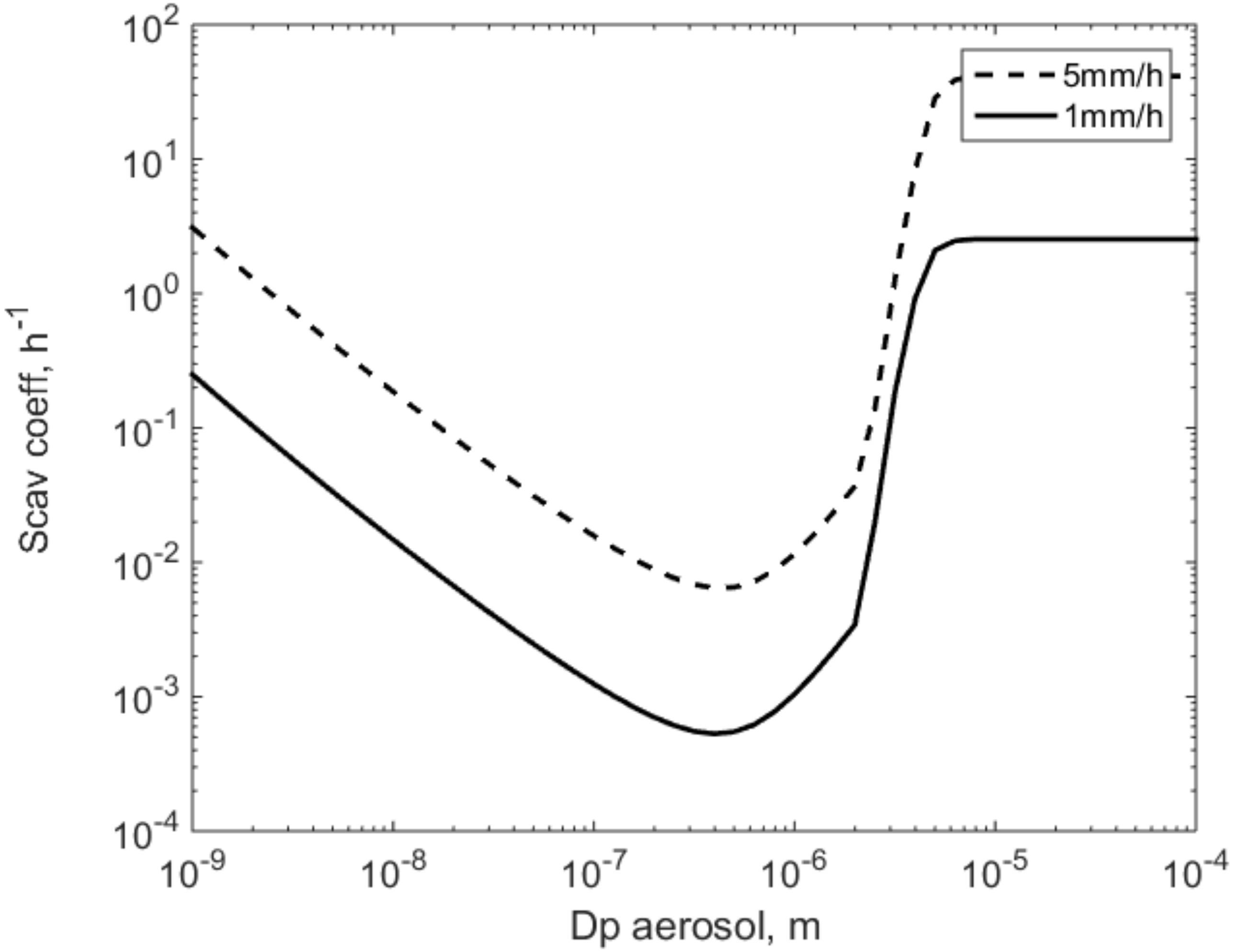


FIG. 2. Distribution function (solid straight lines) compared with results of Laws and Parsons (broken lines) and Ottawa observations (dotted lines).

# Scavengning coefficient, Λ



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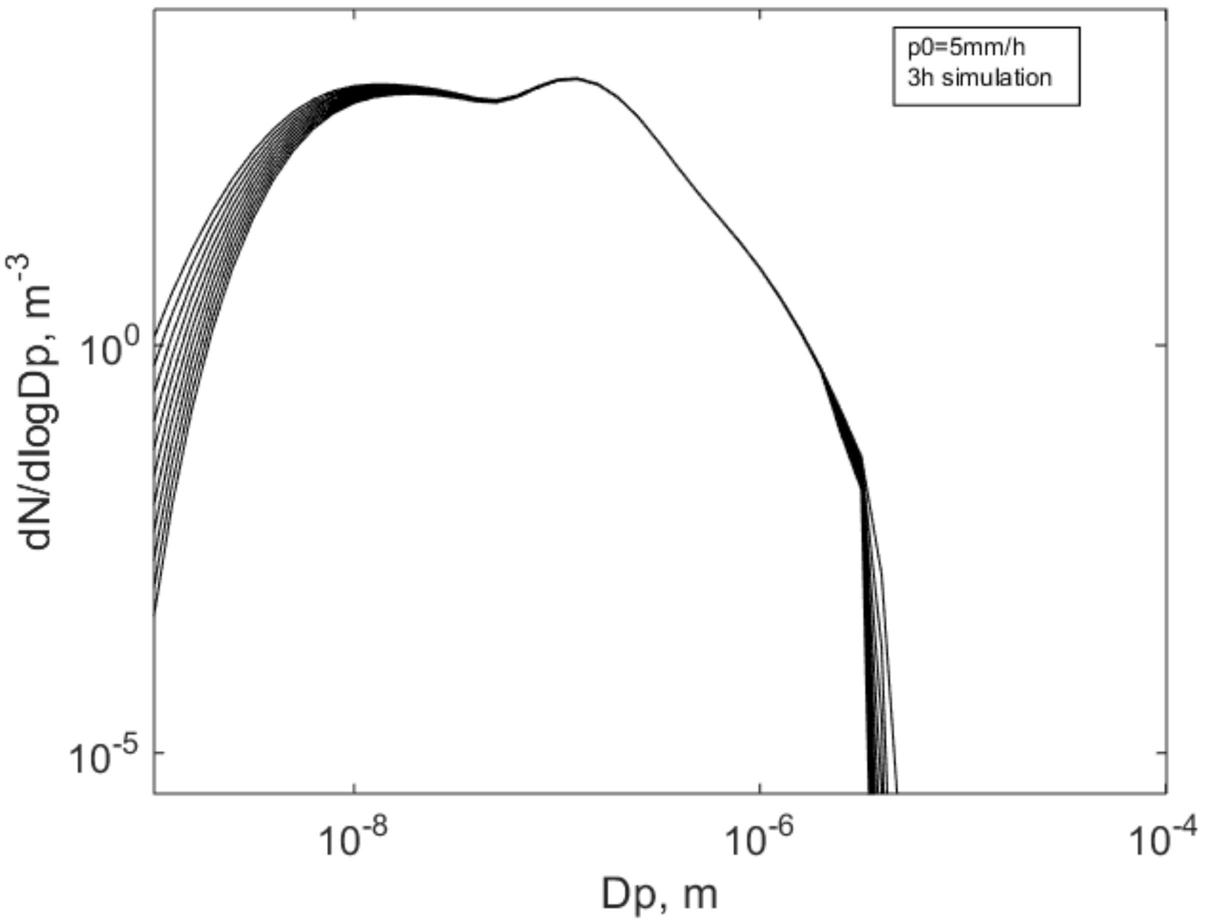
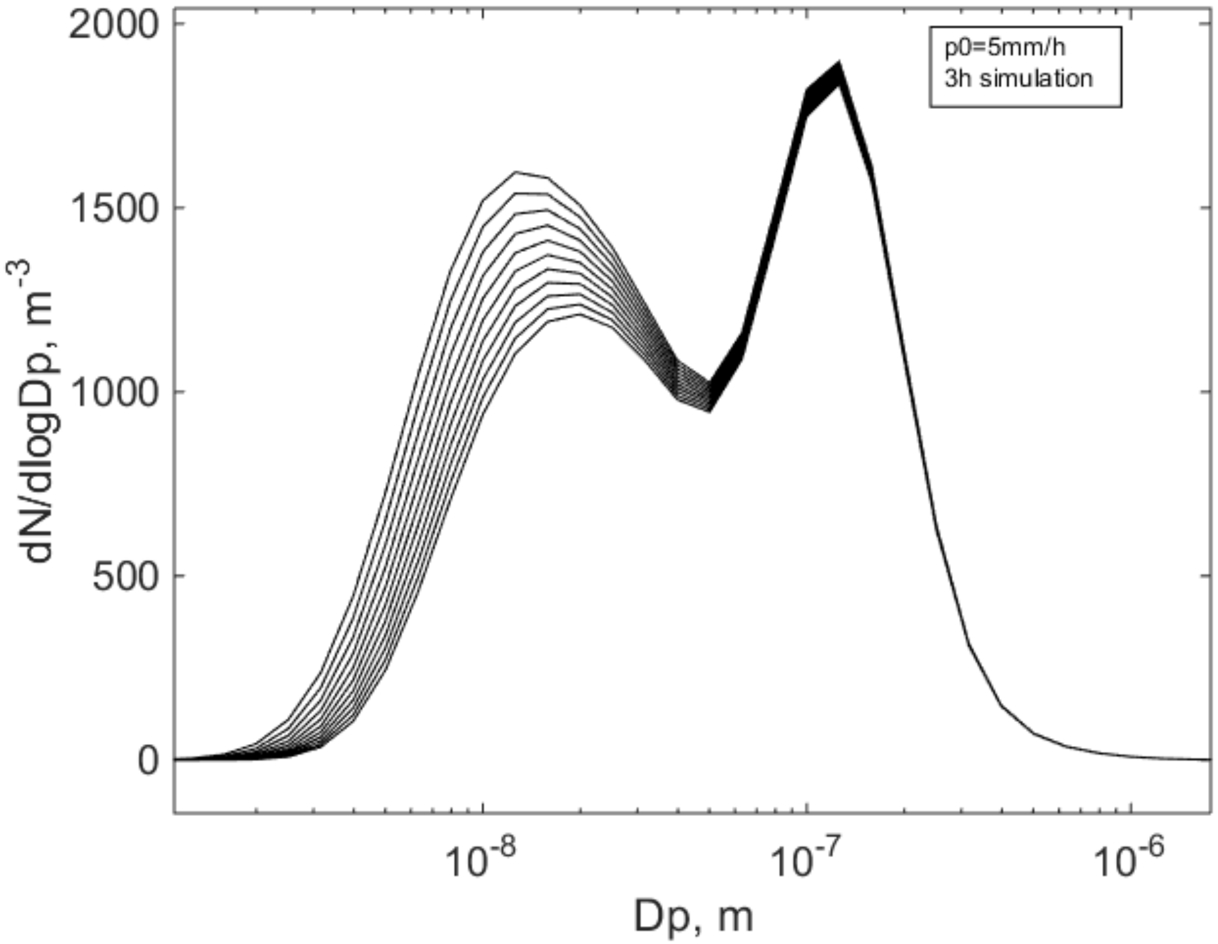
# Simulating below cloud scavengning





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# Simple approach: Assuming constant, linear and irreversible scavengning

$$\frac{\partial C}{\partial t} = -W_{gas/rain} + E + R$$

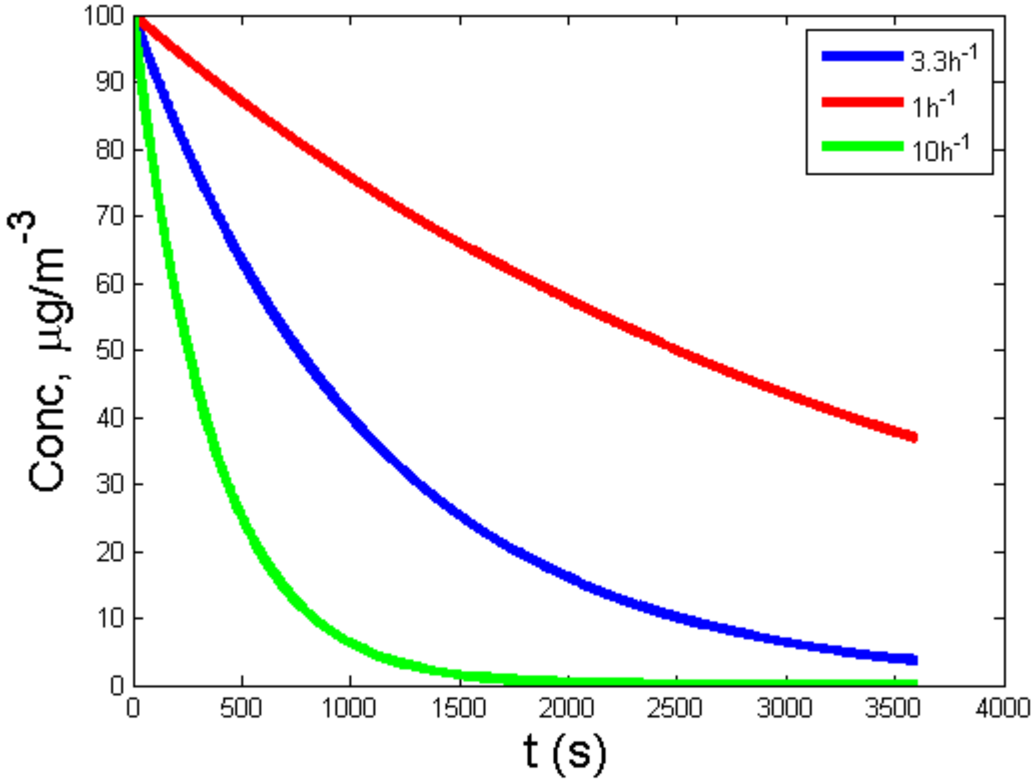
(where R and E are additional reactions and emissions, resp.)

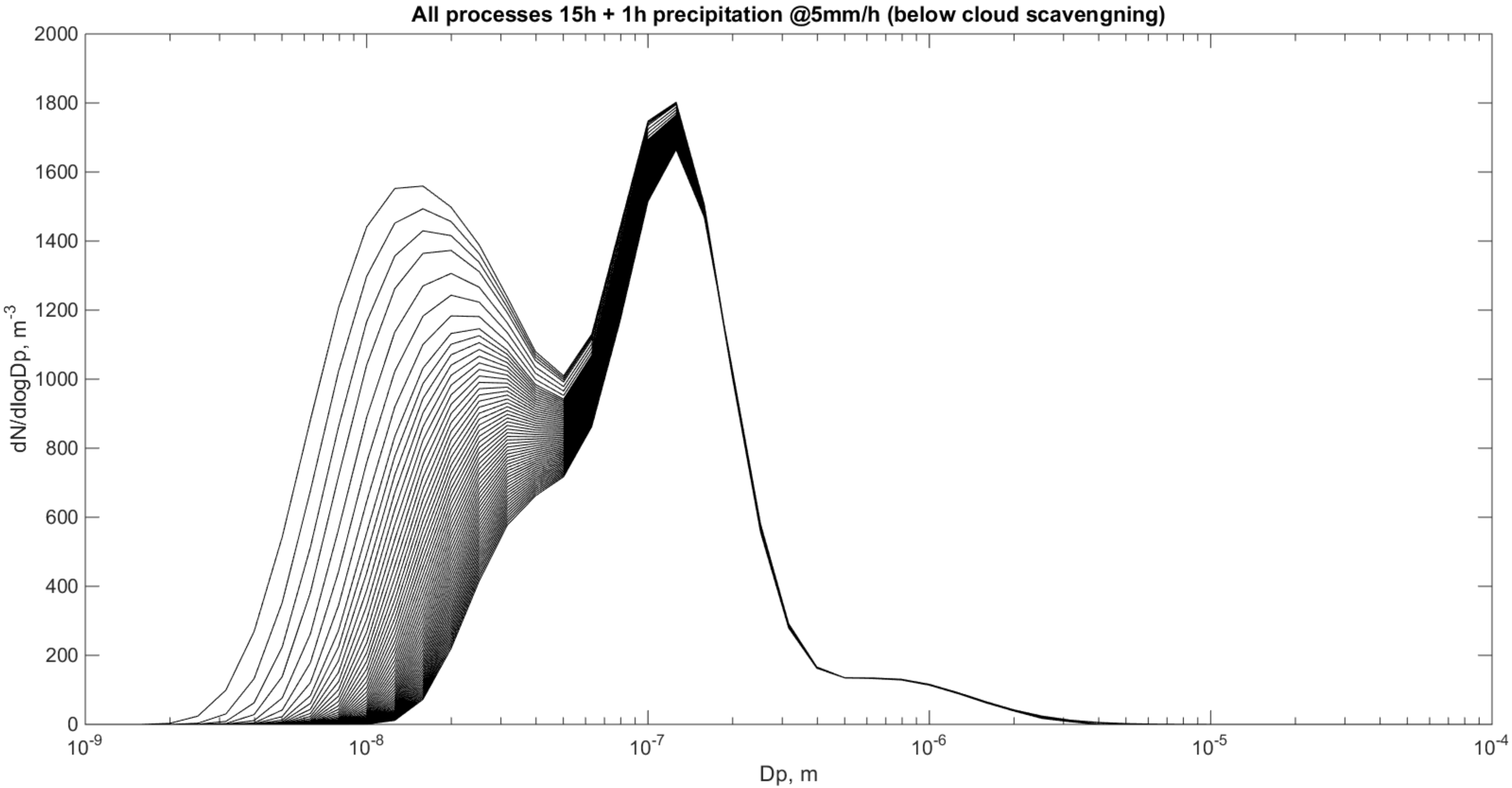
Assuming no R or E, and as :

$$W_{gas/rain} = \Lambda_{i,gas} C_{i,gas} (e.g.\, s^{-1} * \mu g / m^{3})$$

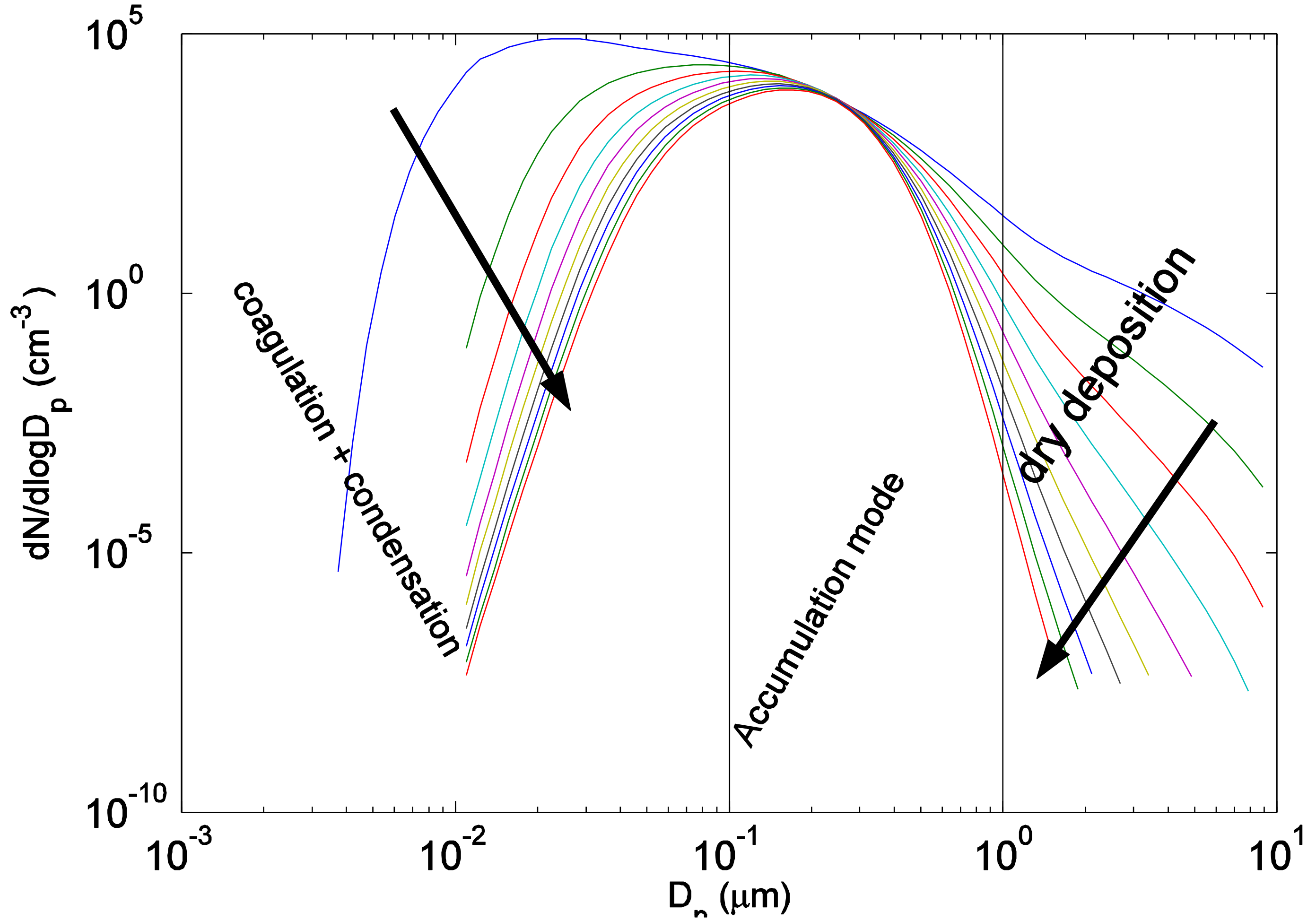
$$\frac{\partial C}{\partial t} = -\Lambda_{i,gas} C_{i,gas}$$

$$C = C_0 e^{-\Lambda_{i,gas} t}$$




All processes 15h + 1h precipitation @5mm/h (below cloud scavengning)
dN/dlogDp, $m^{-3}$
2000
1800
1600
1400
1200
1000
800
600
400
200
0
$10^{-9}$
$10^{-8}$
$10^{-7}$
$10^{-6}$
$10^{-5}$
$10^{-4}$
Dp, m

# Aerosol dynamics: coagulation, condensation and dry deposition



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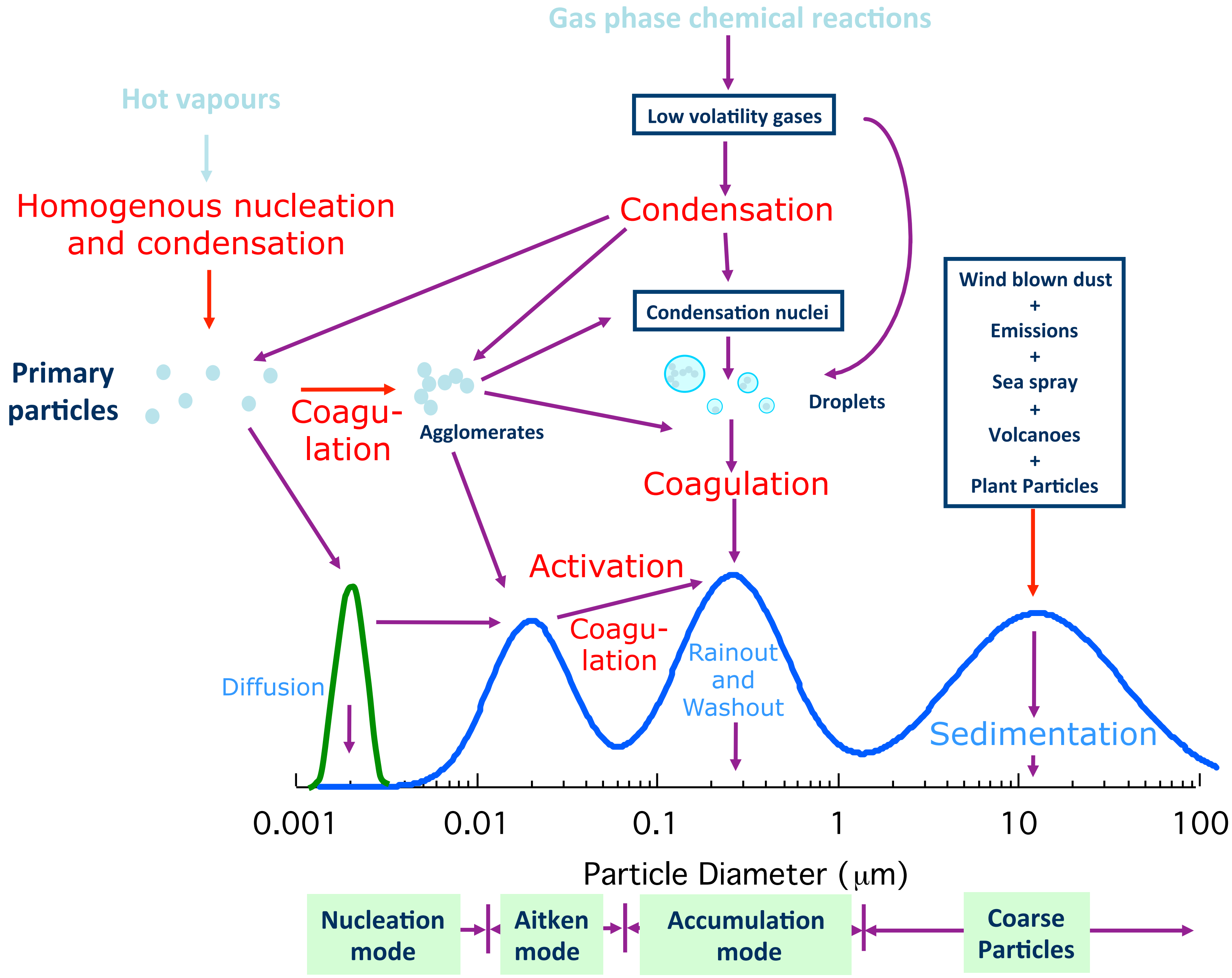

Gas phase chemical reactions

Low volatility gases

Condensation

Condensation nuclei

Droplets

Coagulation

Hot vapours

Homogenous nucleation and condensation

Primary particles

Coagu-lation

Agglomerates

Wind blown dust
+
Emissions
+
Sea spray
+
Volcanoes
+
Plant Particles

Activation

Coagu-lation

Diffusion

Rainout and Washout

Sedimentation

Nucleation mode

Aitken mode

Accumulation mode

Coarse Particles

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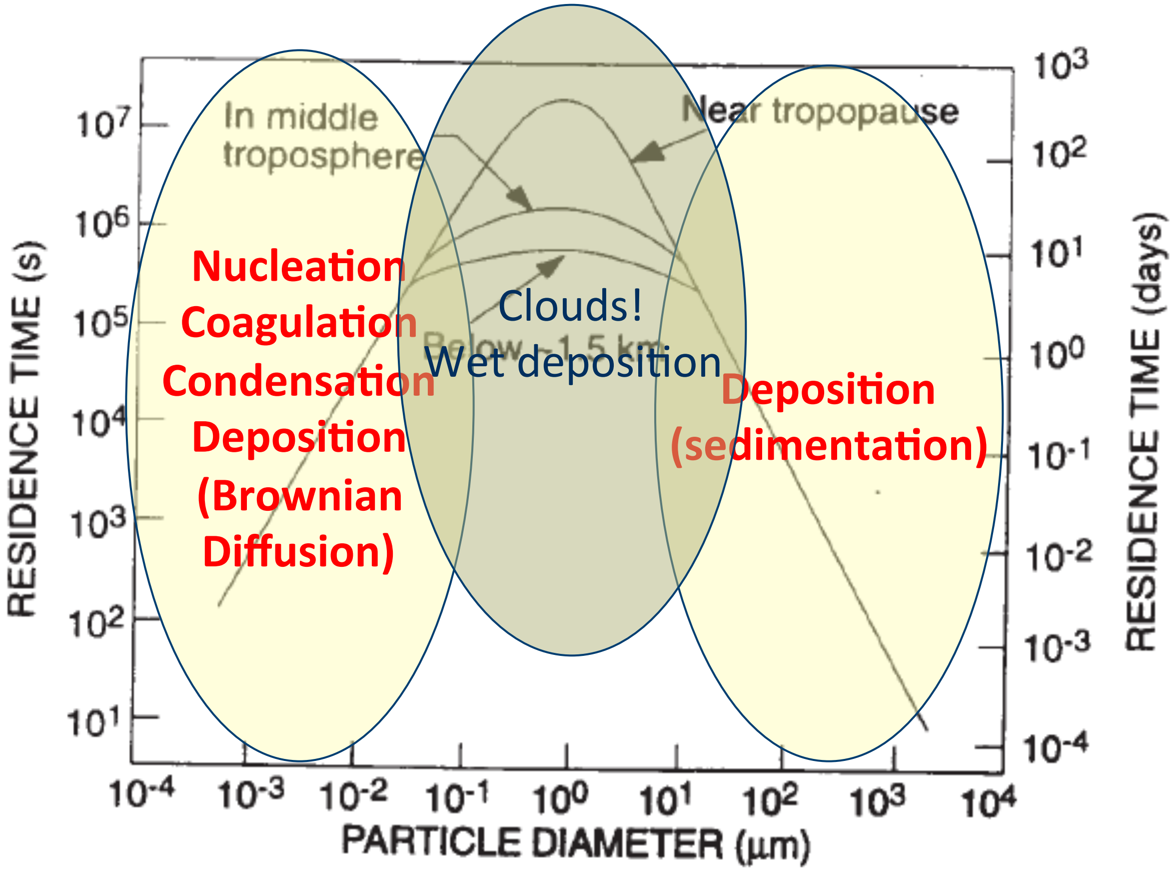
# Explaining the residence time

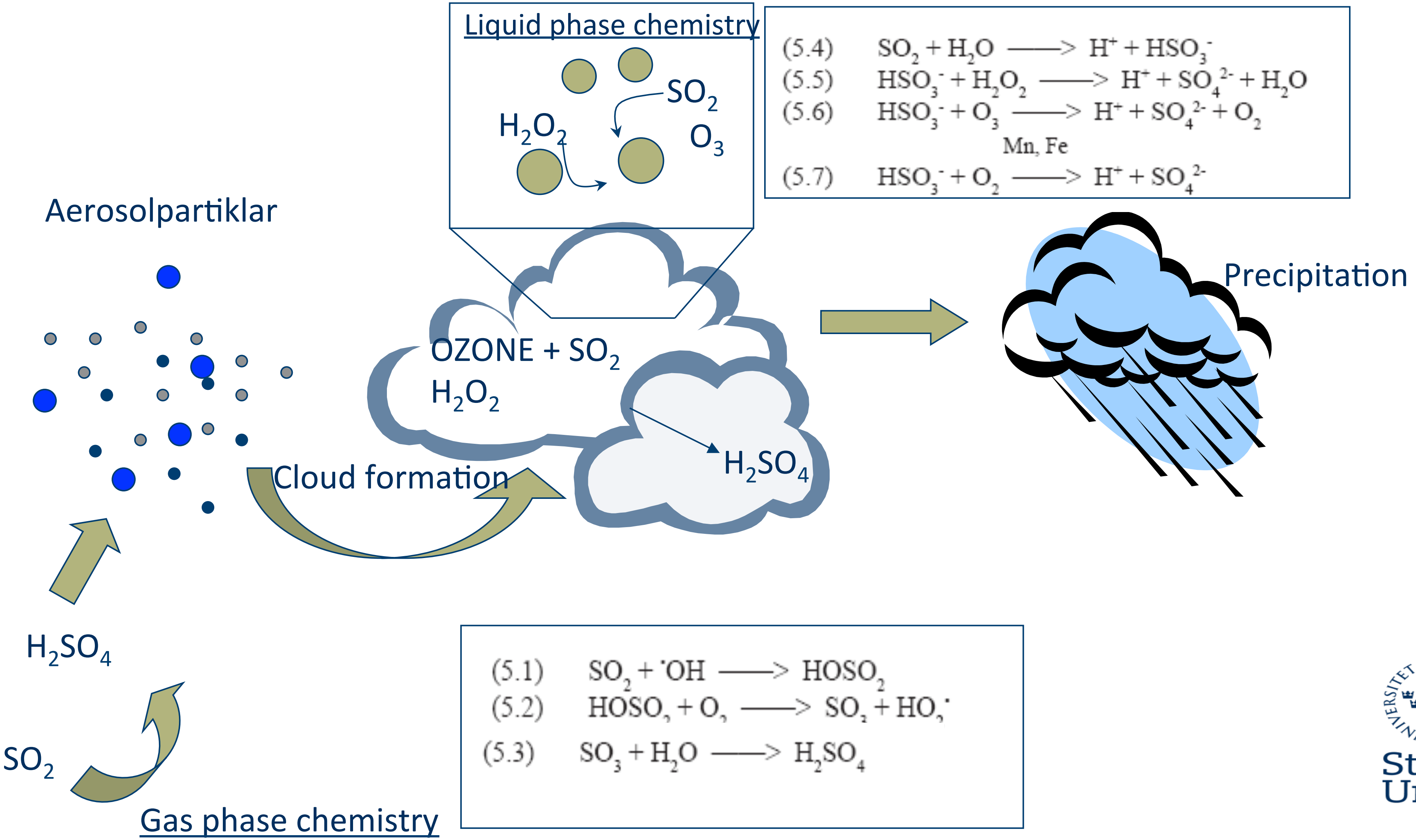


Nucleation
Coagulation
Condensation
Deposition
(Brownian
Diffusion)

Clouds!
Wet deposition

Deposition
(sedimentation)

# Aerosol dynamics: Cloud processing



Liquid phase chemistry

$H_2O_2$

$SO_2$

$O_3$

$$\begin{array}{ll}
(5.4) & SO_2 + H_2O \longrightarrow H^+ + HSO_3^- \\
(5.5) & HSO_3^- + H_2O_2 \longrightarrow H^+ + SO_4^{2-} + H_2O \\
(5.6) & HSO_3^- + O_3 \longrightarrow H^+ + SO_4^{2-} + O_2 \\
(5.7) & HSO_3^- + O_2 \xrightarrow{\text{Mn, Fe}} H^+ + SO_4^{2-}
\end{array}$$

Aerosolpartiklar

OZONE + $SO_2$

$H_2O_2$

$H_2SO_4$

Cloud formation

Precipitation

$H_2SO_4$

$SO_2$

Gas phase chemistry

$$\begin{array}{ll}
(5.1) & SO_2 + {}^{\cdot}OH \longrightarrow HOSO_2 \\
(5.2) & HOSO_2 + O_2 \longrightarrow SO_3 + HO_2^{\cdot} \\
(5.3) & SO_3 + H_2O \longrightarrow H_2SO_4
\end{array}$$

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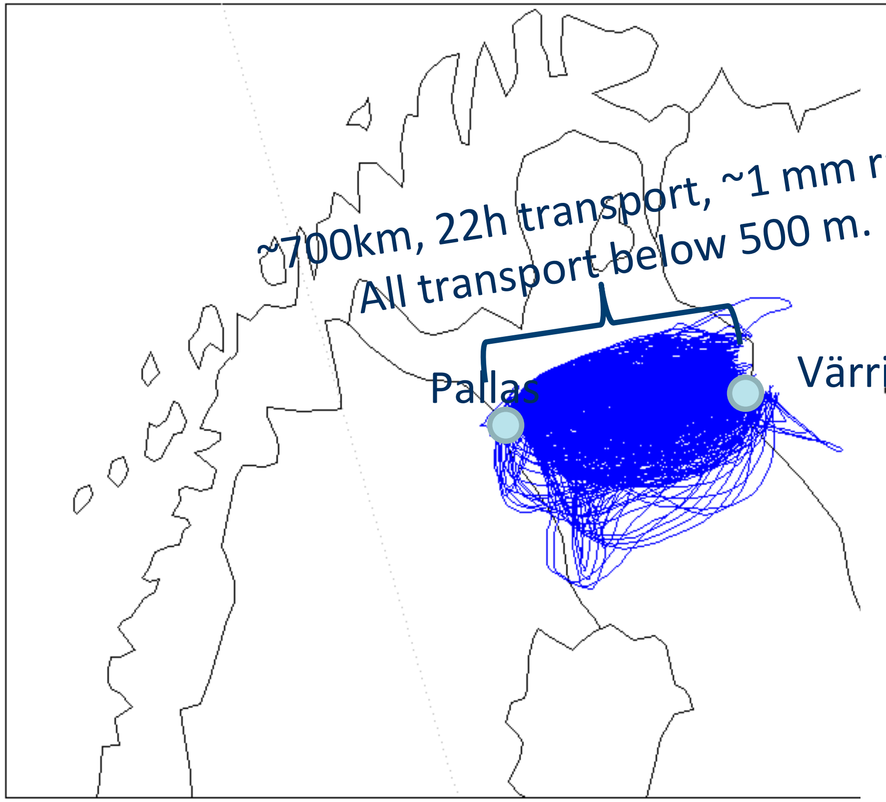
# What can be learnt from Lagrangian experiments: transport between Värriö and Pallas 2006-2008



~700km, 22h transport, ~1 mm rain.
All transport below 500 m.