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CAPES

Modeling of aerosol processes in the atmosphere

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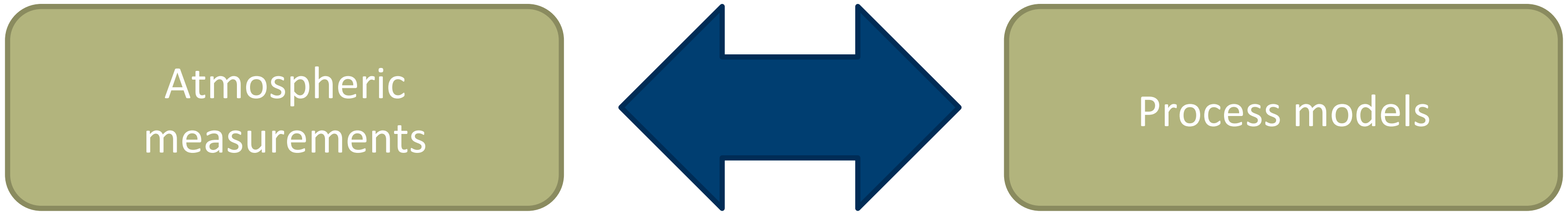
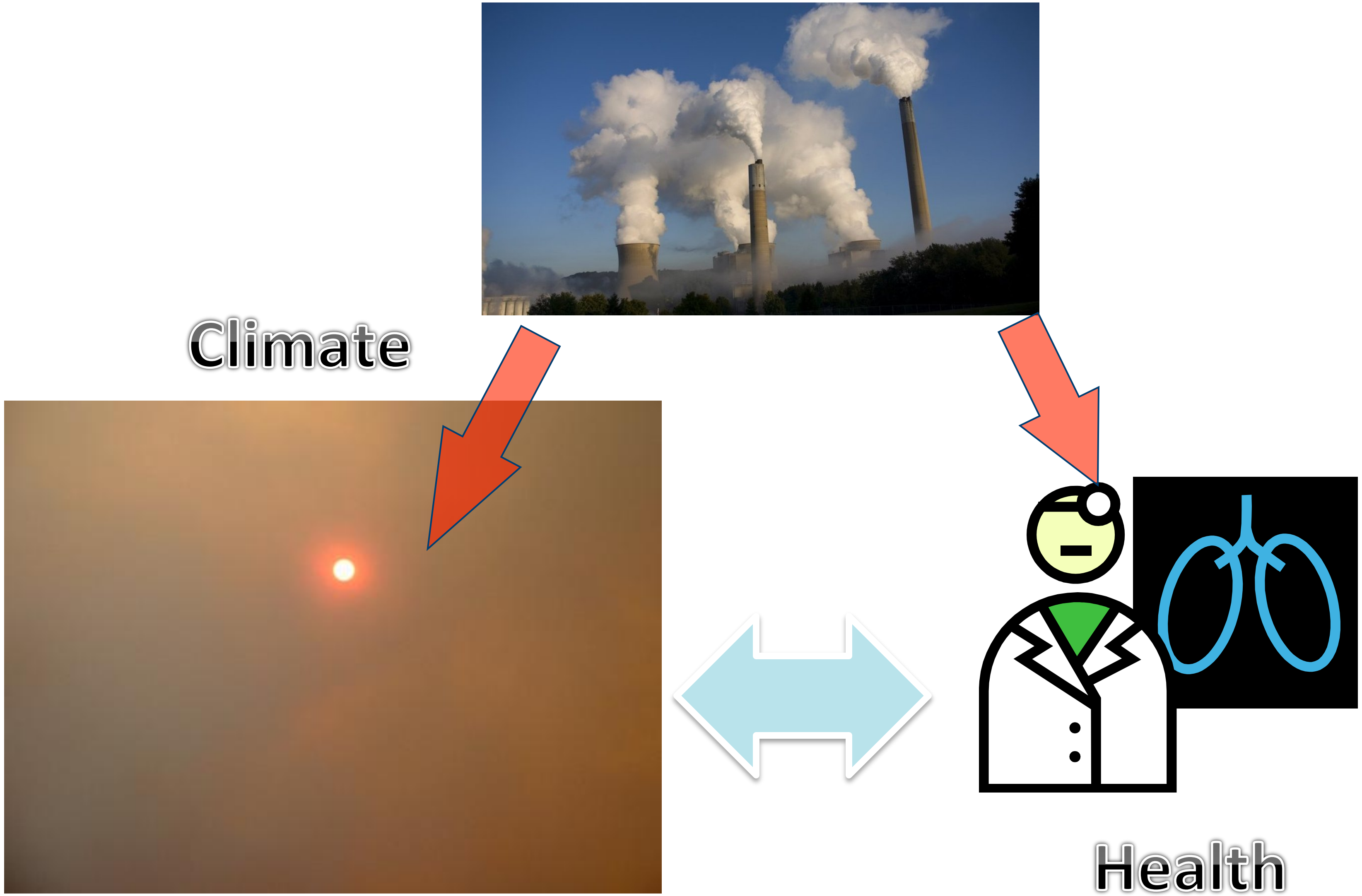
Scope of lecture

- 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

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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

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….

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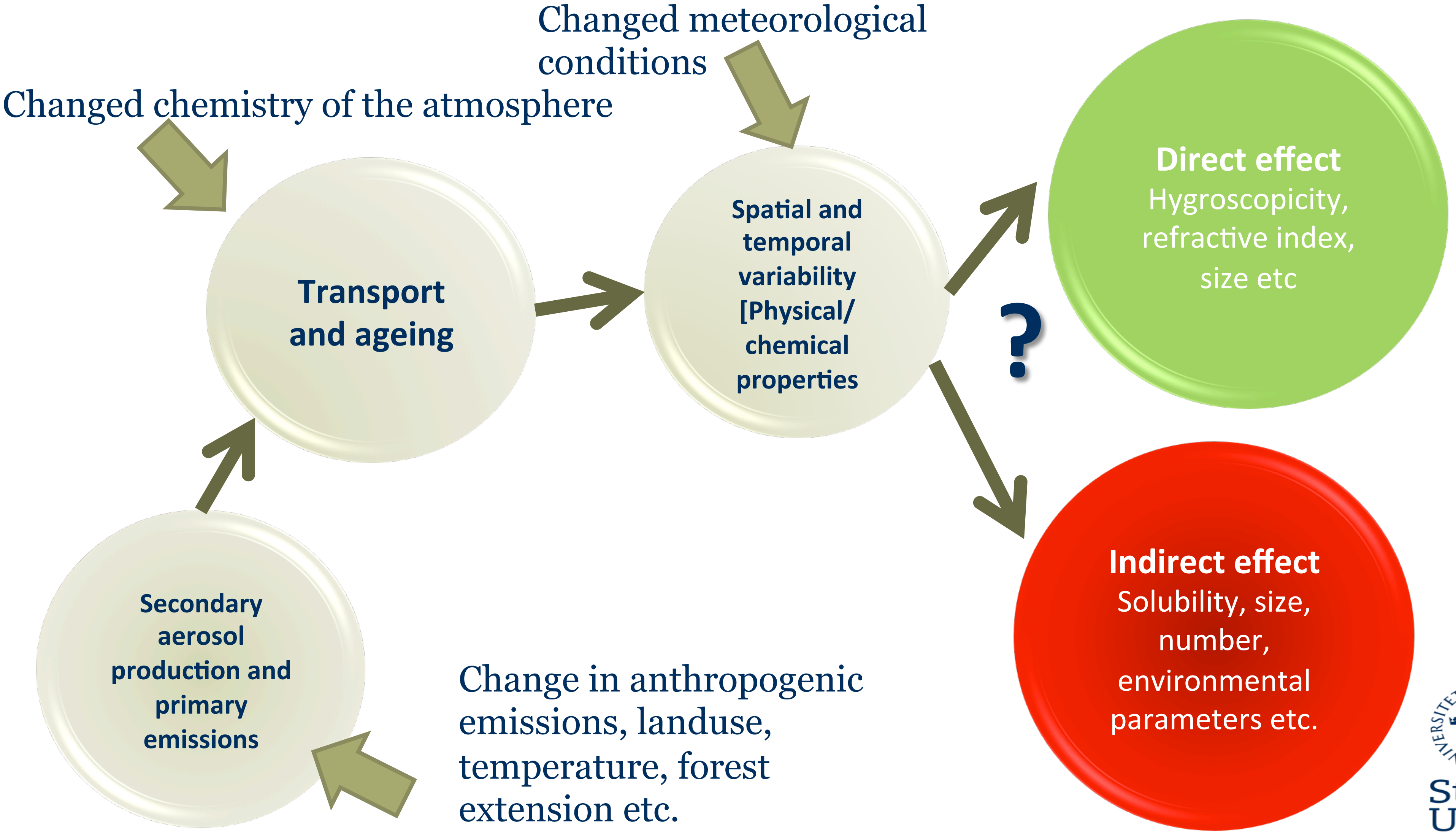
Aerosols and climate in a changing atmosphere: "need-to-knows"



Changed chemistry of the atmosphere

Changed meteorological conditions

Secondary aerosol production and primary emissions

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

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.

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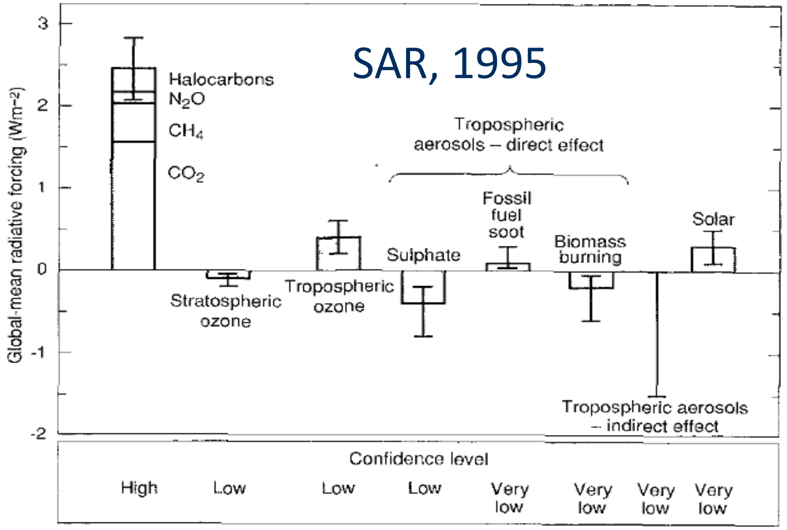
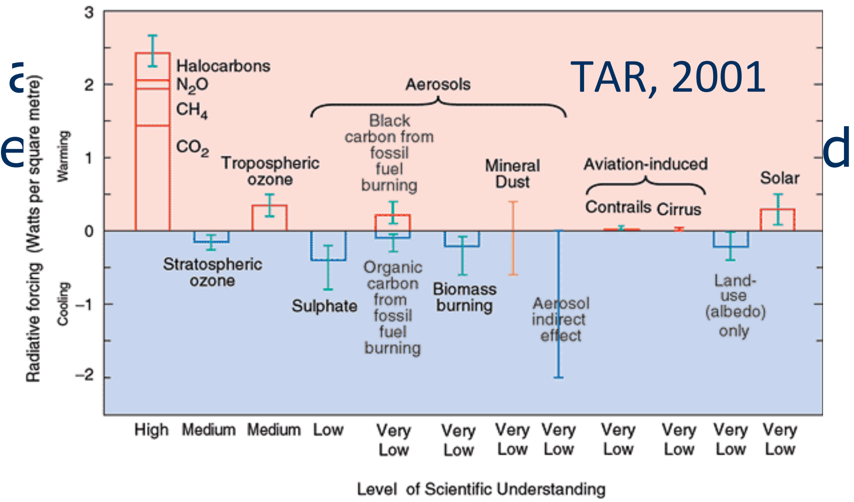
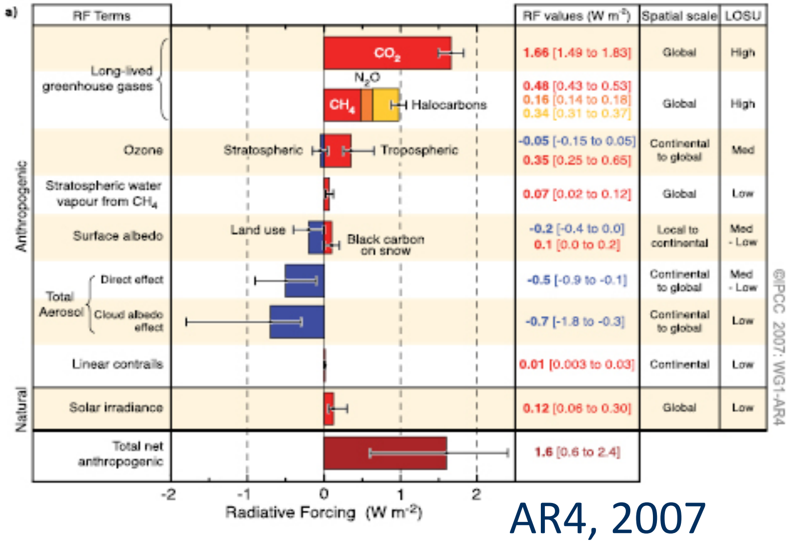
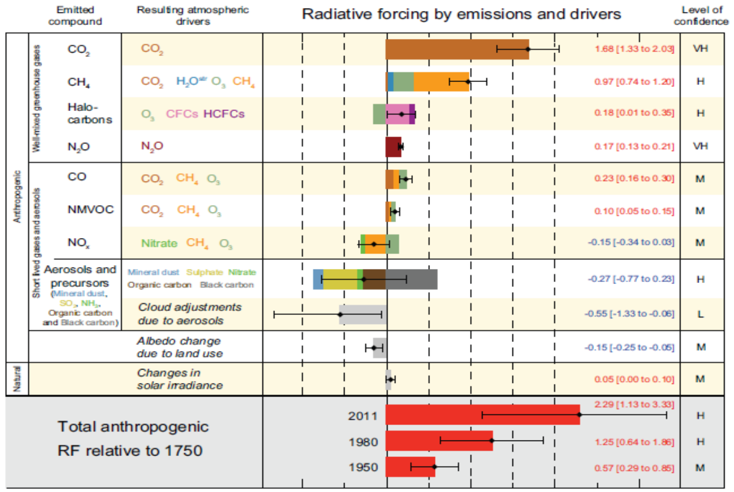
Constraining the aerosol effects







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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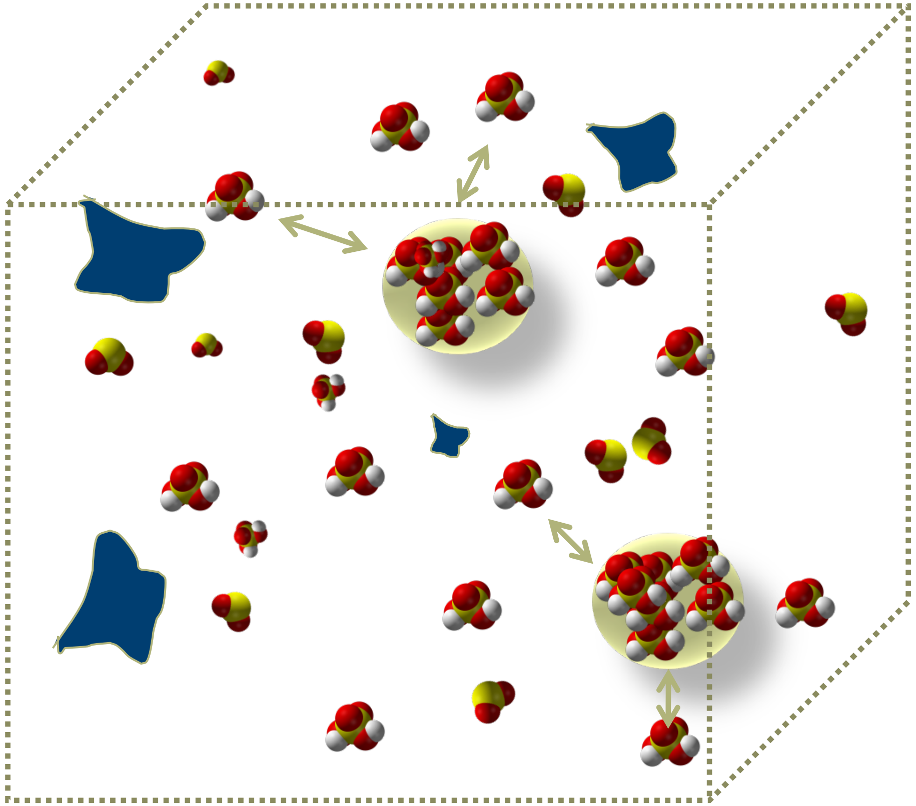
Definition of aerosol



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

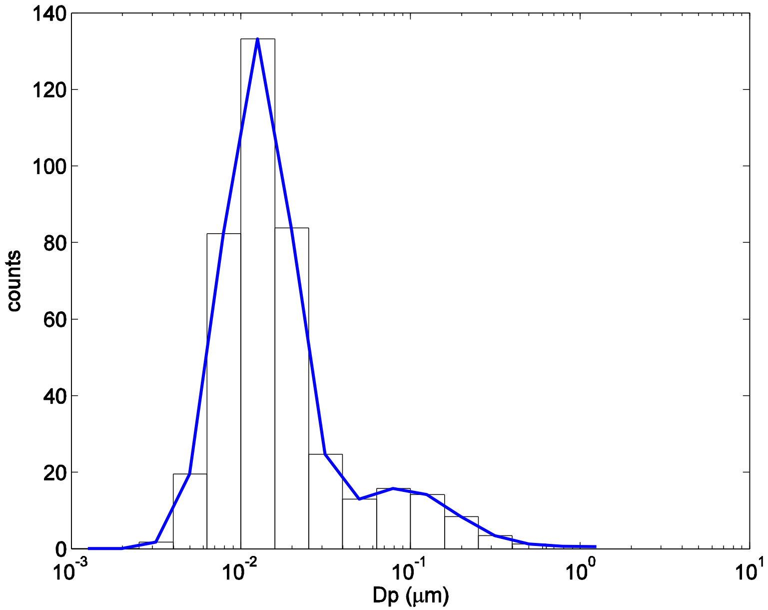
Typical tropospheric liftimes: days-weeks

Observing the aerosol

Mass, number, optical properties, chemical composition

Either as bulk or size distributed

540 cm^{-3} or…



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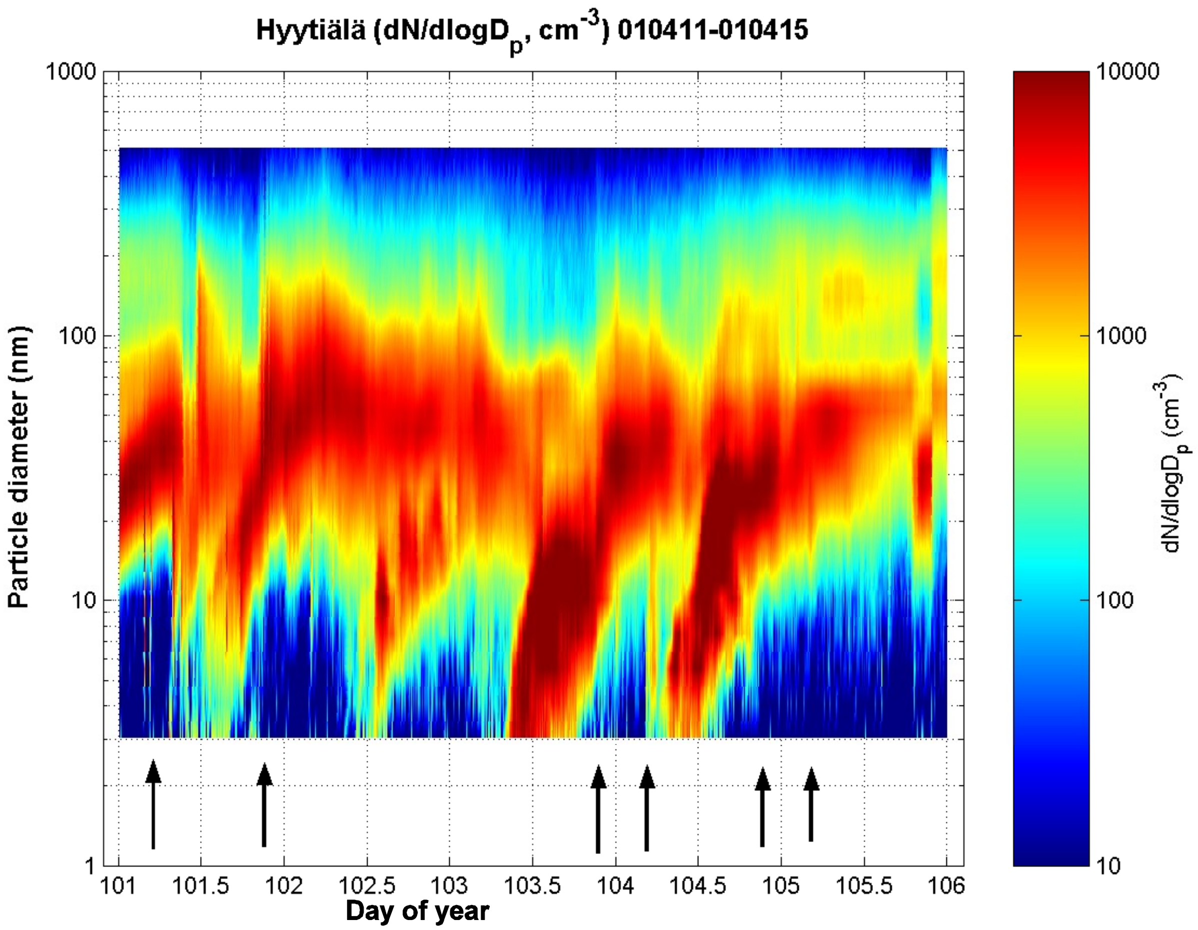
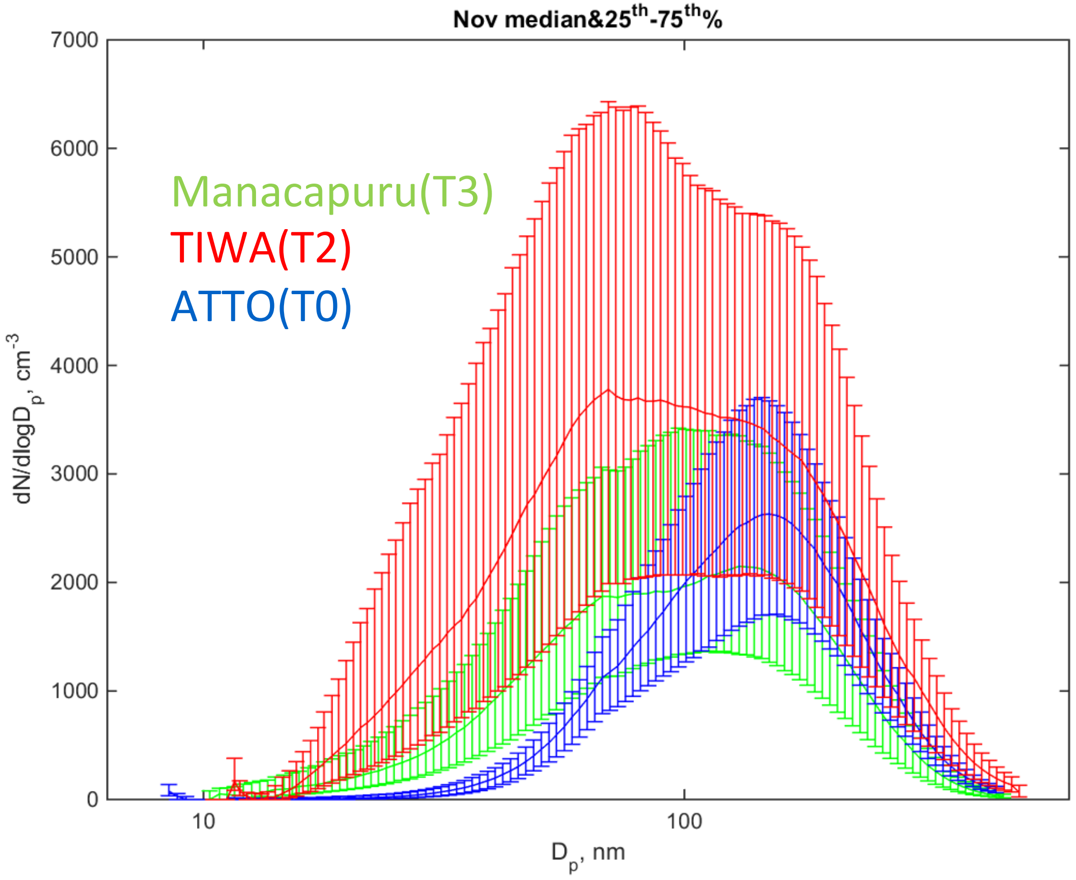
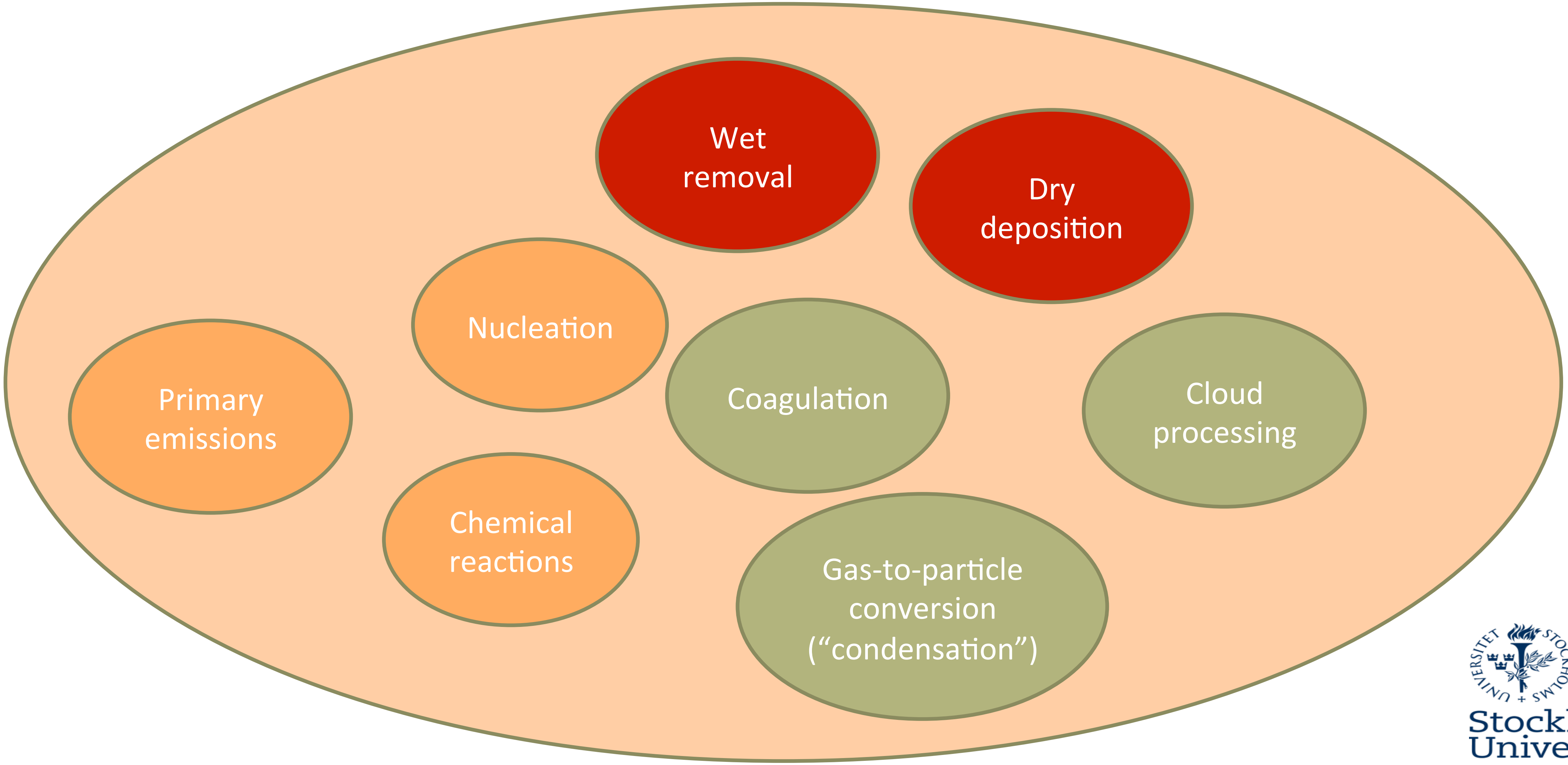
The aerosol is highly variable in space and time





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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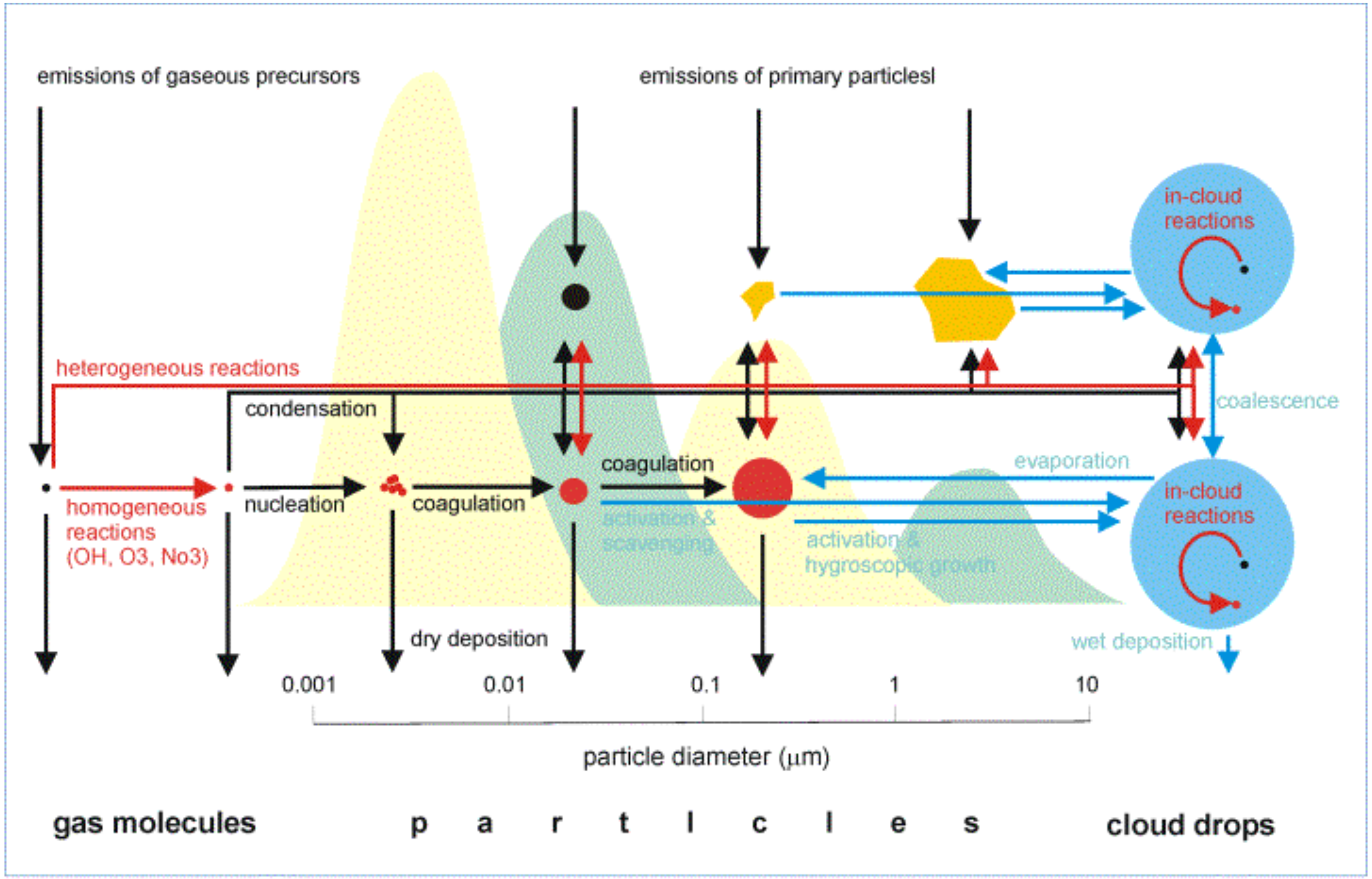
Aerosol processes



Raes et al., Atm. Env., 2000

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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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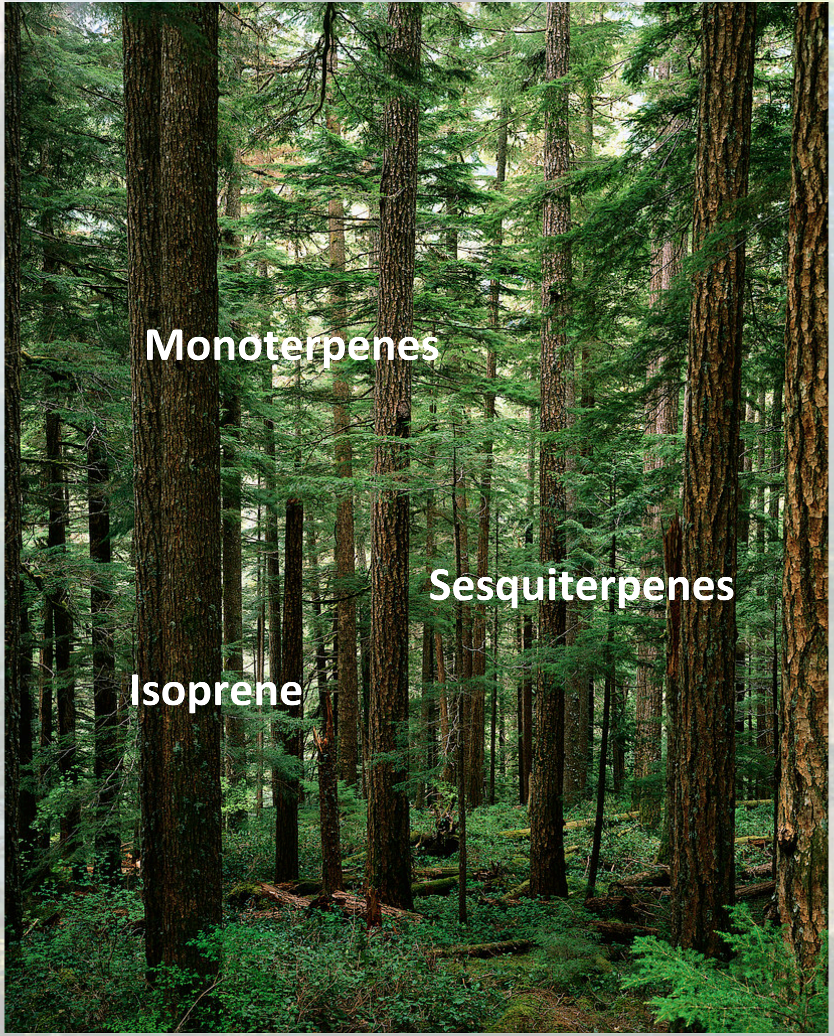
Terpenoids: globally a very important source of secondary aerosols



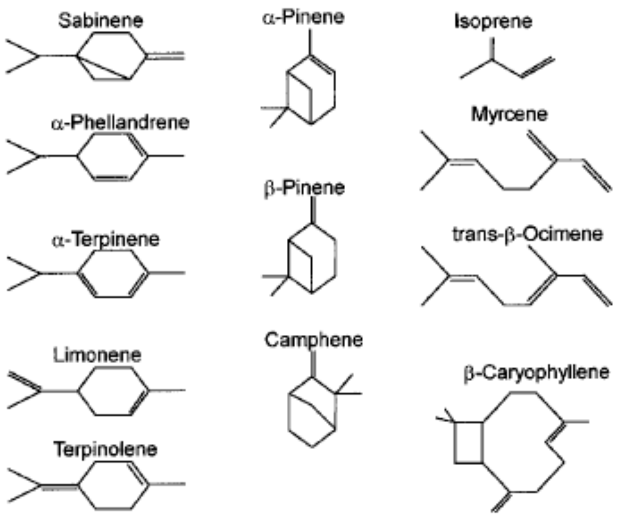
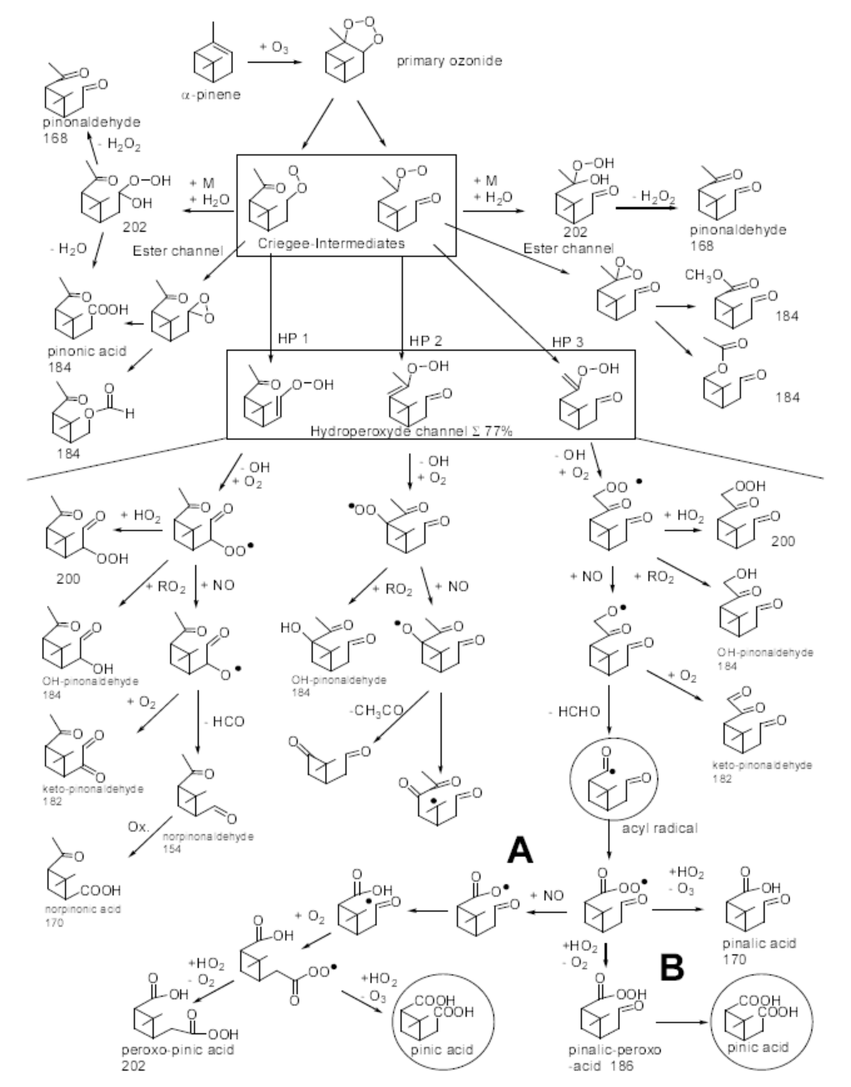


Figure 1. Molecular structures of the volatile hydrocarbons isoprene (C_5), some monoterpenes (C_{10}) and the semivolatile sesquiterpene β-Caryophyllene (C_{15}).

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

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Sinks

Dry deposition

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

Wet deposition

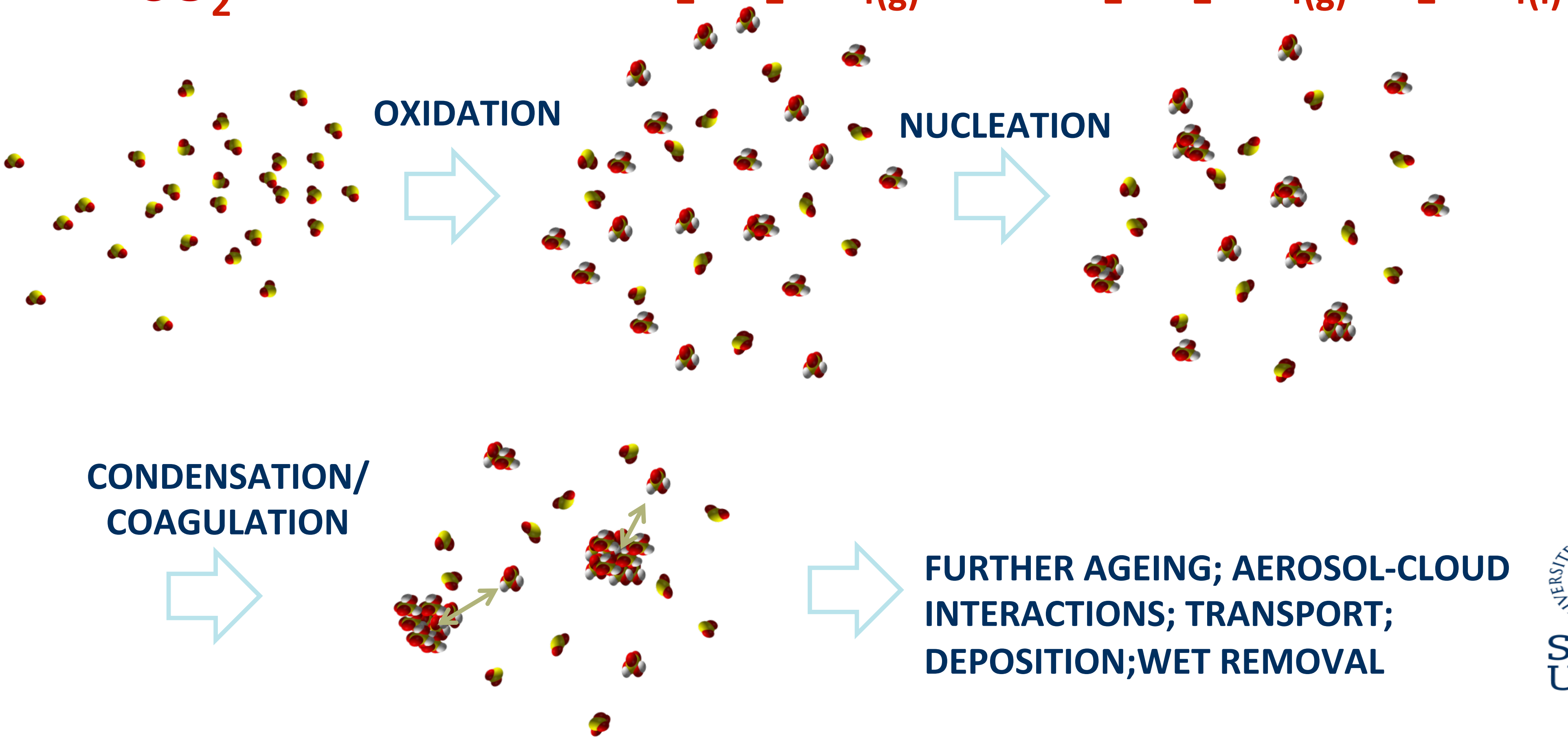
Up-take in cloud droplets (”in-cloud scavenging”), up-take in falling rain droplets (”below-cloud scavenging”)

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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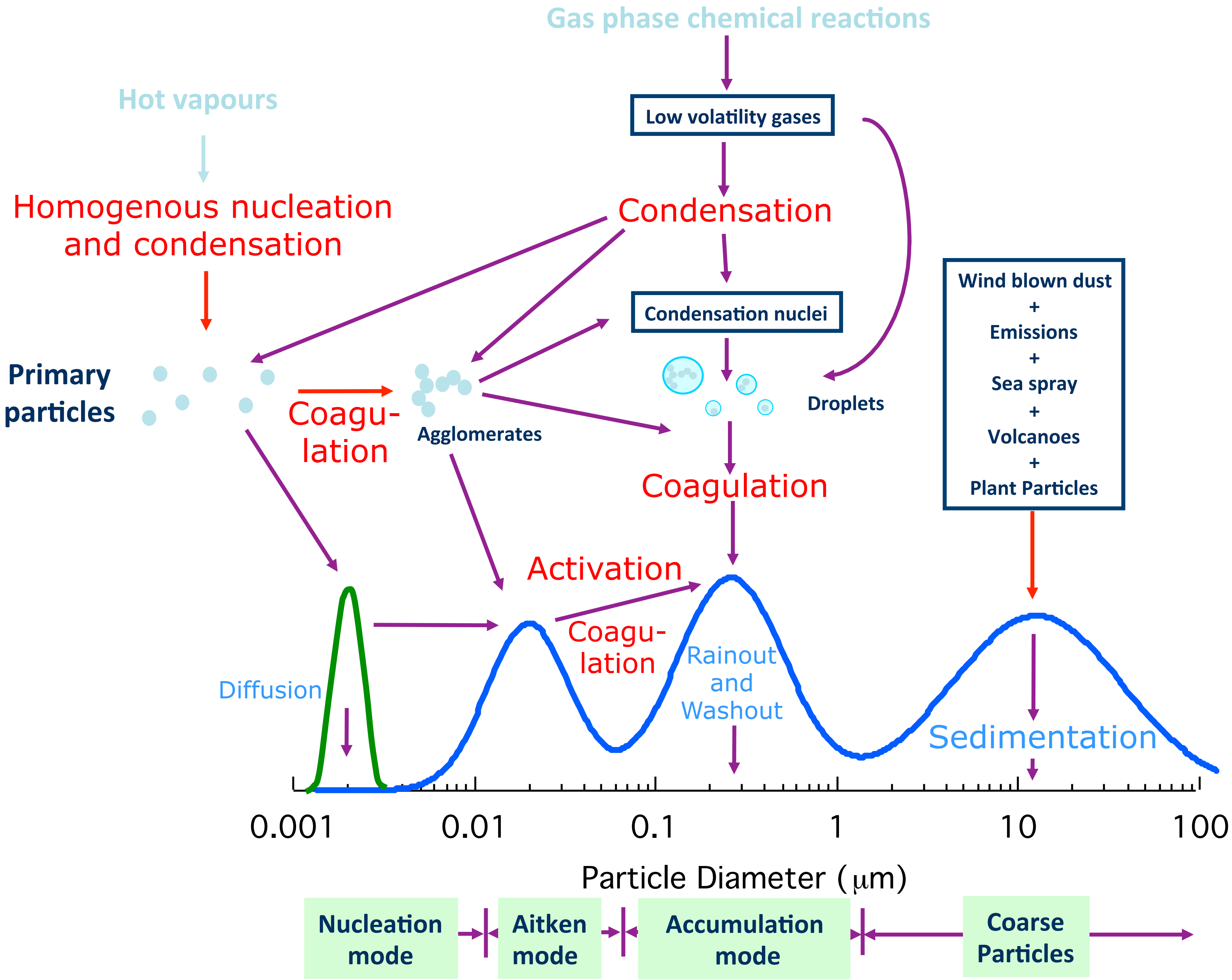

Gas phase chemical reactions

Low volatility gases

Condensation

Condensation nuclei

Droplets

Coagulation

Hot vapours

Homogenous nucleation and condensation

Primary particles

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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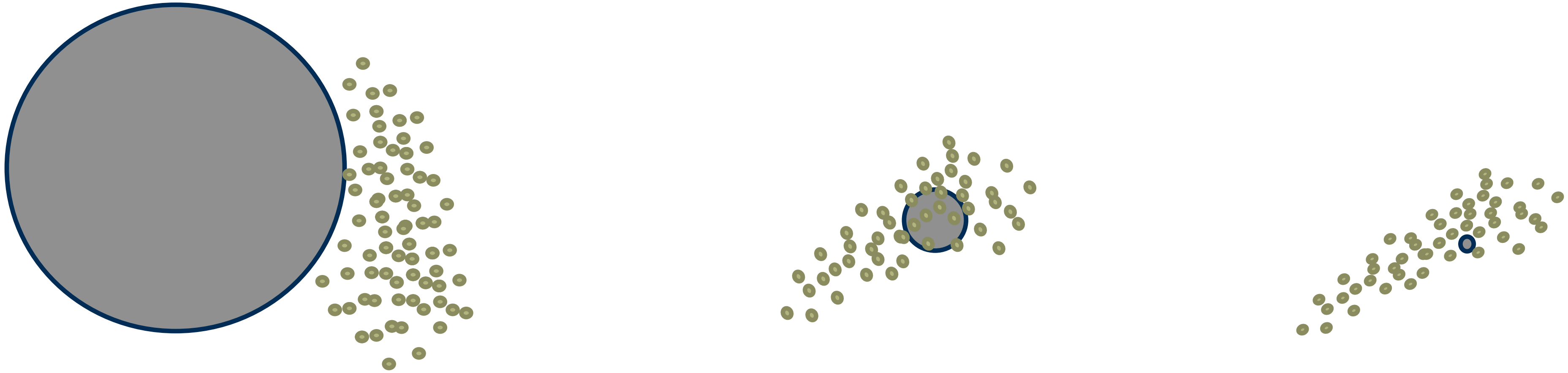
Basic processes acting on single aerosol particles

- Gravitational settling
- Drag force
- Brownian motion

Single particle dynamics and Knudsen number



Continuum regime

$Kn \rightarrow 0$

transition regime

$Kn \approx 1$

Free molecular regime

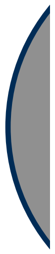
$Kn \rightarrow \infty$

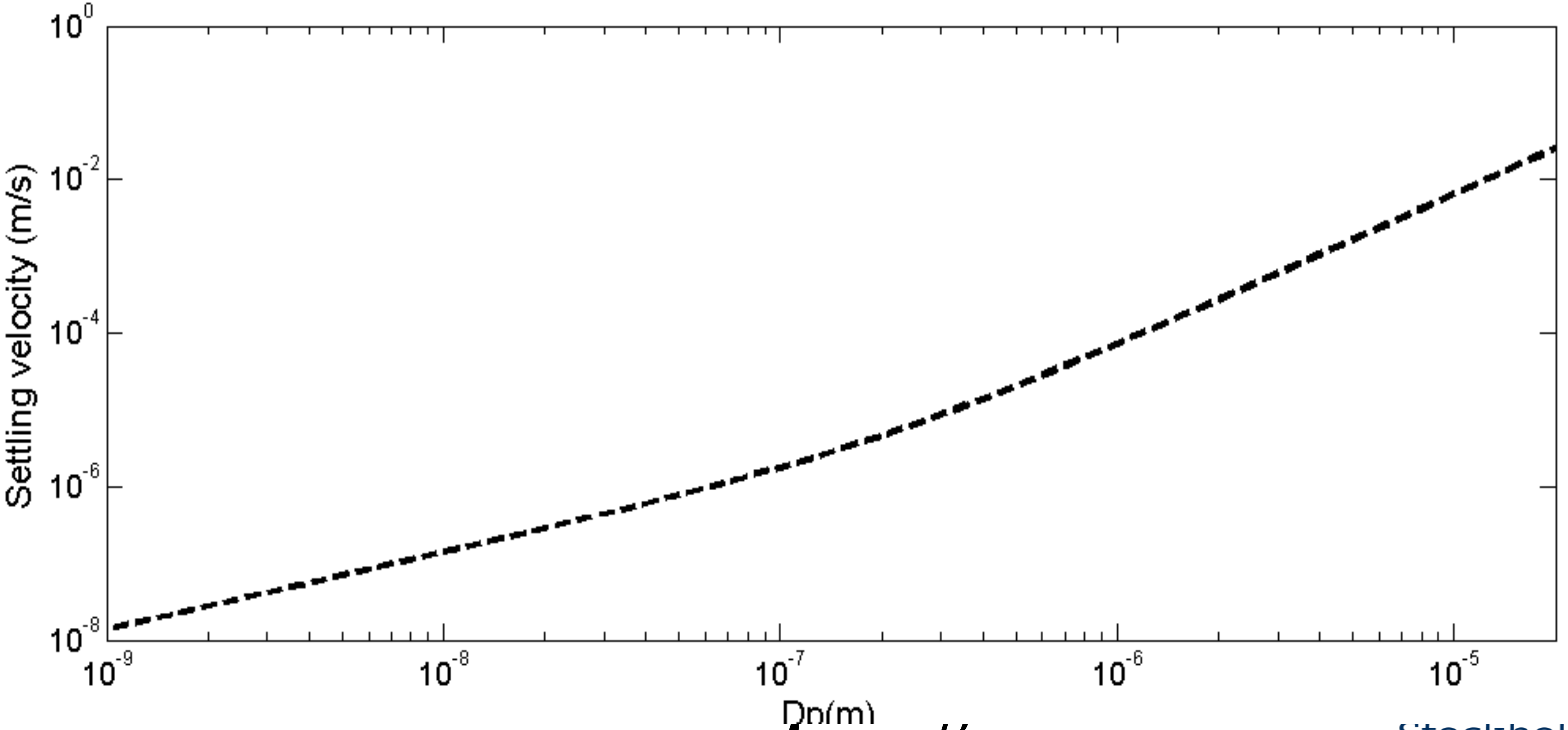
$$Kn = \frac{2\lambda}{D_p}$$

Knudsen number
Where λ is mean free path of air (66nm@293K) and Dp is diameter of particle

Gravitational settling

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





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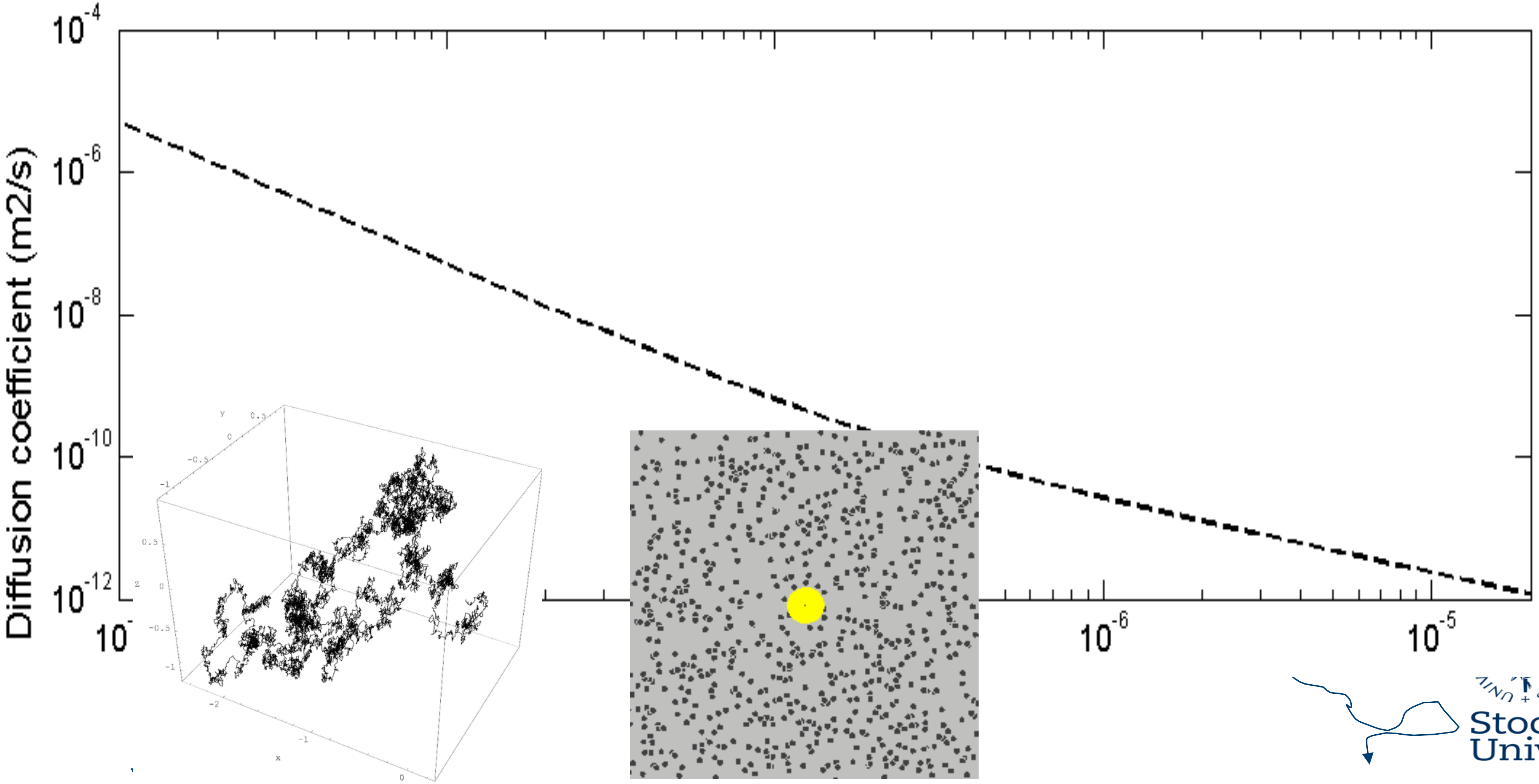
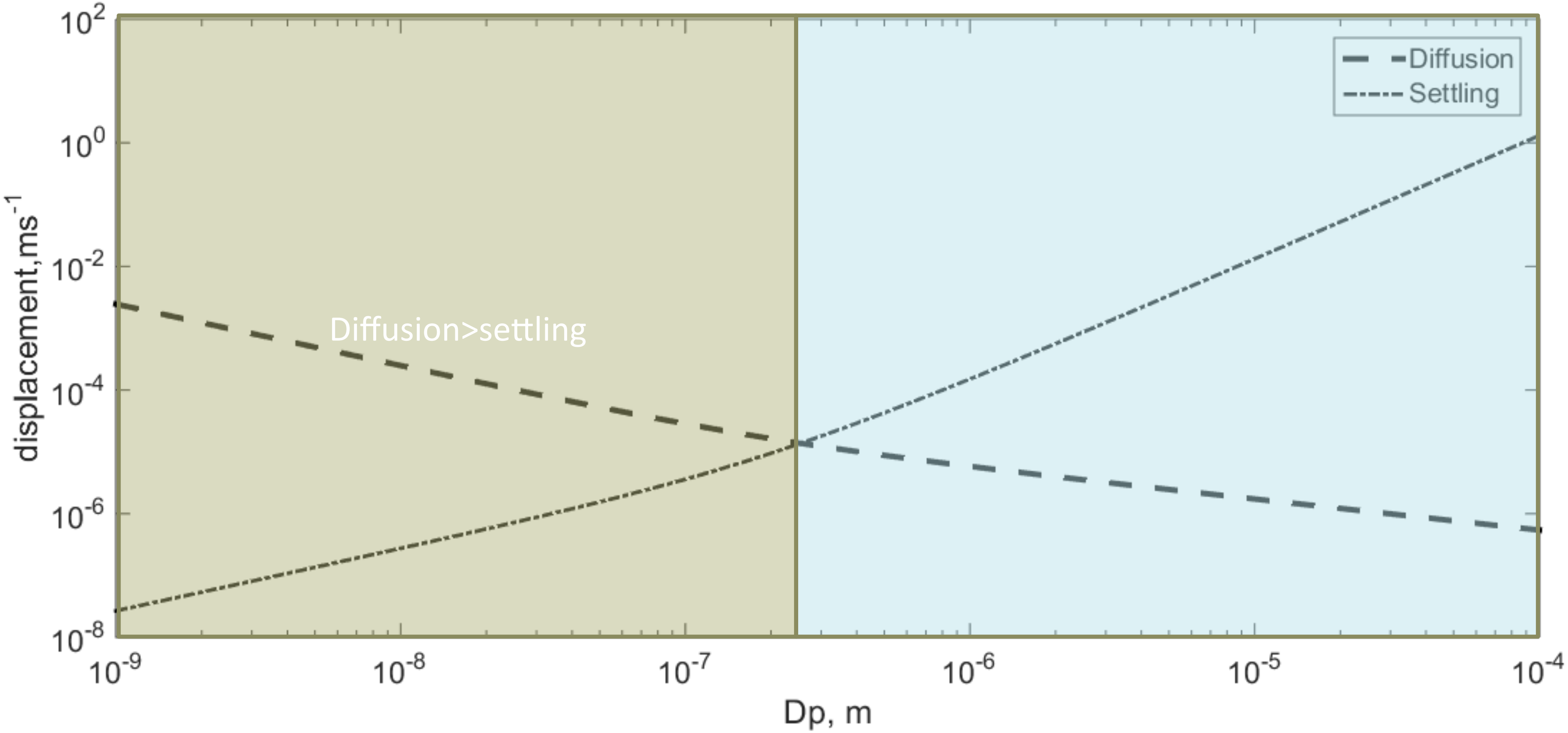
Brownian diffusion



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

$$F=-V_dC$$

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

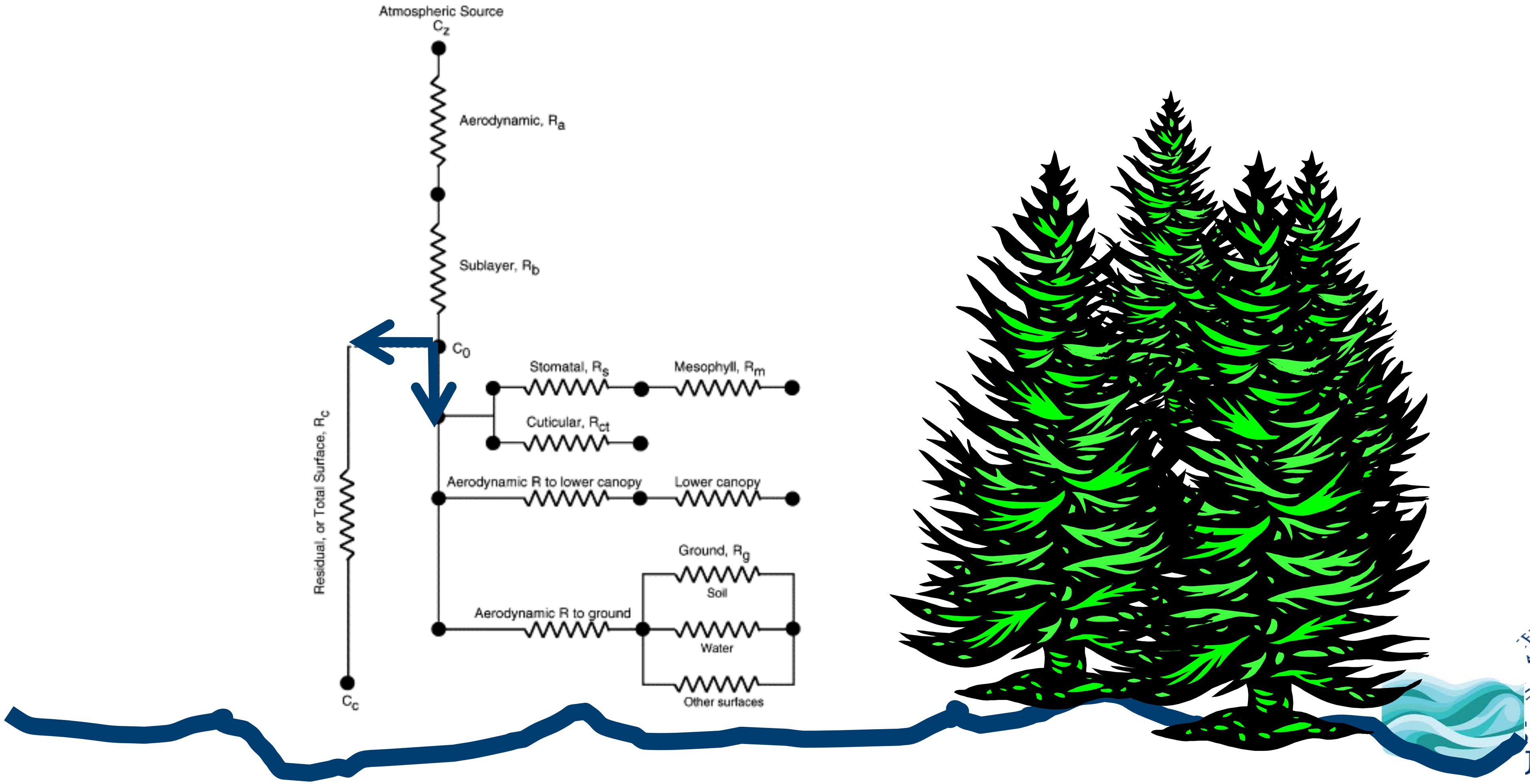
Dry Deposition

Only removal path in the dry atmosphere

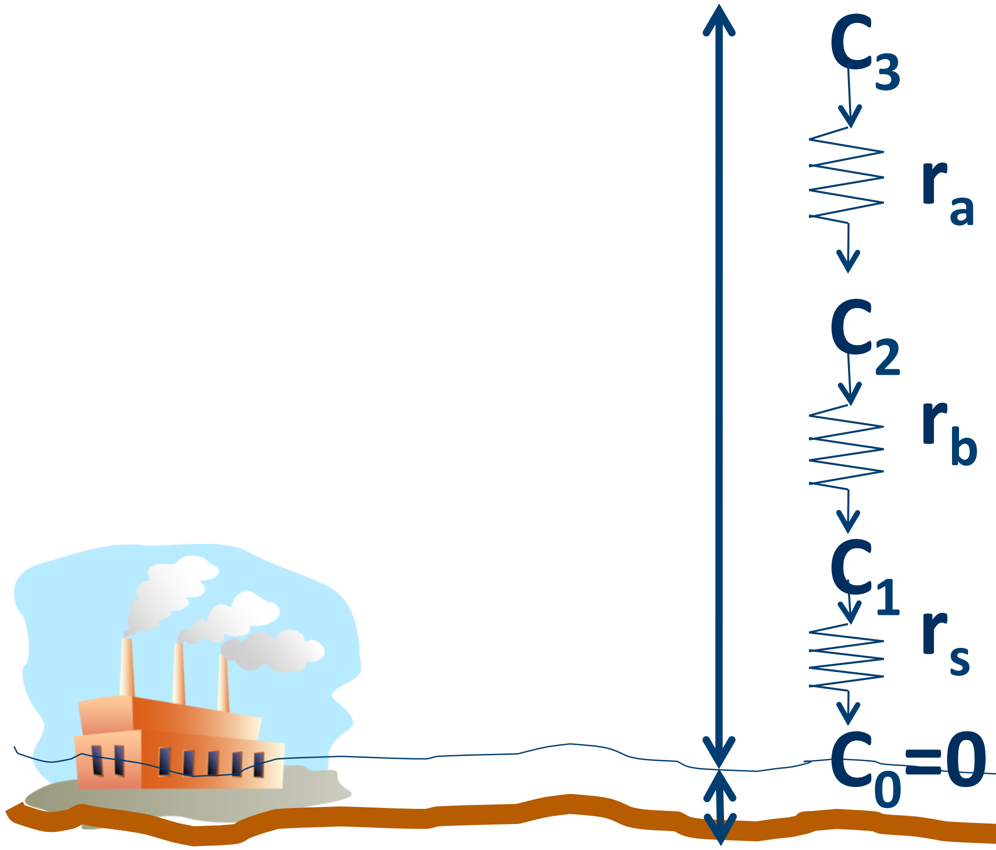
Depends on:

- 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.)

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

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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

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

Turbulent transport

QUASI-LAMINAR RESISTANCE

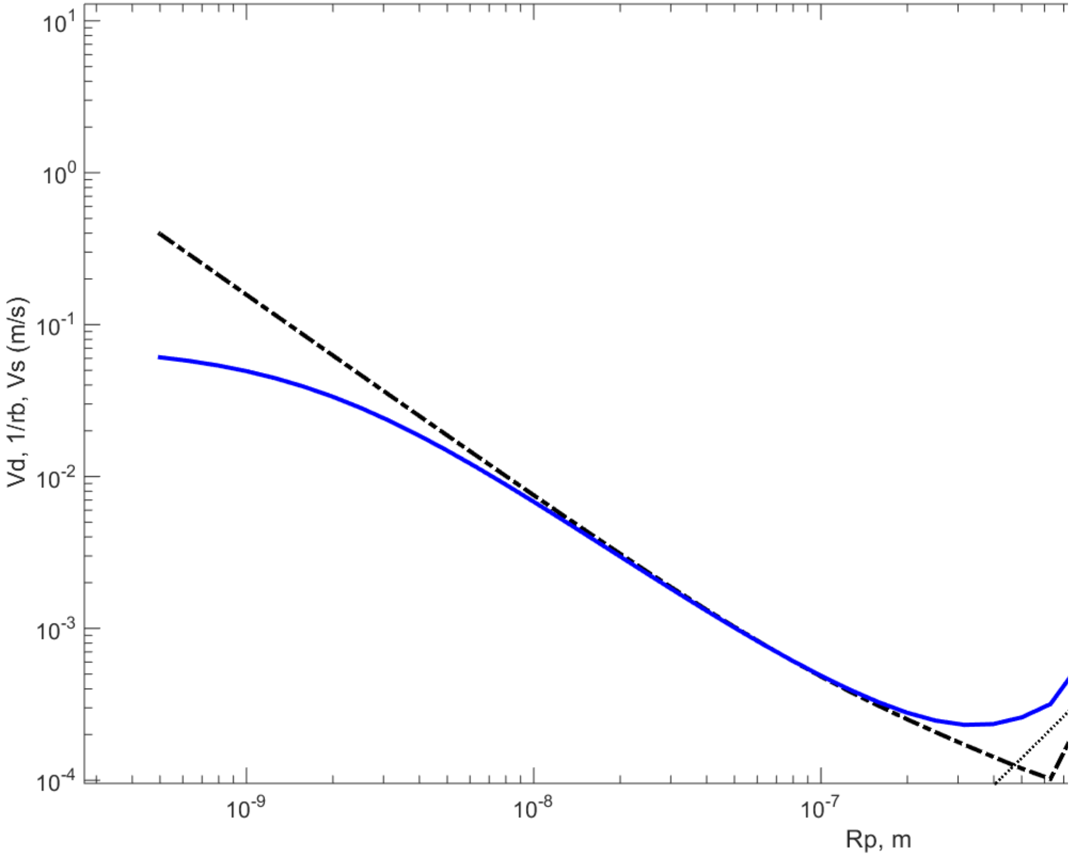
$$r_b = \frac{1}{u*\left(Sc^{-2/3} + 10^{-3/St}\right)}$$

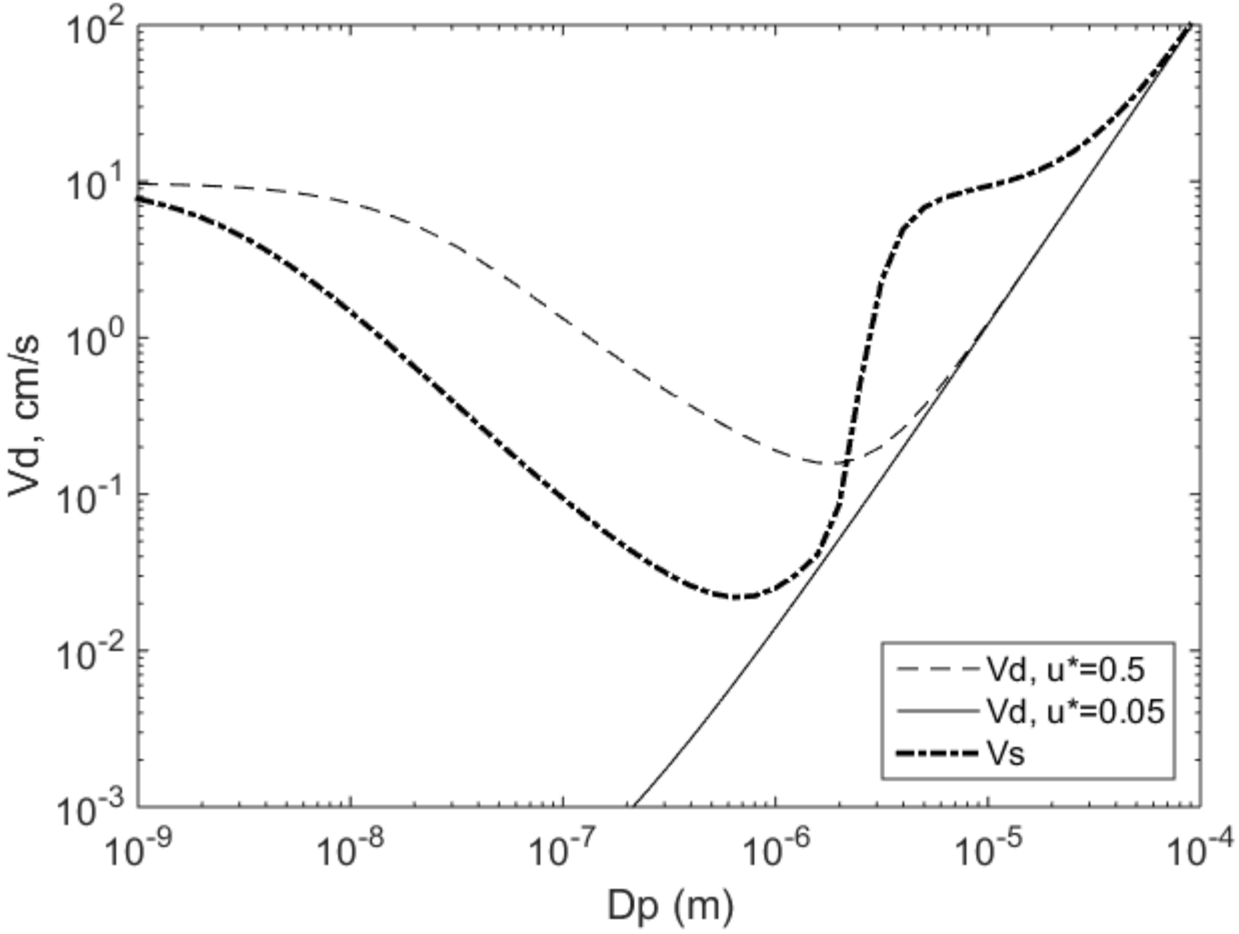
Diffusion

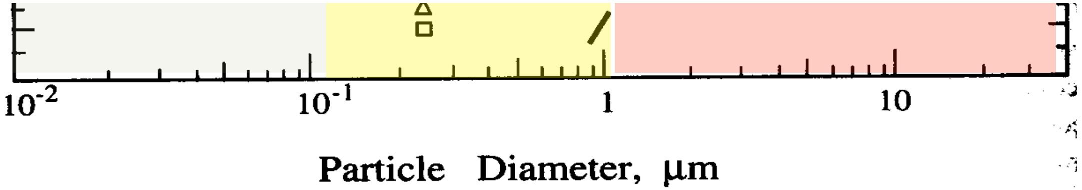
Impaction

$$u^* = friction\ velocity$$

Dry deposition-strongly de







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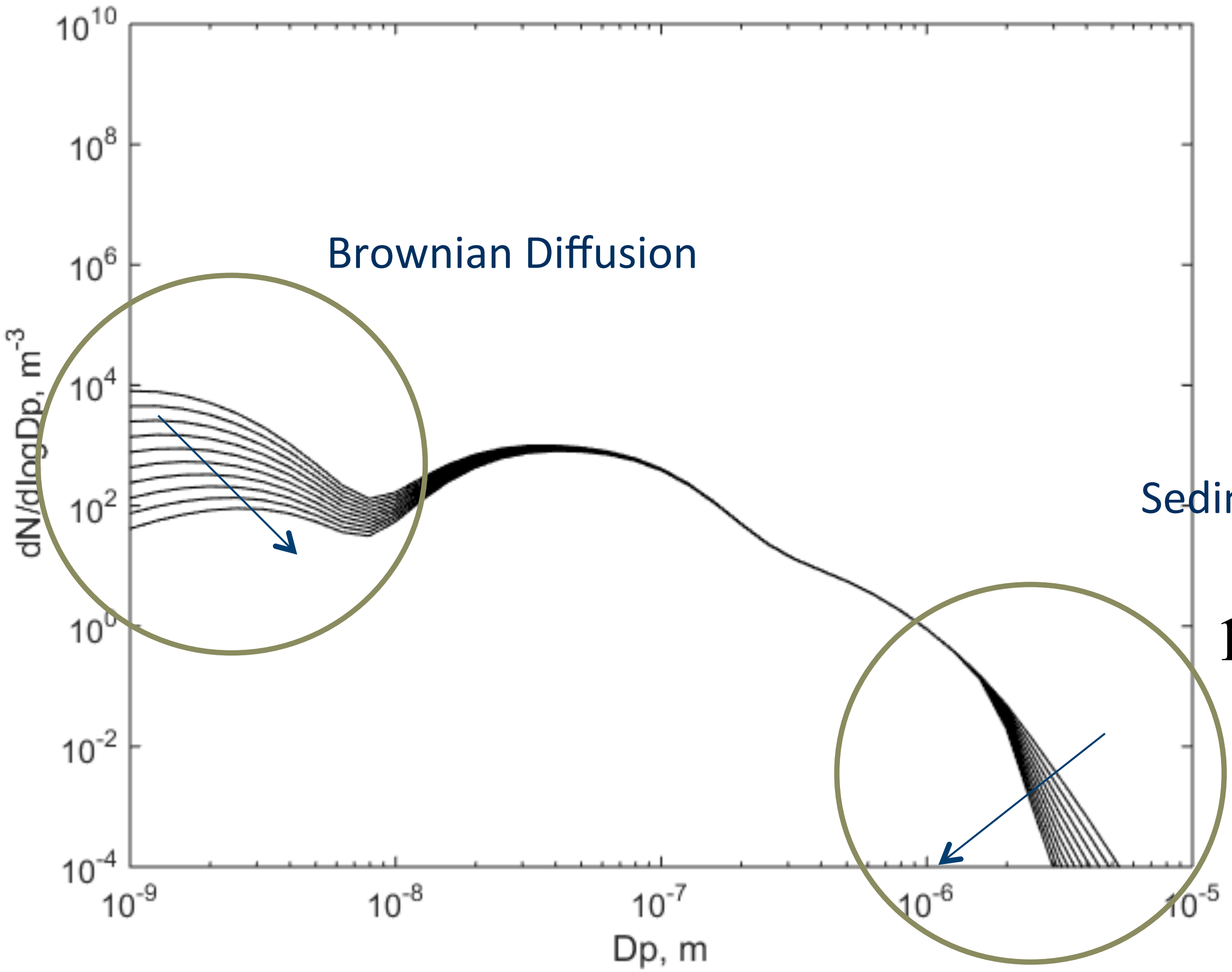
Ageing due to dry deposition

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

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



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

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

Sedimentation, impaction

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

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Coagulation

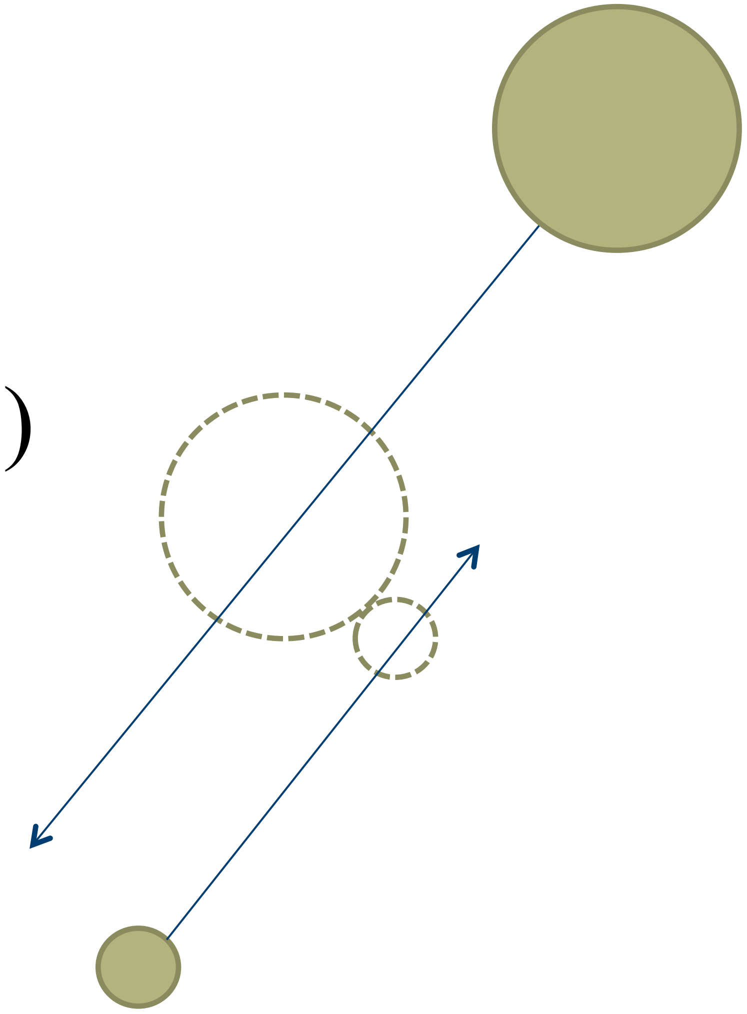
- Mainly the result of Brownian motion, although other forces may come into play (electrical, gravitational etc)
- *Two particles* collide, aggregate and form *one new particle*
- Coagulation does not affect mass, but reduce number
- Most efficient for small particles

Coagulation

- Free molecular regime

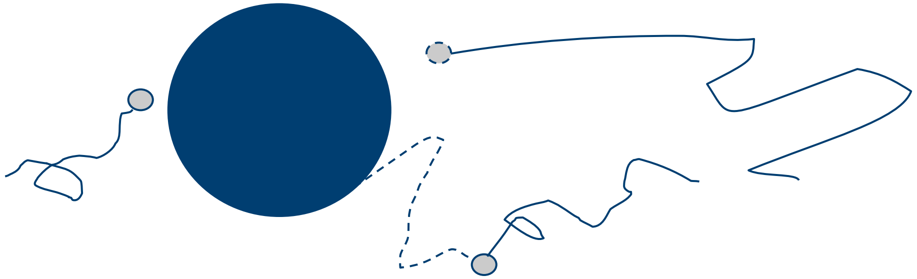
$$RMS = \sqrt{(v_i^{\,2} + v_j^2)}$$

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



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*

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

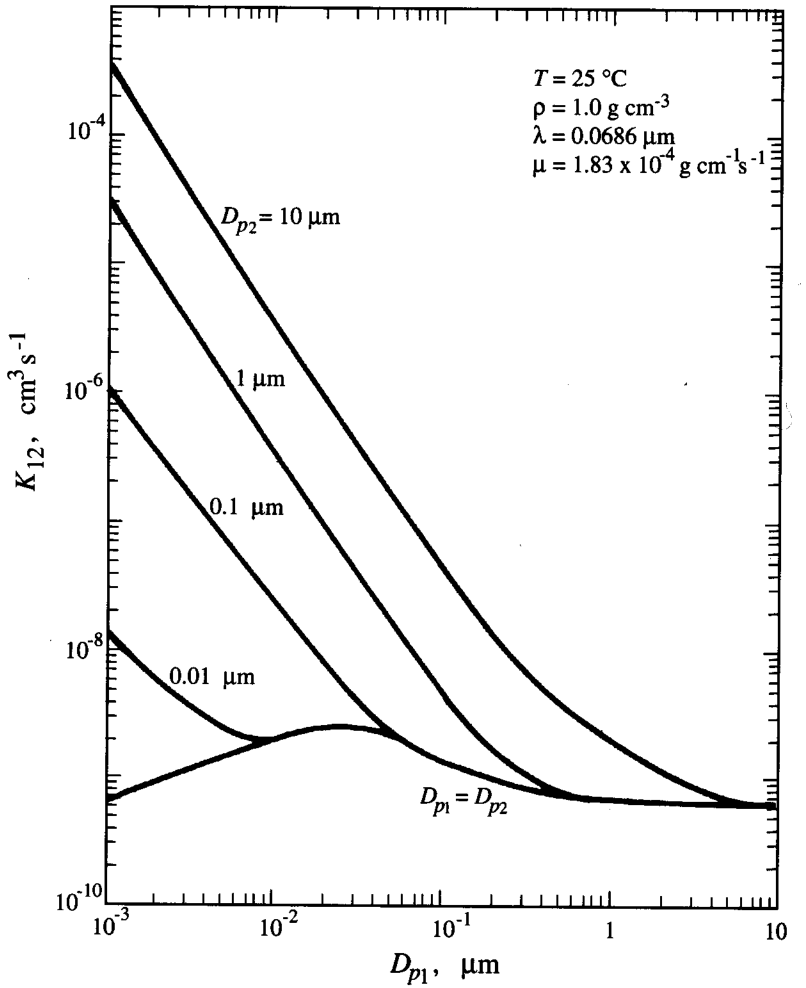
$$K_{12} = 2\pi D_1 D_2 \left(Dp_1 + Dp_2\right)\left(\frac{Dp_1 + Dp_2}{Dp_1 + Dp_2 + 2\left(g_1^2 + g_2^2\right)^{1/2}} + \frac{8\left(D_1 + D_2\right)}{\left(c_1 + c_2\right)^{1/2}\left(Dp_1 + Dp_2\right)}\right)^{-1}$$

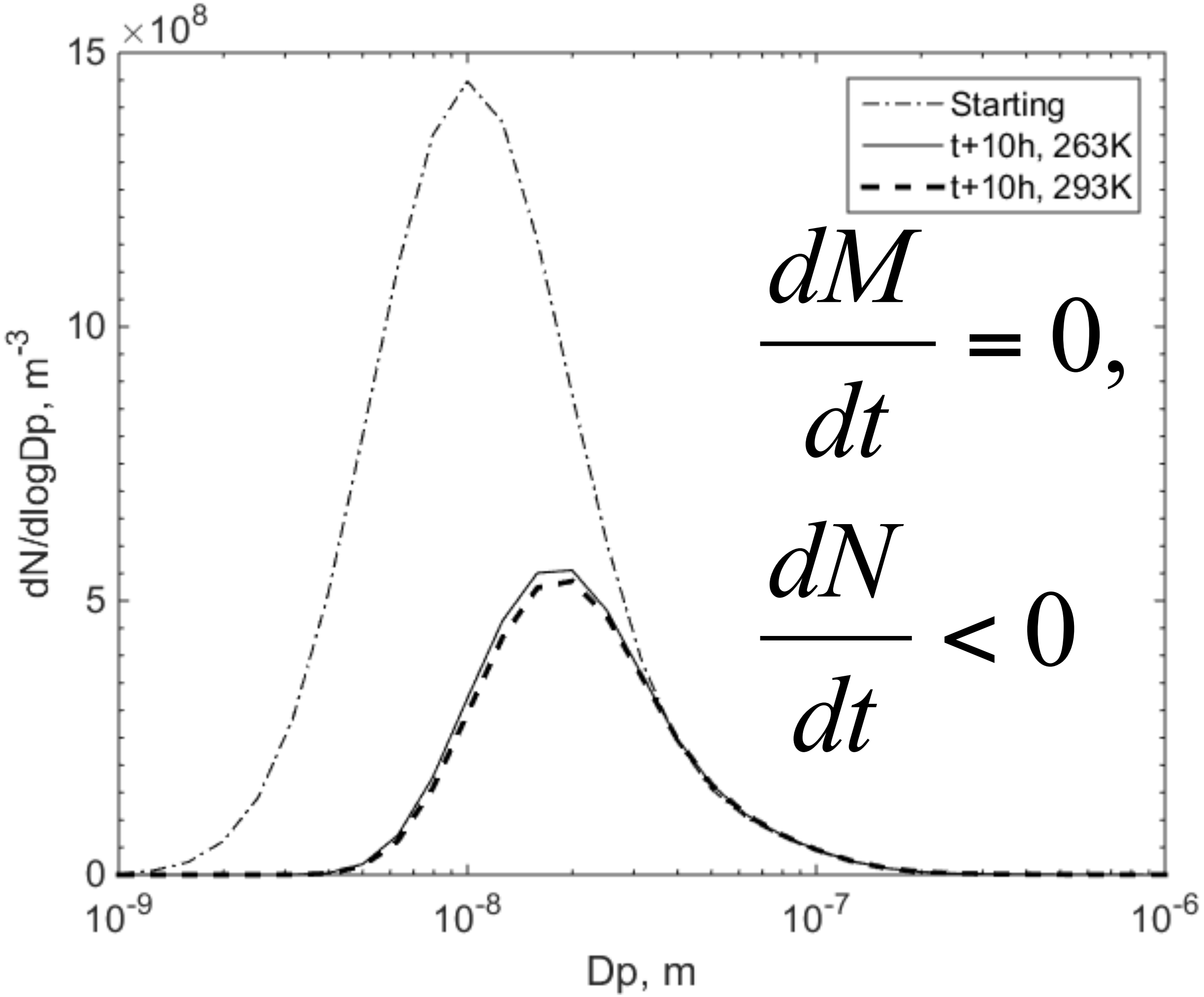
$$D_{1,2} = f\left(T, \frac{1}{Dp}\right)$$

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

$K12=COAG\_COEFF(Dp_{1,} Dp_2, T, P)$

Aerosol dynamics: coagulation

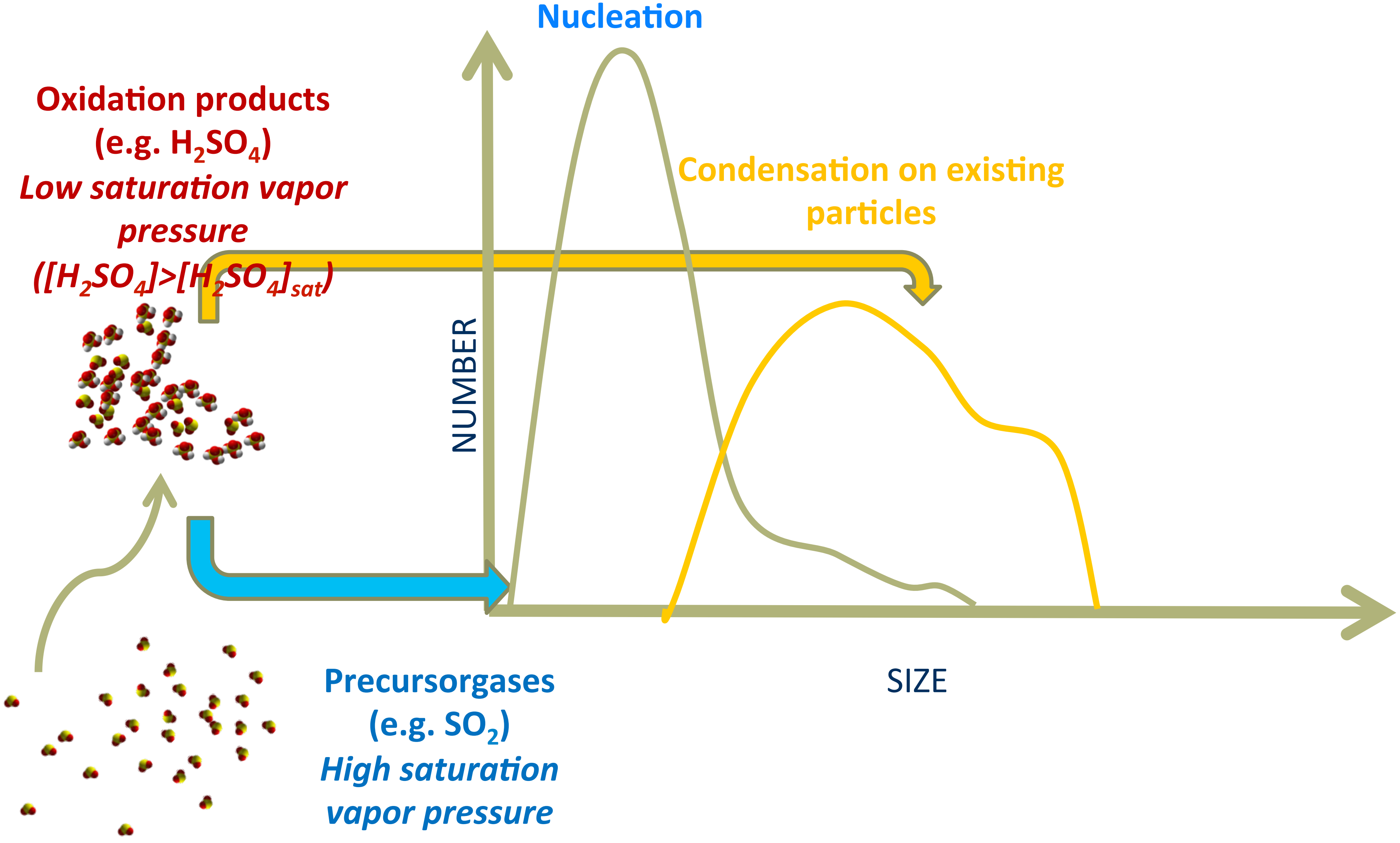




$$\frac{dM}{dt} = 0,$$

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

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

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

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

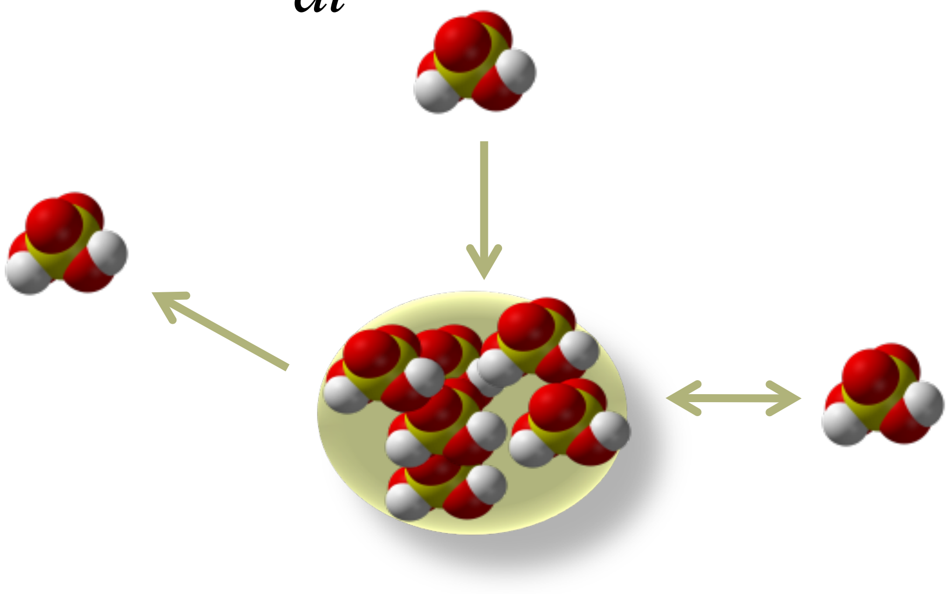
$p_{a=}$partial pressure of a

$p_a{}^s$=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

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

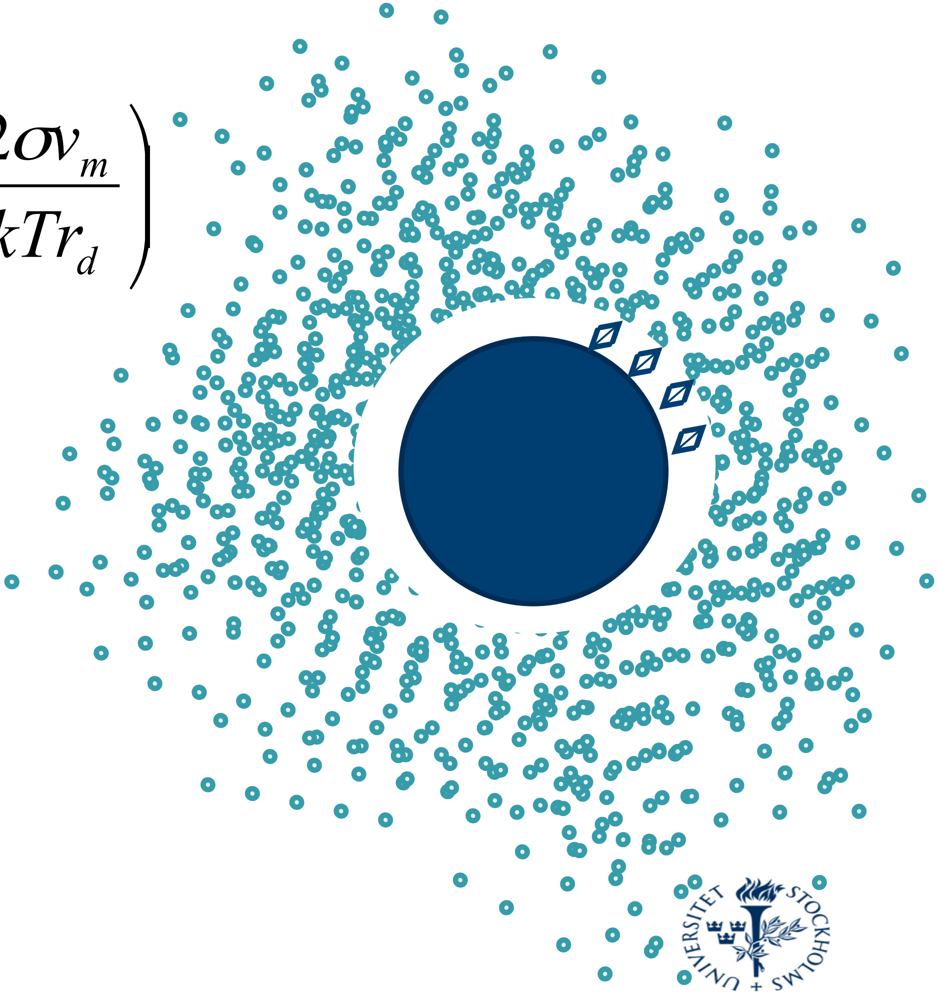
σ = *surface tension*

v_m =*molecular* volume

k=Boltzmanns constant

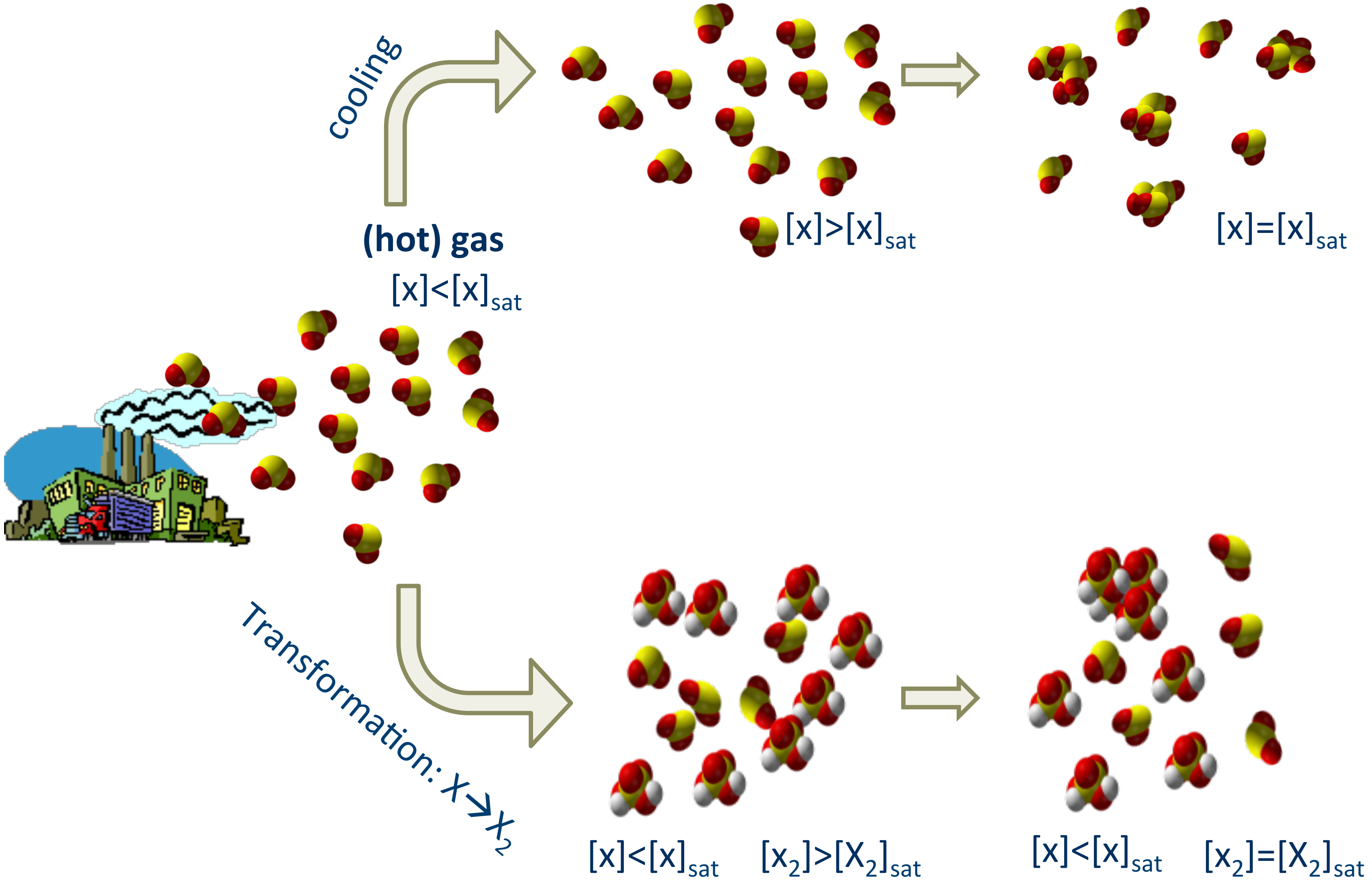
T=Temp

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

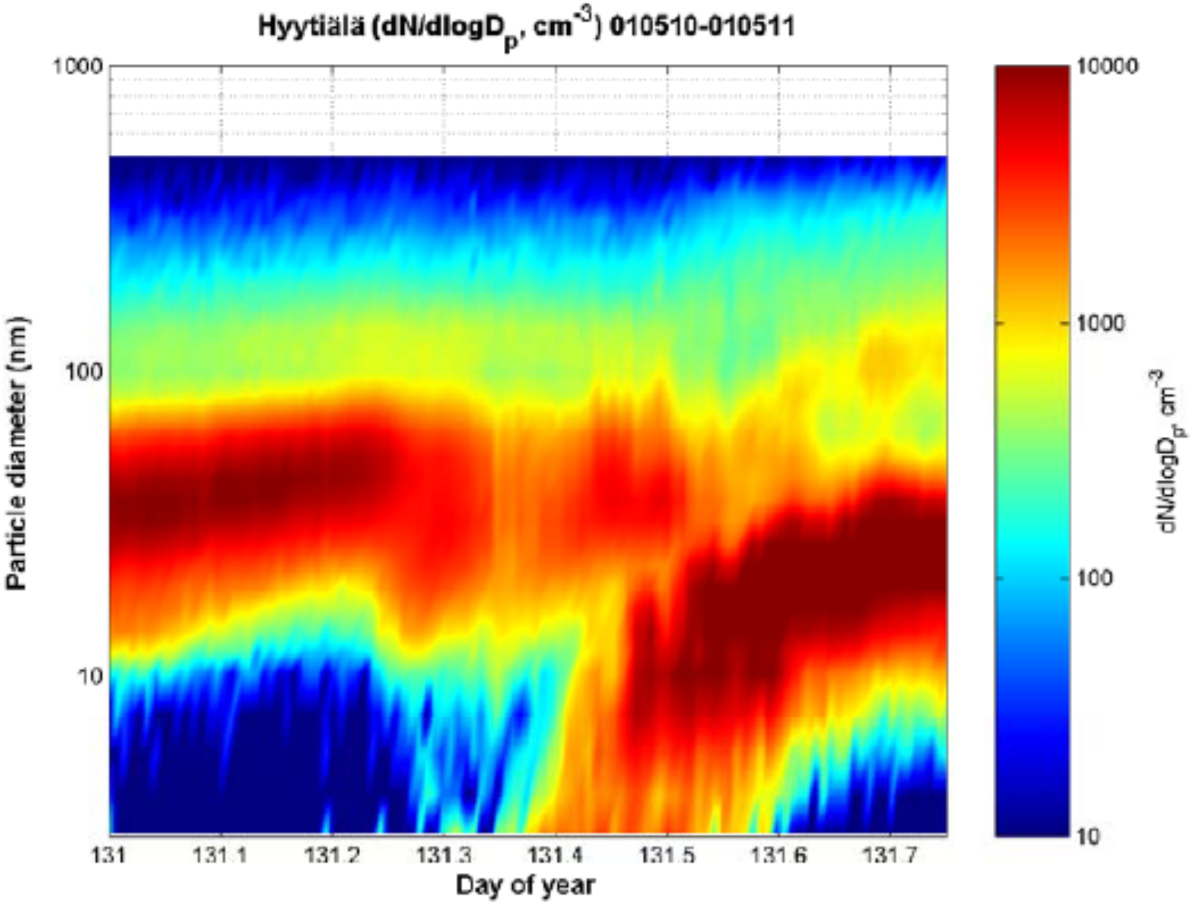

Figure 2: Example of nucleation event observed on 11th May 2001, Hyytiälä (61.51ºN, 24.17ºE).

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

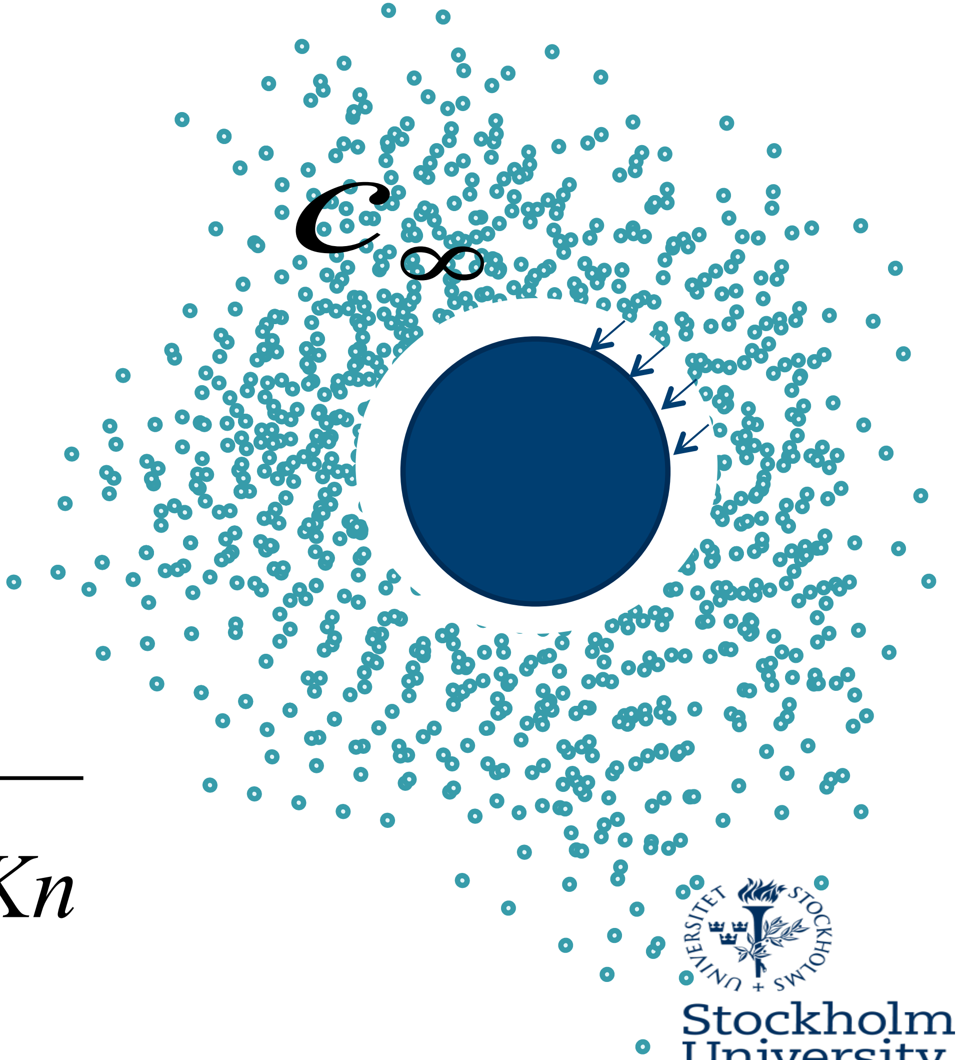
$$\frac{dM}{dt} = 4\pi r_p D_g (c_\infty - c_s)$$

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

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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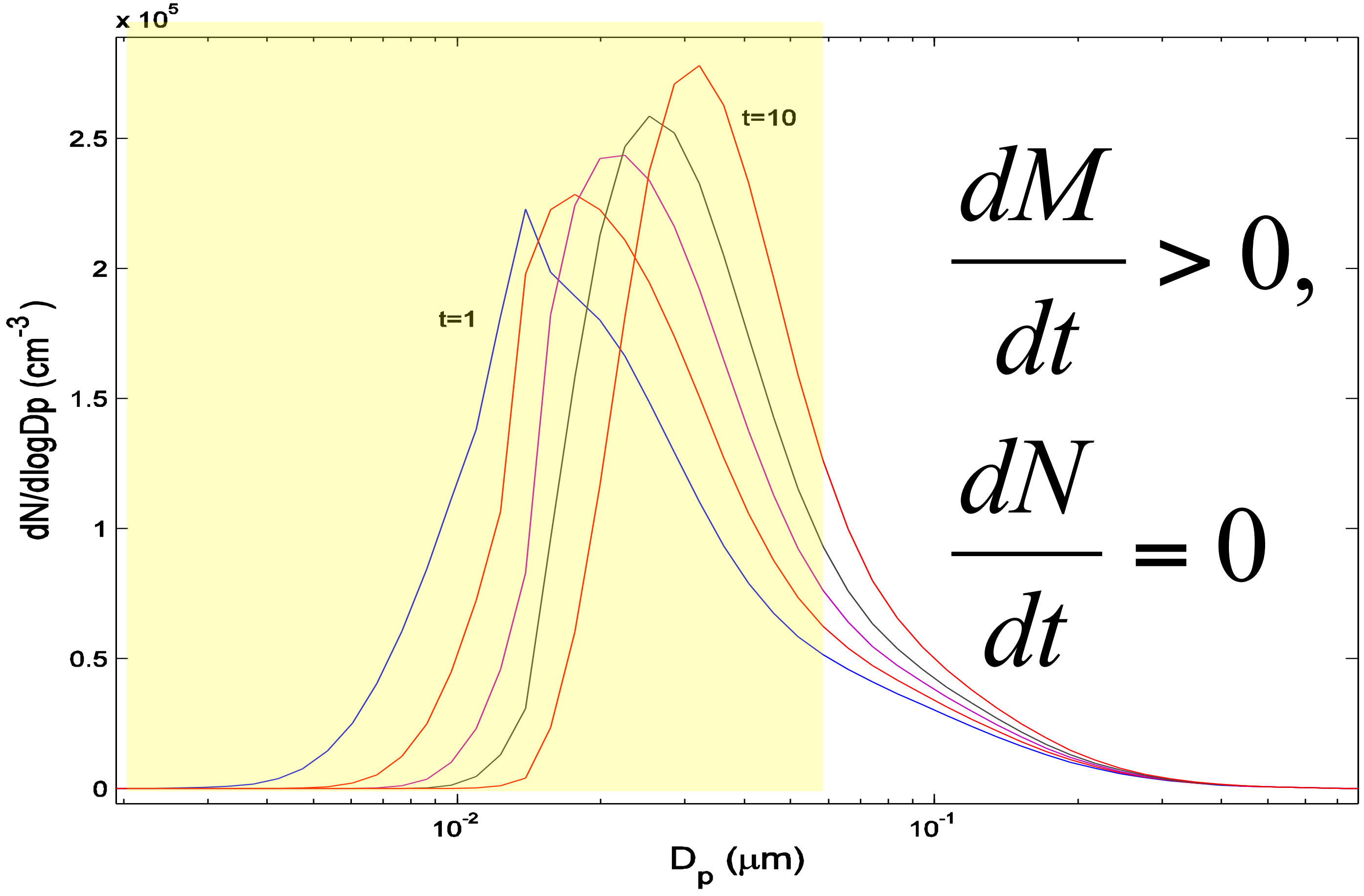
Aerosol dynamics: condensation



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

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

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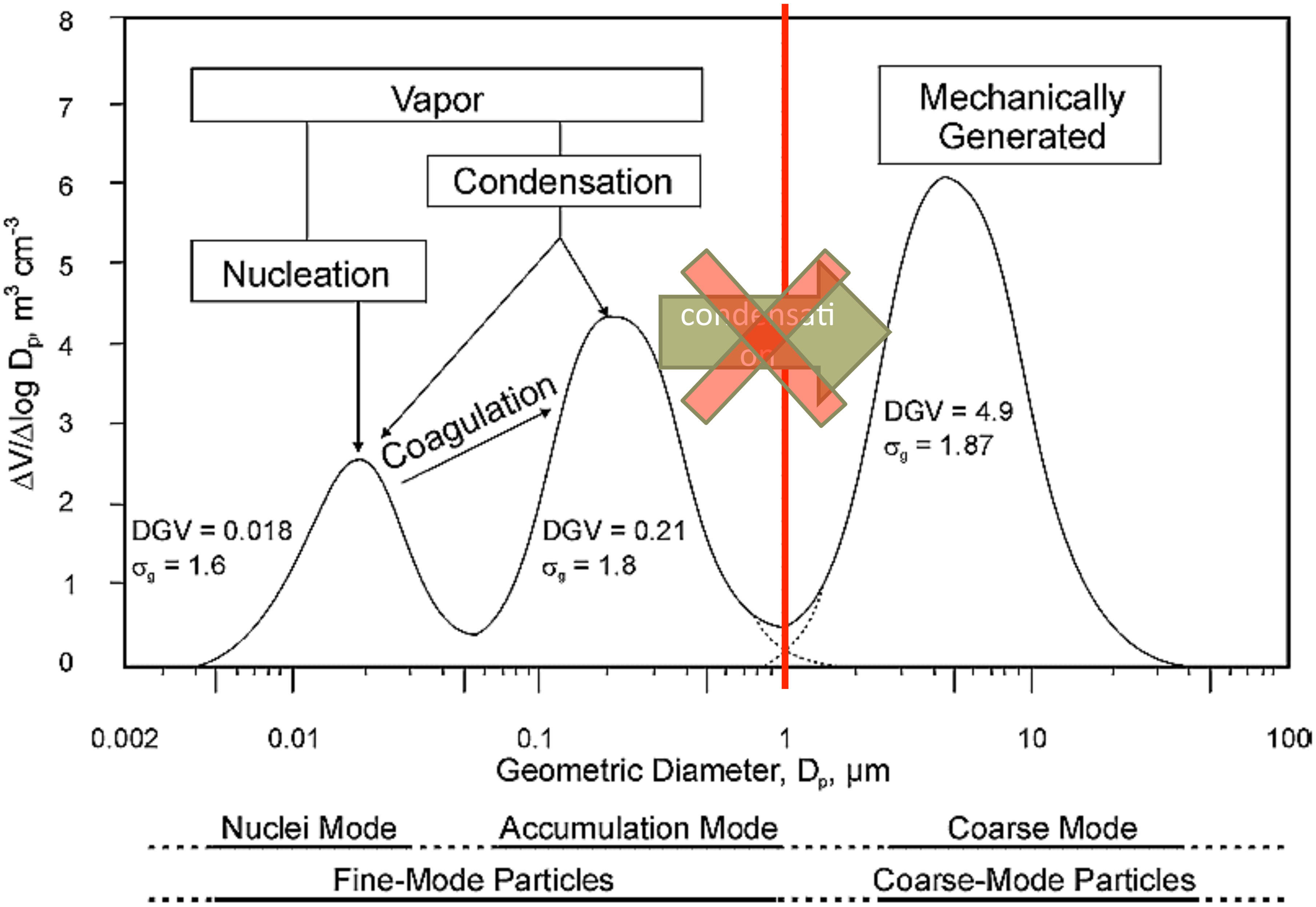

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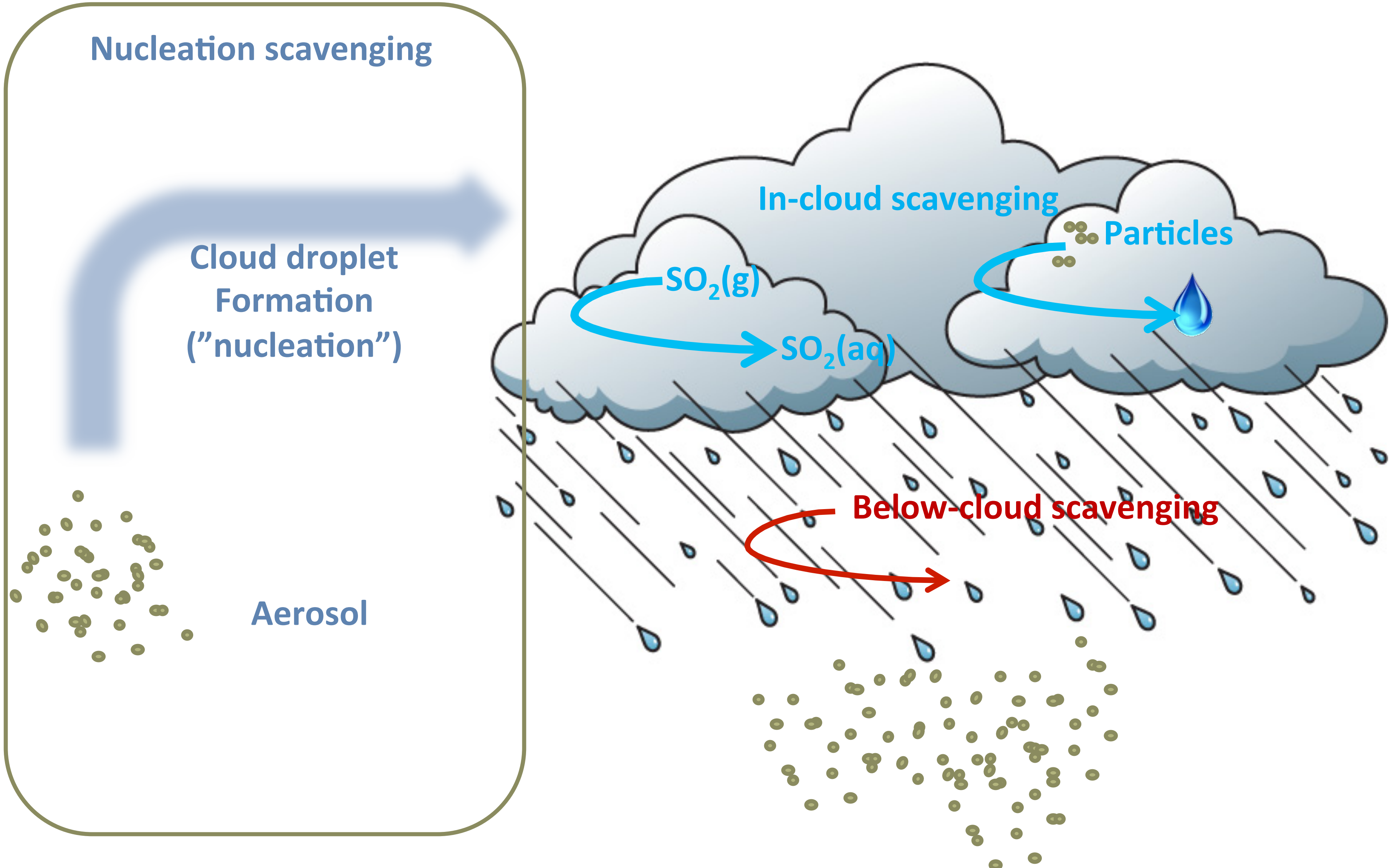
Wet depositon



Nucleation scavenging

Cloud droplet
Formation
(”nucleation”)

Aerosol

In-cloud scavenging

$SO_2(g)$

$SO_2(aq)$

Particles

Below-cloud scavenging

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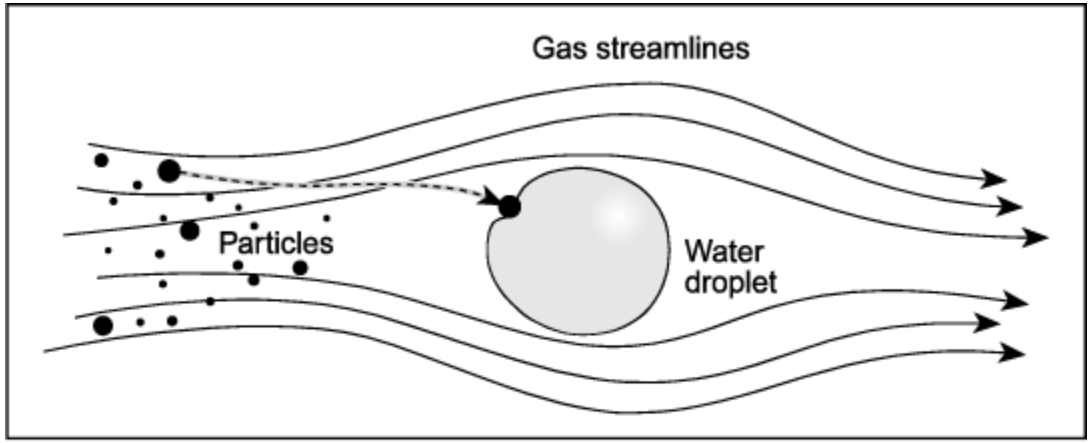
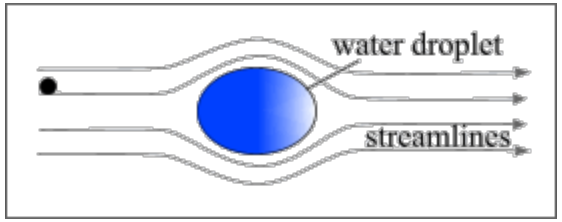
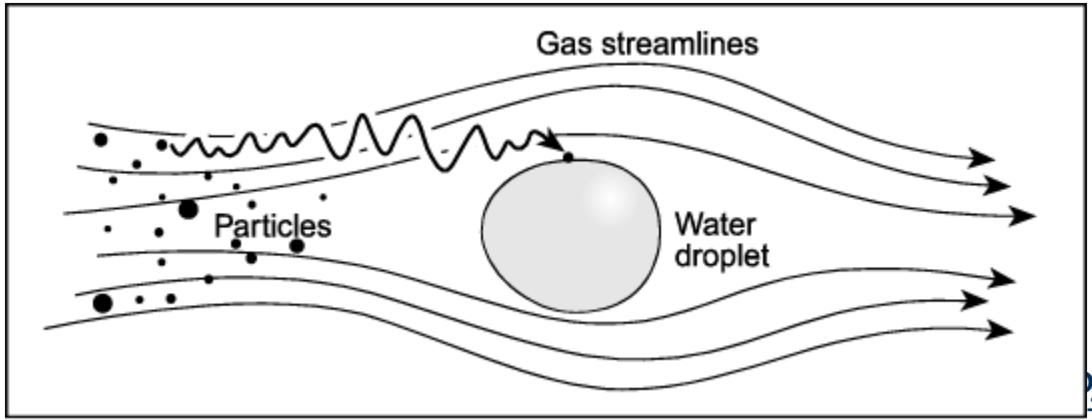
Scavenging of aerosols: Impaction, diffusion and interception







Below cloud scavengning of particles

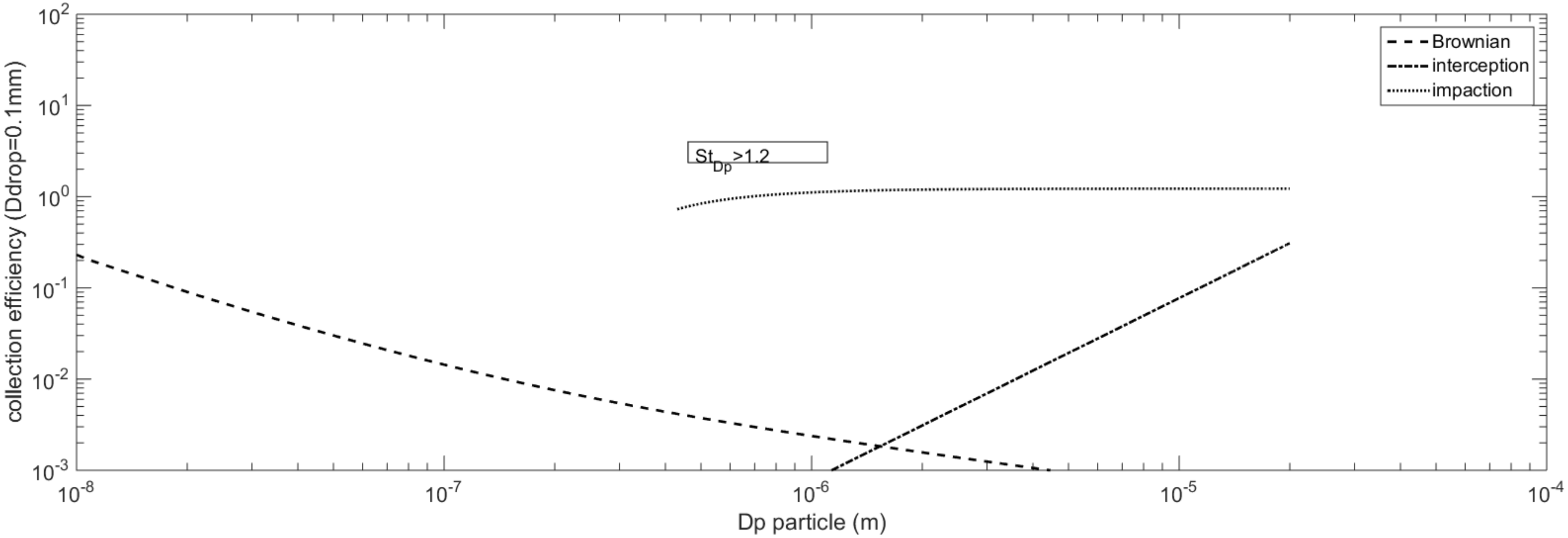
$$\Lambda(d_p) = \int_0^\infty \frac{\pi}{4} D_p^2 U(D_p) E(D_p, d_d) N_{D_p} dD_p$$

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

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

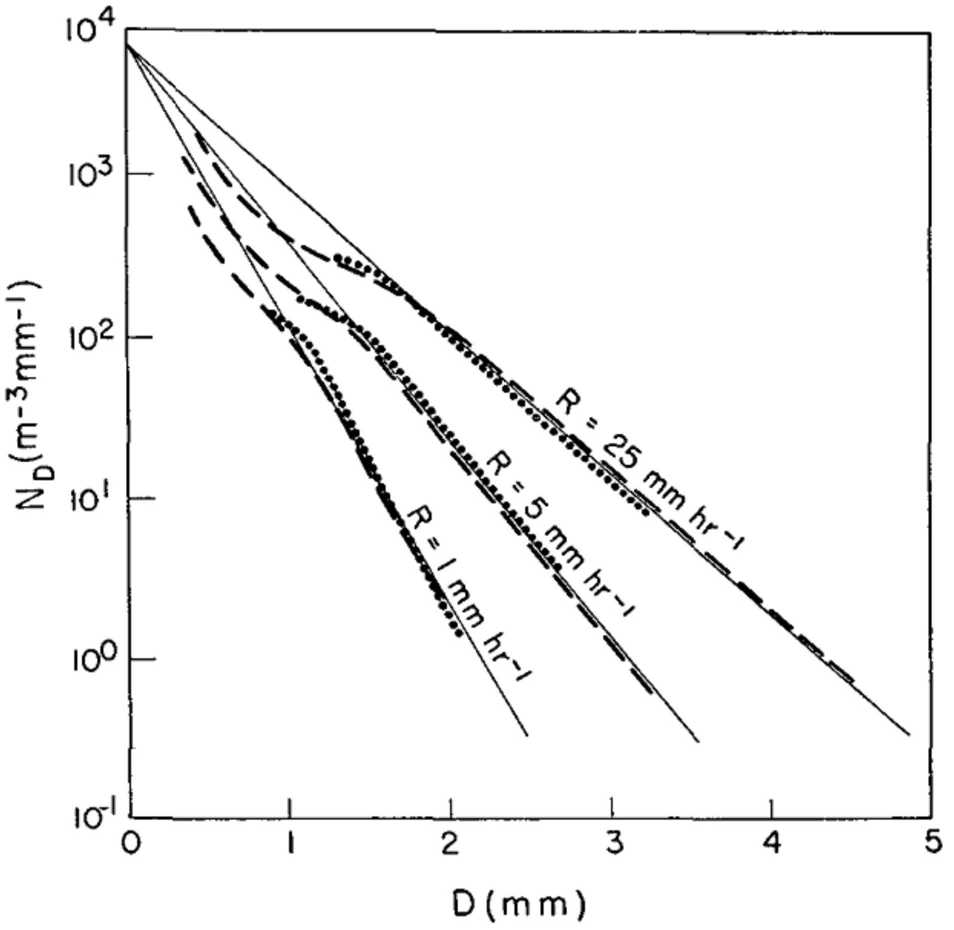
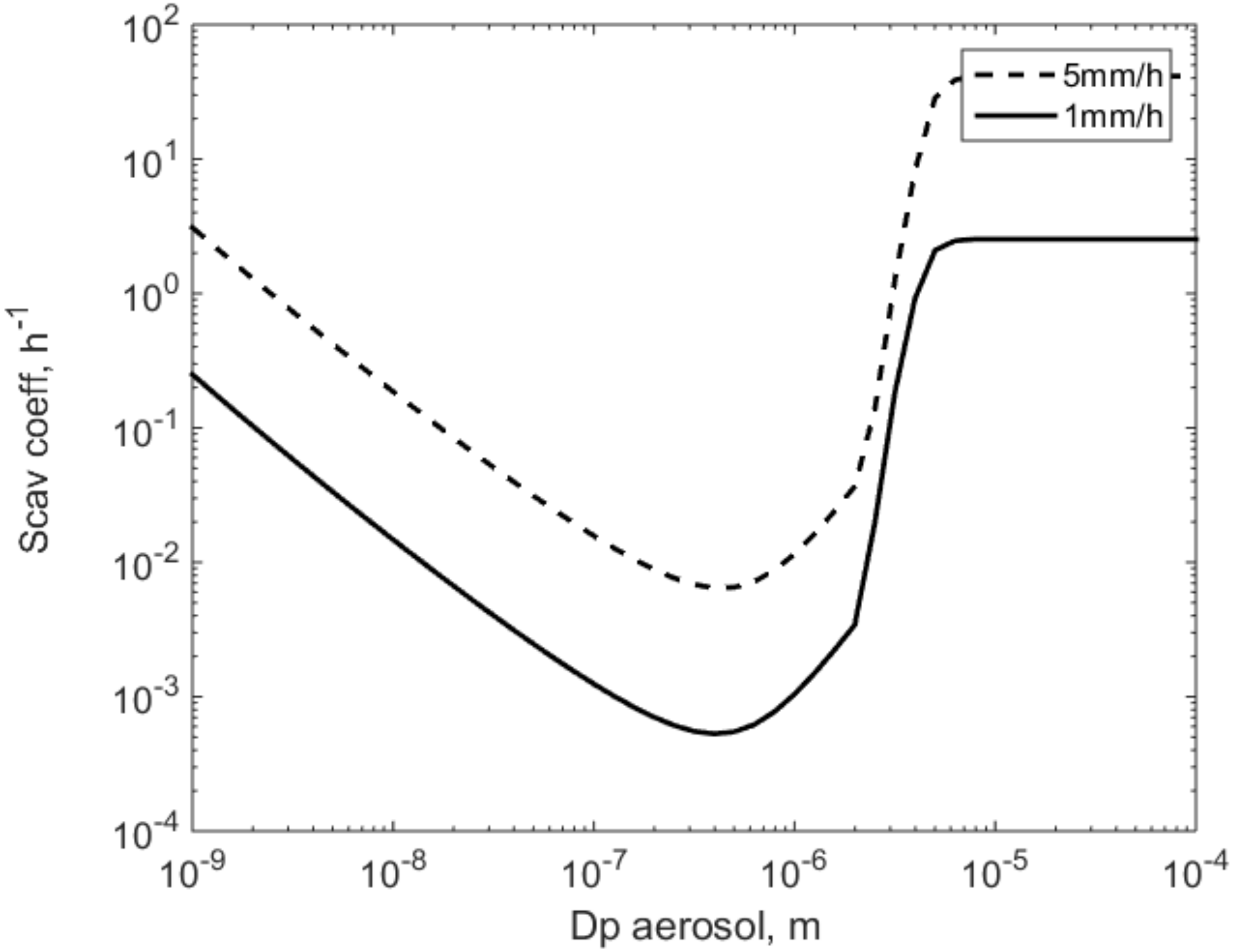
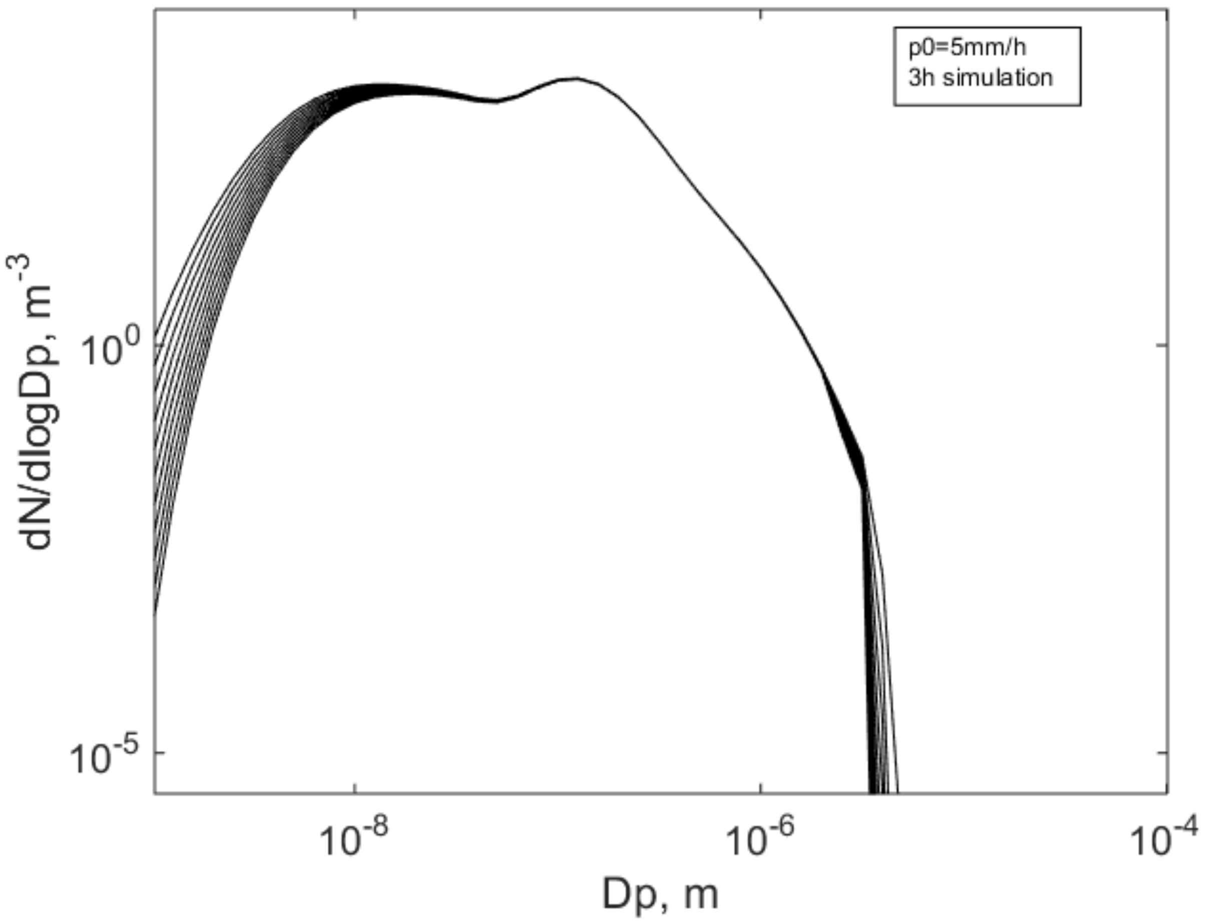


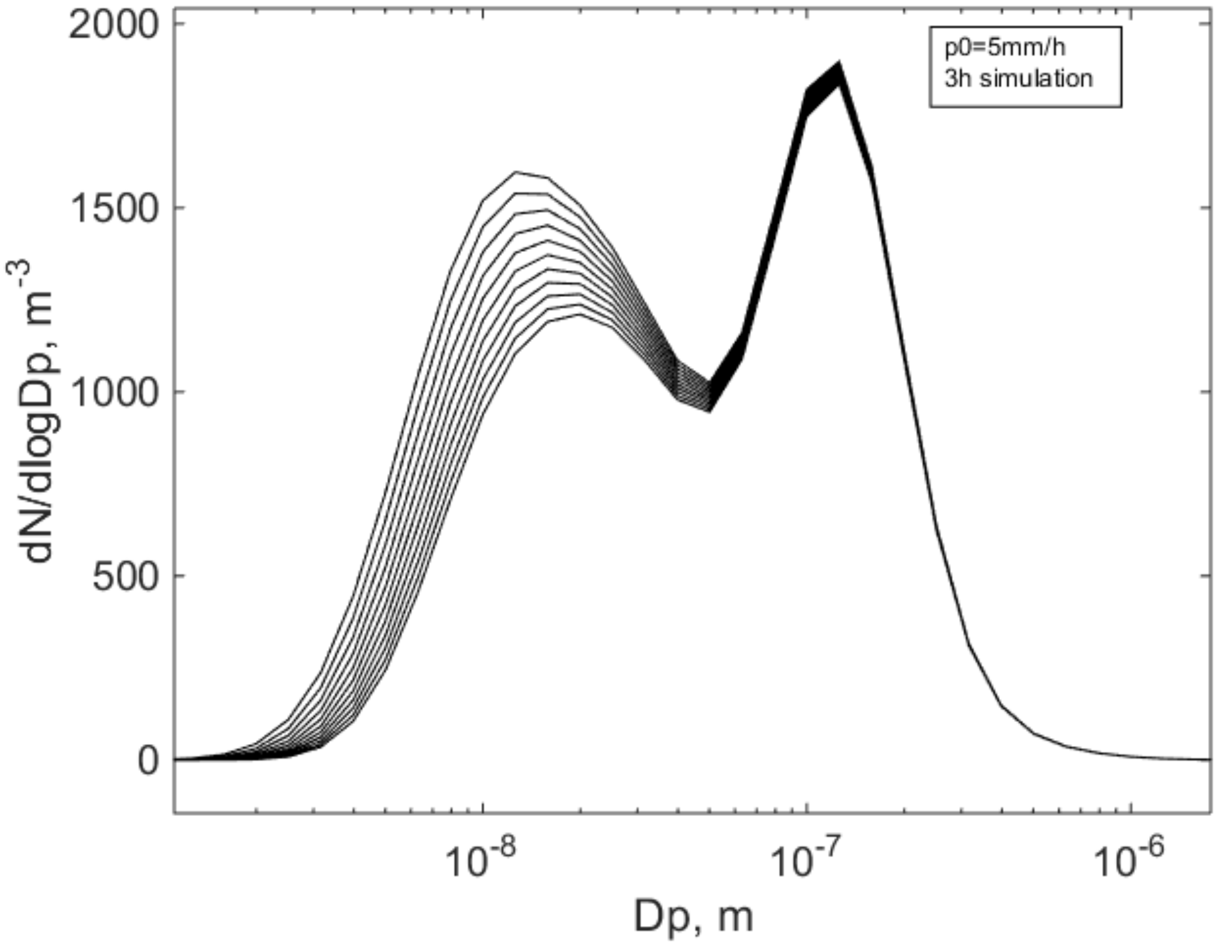
FIG. 2. Distribution function (solid straight lines) compared with results of Laws and Parsons (broken lines) and Ottawa observations (dotted lines).

Scavengning coefficient, Λ



Simulating below cloud scavengning





Simple approach: Assuming constant, linear and irreversible scavengning

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

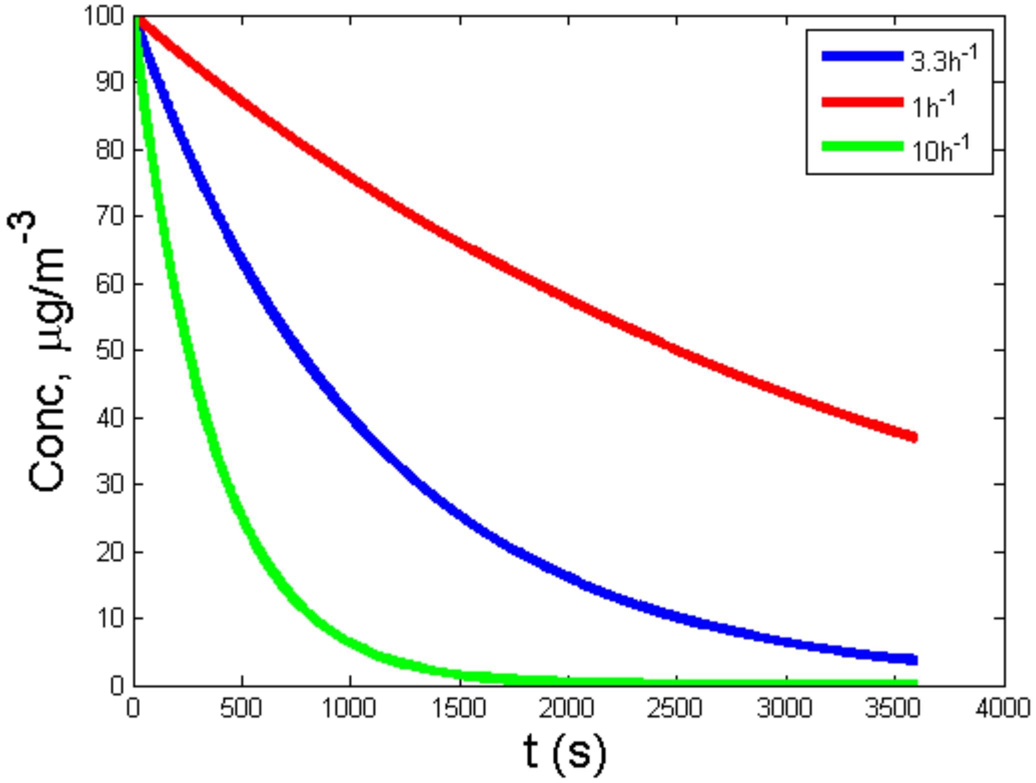
(where R and E are additional reactions and emissions, resp.)

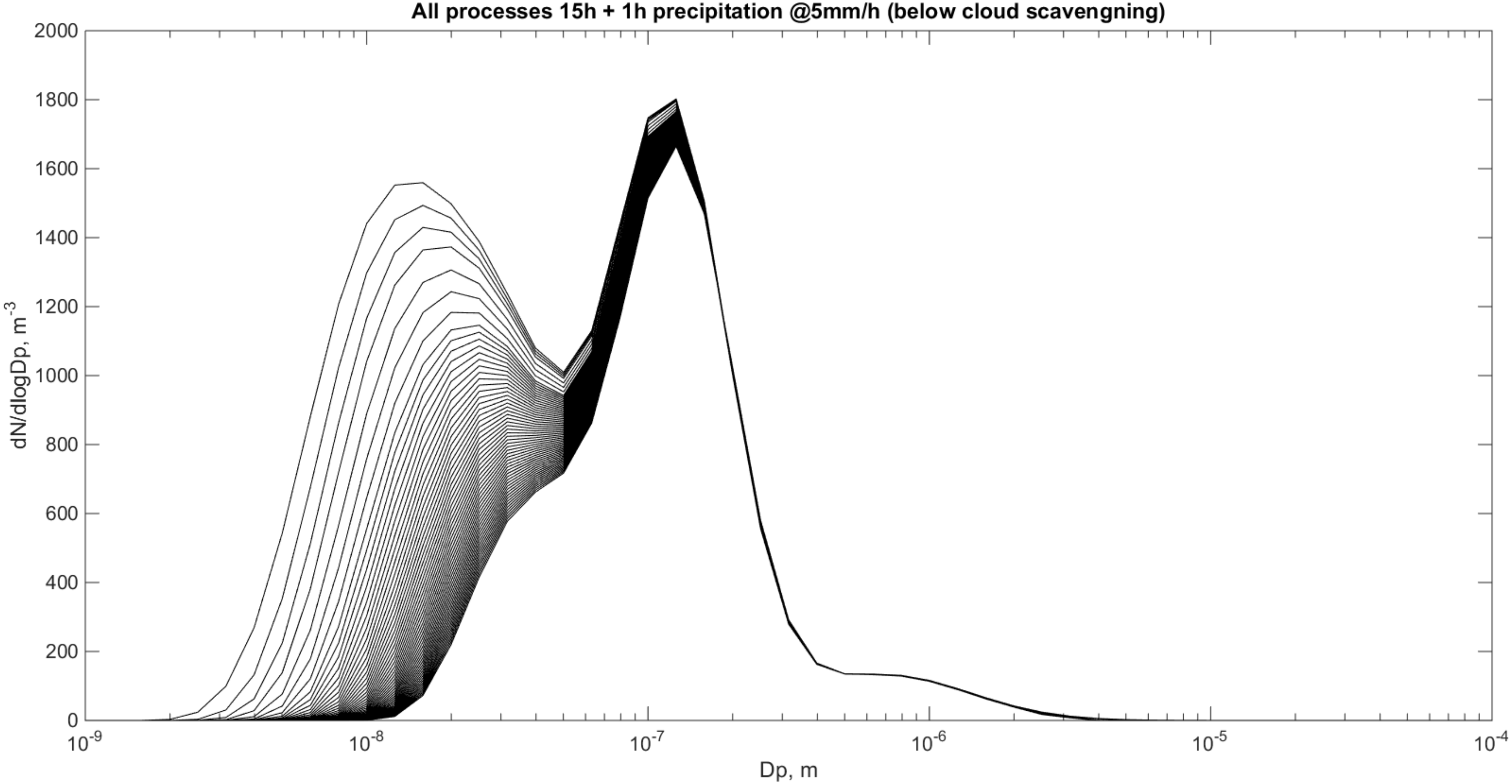
Assuming no R or E, and as :

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

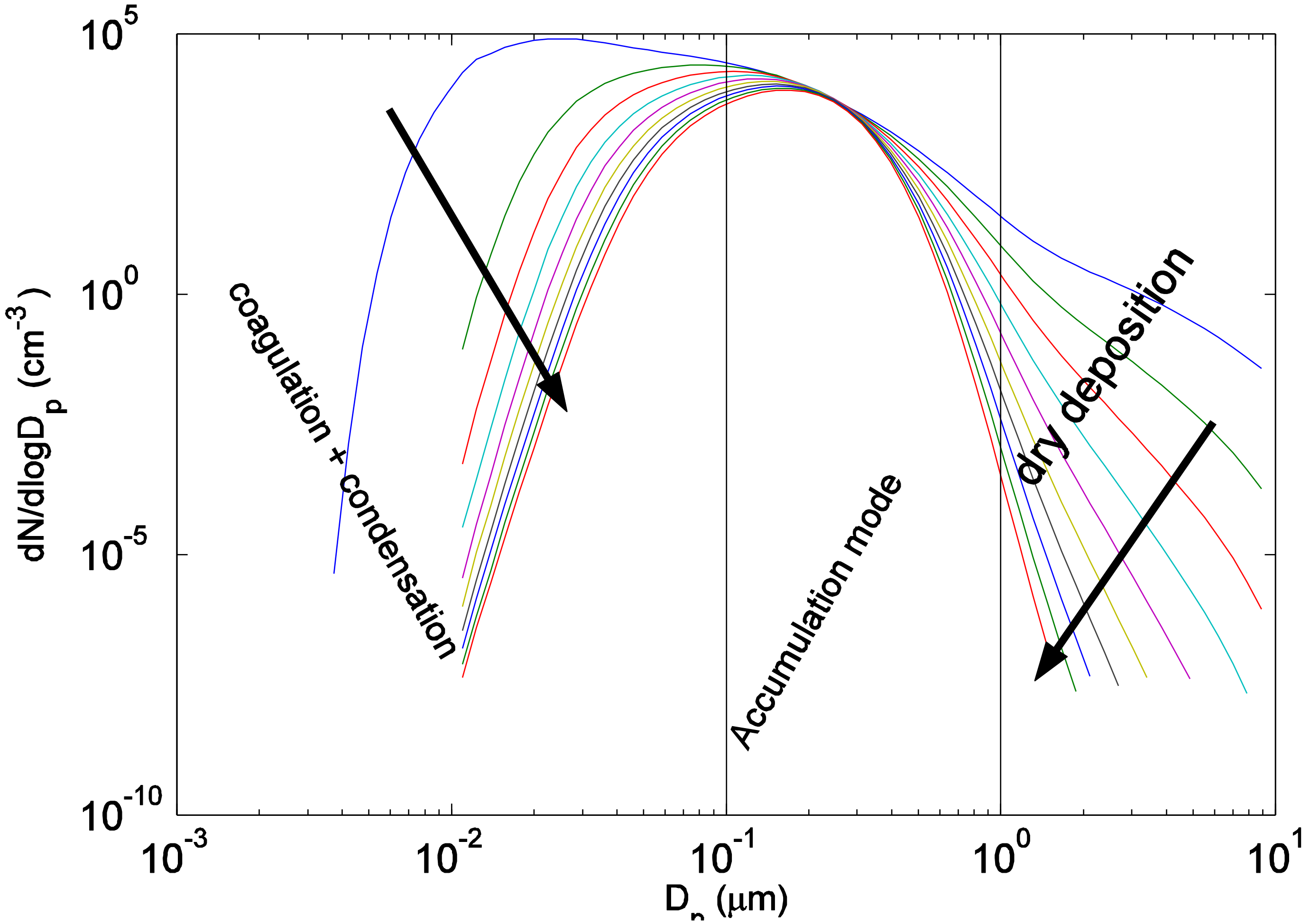
$$\frac{\partial C}{\partial t} = -\Lambda_{i,gas} C_{i,gas}$$

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




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

Aerosol dynamics:
coagulation, condensation and dry deposition



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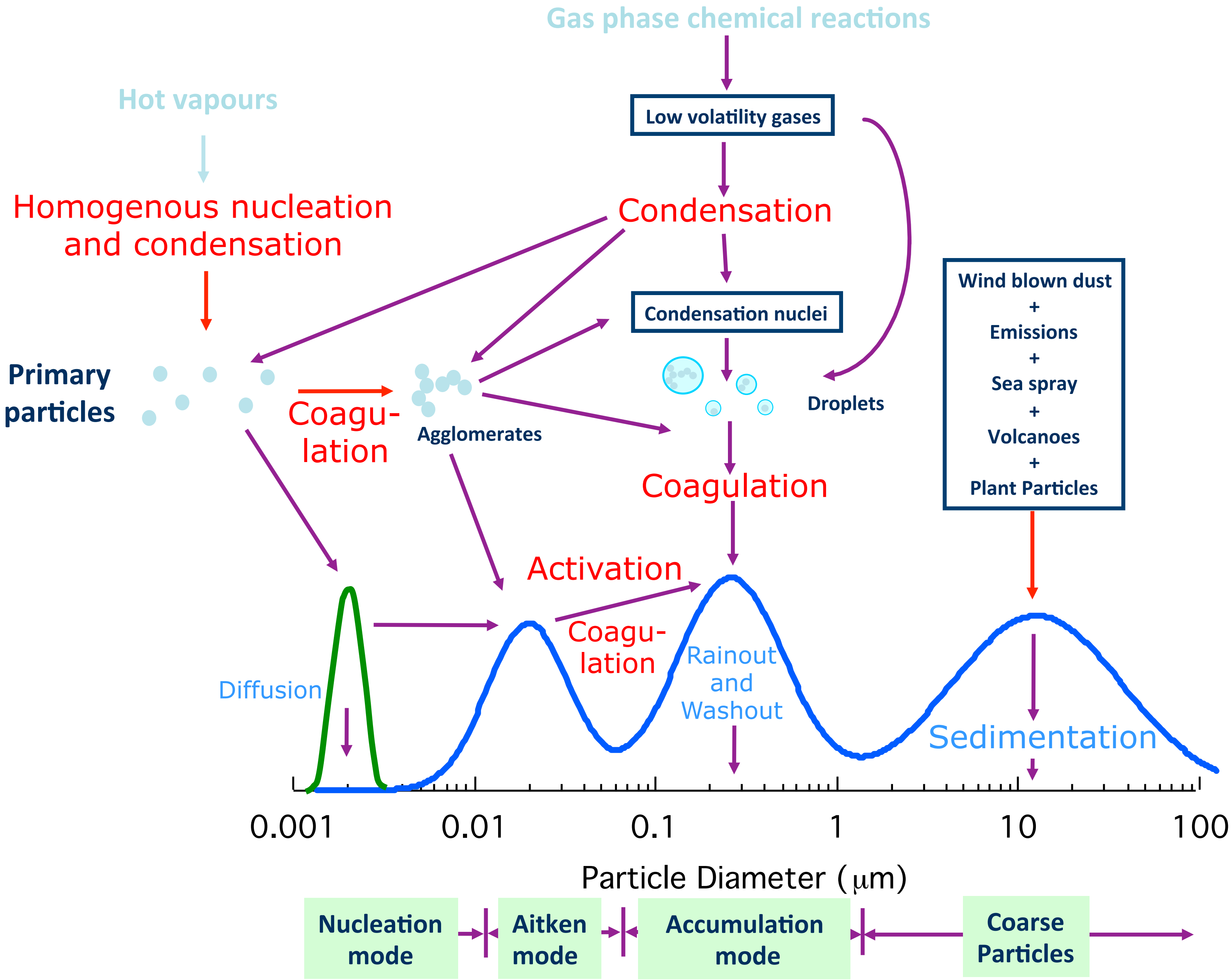

Gas phase chemical reactions

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

Particle Diameter (μm)

Nucleation mode

Aitken mode

Accumulation mode

Coarse Particles

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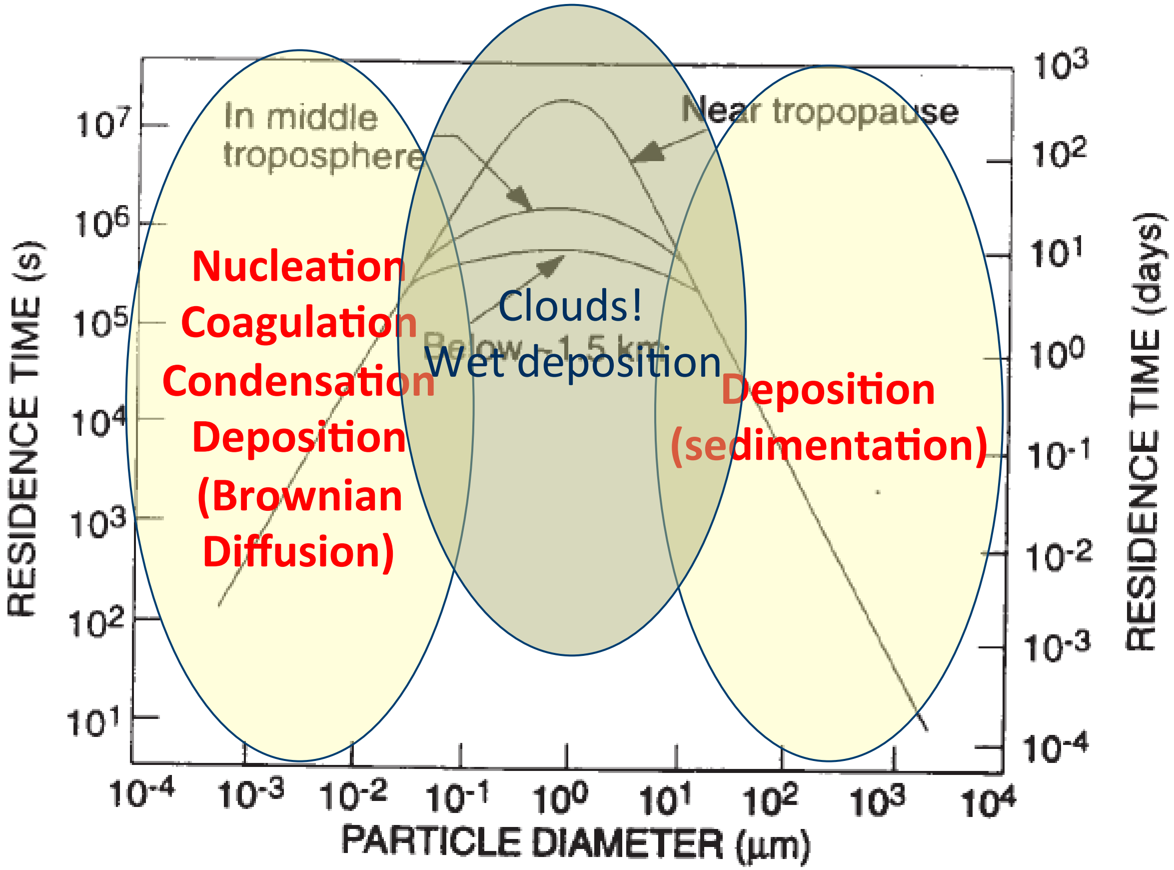
Explaining the residence time

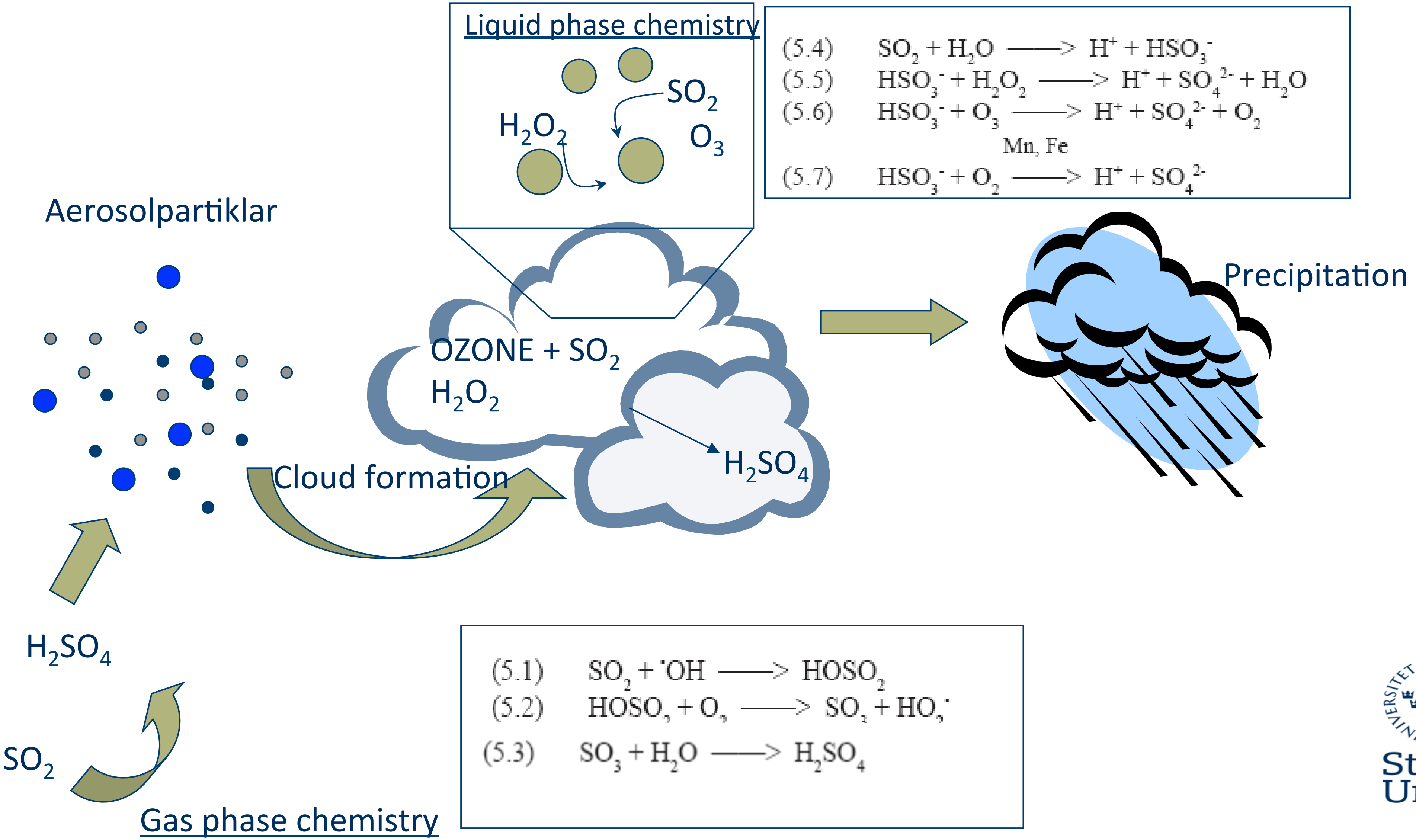


Nucleation
Coagulation
Condensation
Deposition
(Brownian
Diffusion)

Clouds!
Wet deposition

Deposition
(sedimentation)

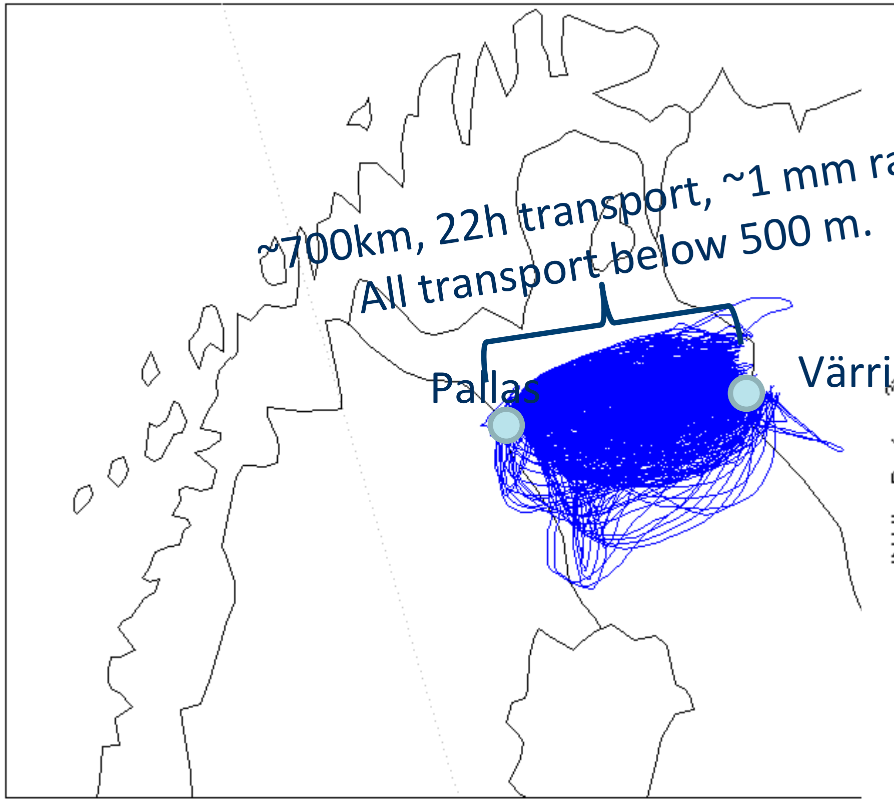
Aerosol dynamics: Cloud processing



(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) $HSO_3^- + O_2 \xrightarrow{\text{Mn, Fe}} H^+ + SO_4^{2-}$

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

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.