The Abdus Salam
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United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

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Workshop on Aerosol Impact in the Environment: from Air Pollution to Climate Change

8 - 12 August 2011

Aerosol processing in the atmosphere: emissions, dynamics and deposition

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Aerosol processes in the atmosphere: emissions, dynamics and deposition

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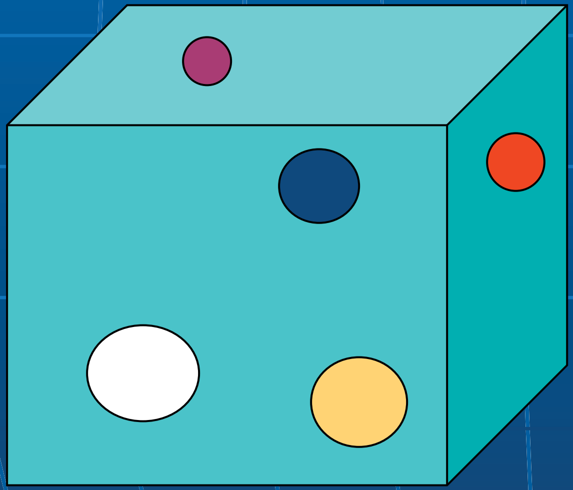
Trieste, 8-12 August 2011

Aerosols

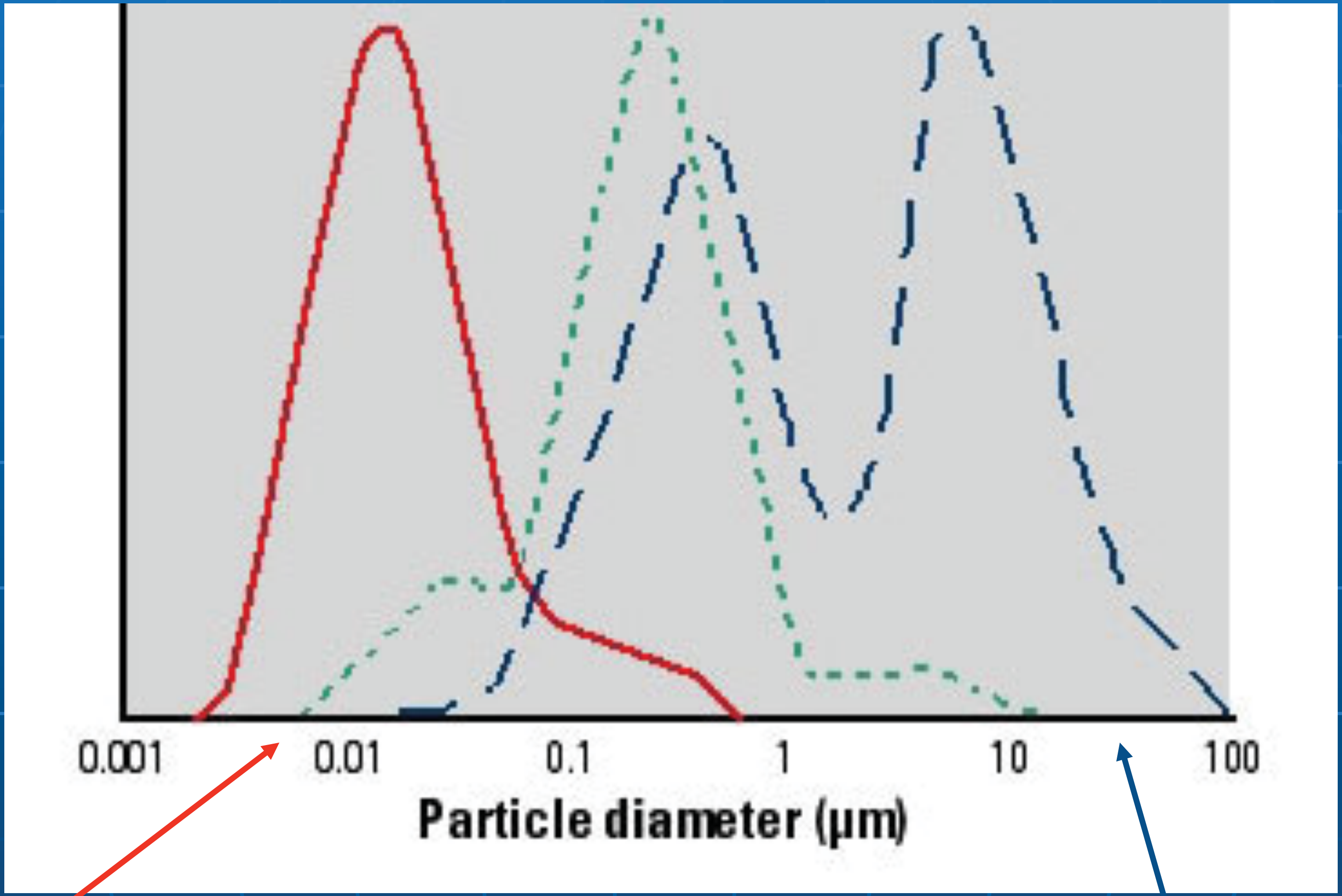
- definition



Volume of air that contains particles in suspension, in liquid or solid phase

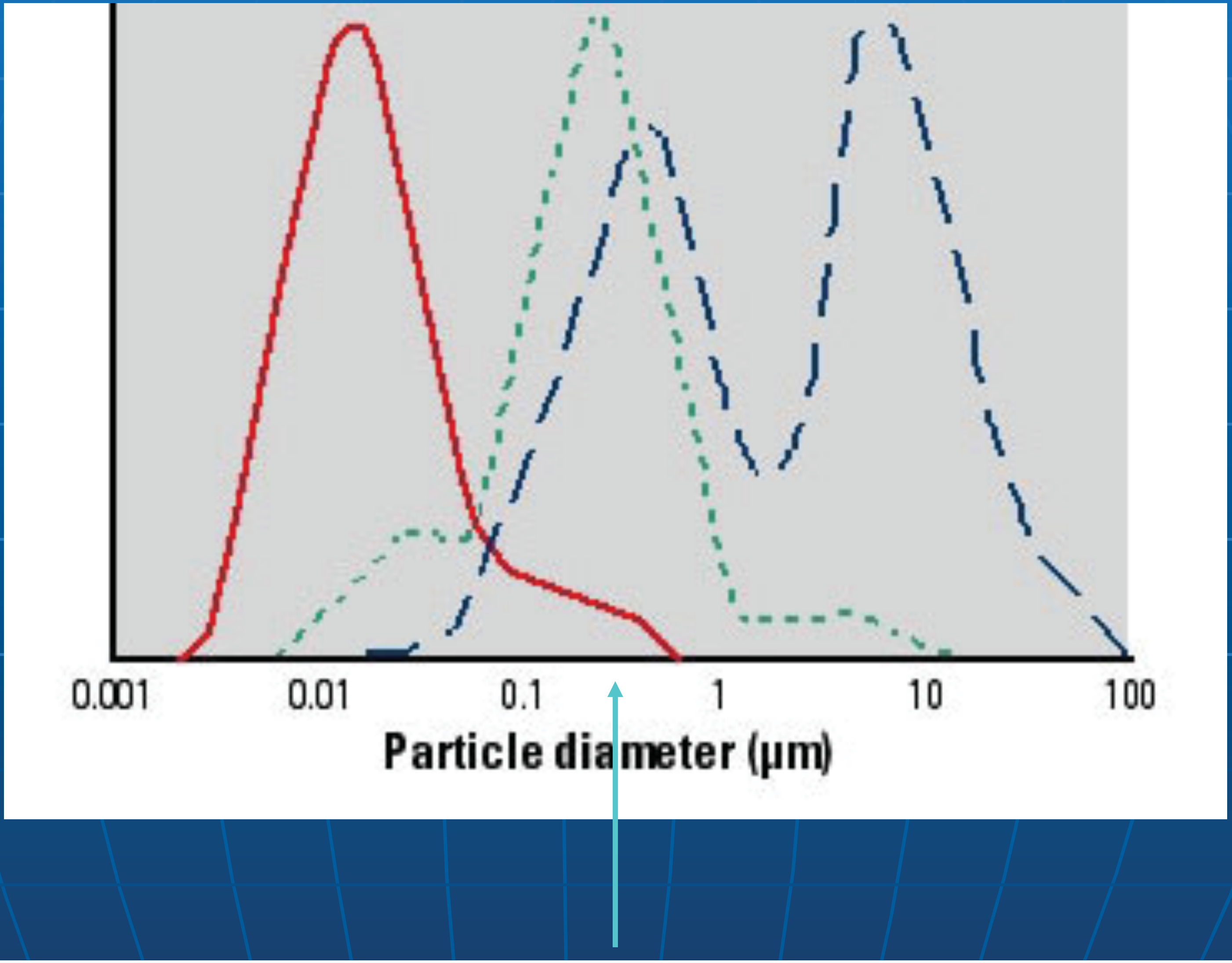
Aerosol dynamics

- Nucleation
- Condensation/Evaporation
- Coagulation

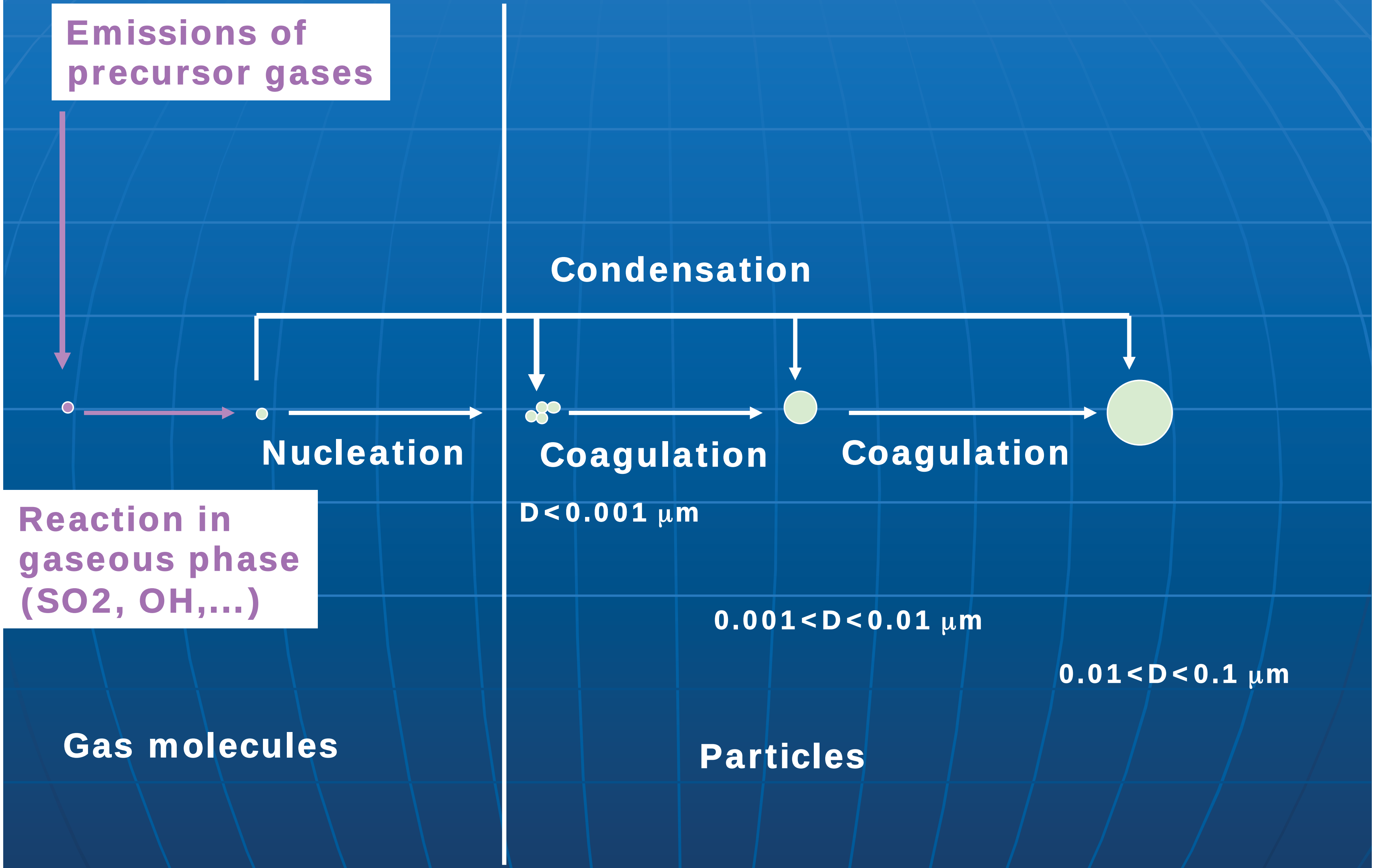


very mobile
rapidly evaporating

gravitational fall is important
large inertia



too large to be easily diffused
Too small for effective inertia and gravitational fall



Emissions of precursor gases

Reaction in gaseous phase (SO2, OH,...)

Condensation

Nucleation

Coagulation

Coagulation

D<0.001 µm

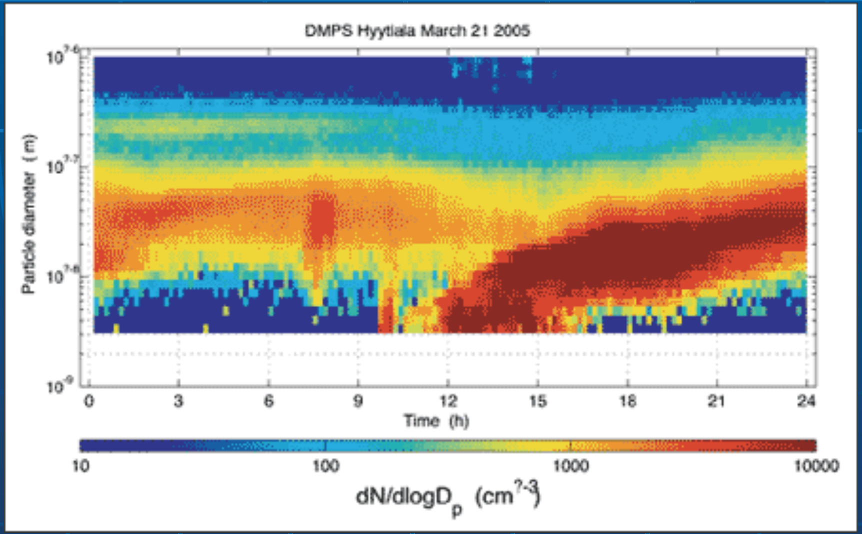
0.001<D<0.01 µm

0.01<D<0.1 µm

Gas molecules

Particles

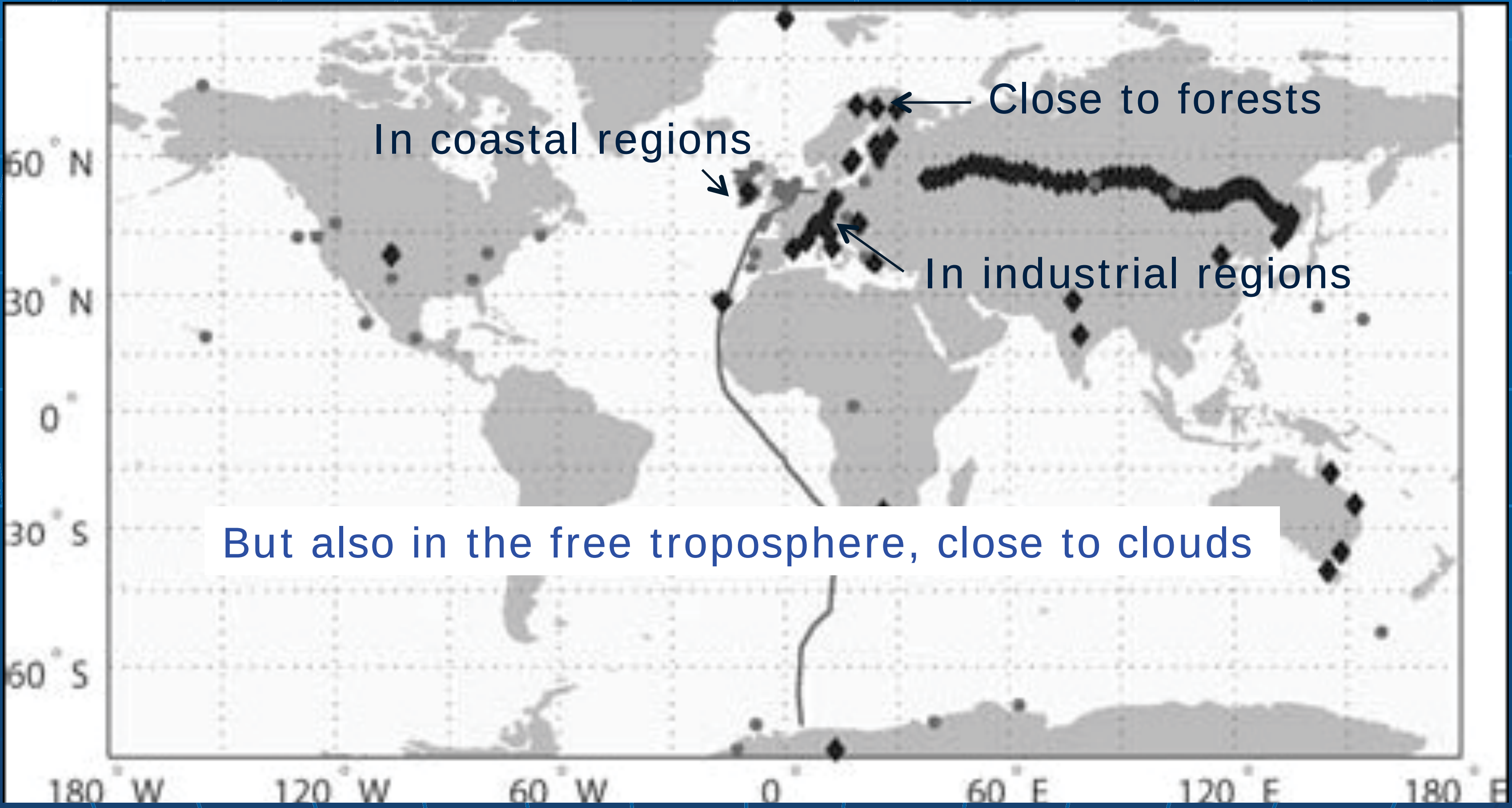
Nucleation


DMPS Hyytiala March 21 2005
Particle diameter (m)
$10^{?-6}$
$10^{?-7}$
$10^{?-8}$
10^{-9}
0
3
6
9
12
15
18
21
24
Time (h)
10
100
1000
10000
dN/dlogD$_p$ (cm$^{?-3}$)

Nucleation

- Phase transformation of substances from the gaseous to the liquid or solid phase
- In 1897 first evidences of particle formation in the atmosphere, but only around 2000 instrumentation to quantitatively measure it appeared
- Two important phases in the new particle formation: the nucleation itself, and the growth in dimention to a size that can be observed

Where were new particles observed?



In coastal regions

Close to forests

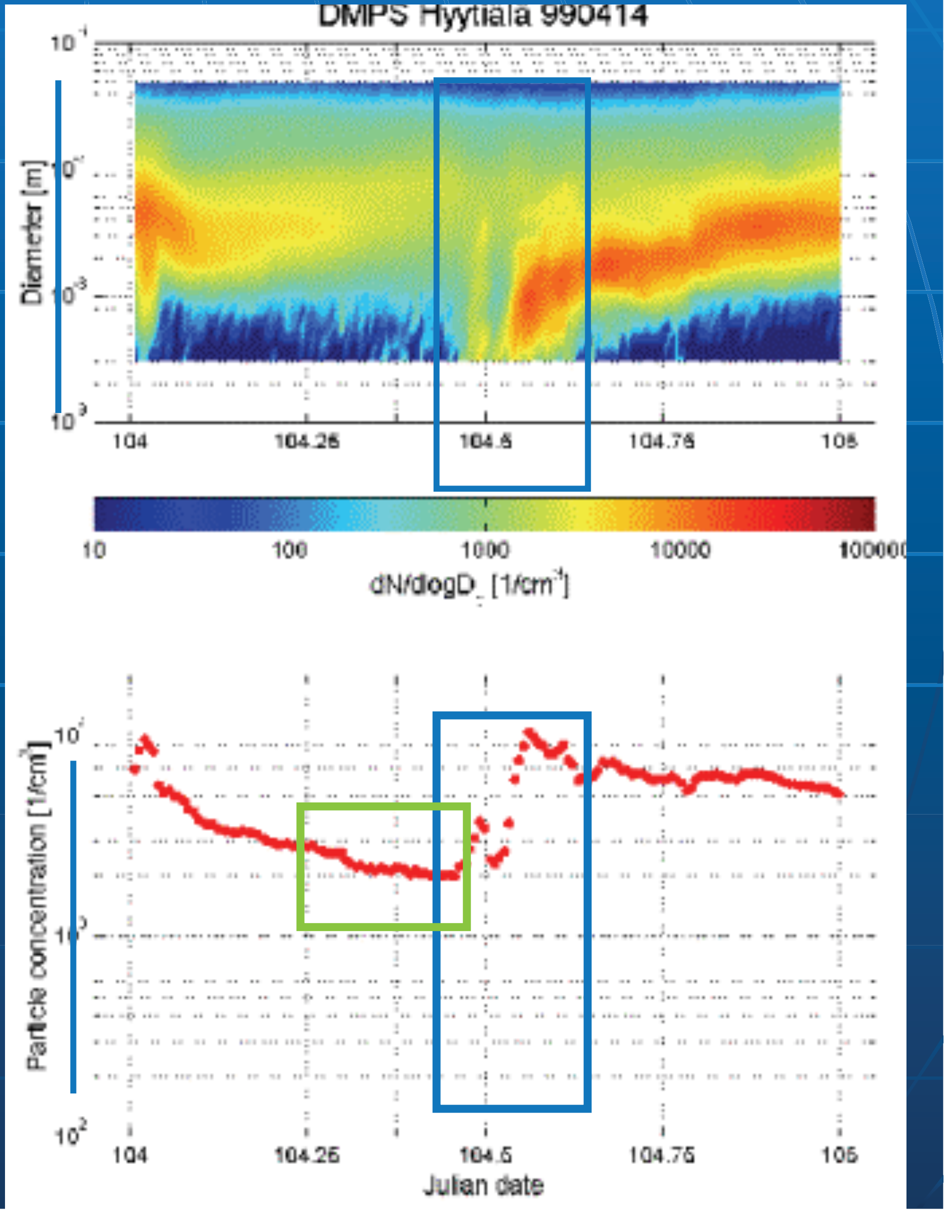
In industrial regions

But also in the free troposphere, close to clouds

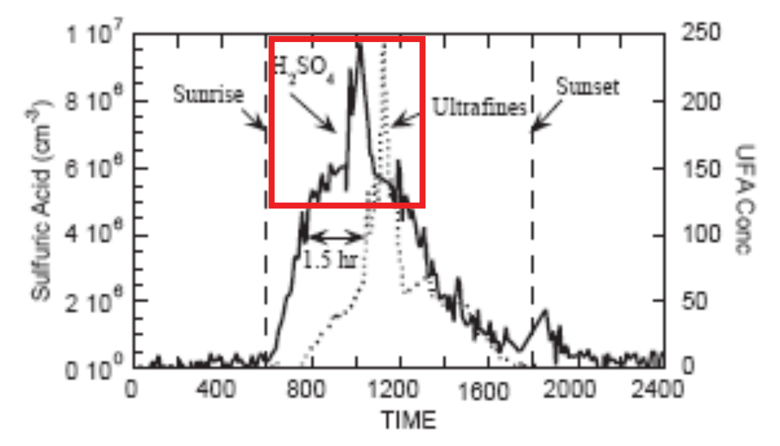
Kulmala et al., 2008

Particle formation takes place:

- During daytime, suggesting that photochemistry plays an important role
- In presence of only a few pre-existent particles



- In presence of a large source of precursor vapour, photochemical or of biogenic origin



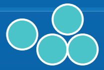
- Sometimes at low temperatures

What is the formation rate of new particles in the atmosphere?

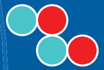
- At regional scale tipically: 0.01-10 $cm^{-3}s^{-1}$
- Up to 100 $cm^{-3}s^{-1}$ in urban areas
- Up to 10^4-10^5 $cm^{-3}s^{-1}$ in coastal zones and industrial plumes

Nucleation types

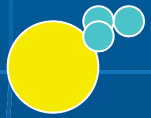
- Nucleation of a single species (homogeneous-homomolecular)



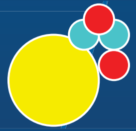
- Nucleation of two or more species (homogeneous-heteromolecular)



- Nucleation of a single species onto another substance (heterogeneous-homomolecular)

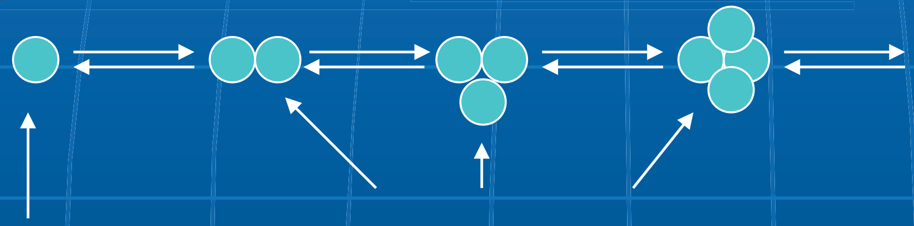


- Nucleation of two or more species onto another substance (heterogeneous-heteromolecular)



Nucleation mechanism

- Vapour A at saturation



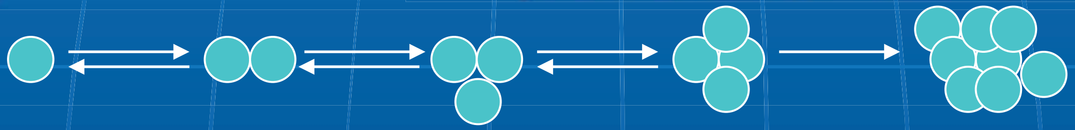
molecule=
monomers

cluster

  - mean cluster concentration is stable
  - presence of larger clusters is rare

Nucleation mechanism

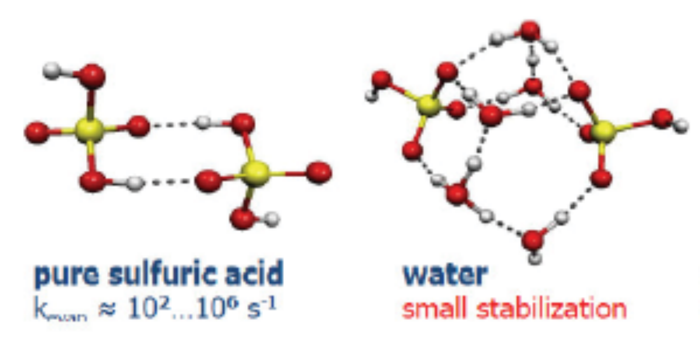
- Vapour A at supersaturation



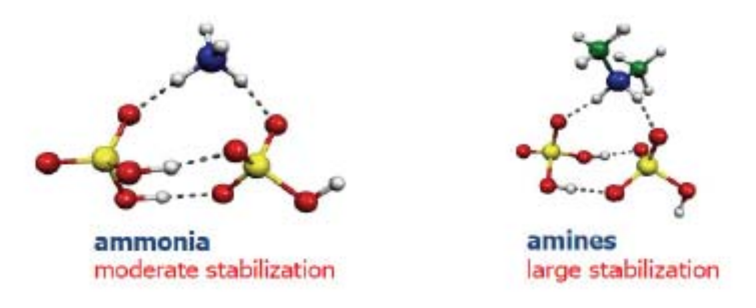
  - there is an excess of monomers compared to saturation
  - a larger number of larger clusters is produced
  - some may then grow beyond a certain critical dimension to give rise to a new phase

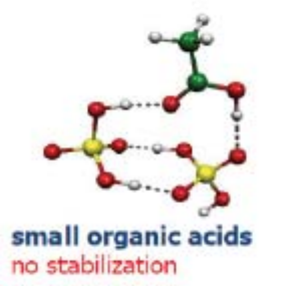
The suspected couple: H_2SO_4-H_2O

- Sulphuric acid and water constitute the cluster



- Other compounds stabilise them and make them grow





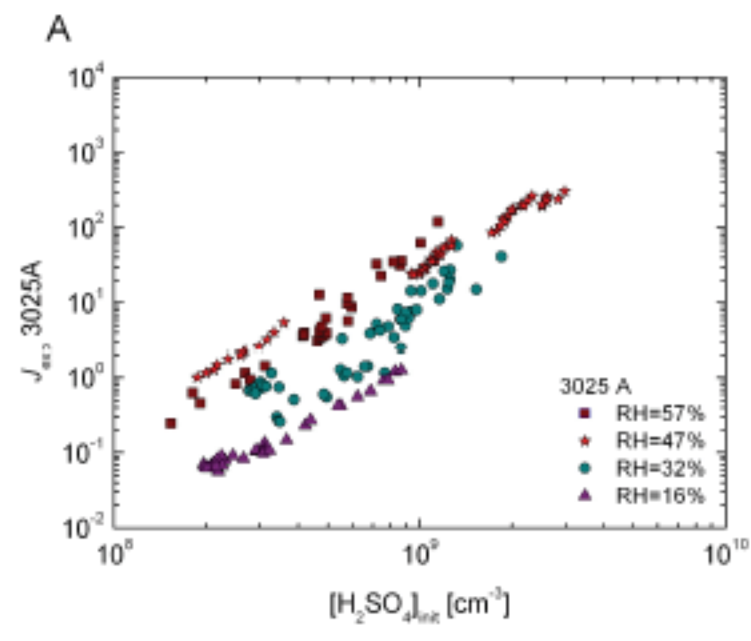
Kerminen et al., 2010

Measured characteristics of the couple

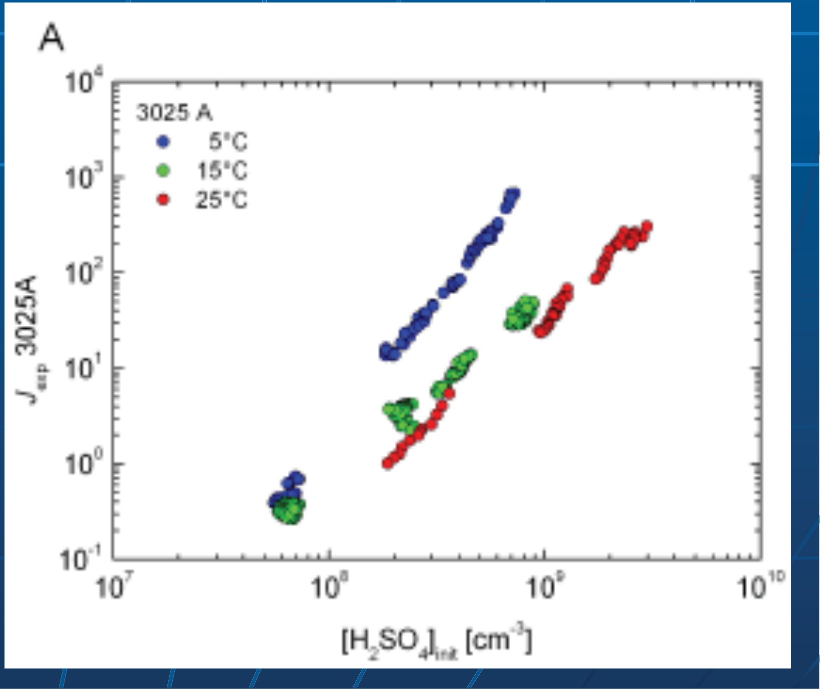
- Binary nucleation
  - taking place most of all in free troposphere and in industrial plumes,...)

Measured formation rate vs sulphuric acid (Brus et al. 2010)

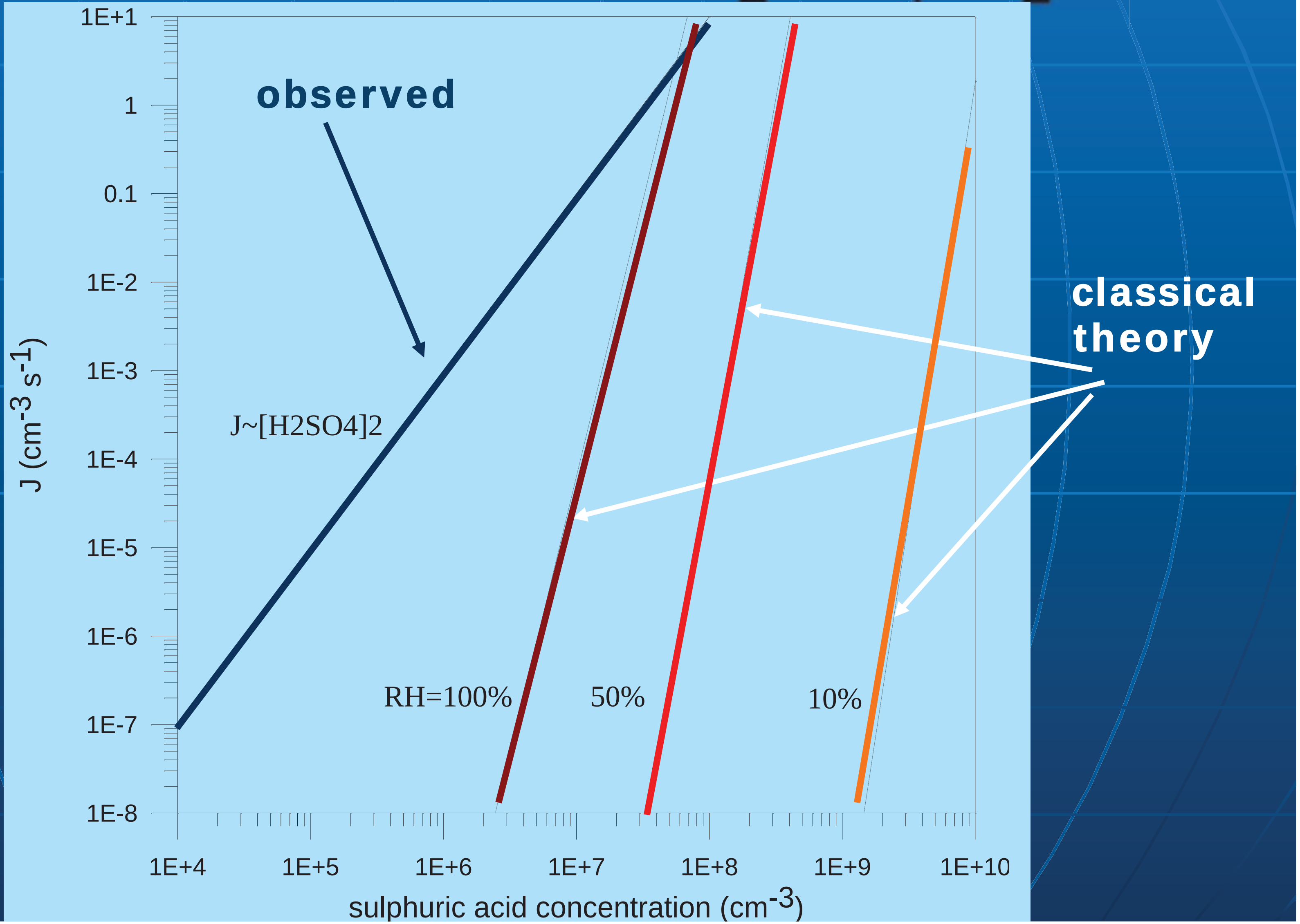
Dipendence on relative humidity



Dipendence on temperature

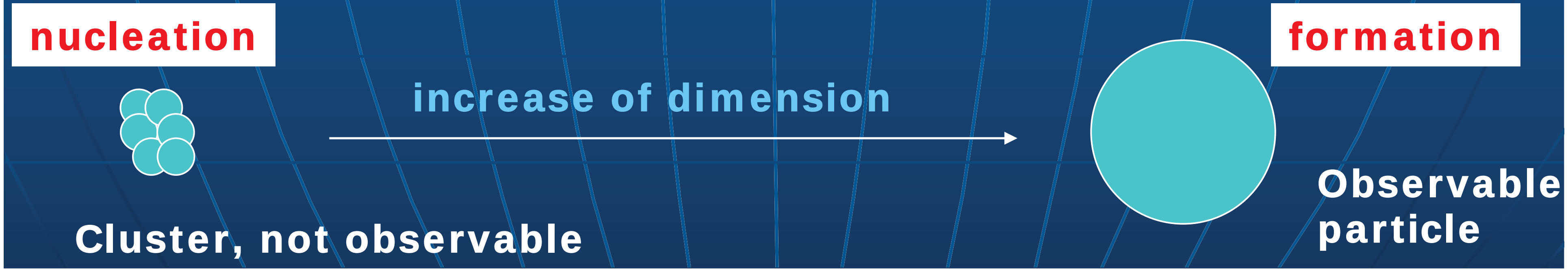


Measured and calculated nucleation rates for H_2SO_4-H_2O



Why we do not understand the mechanism yet

- Critical clusters are too small and cannot be measured
- We cannot measure directly the nucleation rate, but only a “formation” rate of particles with larger diameters
- Theoretically we derive a relation between nucleation rate of cluster and the “formation” rate of measurable particles



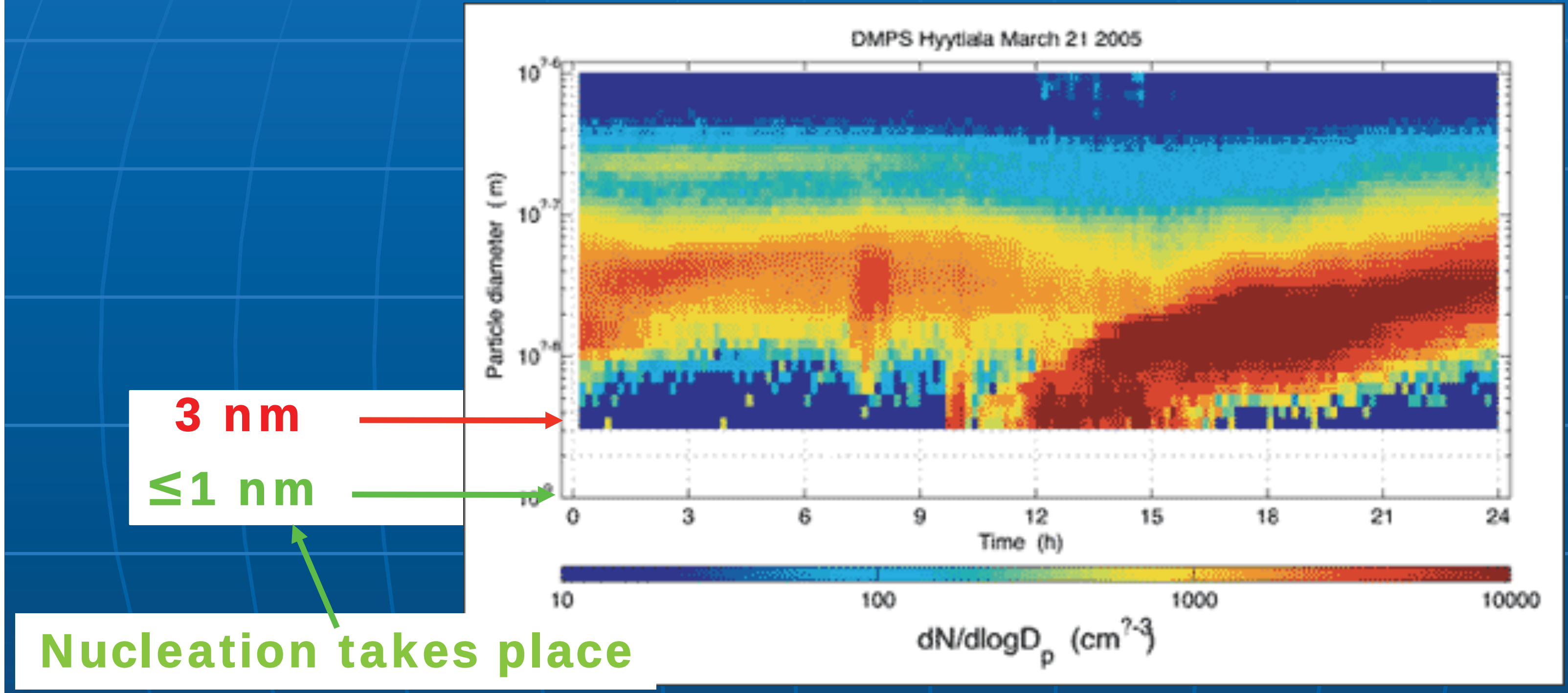
nucleation

increase of dimension

formation

Cluster, not observable

Observable particle

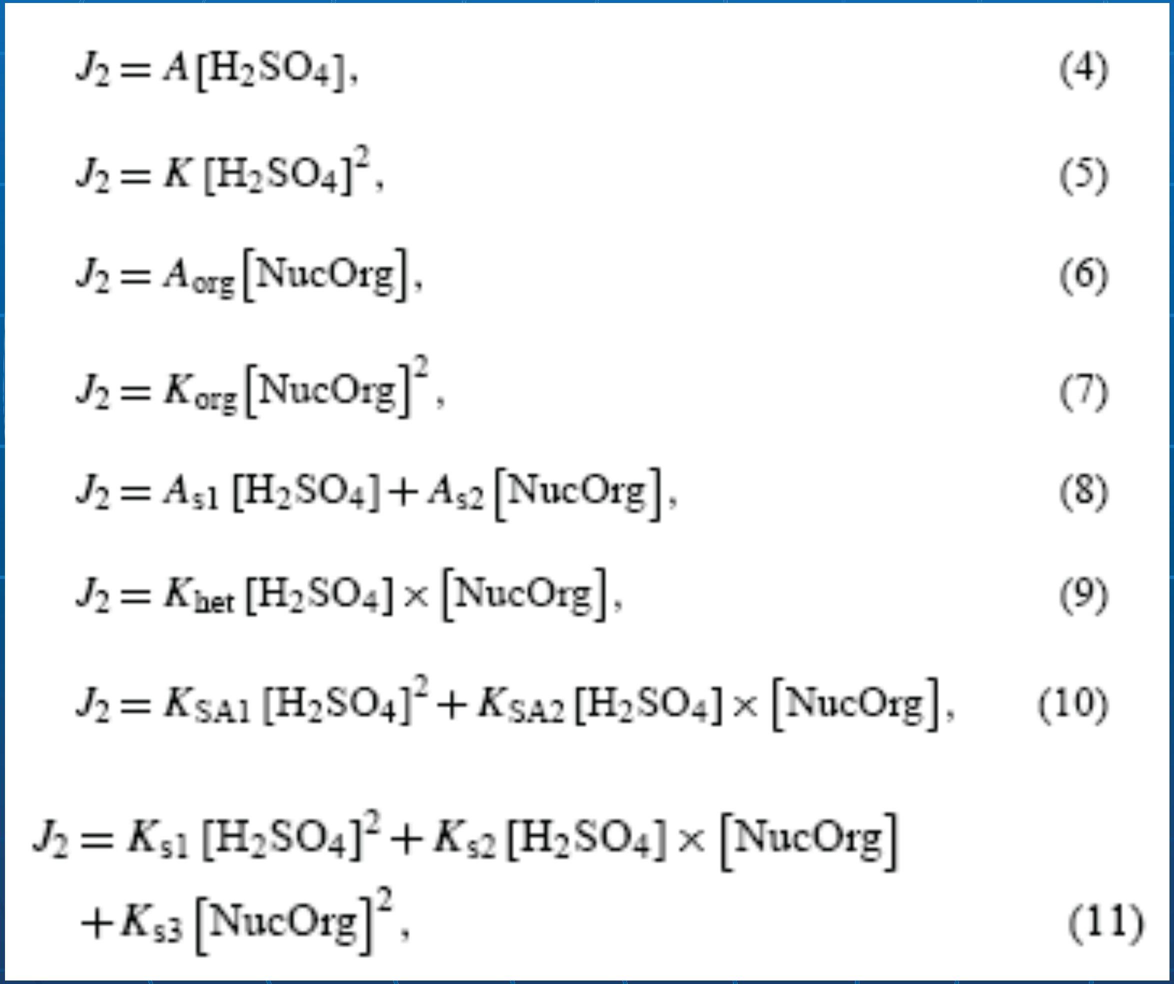


3 nm

≤1 nm

Nucleation takes place

Formulation of candidate mechanisms for particle formation:



$$J_2 = A\,[\mathrm{H_2SO_4}], \tag{4}$$

$$J_2 = K\,[\mathrm{H_2SO_4}]^2, \tag{5}$$

$$J_2 = A_{\mathrm{org}}\,[\mathrm{NucOrg}], \tag{6}$$

$$J_2 = K_{\mathrm{org}}\,[\mathrm{NucOrg}]^2, \tag{7}$$

$$J_2 = A_{\mathrm{s1}}\,[\mathrm{H_2SO_4}] + A_{\mathrm{s2}}\,[\mathrm{NucOrg}], \tag{8}$$

$$J_2 = K_{\mathrm{het}}\,[\mathrm{H_2SO_4}] \times [\mathrm{NucOrg}], \tag{9}$$

$$J_2 = K_{\mathrm{SA1}}\,[\mathrm{H_2SO_4}]^2 + K_{\mathrm{SA2}}\,[\mathrm{H_2SO_4}] \times [\mathrm{NucOrg}], \tag{10}$$

$$J_2 = K_{\mathrm{s1}}\,[\mathrm{H_2SO_4}]^2 + K_{\mathrm{s2}}\,[\mathrm{H_2SO_4}] \times [\mathrm{NucOrg}] + K_{\mathrm{s3}}\,[\mathrm{NucOrg}]^2, \tag{11}$$

None works in
all tested environments!

Mechanisms different
depending on the
conditions!

Large uncertainties
in observations

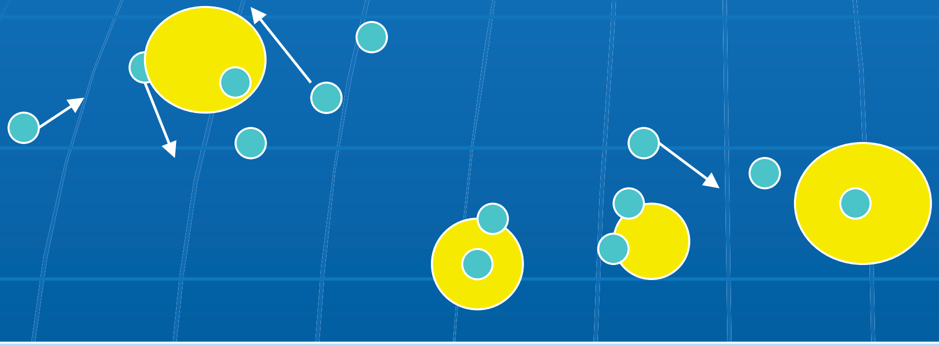
Kerminen et al., 2010

Coagulation

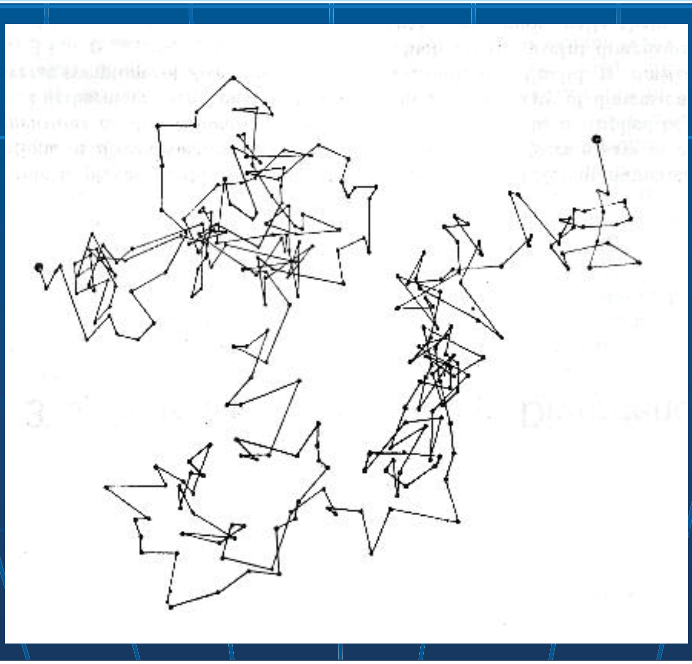
Coagulation

- It is the process by which particles collide among them due to their relative motion and adhere to form a larger particle
  - Thermal coagulation – brownian motion
  - Cinematic coagulation – external actions: gravity, electric forces, aerodynamical effects

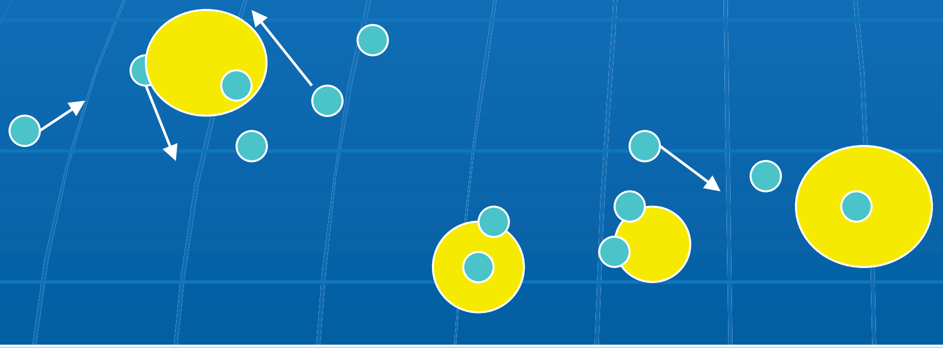
Brownian coagulation



Brownian motion = irregular motion of a particle in the steady air, caused by random variations in the continuous bombing of the gas molecules against particle



Brownian coagulation



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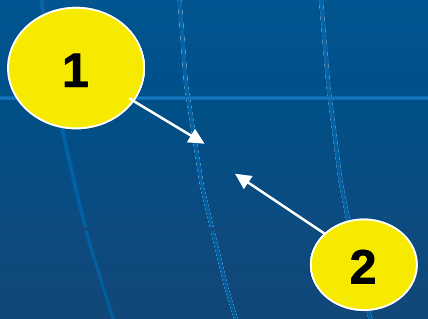


$$\left(\frac{\partial n}{\partial t}\right)_{coag} = -\frac{1}{2}\int_0^\infty\int_0^\infty K_{1,2}\, n(r_1)\, n(r_2)\, dr_1\, dr_2$$

$n(r_1), n(r_2)$ = number concentration of particles with radius r_1 and r_2
$K_{1,2}$ = coagulation coefficient

Coagulation coefficient

$$K_{1,2} = 4\pi\left(r_1 + r_2\right)\left(D_1 + D_2\right)\beta$$

D = diffusion coefficient of particles

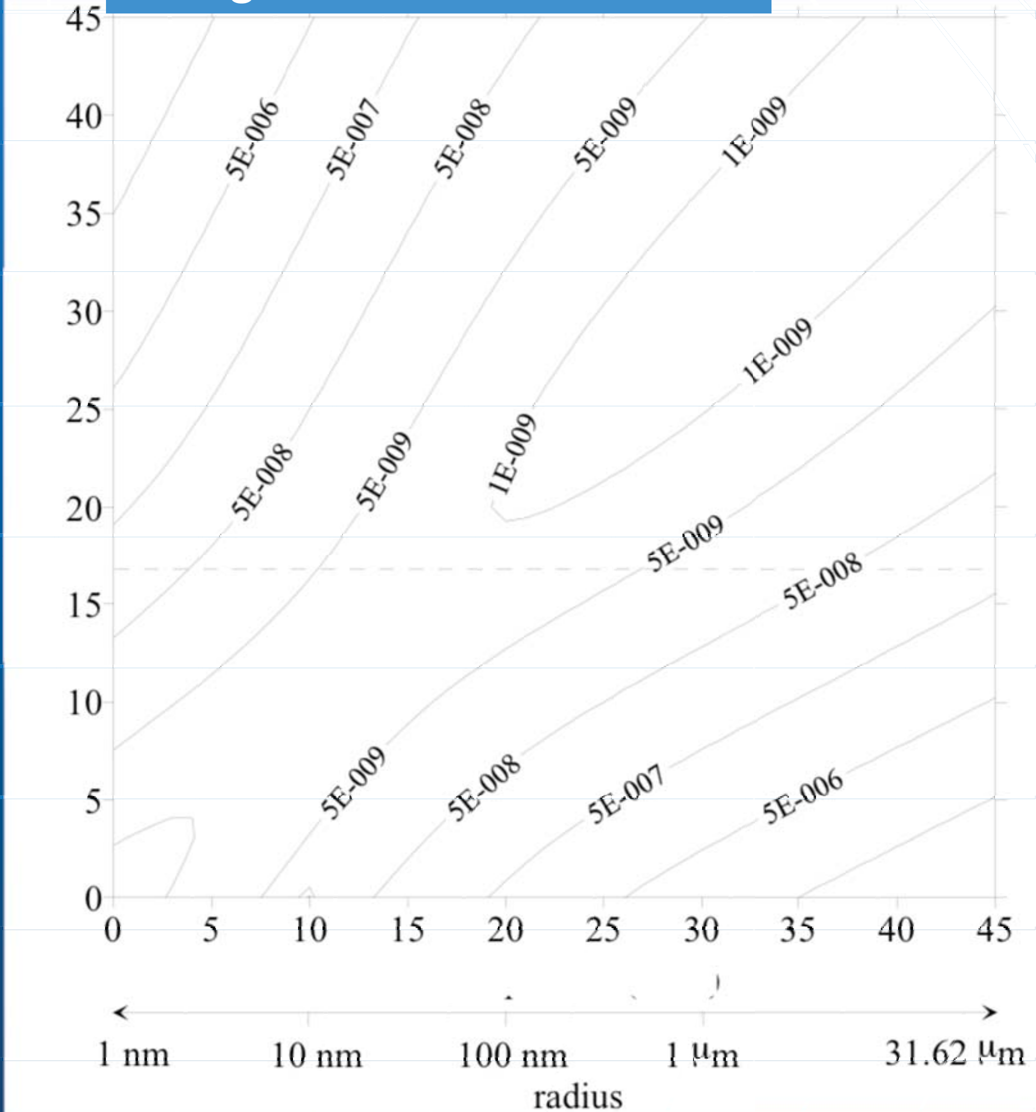
$$D = \frac{k_B T C_c}{6\pi\eta r}$$

β = Fuchs' correction factor

K depends on temperature, air viscosity, particle mean thermal, particle radius and mass, ...

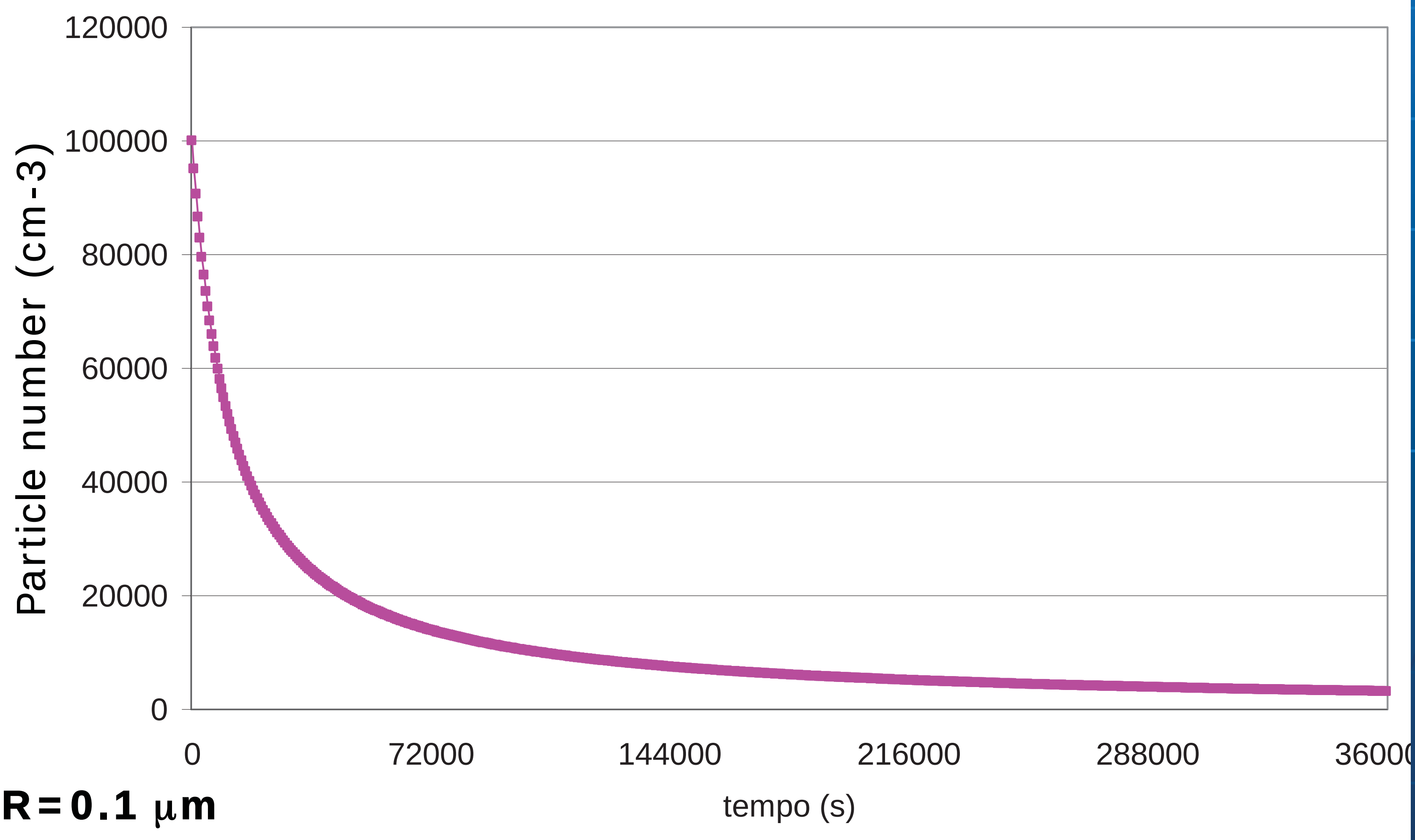
- Symmetric matrix
- Minimum values along the diagonal line
- Maximum values for coagulation of a very small particle with a very large one

Coagulation coefficient



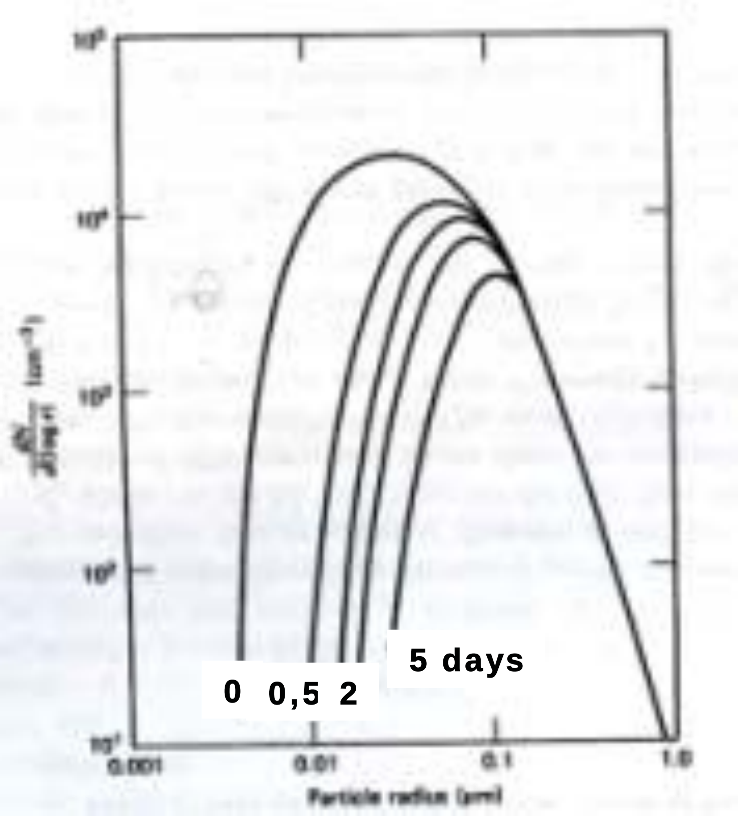
$cm^3\ s^{-1}$

How does coagulation affect particle number?



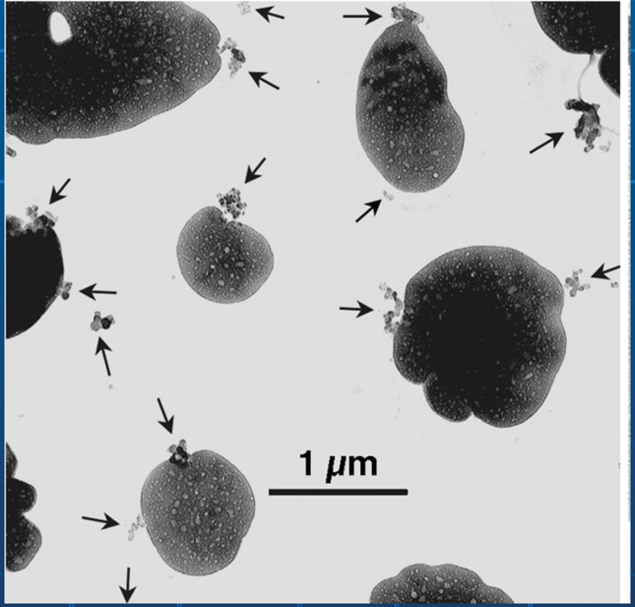
R=0.1 μm

… and effects on number size distribution?

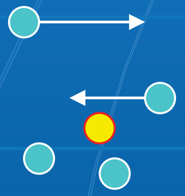


Hinds, 1982

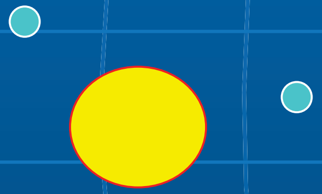
Condensation



Condensation regimes



r < mean molecular path
Particle grow is determined by the rate of random collisions with the gas molecules (cinetic regime)



r > mean molecular path
Particle grow is determined by the rate of gas molecule diffusione to the particle surface
(continuous regime)

- If the particle is not in equilibrium with the surrounding gas, a mass flux between the particle and the gas starts

How do we model condensation (evaporation) to a particle?

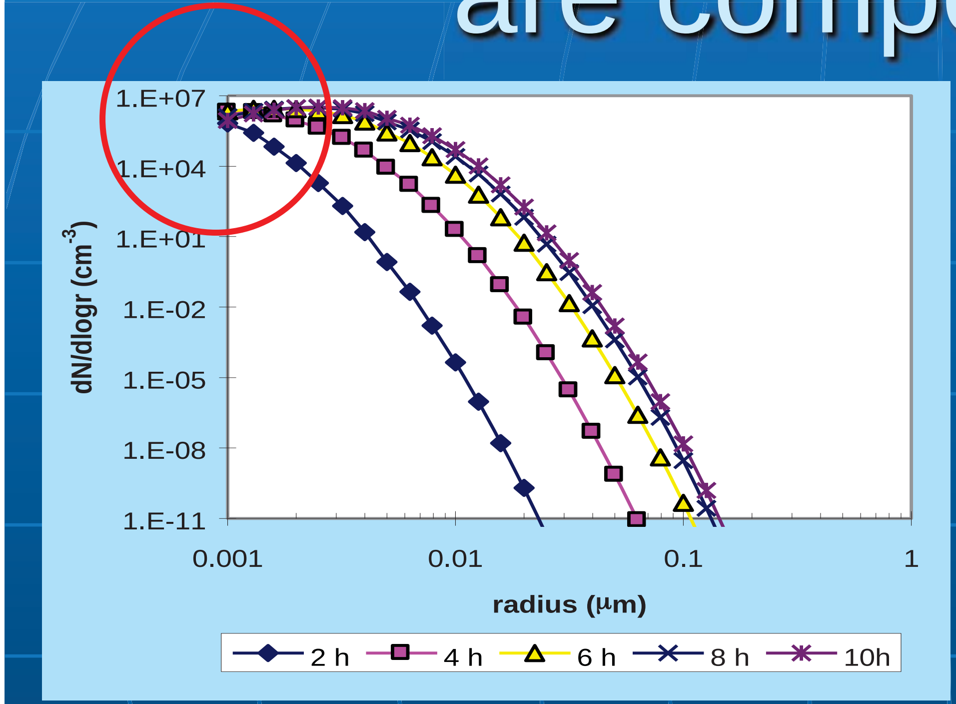
- The flux of a gas that condenses on a particle of radius r (for both kinetic and continuous regimes):

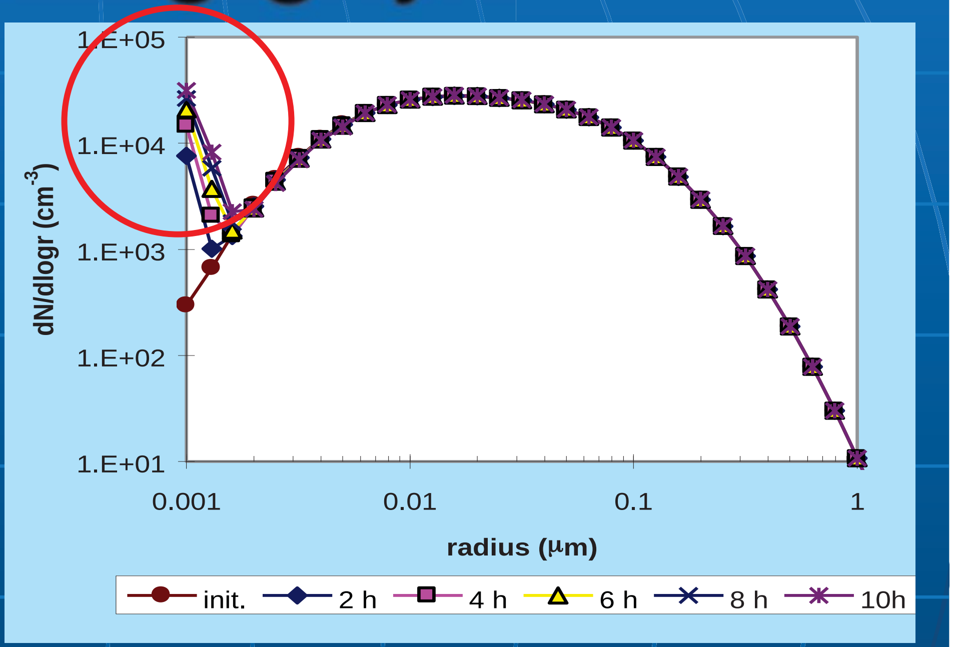
$$\frac{dm}{dt} = C_{cond}$$

$$C_{cond} = \underbrace{\frac{4\pi D_m r}{\frac{4D_m}{\alpha v r} + \frac{r}{r+\Delta}}}_{A} \left(C_\infty - C_s\right)$$

D_m = molecular diffusion coefficient
ν = molecular thermal velocity
Δ = can be the molecular mean path
r = particle radius
α = accomodation coefficient ($0 \leq \alpha \leq 1$)
C_∞ = gas concentration
C_s = gas concentration at particle surface

Nucleation and condensation are competing guys





Nucleation without pre-existing particles

Nucleation in presence of pre-existing particles

Nucleation is less efficient!!!
Condensation subtracts gas

Emissions of primary particles

Black carbon
Organic Carbon
Sea salt
Dust

Black carbon

- **Large scale biomass burning**:

≈ 3 TgC yr-1

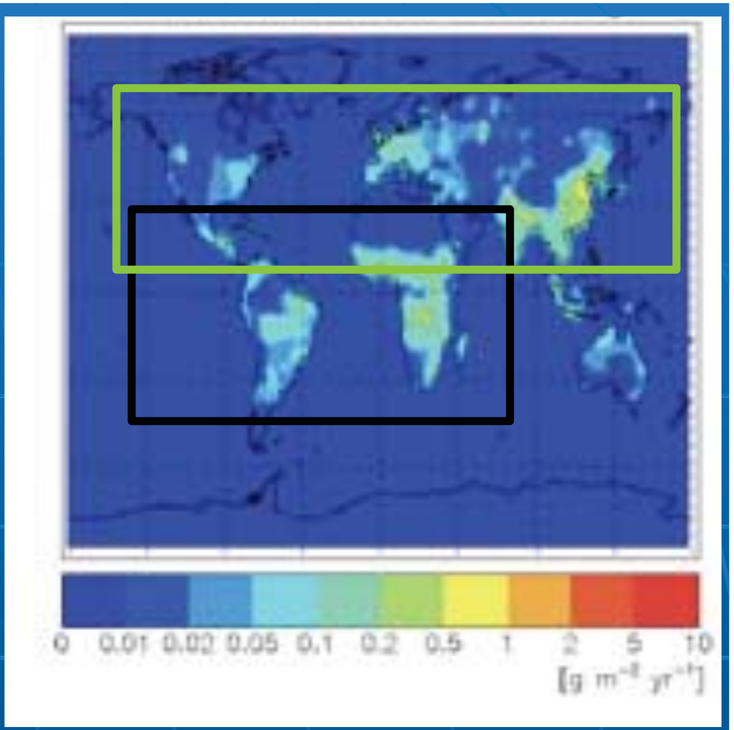
- **Anthropogenic sources (fossil and biofuels)**:

≈ 5.4 TgC yr-1

A) Domestic use

B) Road transport

C) Industry



Uncertainty of a factor of 2

Organic Carbon

- **Large scale biomass burning**:

  ≈ 34.7 Tg yr-1

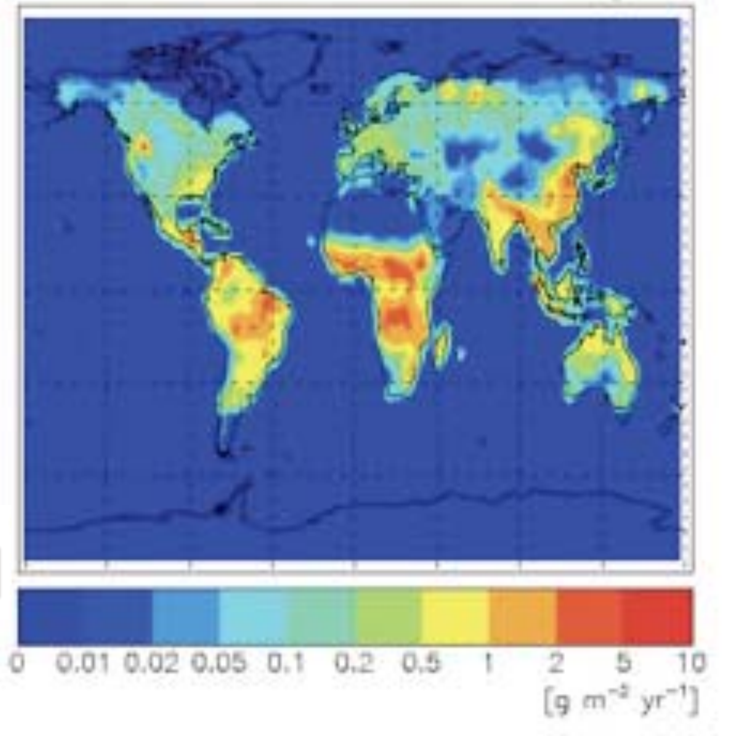
- **Anthropogenic sources (fossil and biofuels)**:

  ≈ 19.1 Tg yr-1

A) Domestic use

B) Road transport

C) Industry

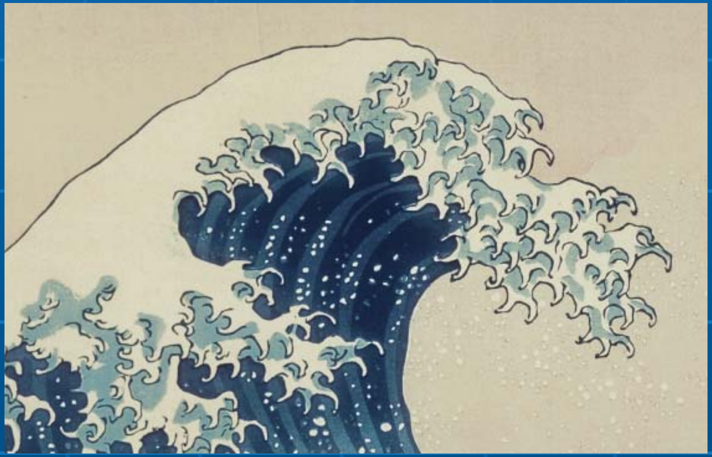


Uncertainty of a factor of 2

Sea Salt

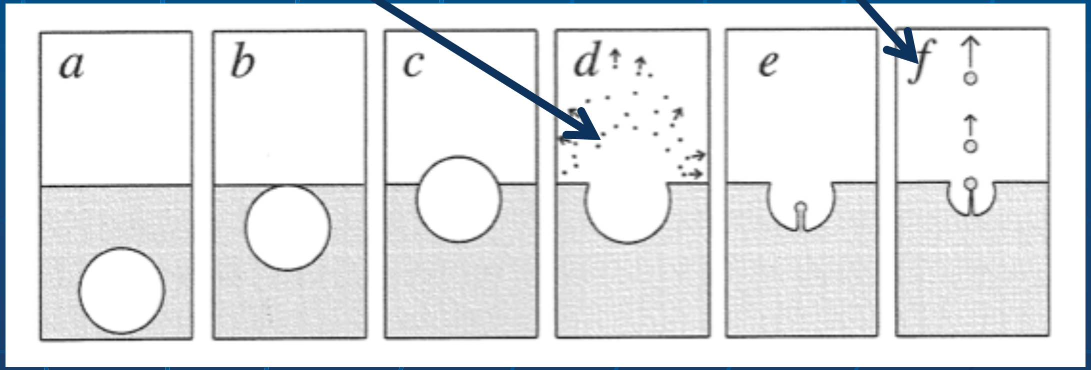
Mechanism of production

Air entrainment

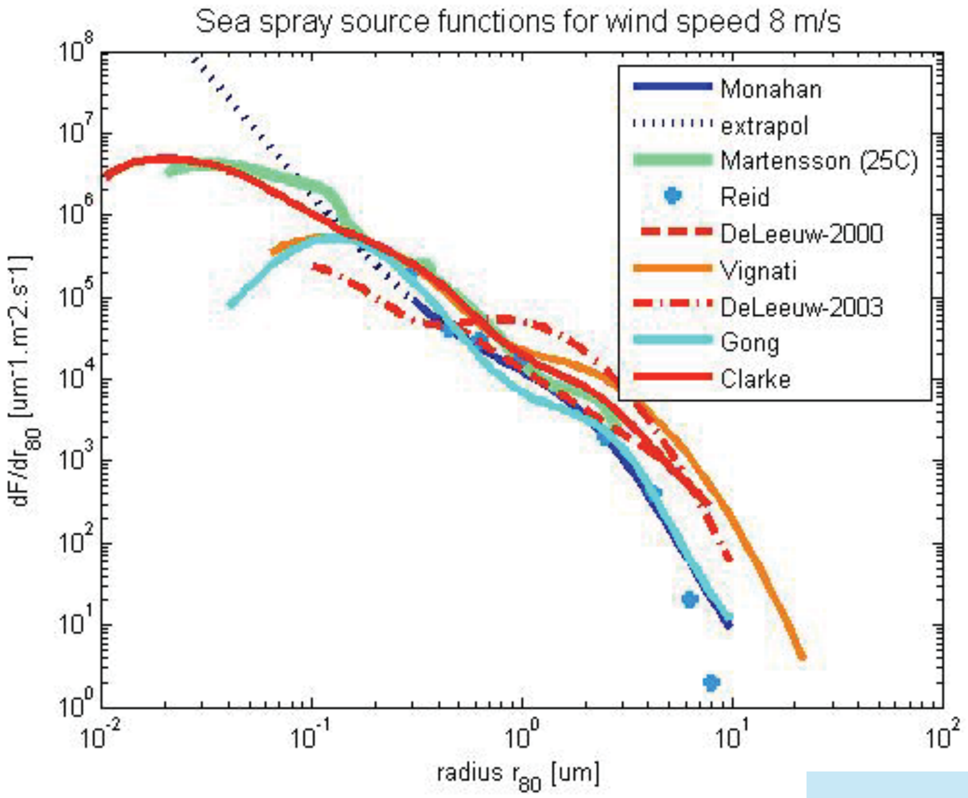


Film droplet injection Jet droplet injection

Bubble bursting

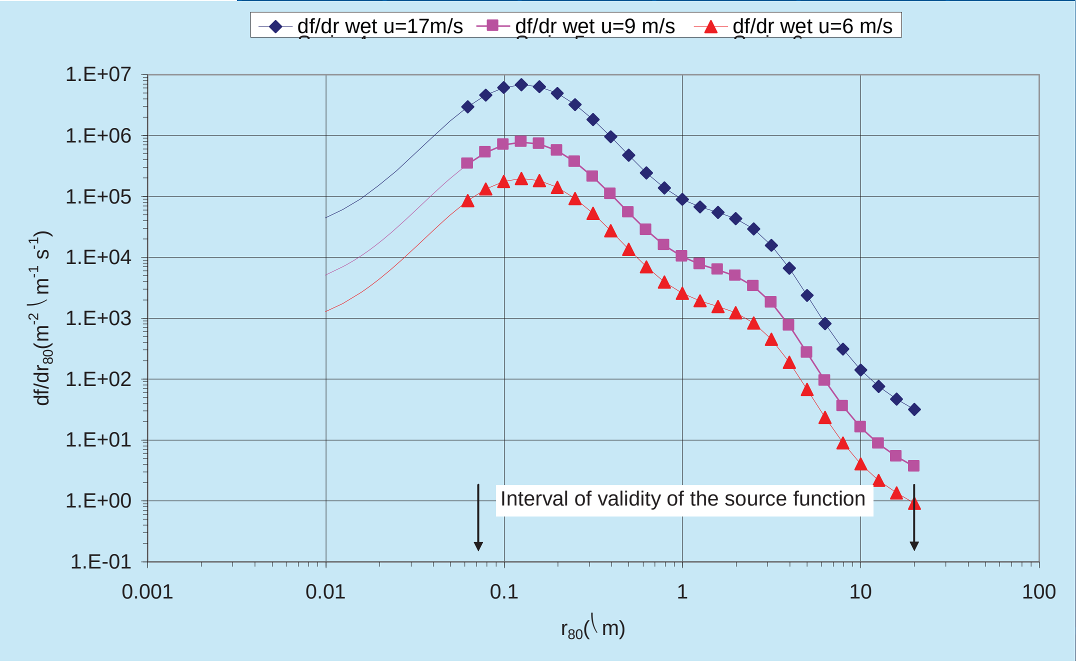


(Schwarz and Lewis, 2004)



(De Leeuw et al, 2011)

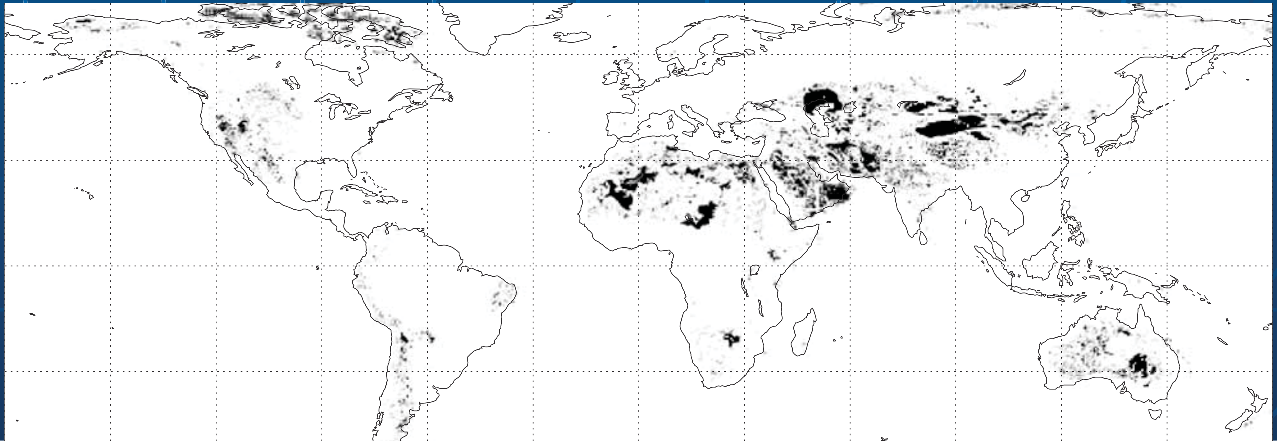
Dependence of wind speed



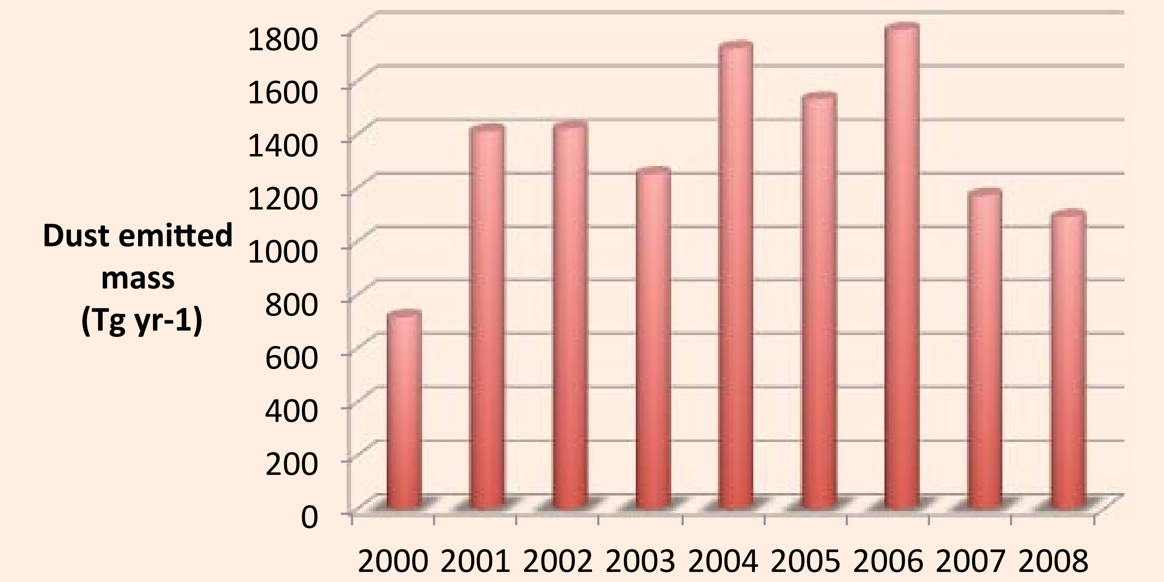
Gong, 2003

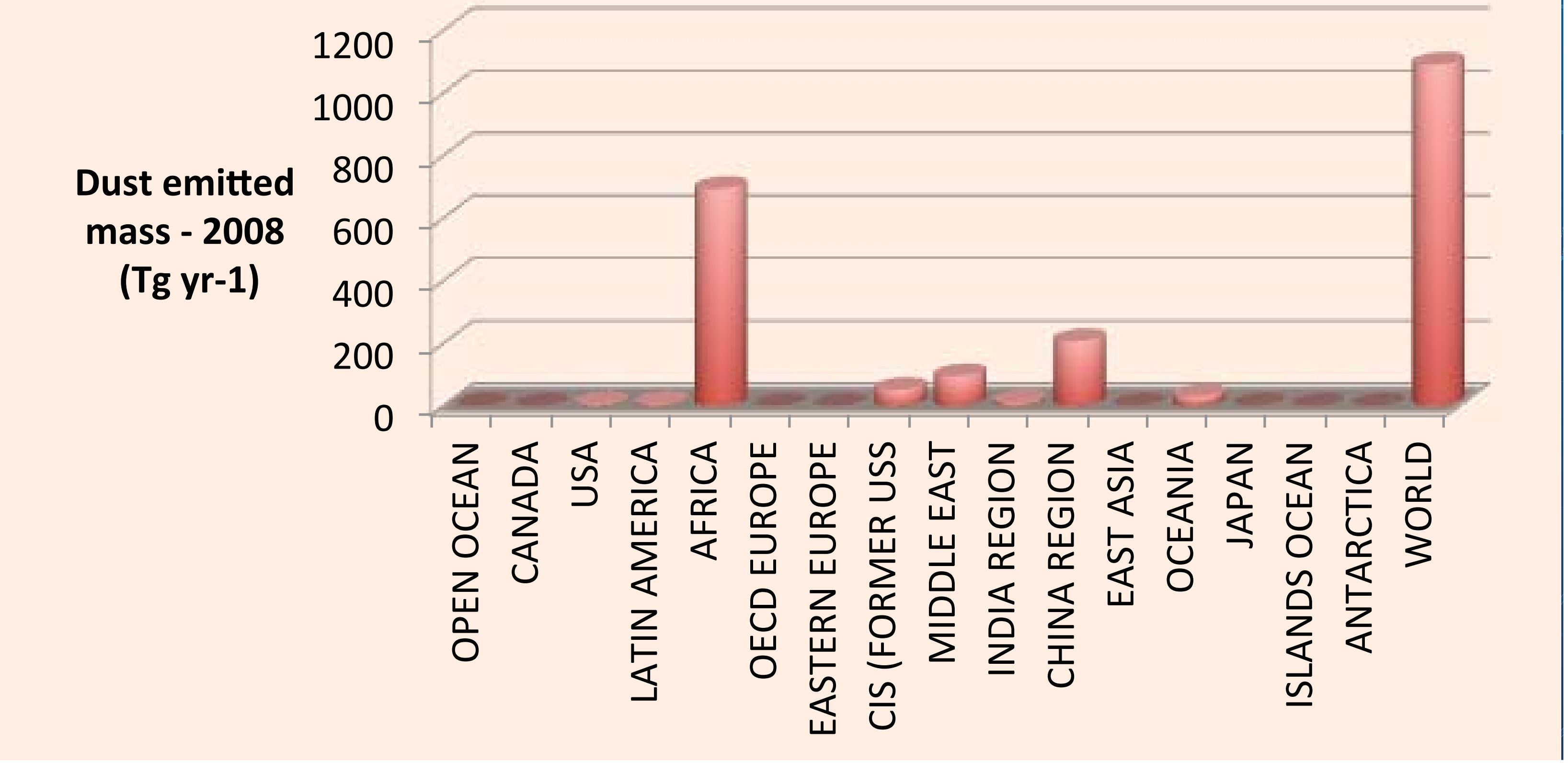
Dust

- Mechanism of production: soil deflation from bare surface when wind exceeds a certain threshold
- from dust potential sources (using vegetation maps, dust grain types, low surface roughness,...)



Tegen et al., 2002


Dust emitted mass (Tg yr-1)
1800
1600
1400
1200
1000
800
600
400
200
0
2000
2001
2002
2003
2004
2005
2006
2007
2008


Dust emitted mass - 2008 (Tg yr-1)
1200
1000
800
600
400
200
0
OPEN OCEAN
CANADA
USA
LATIN AMERICA
AFRICA
OECD EUROPE
EASTERN EUROPE
CIS (FORMER USS
MIDDLE EAST
INDIA REGION
CHINA REGION
EAST ASIA
OCEANIA
JAPAN
ISLANDS OCEAN
ANTARCTICA
WORLD

Removals

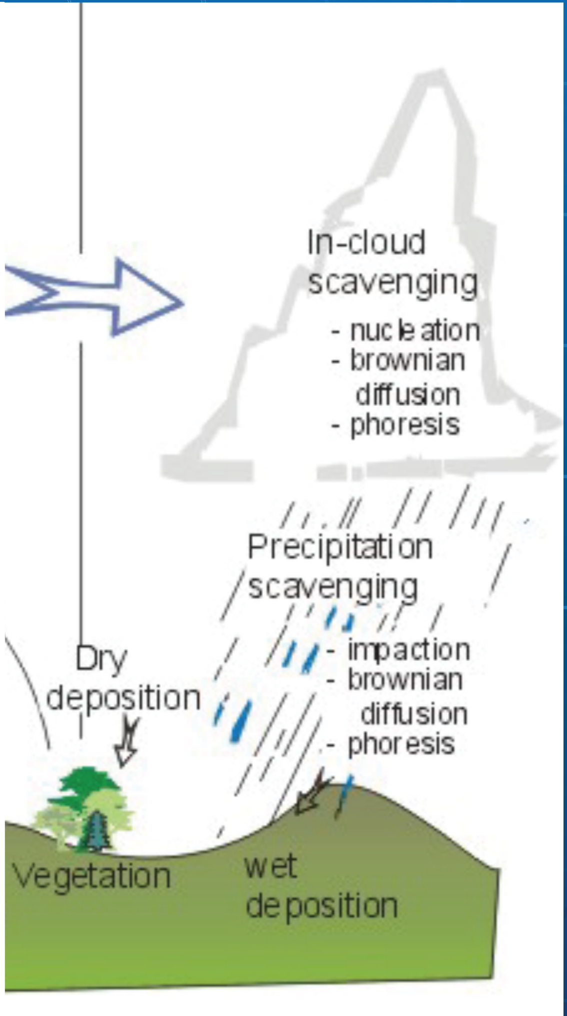
Types of removals

Dry deposition: Transport of particles from the atmosphere onto surfaces when precipitation is not present

Wet deposition: Process by which particles are removed by cloud (and fog) droplets, rain and snow and transported on Earth's surface;

divided in:
- In-cloud scavenging

- Below-cloud scavenging



Dry removal

- Not practical to implement a formulation of all microphysical processes that lead particles from the atmosphere to the surface
- Most used formulation

$$F = -v_d C$$

F= dry deposition flux; v_d deposition velocity; C concentration

Dry removal

$$F = -v_d C$$

F= dry deposition flux; v_d deposition velocity; C concentration

F = material deposited per unit of surface and time

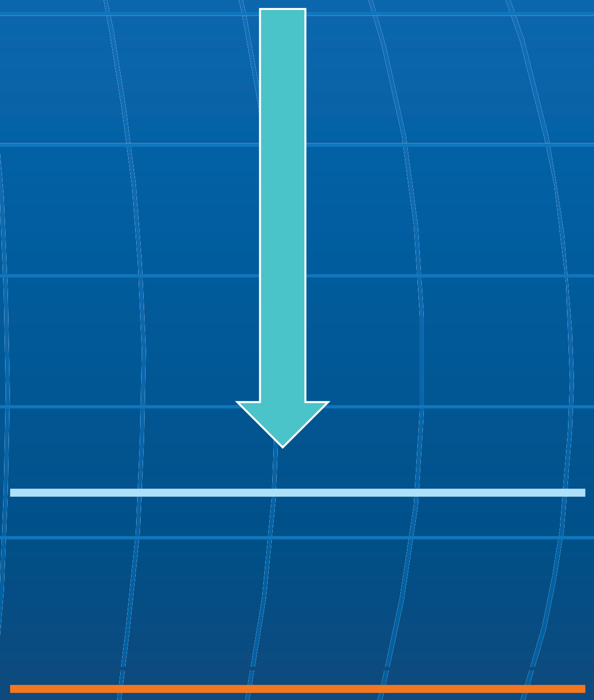
C is given a certain height and v_d as well

Advantages!
All processes are represented with v_d

Disadvantages!
It is difficult to correctly represent all processes with v_d

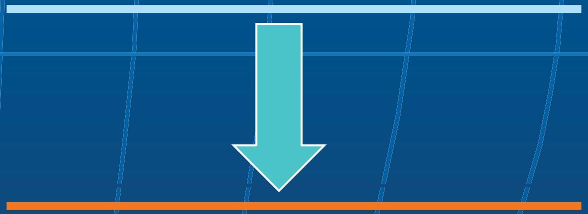
Dry deposition: 3 step process

- Aerodynamic transport through the surface layer



Dry deposition: 3 step process

- Brownian transport through stagnant *quasi-laminar sublayer*



Dry deposition: 3 step process

- Uptake at the surface

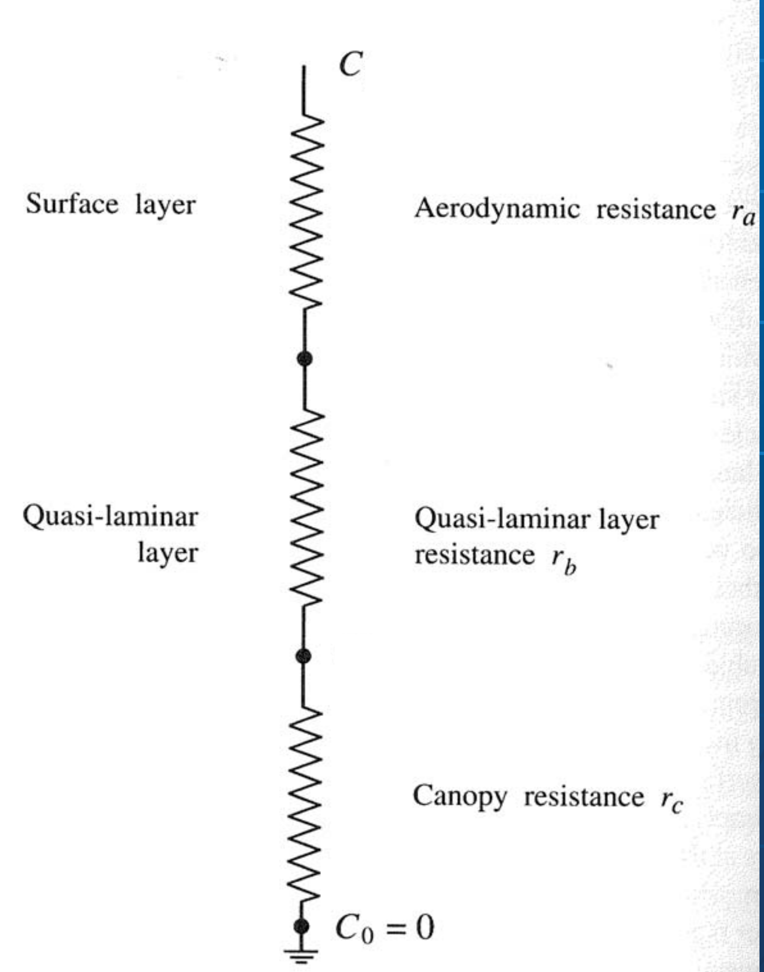
Resistant model for dry dep.

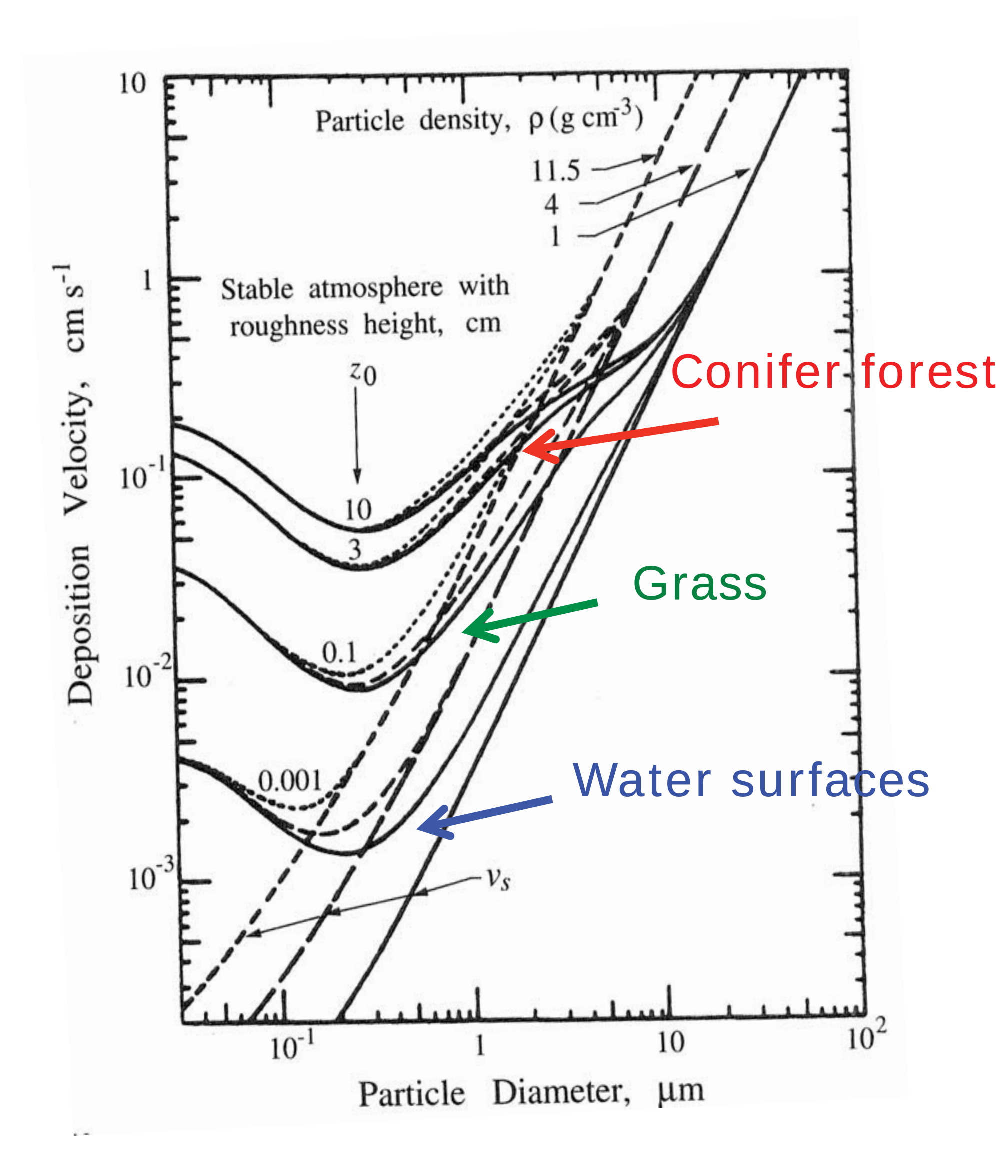
- In analogy with electrical resistance:

$$v_d^{-1} = r_t = r_a + r_b + r_c$$

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

v_s = particle settling velocity



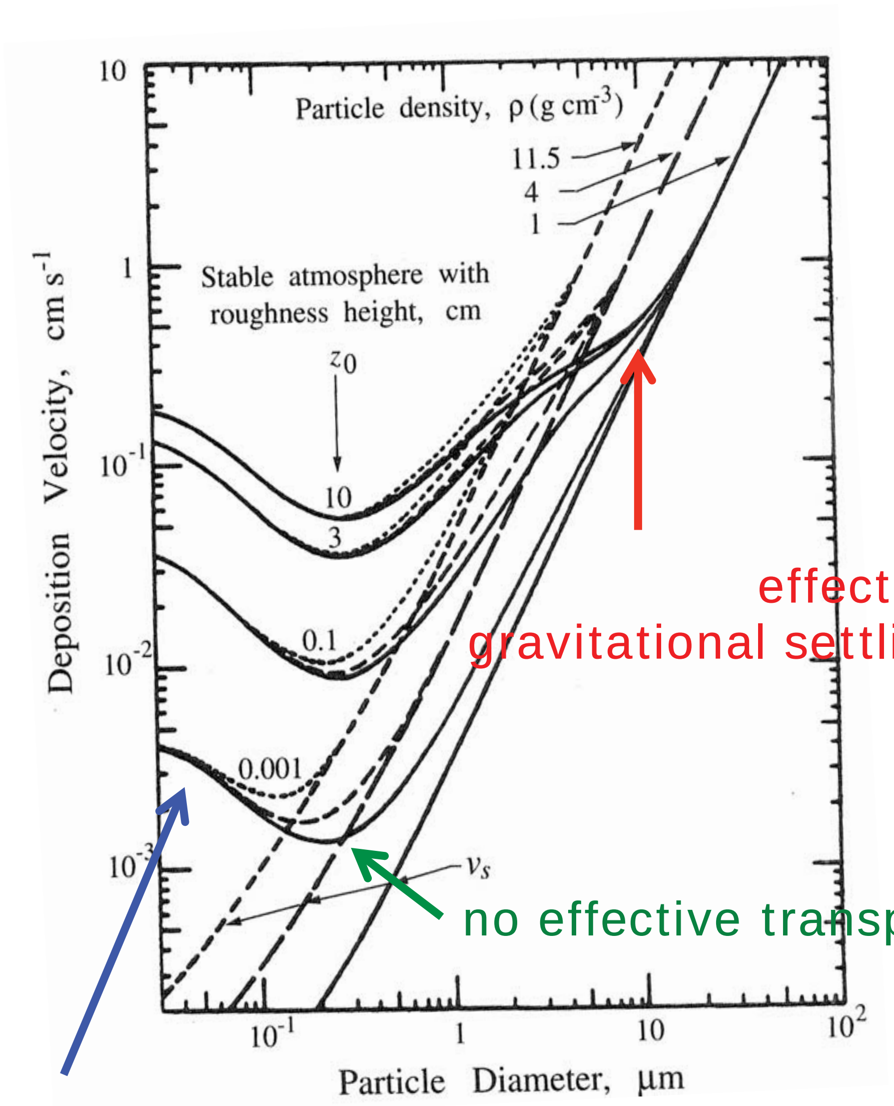


Conifer forest

Grass

Water surfaces

Sehmel, 1980



effective
gravitational settling

no effective transport

effective transport in ql layer (brownian)

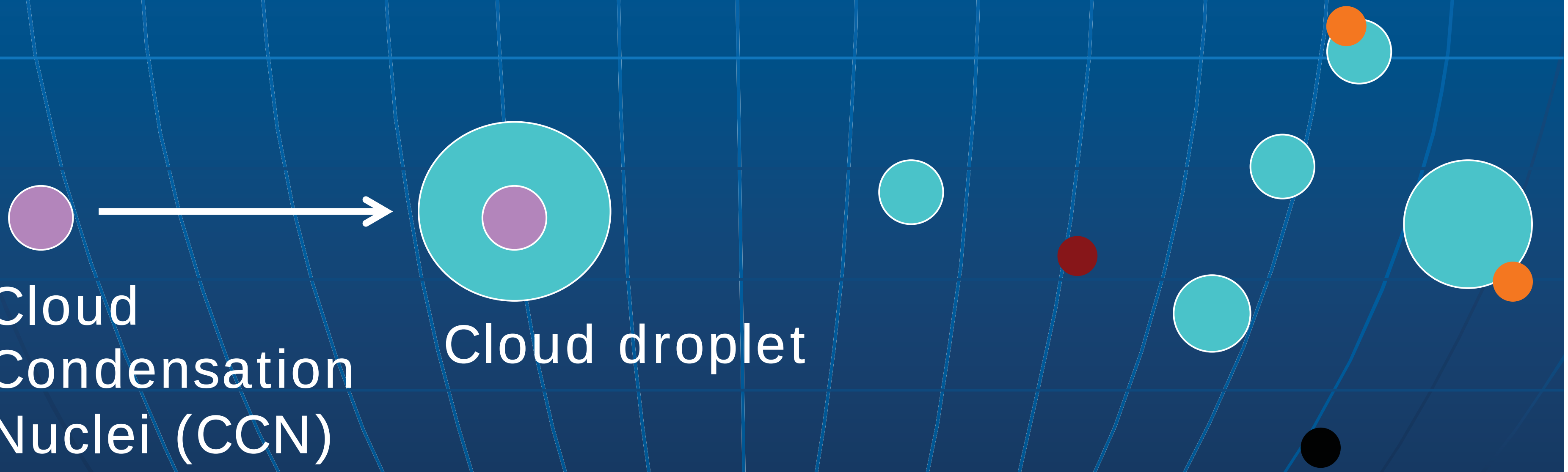
Sehmel, 1980

Wet removal

- One of the most complex process to model; for aerosols is the most uncertain:
  - various phases (aerosol, aqueous, cloudwater, rain, snow, ice cristal,...)
  - aerosol particles, cloud droplets, rain droplets, with their size distributions
  - clouds are a sub-grid scale phenomena
  - processes are reversible: cloud droplets may evaporate and release the particle

In-cloud scavenging

- Particles can be incorporated into cloud droplets (and rain droplets) inside a cloud by
    - Homogeneous nucleation
    - collection



Cloud Condensation Nuclei (CCN)

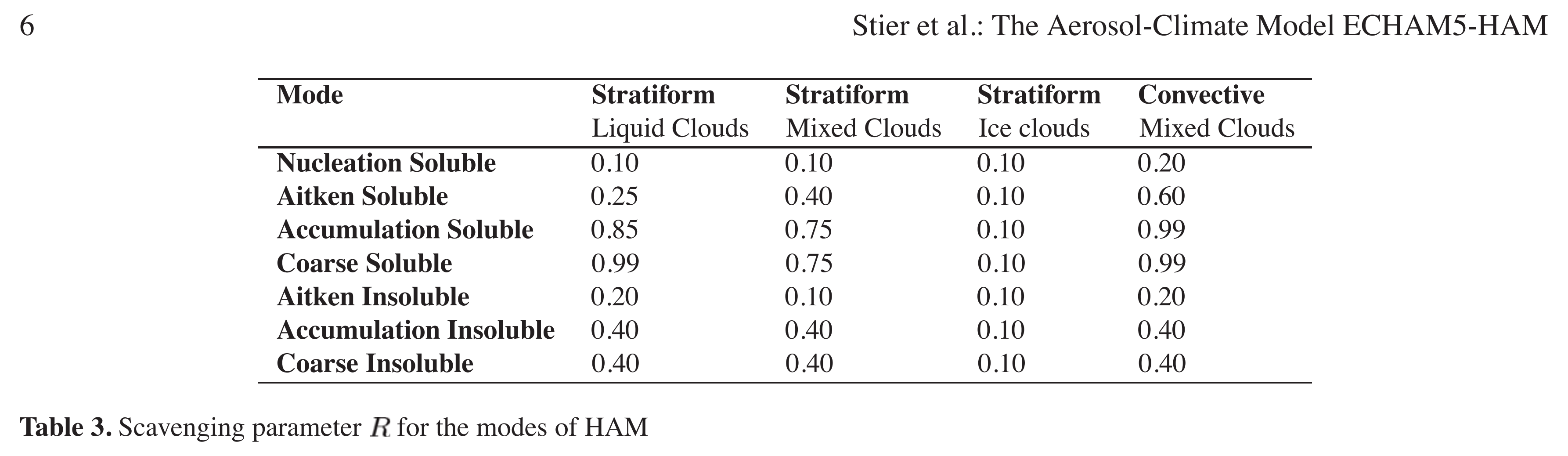
Cloud droplet

Removal of particles in models:

Scavenging parameter R:

$$\frac{\Delta C}{\Delta t} \propto R, f_{cl}, C, \ldots\ldots$$

C = aerosol concentration; f_{cl} = cloud fraction



6

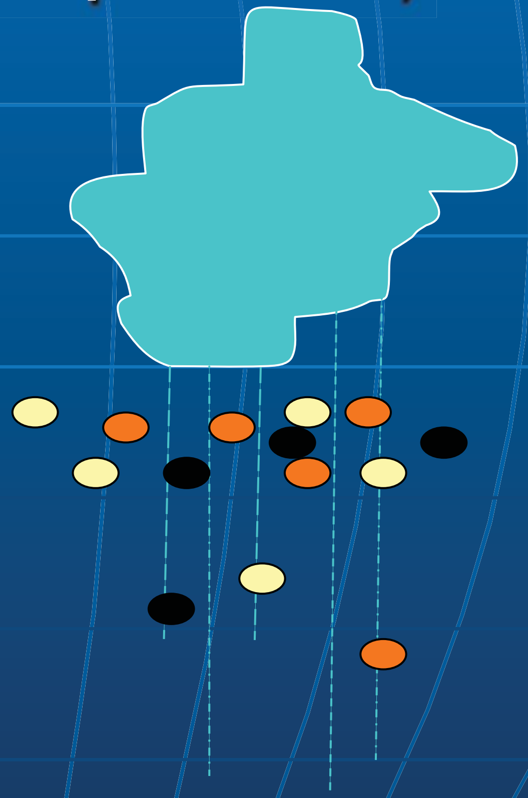
Stier et al.: The Aerosol-Climate Model ECHAM5-HAM

Mode	**Stratiform** Liquid Clouds	**Stratiform** Mixed Clouds	**Stratiform** Ice clouds	**Convective** Mixed Clouds
Nucleation Soluble	0.10	0.10	0.10	0.20
Aitken Soluble	0.25	0.40	0.10	0.60
Accumulation Soluble	0.85	0.75	0.10	0.99
Coarse Soluble	0.99	0.75	0.10	0.99
Aitken Insoluble	0.20	0.10	0.10	0.20
Accumulation Insoluble	0.40	0.40	0.10	0.40
Coarse Insoluble	0.40	0.40	0.10	0.40

Table 3. Scavenging parameter R for the modes of HAM

Below cloud scavenging

- Removal by precipitation of particles below cloud base by impaction, diffusion, ….



How do we model it?

$$\frac{\Delta C}{\Delta t} \propto R_r, R_s, f_{precipitation}, C, \ldots\ldots.$$

C = aerosol concentration;

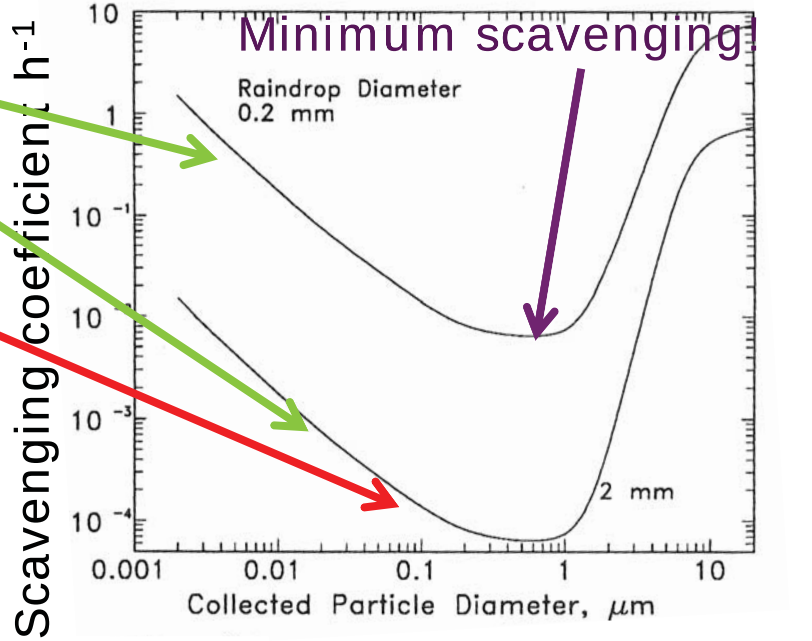
$f_{precipitation}$ = fraction of gridbox affected by precipitation;

R = scavenging efficiency for rain and snow

Rain droplet size distribution

Aerosol size distribution

For rainfall intensity of 1 mm h^{-1}



Minimum scavenging!

Seinfeld and Pandis, 1998

Thank you!!!

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