Aerosol physics

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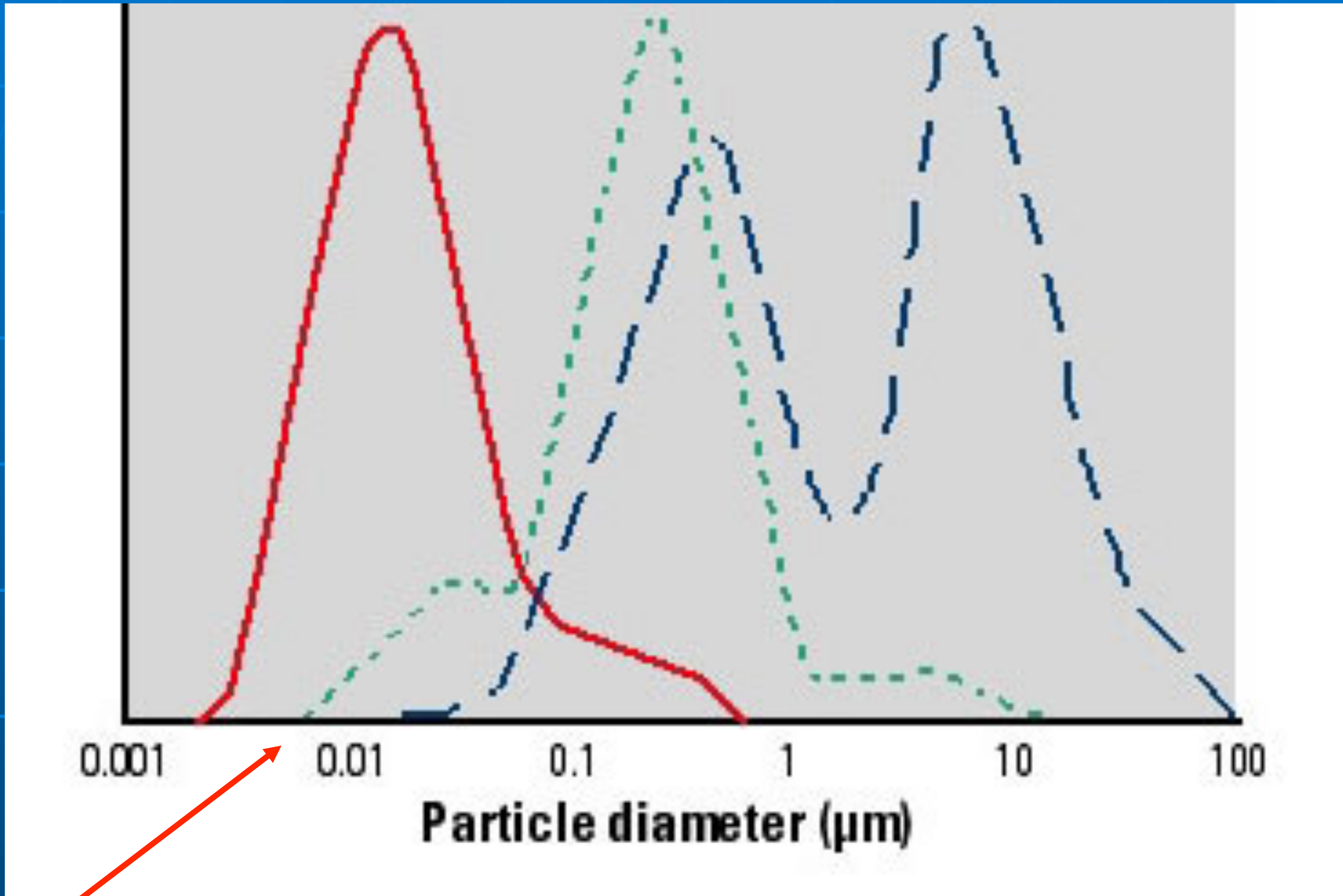
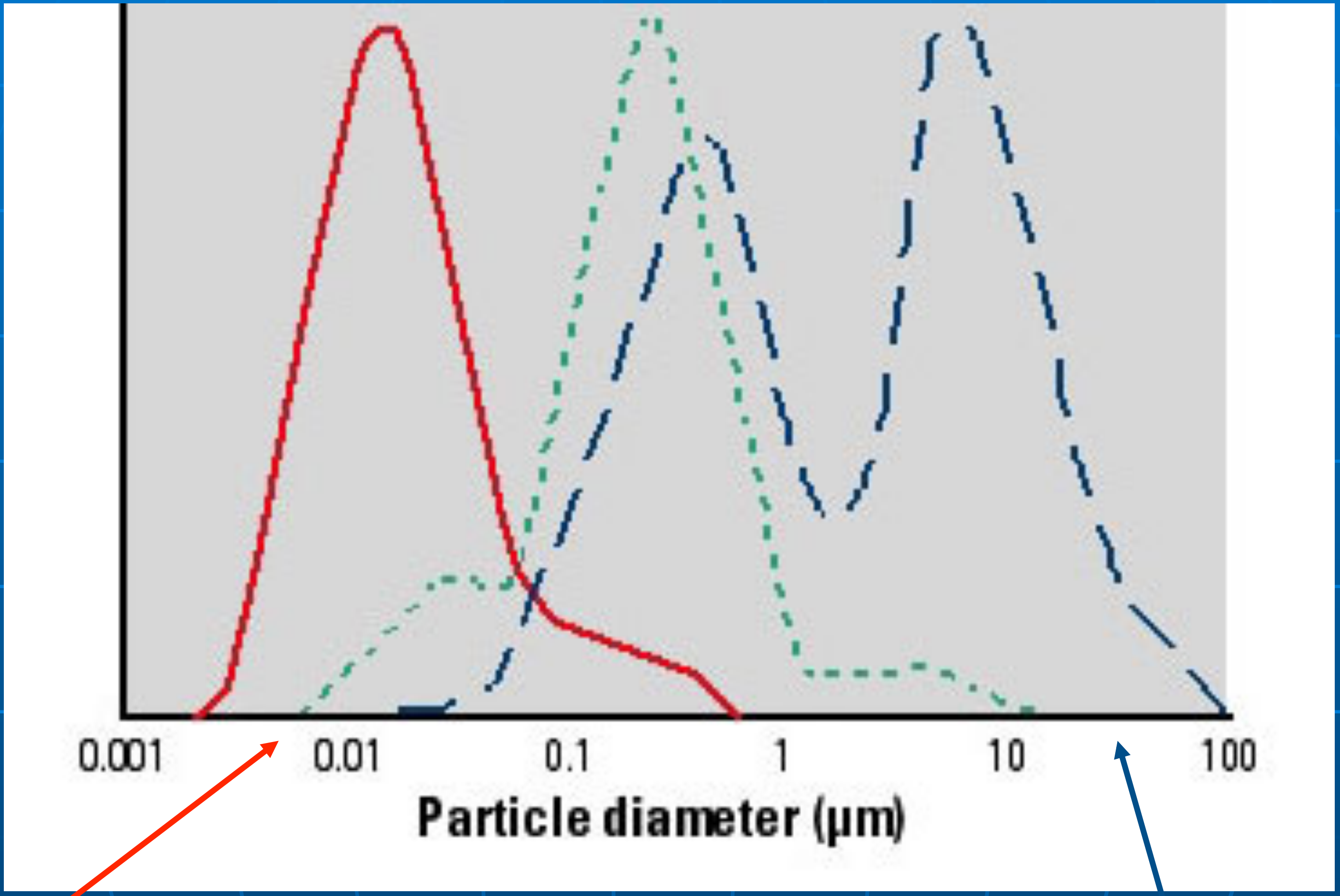
Aerosol dynamics

- Nucleation
- Condensation/Evaporation
- Coagulation

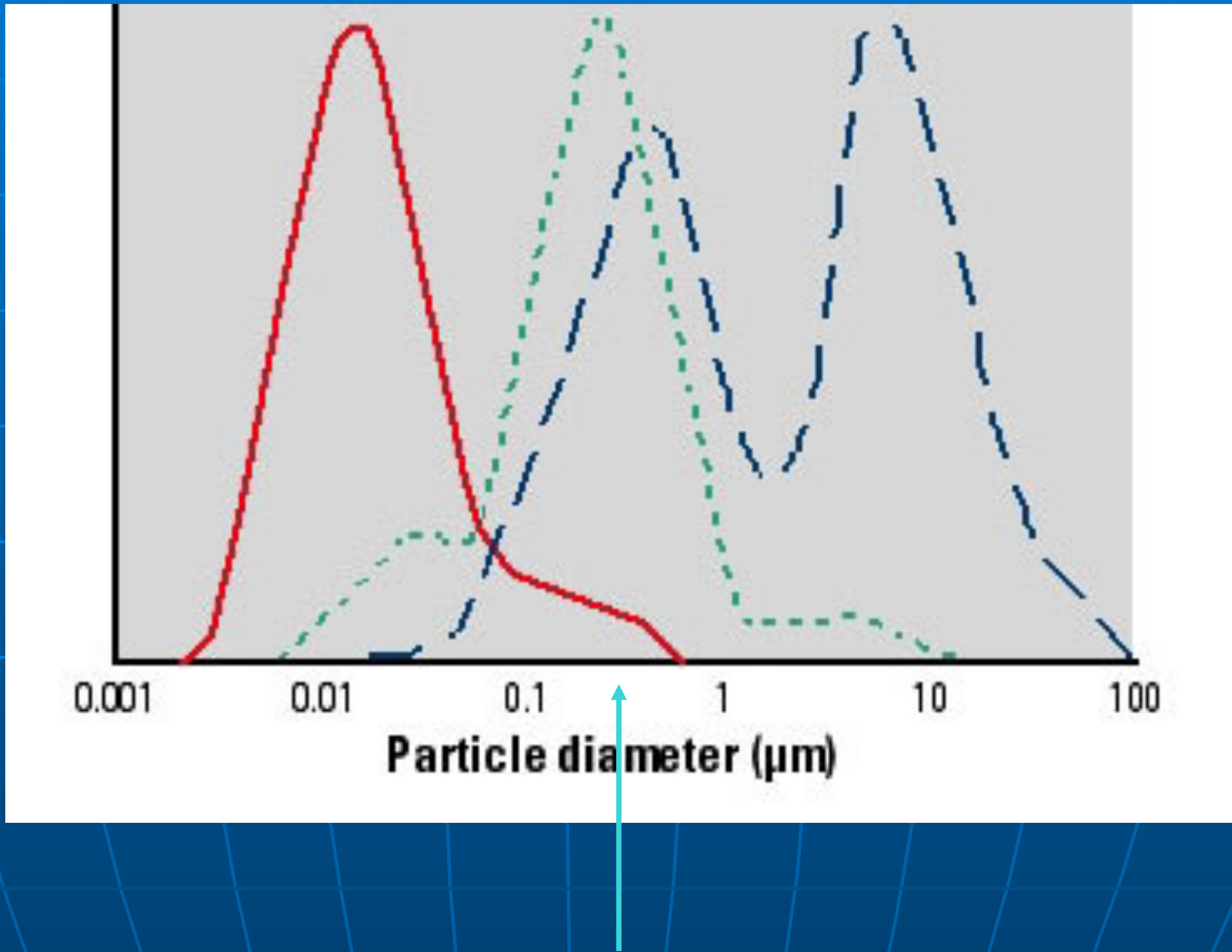


very mobile
rapidly evaporating



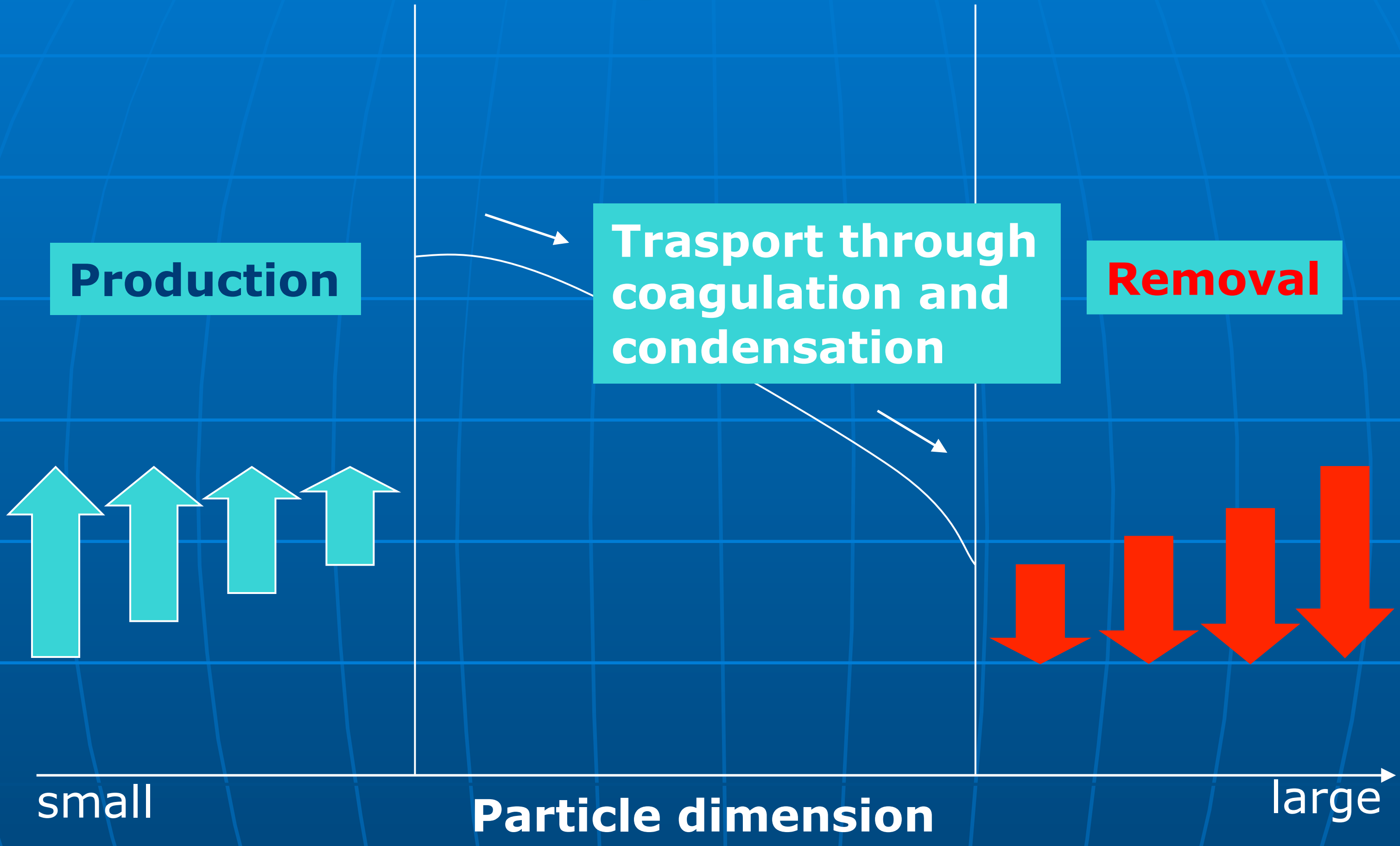
very mobile
rapidly evaporating

gravitational fall is important
large inertia



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

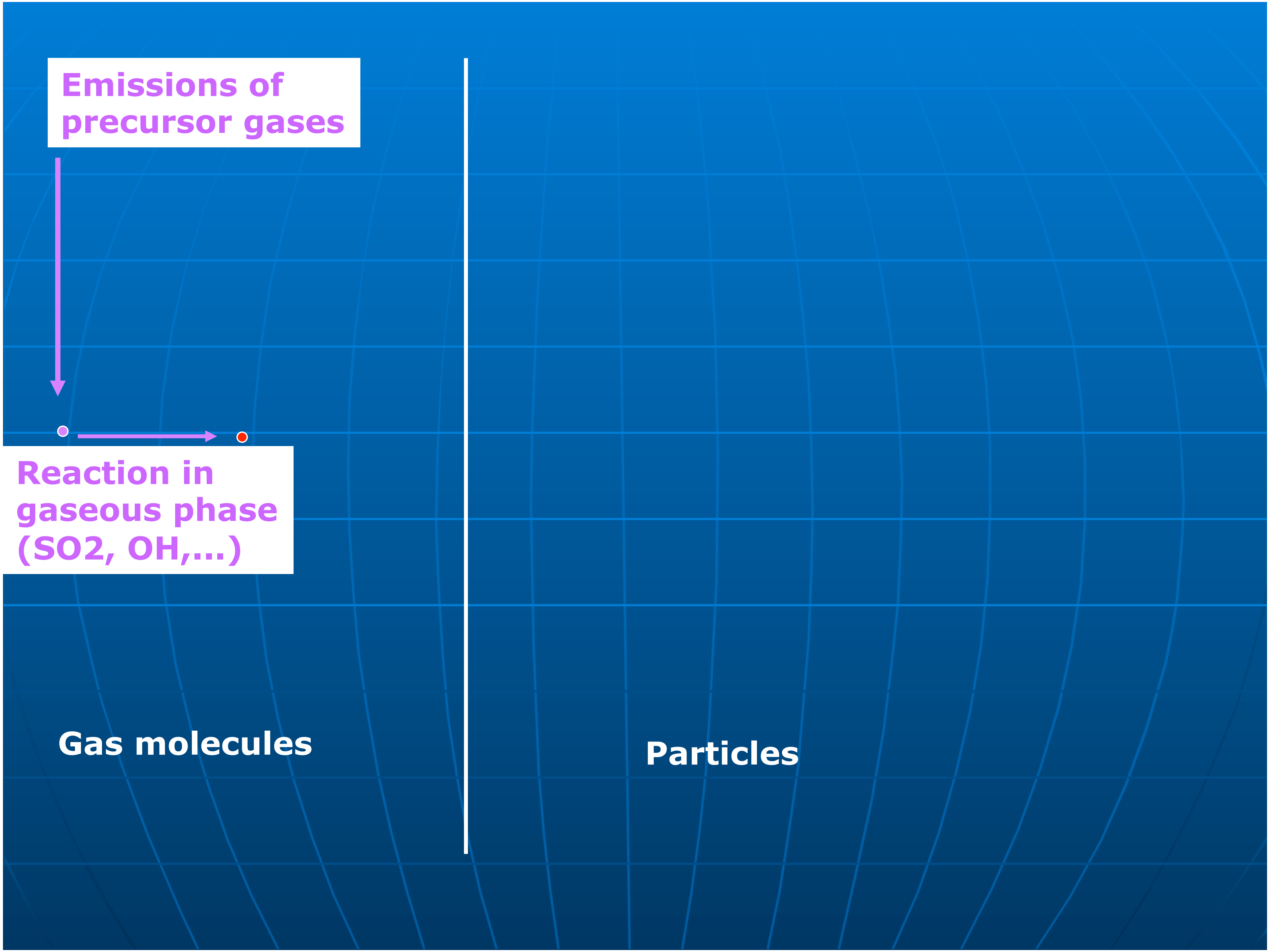
Mass flux along the size spectrum

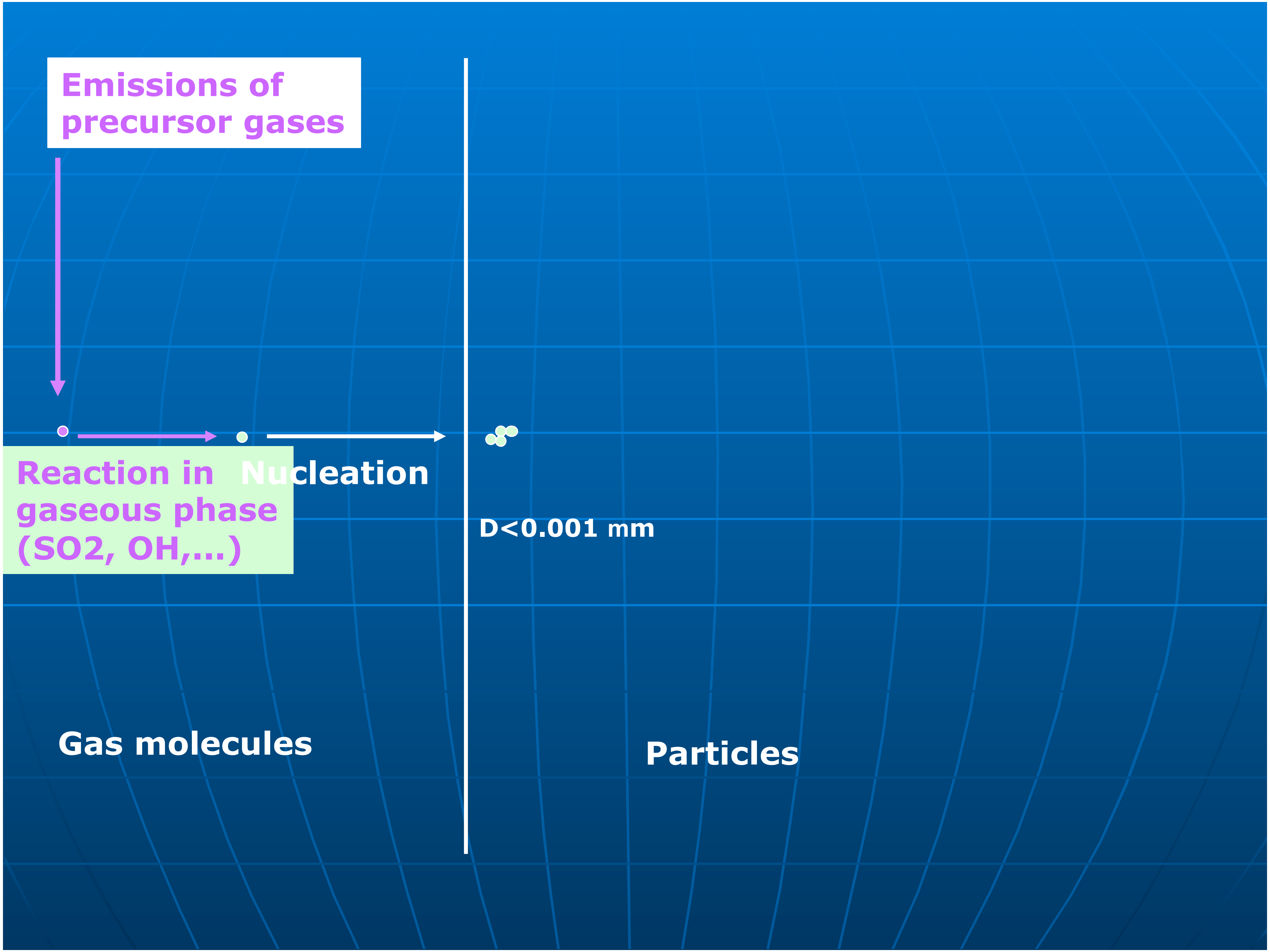


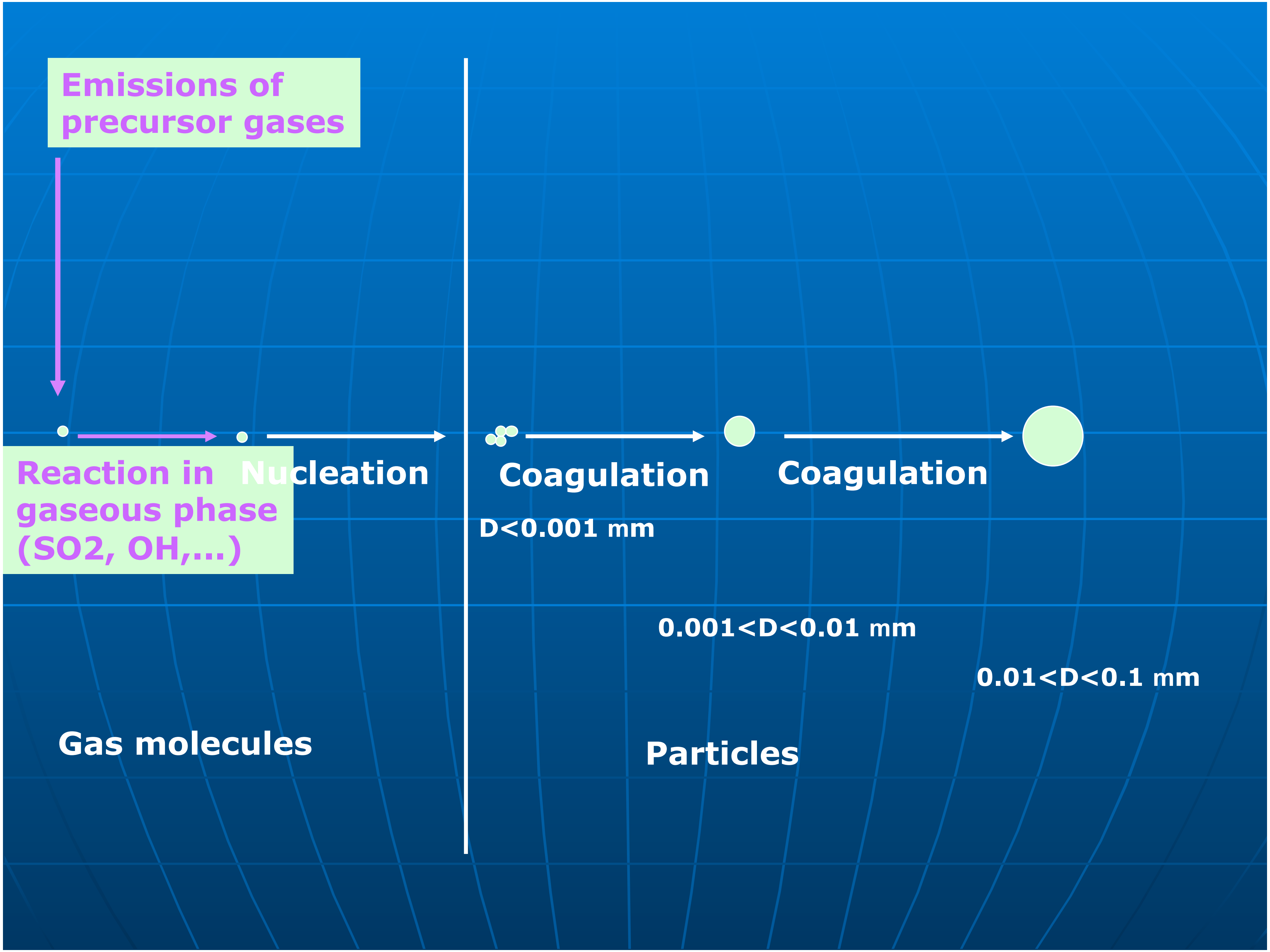
(Twomey, 1977)

Gas molecules

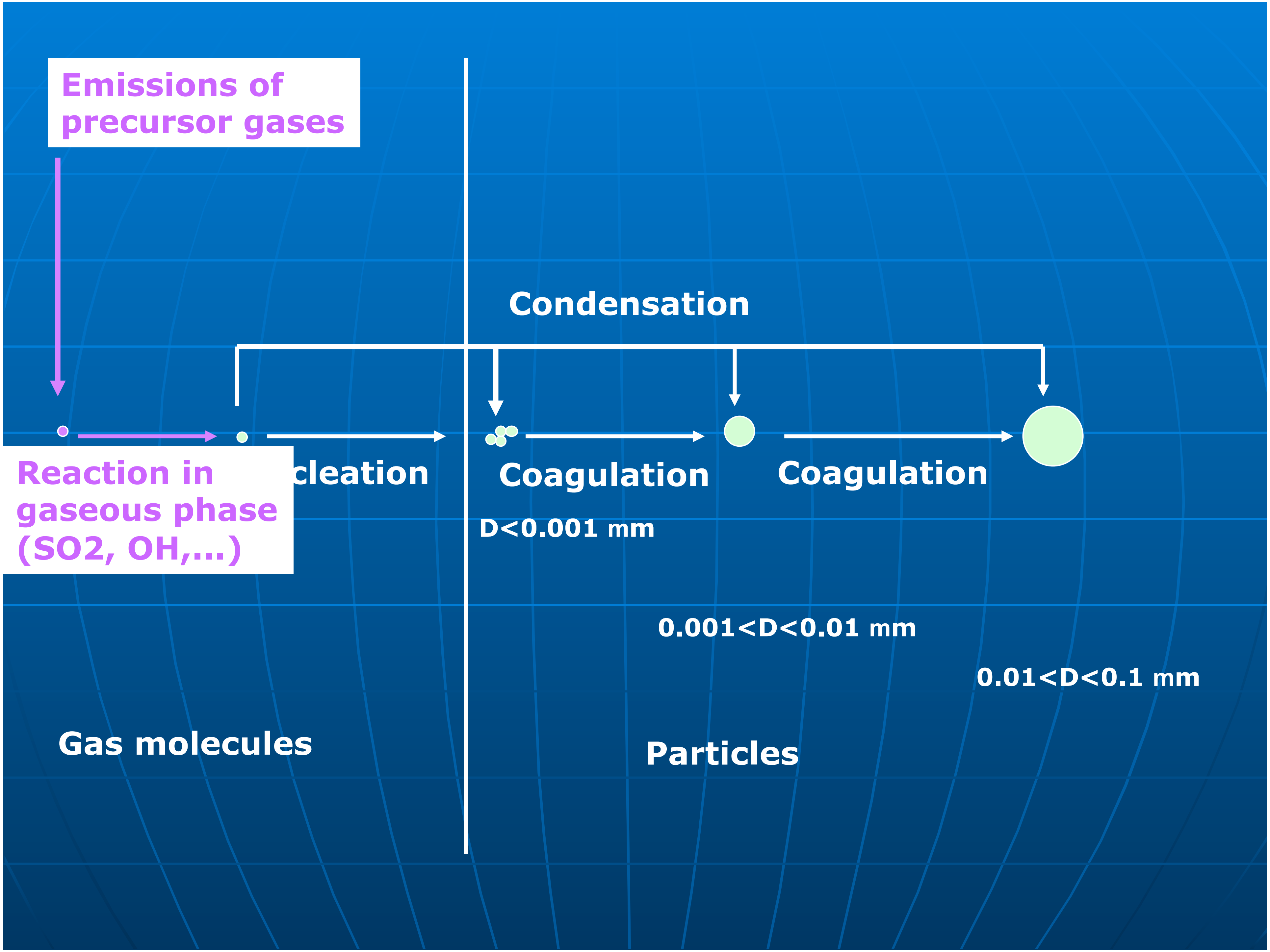
Particles


Emissions of precursor gases
Reaction in gaseous phase (SO2, OH,…)
Gas molecules
Particles


Emissions of precursor gases
Reaction in gaseous phase (SO2, OH,…)
Nucleation
D<0.001 mm
Gas molecules
Particles



Emissions of precursor gases
Reaction in gaseous phase (SO2, OH,...)
Nucleation
Coagulation
Coagulation
D<0.001 mm
0.001<D<0.01 mm
0.01<D<0.1 mm
Gas molecules
Particles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Gas molecules
Particles

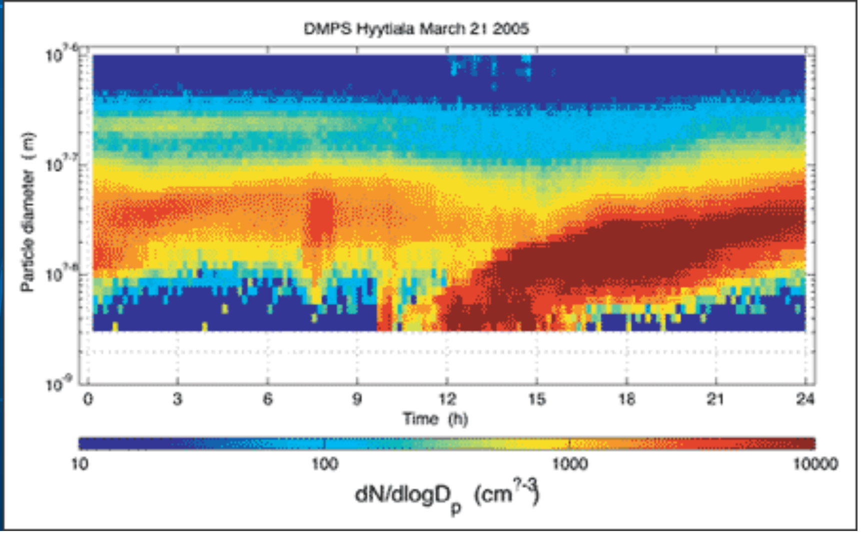
Dynamics general equation

$$\frac{\partial n_i}{\partial t} = \left(\frac{\partial n_i}{\partial t}\right)_{cond\,/\,evap} + \left(\frac{\partial n_i}{\partial t}\right)_{coag} + \left(\frac{\partial n_i}{\partial t}\right)_{nucl}$$

$$\frac{\partial m_i}{\partial t} = \left(\frac{\partial m_i}{\partial t}\right)_{cond\,/\,evap} + \left(\frac{\partial m_i}{\partial t}\right)_{coag} + \left(\frac{\partial m_i}{\partial t}\right)_{nucl}$$

n_i : number of particles
m_i : mass of specie i

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/dlogDp (cm?-3)

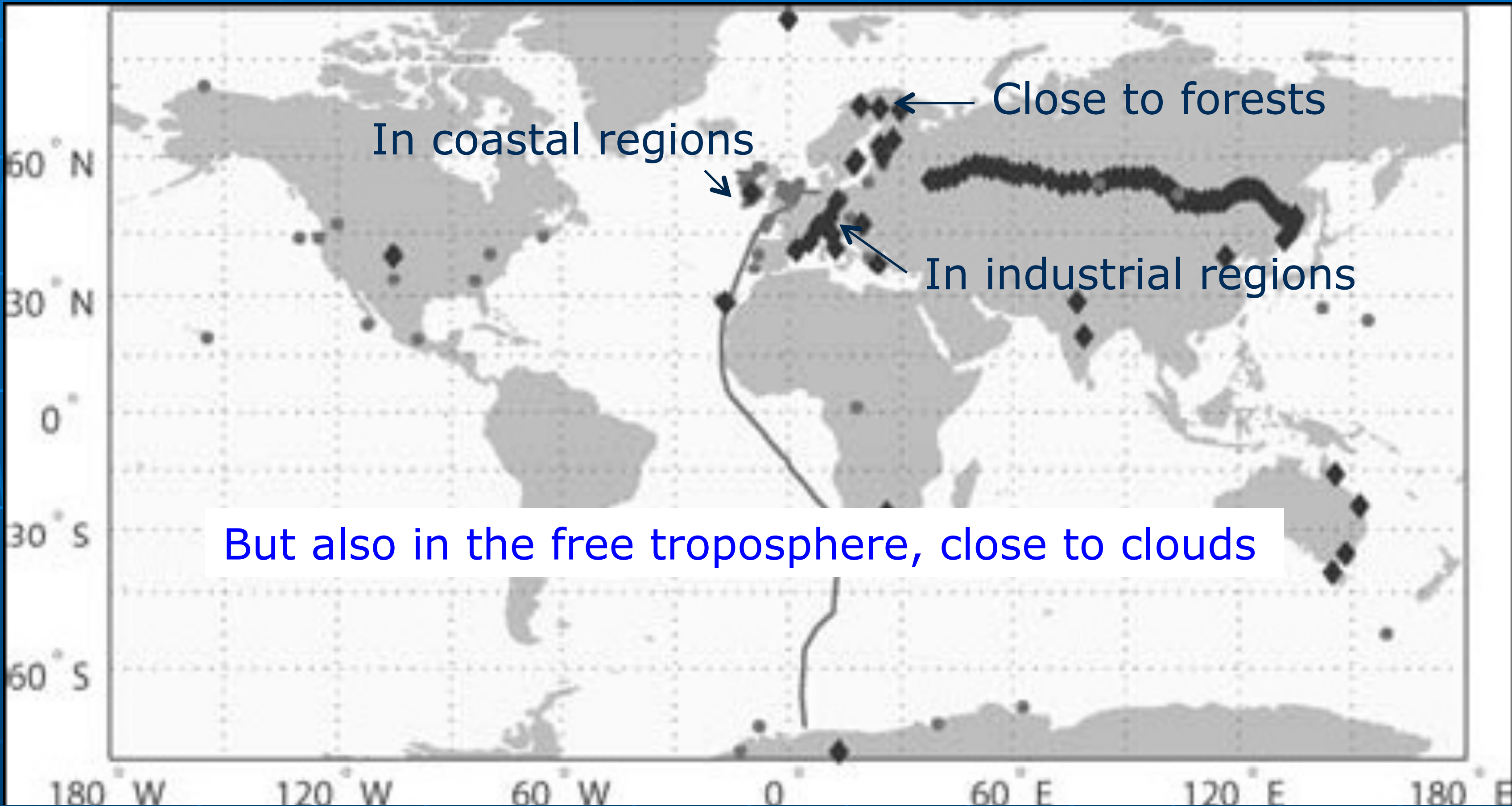
Nucleation

- 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

Nucleation

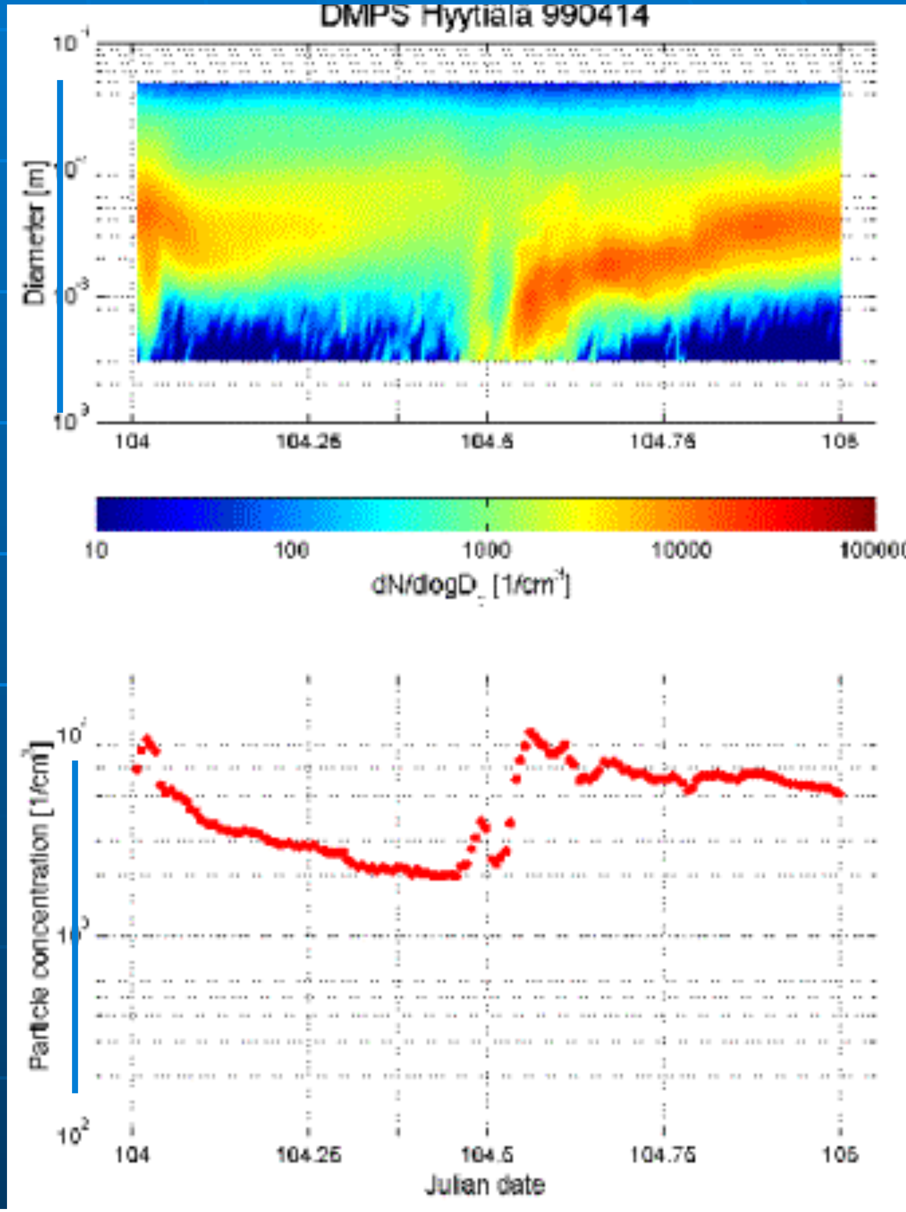
- Phase transformation of substances from the gaseous to the liquid or solid phase
- In 1897 first evidences of particle formation in the atmosphere, but only around 2000 instrumentation to quantitatively measure it appeared
- Two important phases in the new particle formation: the nucleation itself,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

Where were new particles observed?



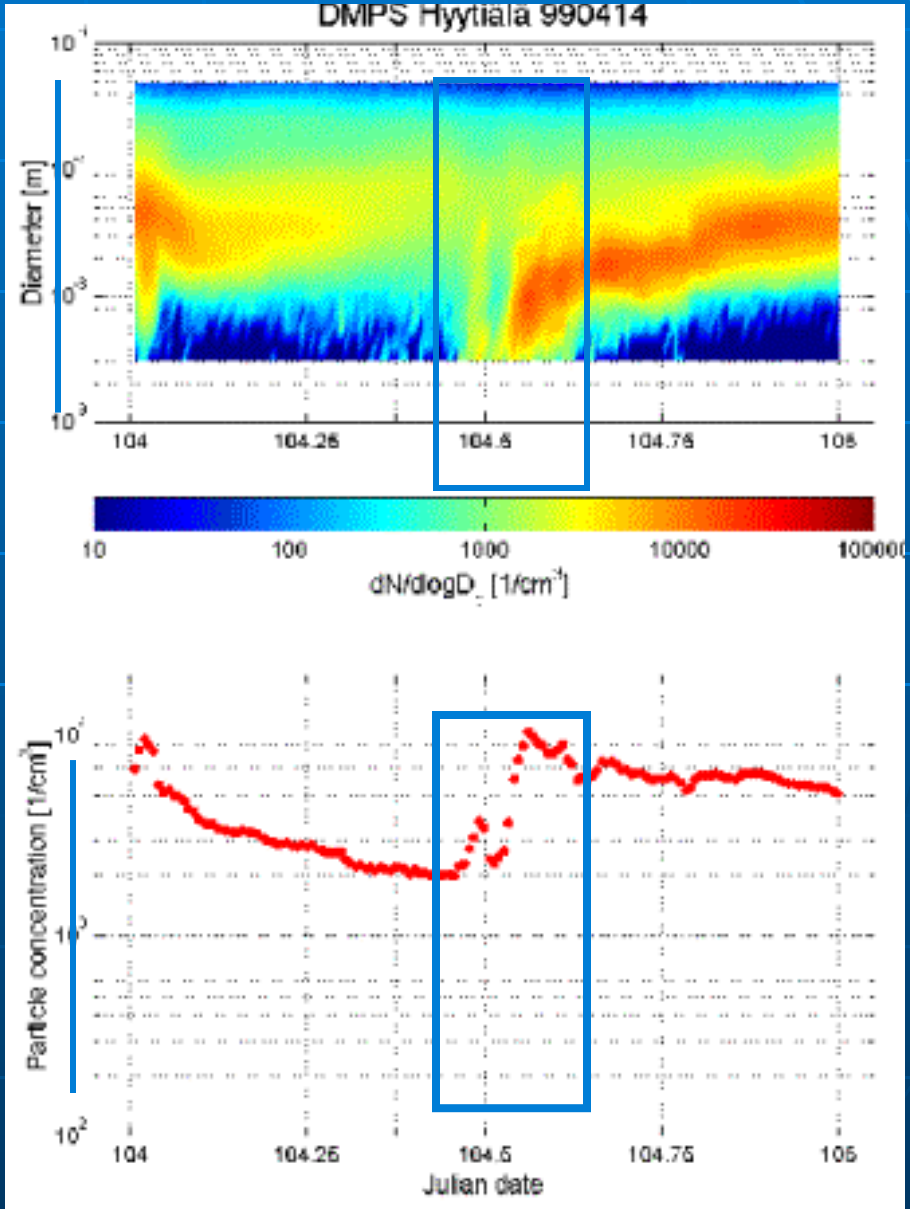
Kulmala et al., 2008

Particle formation takes place:



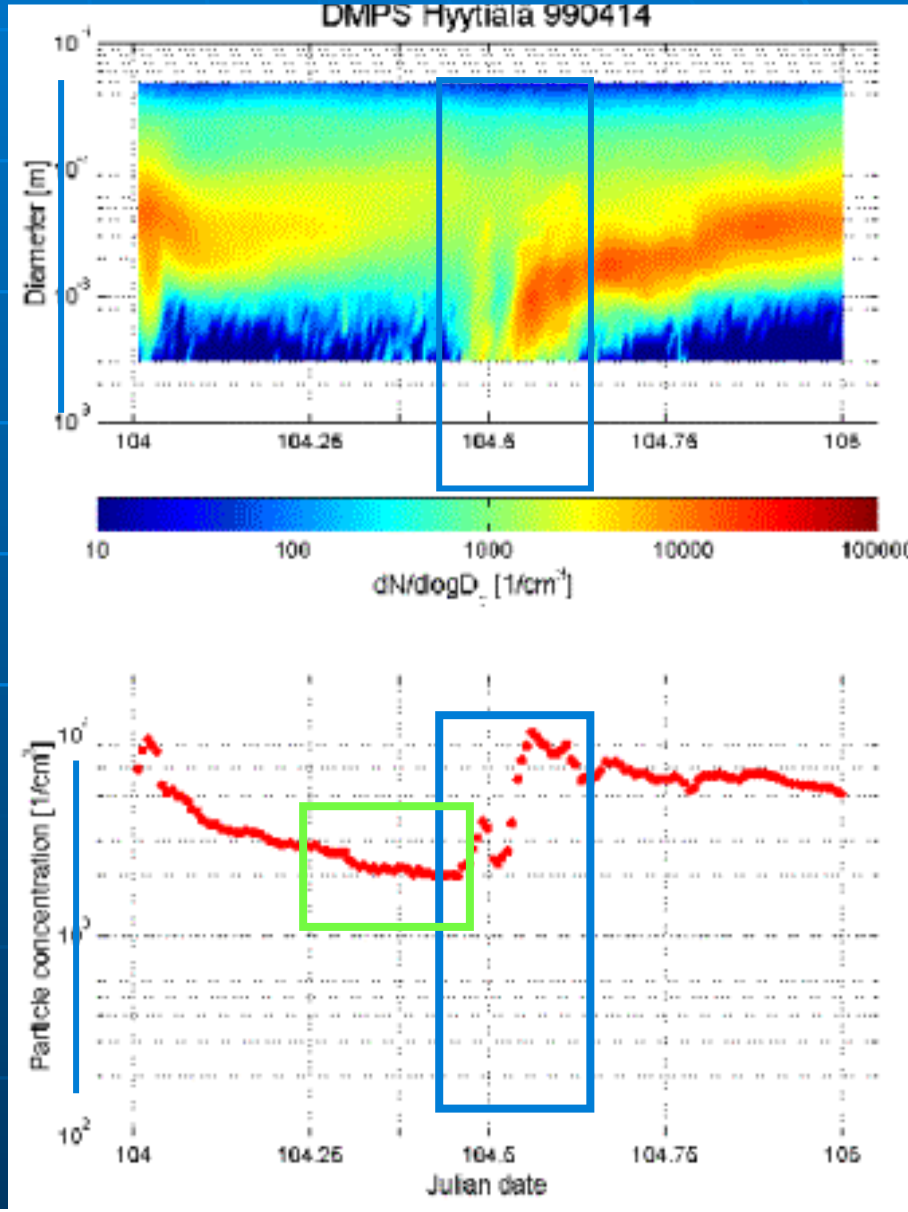
Particle formation takes place:

- During daytime, suggesting that photochemistry plays an important role

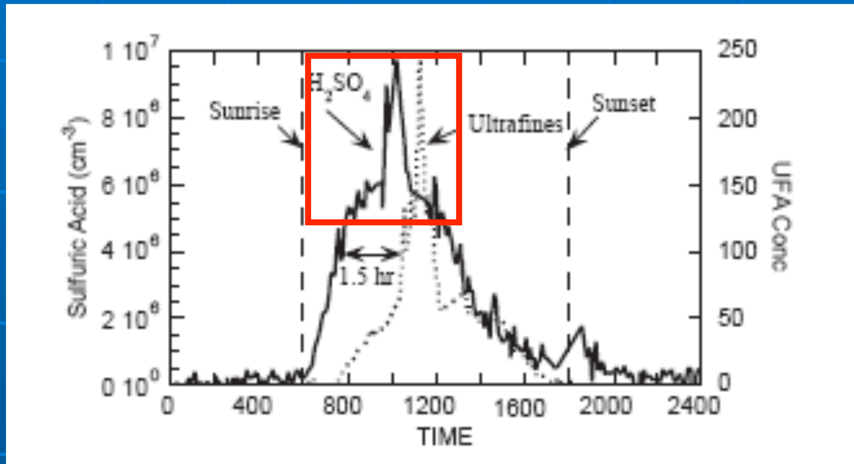


Particle formation takes place:

- 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



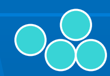
- Sometimes at low temperatures

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

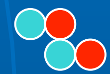
- At regional scale tipically: 0.01-10 $cm^{-3}s^{-1}$
- Up to 100 $cm^{-3}s^{-1}$ in urban areas
- Up to 10^4-10^5 $cm^{-3}s^{-1}$ in coastal zones and industrial plumes

Nucleation types

- Nucleation of a single species (homogeneous-homomolecular)



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



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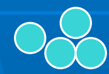
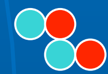
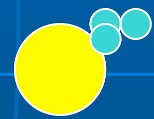


- Nucleation of two or more species (homogeneous-heteromolecular)



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



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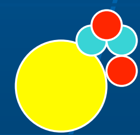
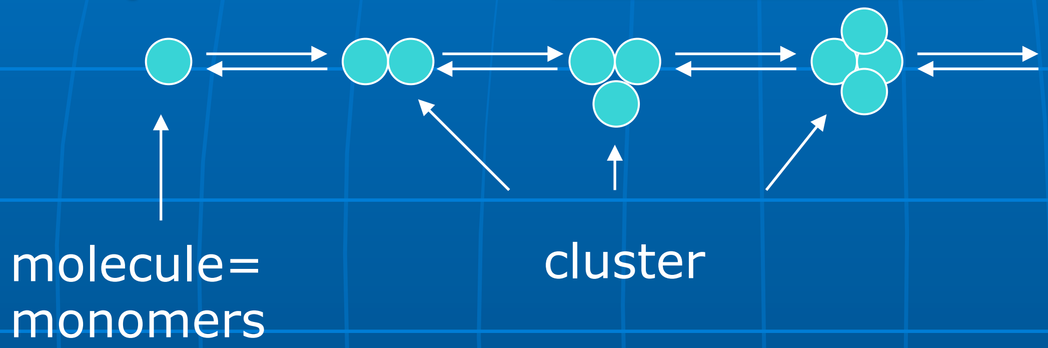


Nucleation mechanism

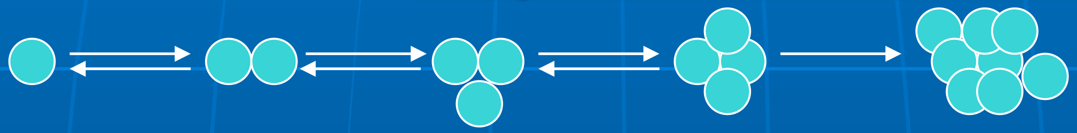
- Vapour A at saturation



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

Nucleation mechanism

- Vapour A at <u>supersaturation</u>



  - 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

Classical theory of homogeneous nucleation

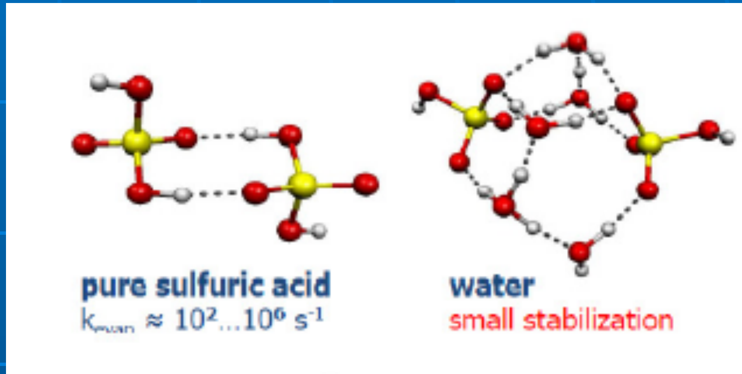
- It solves a set of equations for the cluster concentration (N(t)) of different dimensions

$$\frac{dN_i}{dt} = \beta_{i-1}N_{i-1}(t) - \gamma_i N_i(t) - \beta_i N_i(t) + \gamma_{i+1}N_{i+1}(t)$$

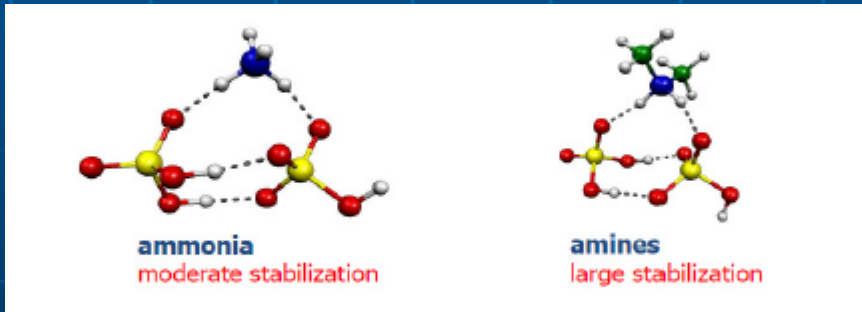
β **: costant for collision of a monomer with the cluster**
γ: **costant for evaporation of a monomer from a cluster**

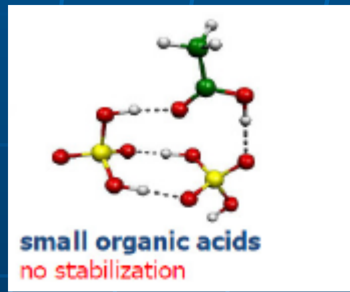
The suspected couple: H_2SO_4-H_2O

- Sulphuric acid and water constitute the cluster



- Other compounds stabilise them and make them grow





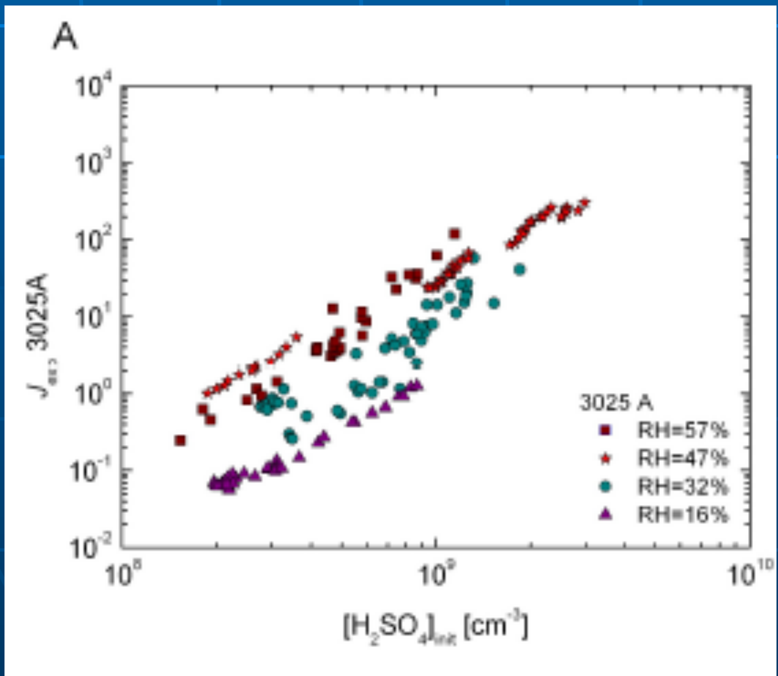
Kerminen et al., 2010

Measured characteristics of the couple

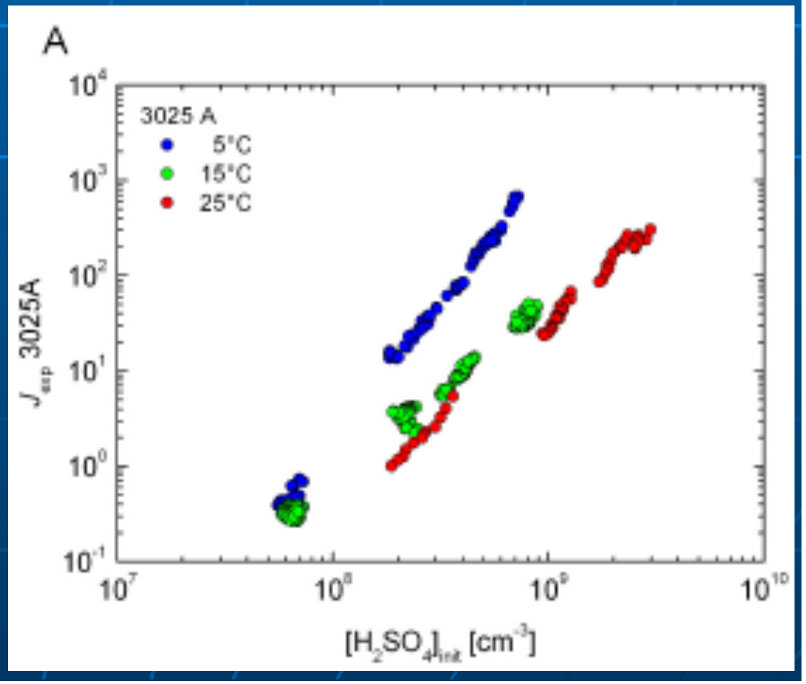
- Binary nucleation
  - taking place most of all in free troposphere and in industrial plumes,…)

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

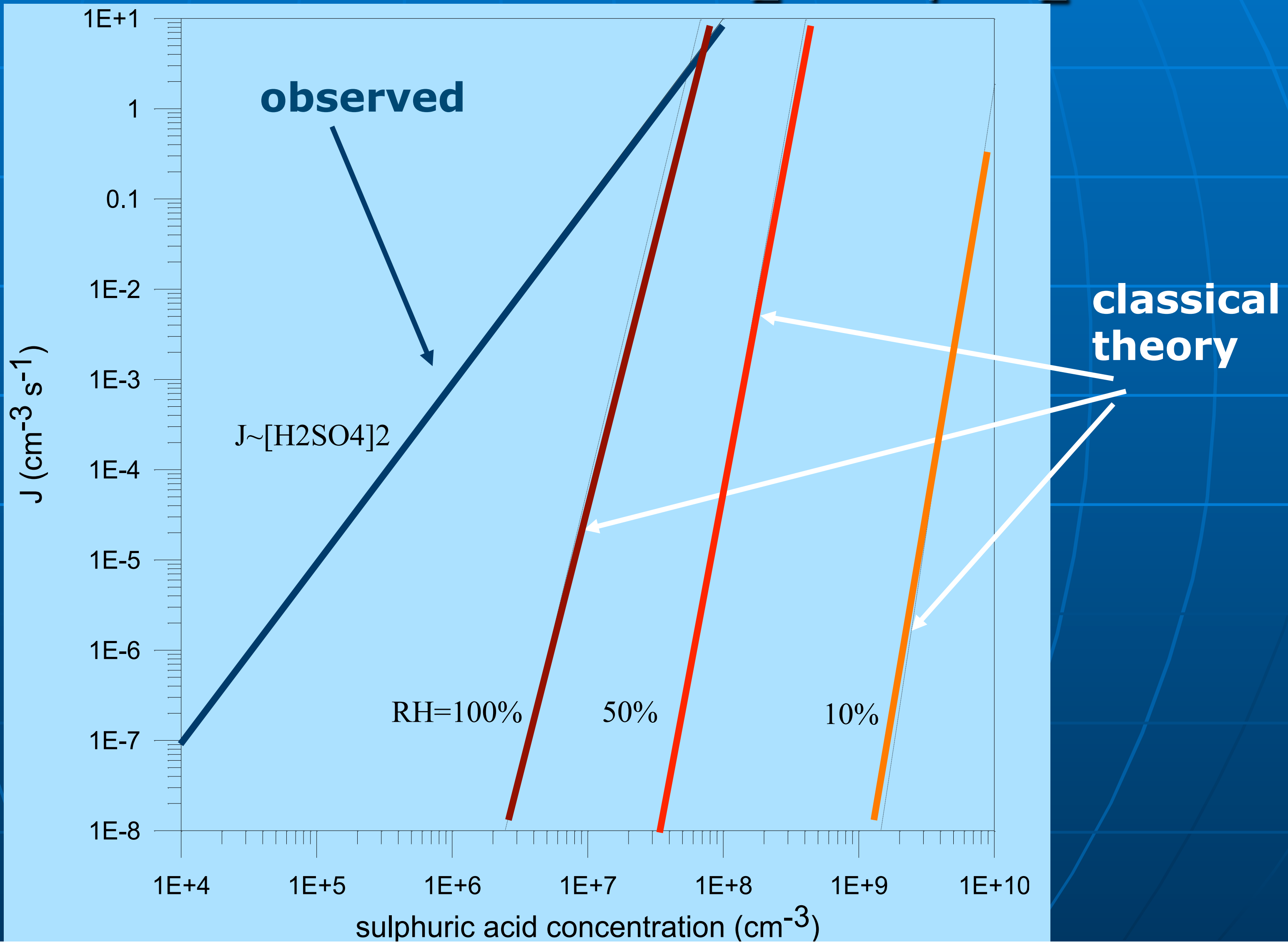
Dipendence on relative humidity



Dipendence on temperature

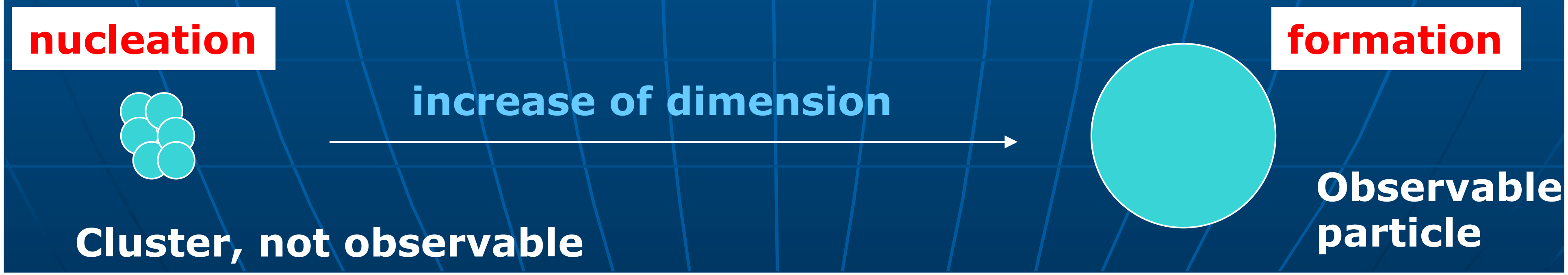


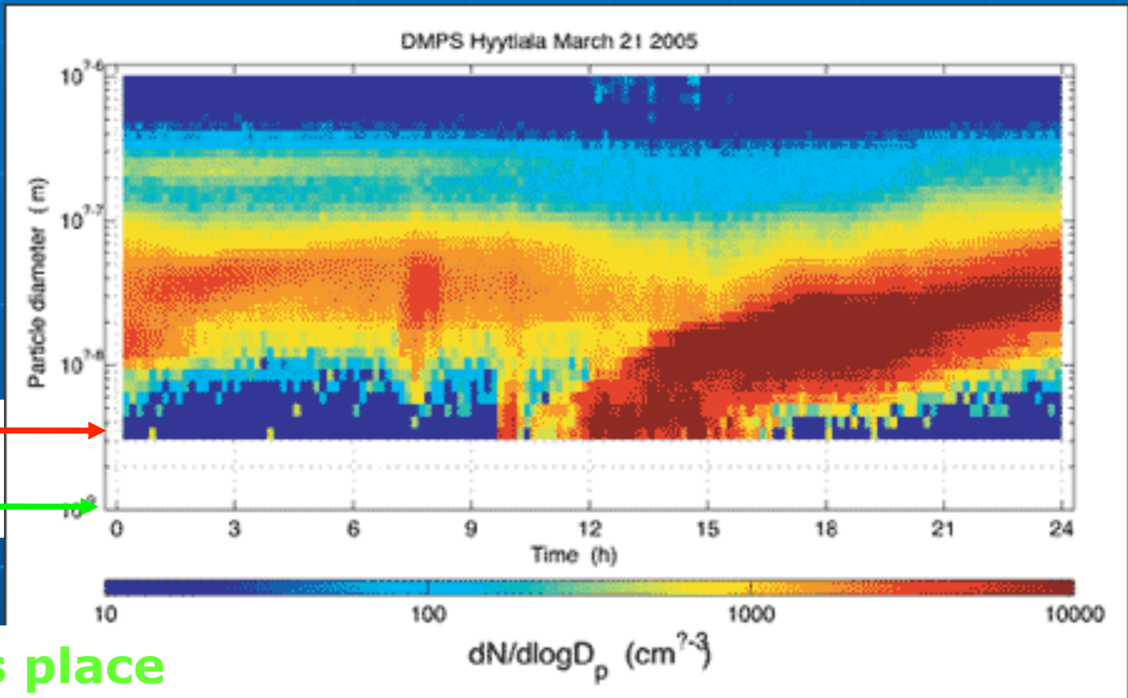
Measured and calculated nucleation rates for H_2SO_4-H_2O



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





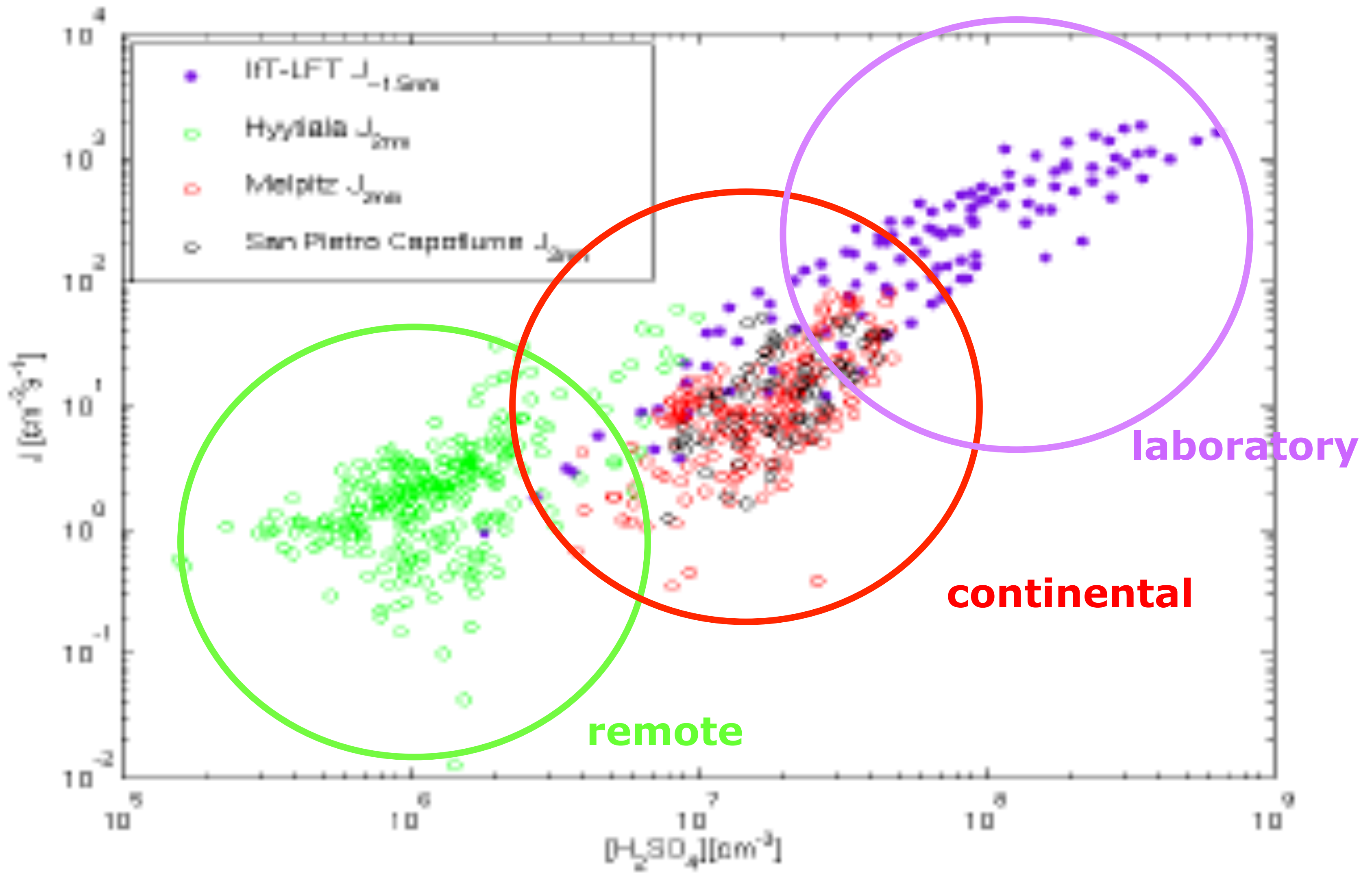
3 nm

≤1 nm

Nucleation takes place

How can we then include
a reasonable nucleation scheme in models?

Formation rate of particles measured in different environment



- Formulation of candidate mechanisms for particle formation:

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

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

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

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

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

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

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

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

None works in
all tested environments!

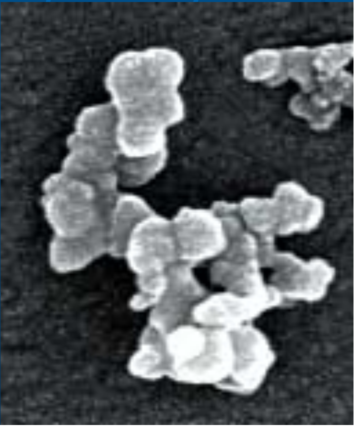
Mechanisms different
depending on the
conditions!

Large uncertainties
in observations

Nucleation: take-home message

- Particle formation is important because it
  - Influences particle number in atmosphere
  - Increases number of CCN, therefore influences climate
- It is present in many parts of the globe
- The principal mechanism of formation is still poorly understood

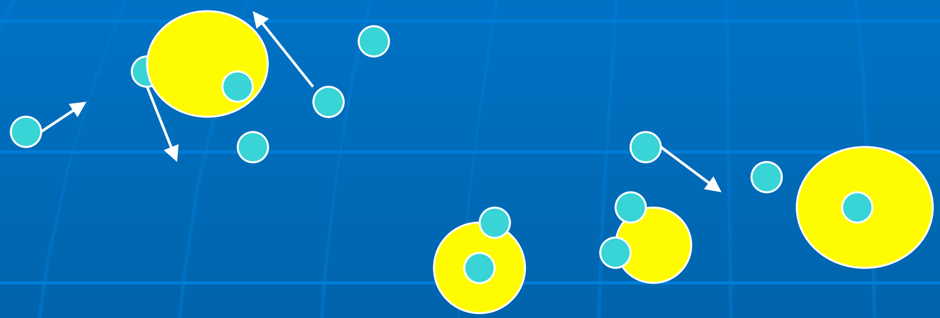
Coagulation



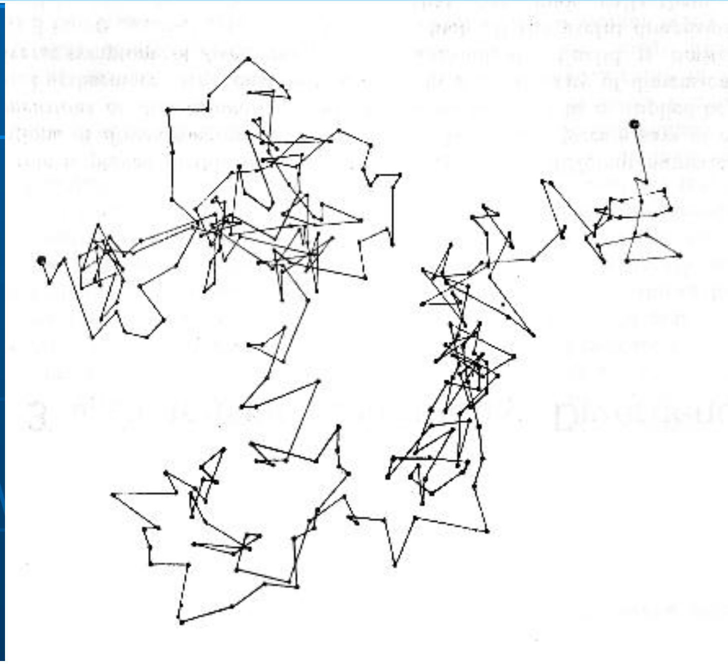
Coagulation

- 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

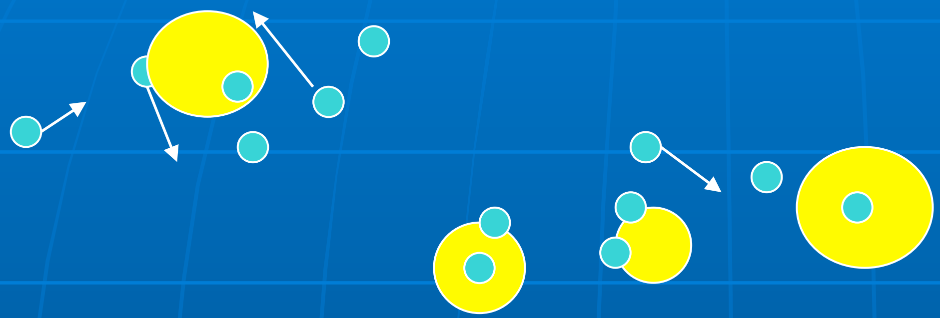
Brownian coagulation



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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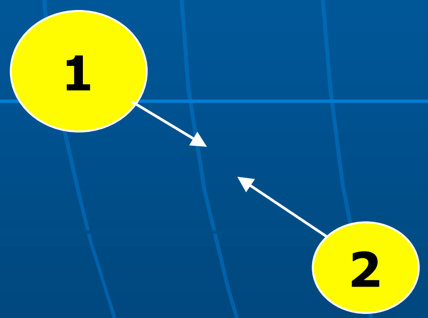


$$\left(\frac{\partial n}{\partial t}\right)_{coag} = -\frac{1}{2}\int_0^\infty\int_0^\infty K_{1,2}\, n(r_1)\, n(r_2)\, dr_1\, dr_2$$

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

Coagulation coefficient

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

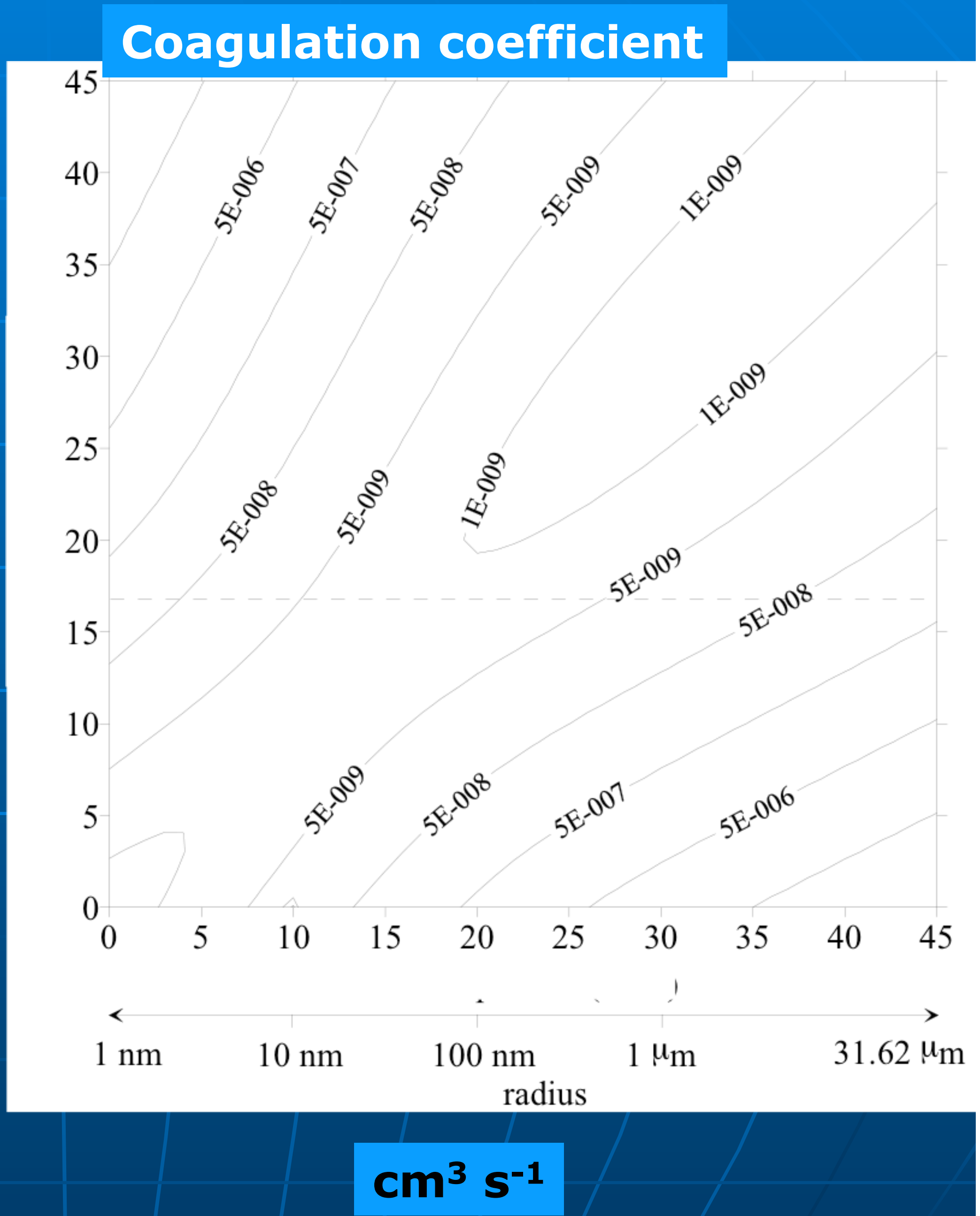
D = diffusion coefficient of particles

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

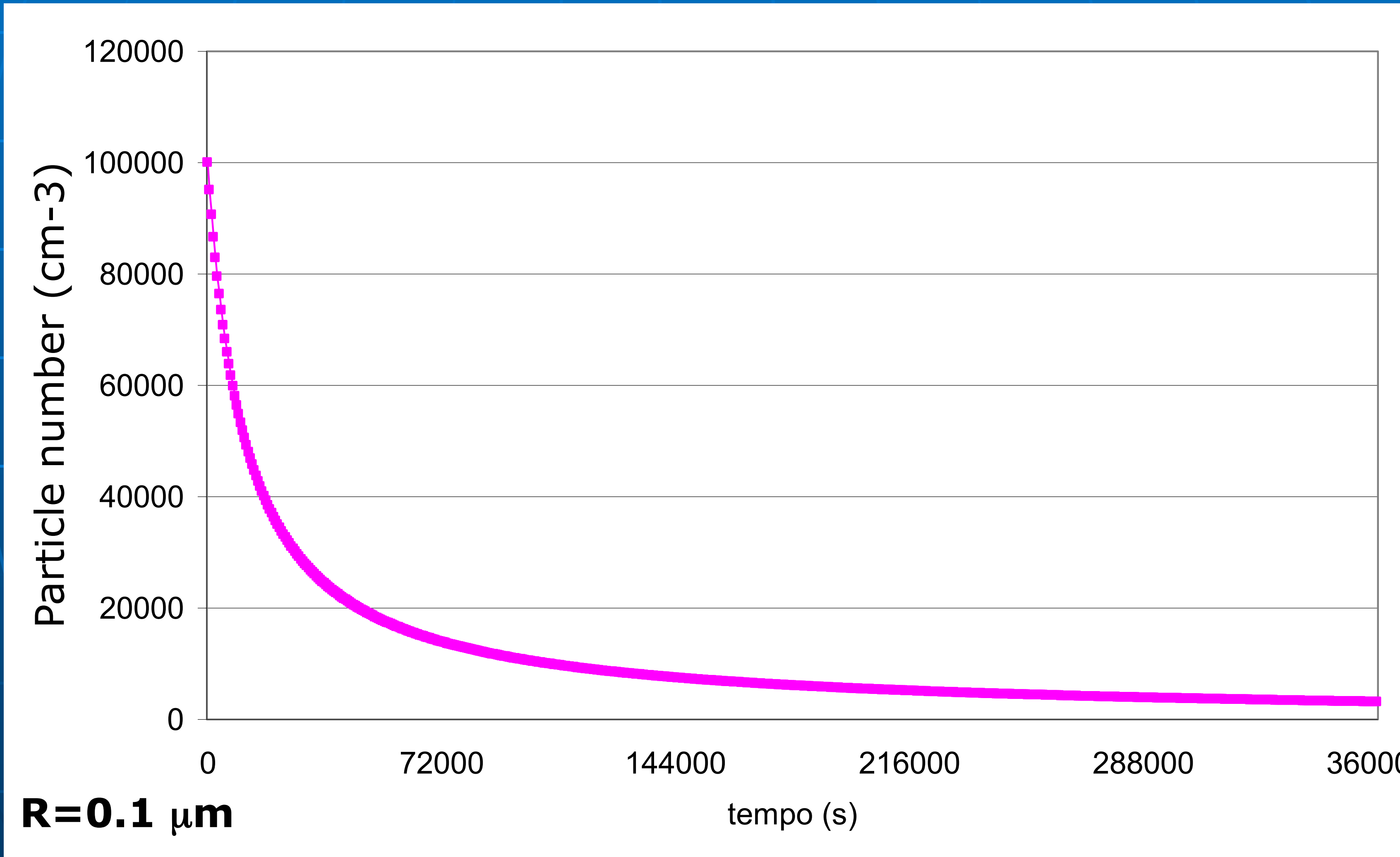
β **= Fuchs' correction factor**

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

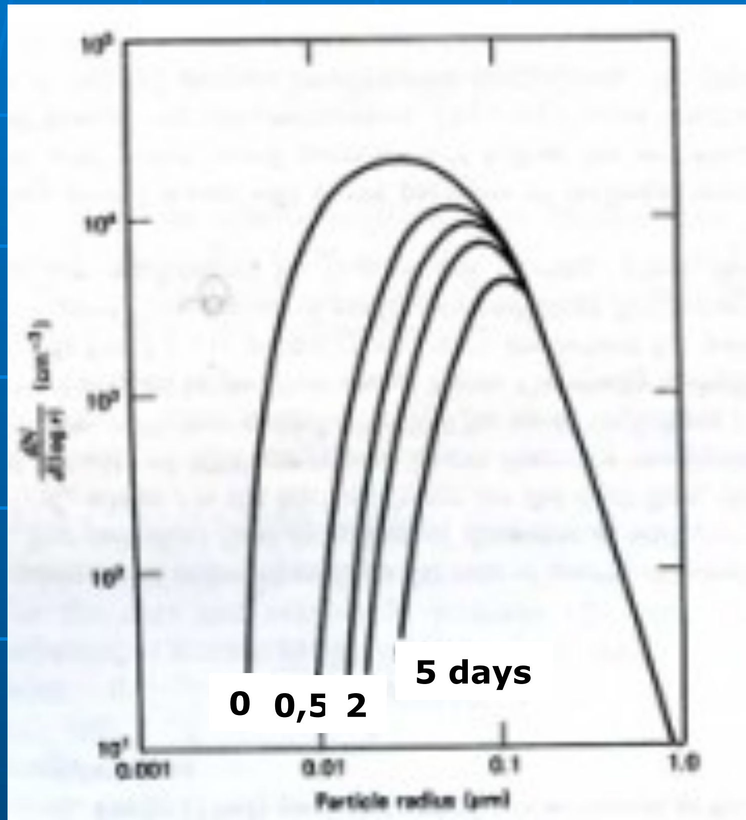
- Symmetric matrix
- Minimum values along the diagonal line
- Maximum values for coagulation of a very small particle with a very large one



How does coagulation affect particle number?



… and effects on number size distribution?

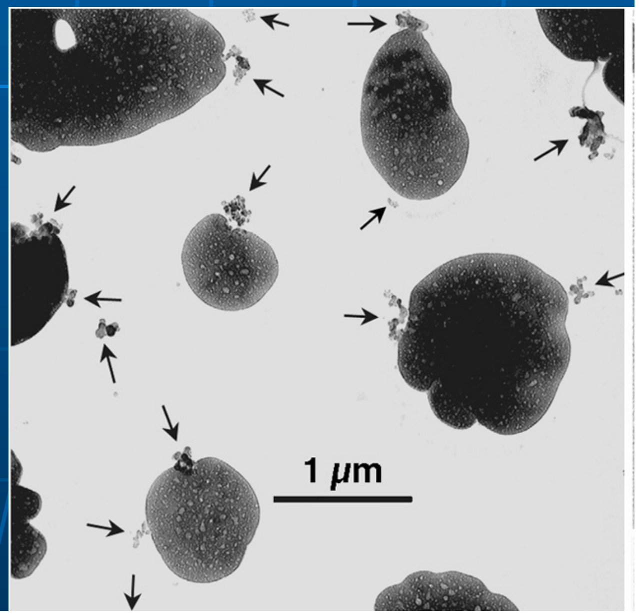


Hinds, 1982

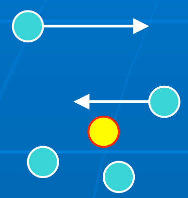
Coagulation: take-home message

- It is the process that determines the mass flux from smaller dimensions to larger ones
- It is important in high particle concentration conditions and in presence of a distribution spanning on a large dimension range
- It is a source of particles of mixed chemical composition

Condensation

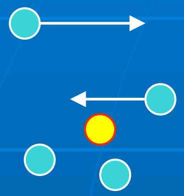


Condensation regimes



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

Condensation regimes



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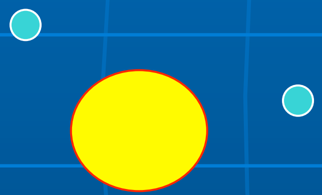


r > mean molecular path
Particle grow is determined by the rate of gas molecule diffusion to the particle surface
(continuous regime)

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):

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

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

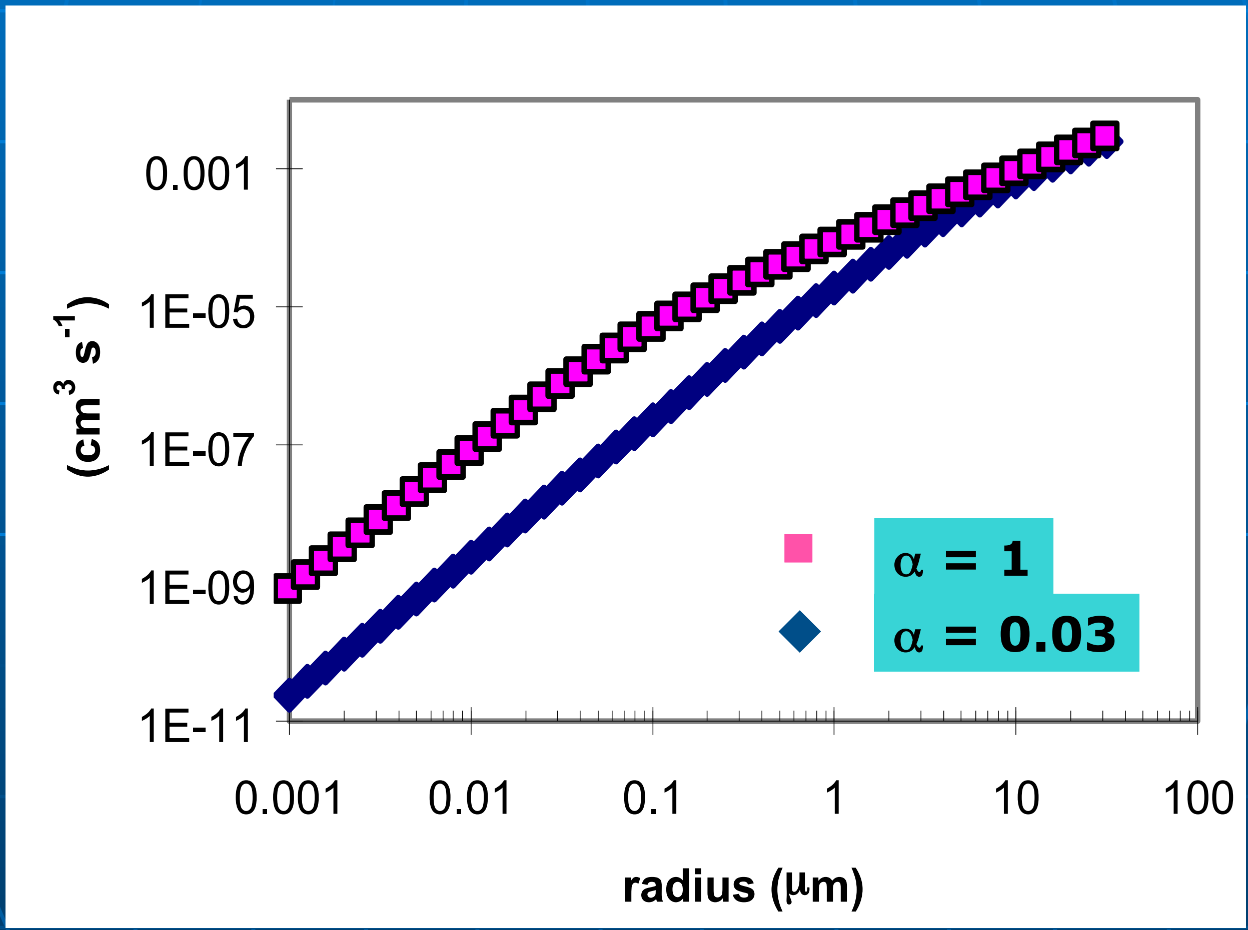
- The flux of a gas that condenses on a particle of radius r (for both kinetic and continuous regimes):

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

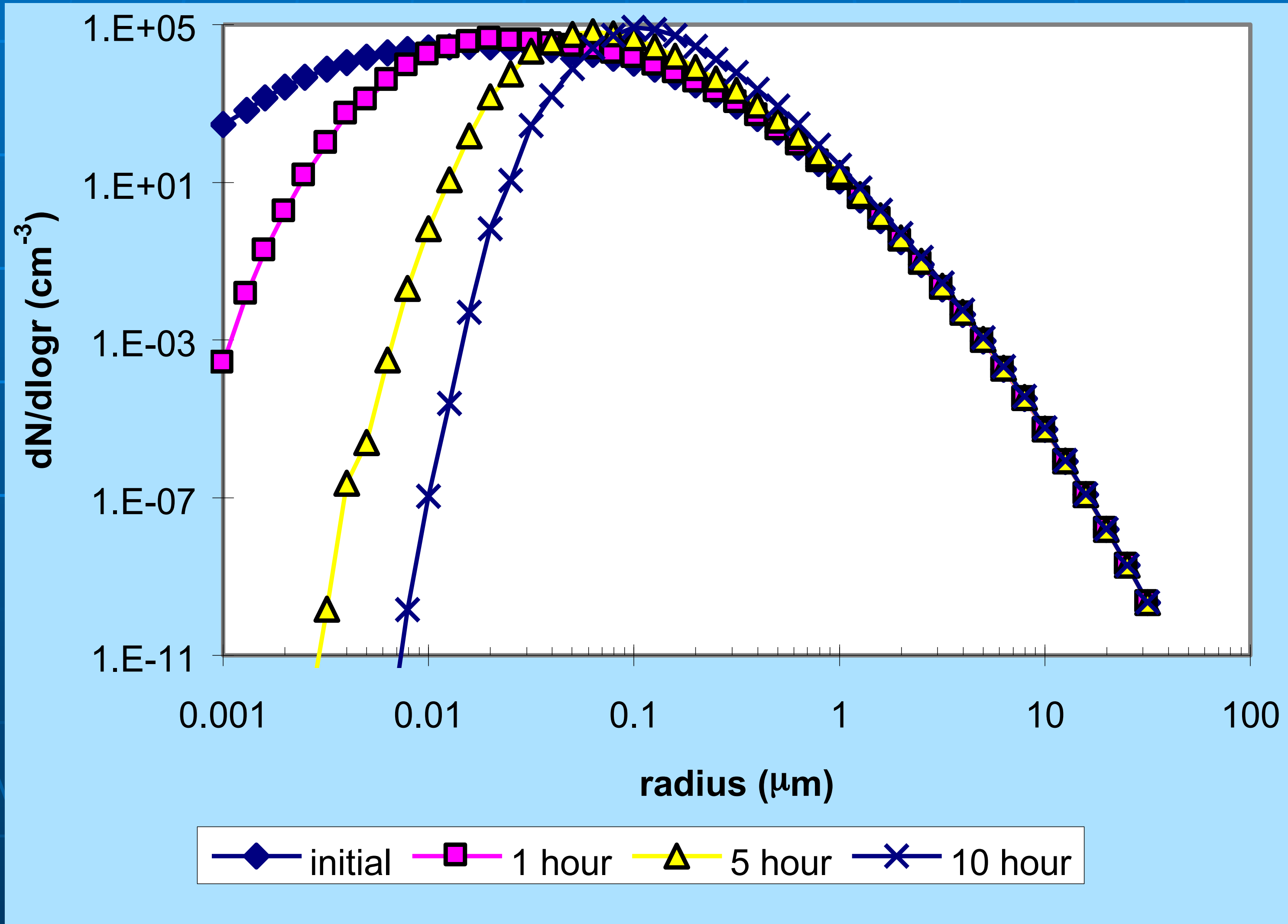
$$C_{cond} = \frac{4\pi D_m r}{\underbrace{\frac{4D_m}{\alpha v r} + \frac{r}{r+\Delta}}_{A}}\left(C_\infty - C_s\right)$$

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

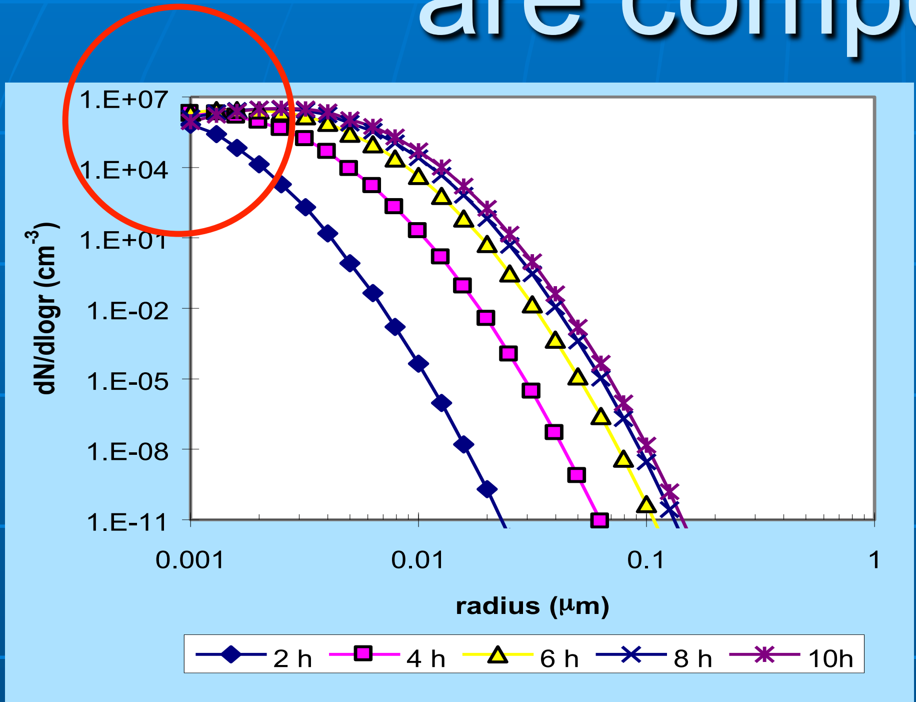
Accomodation coefficient α, a troublemaker beast



Condensation of sulphuric acid (H_2SO_4), effect on size distribution

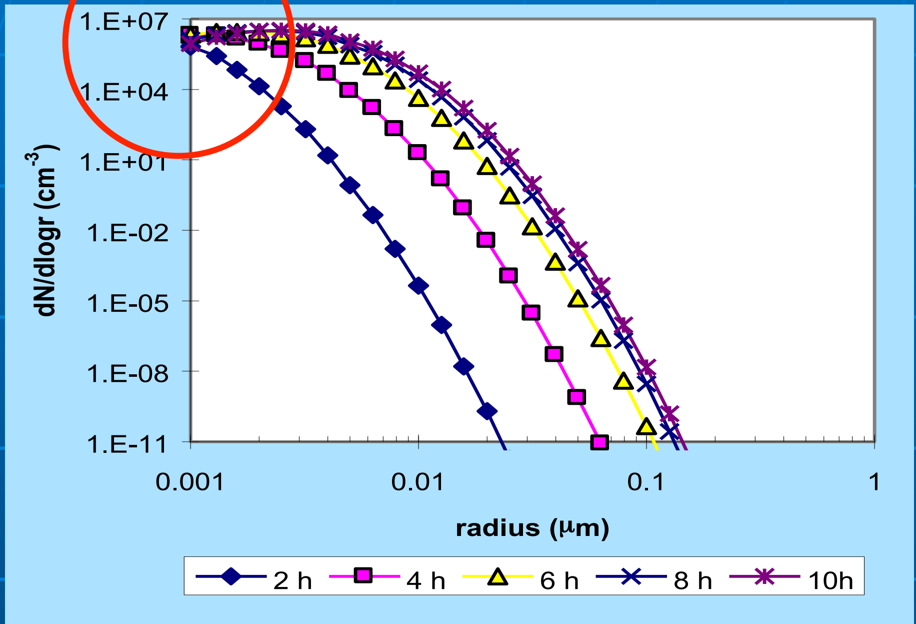


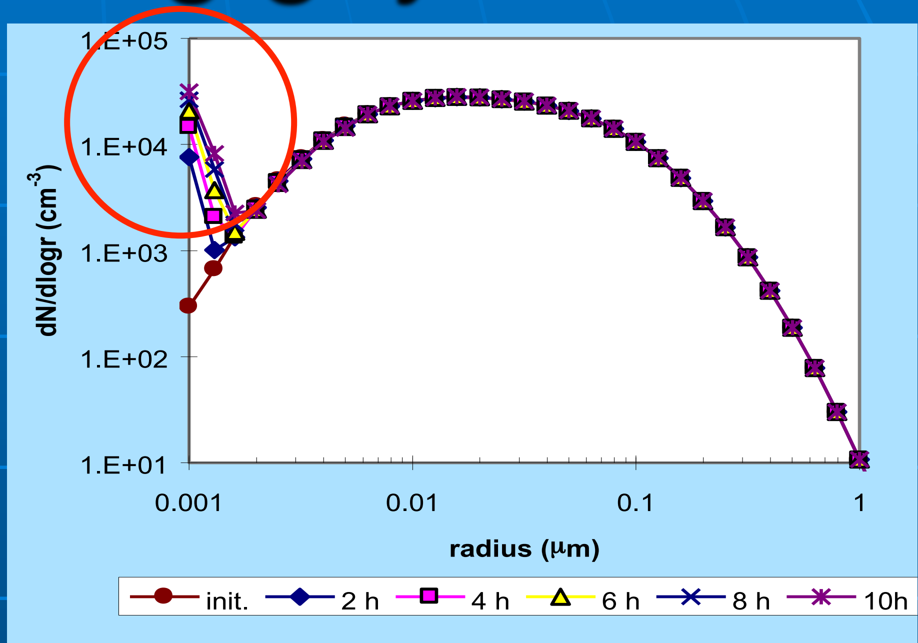
Nucleation and condensation are competing guys



Nucleation without pre-existing particles

Nucleation and condensation are competing guys





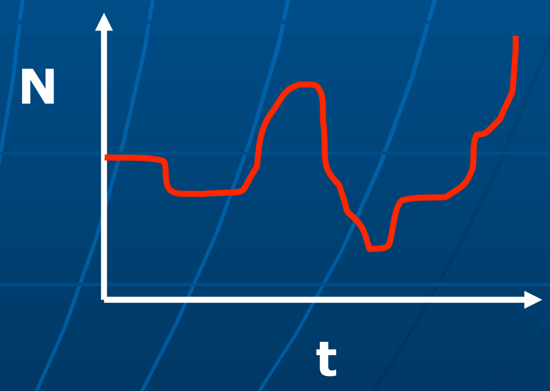
Nucleation without pre-existing particles

Nucleation in presence of pre-existing particles

Nucleation is less efficient!!!
Condensation subtracts gas

Let's build a 0-dimensional aerosol model

0-D spatial, time is the only dimension



Our problem

- Trasformation of particles emetted by a car in a street:
  - Which is the role of coagulation in the plume emetted by a vehicle?

Vignati et al., 1999

Our problem

- Trasformation of particles emetted by a car in a street:
  - Which is the role of coagulation in the plume emetted by a vehicle?

Vignati et al., 1999

S= plume section

The particle we have to model

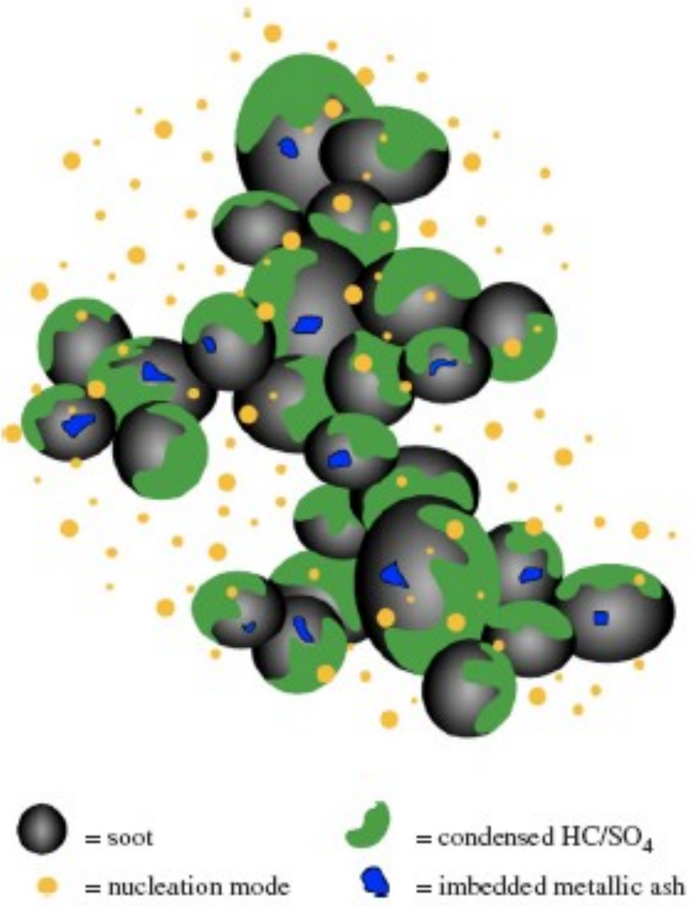
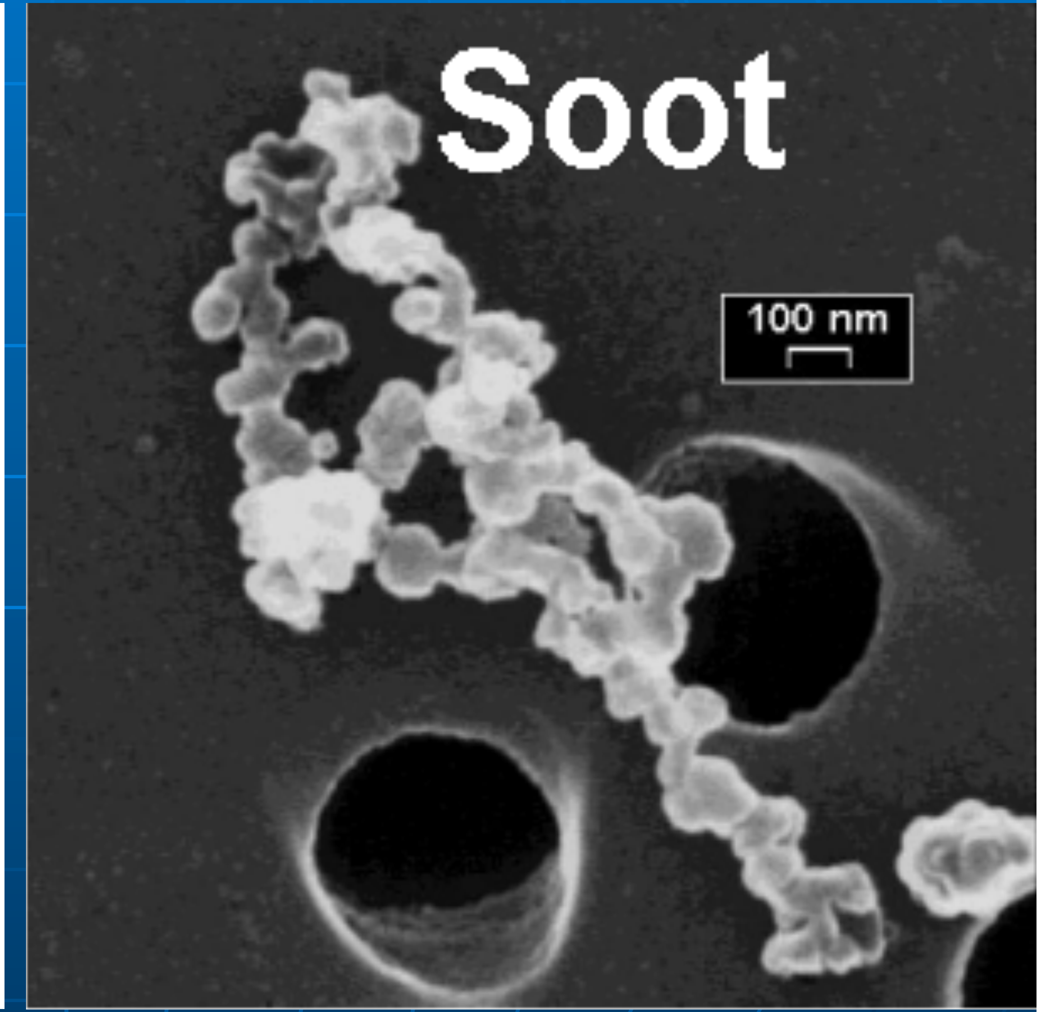


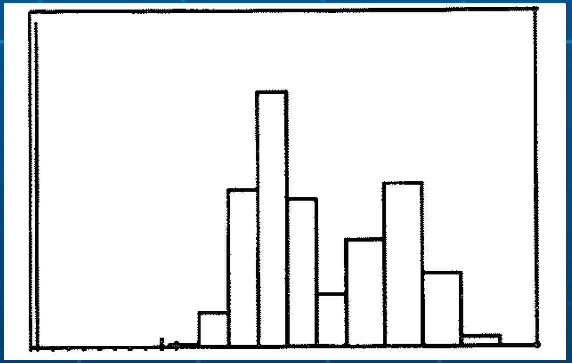
Fig. 1. Artist's conception of diesel PM.



Matti Maricq, 2007

How do we construct the model?

1. Our particles are supposed to be spheres
2. We do not have restriction for computer time → sectional model

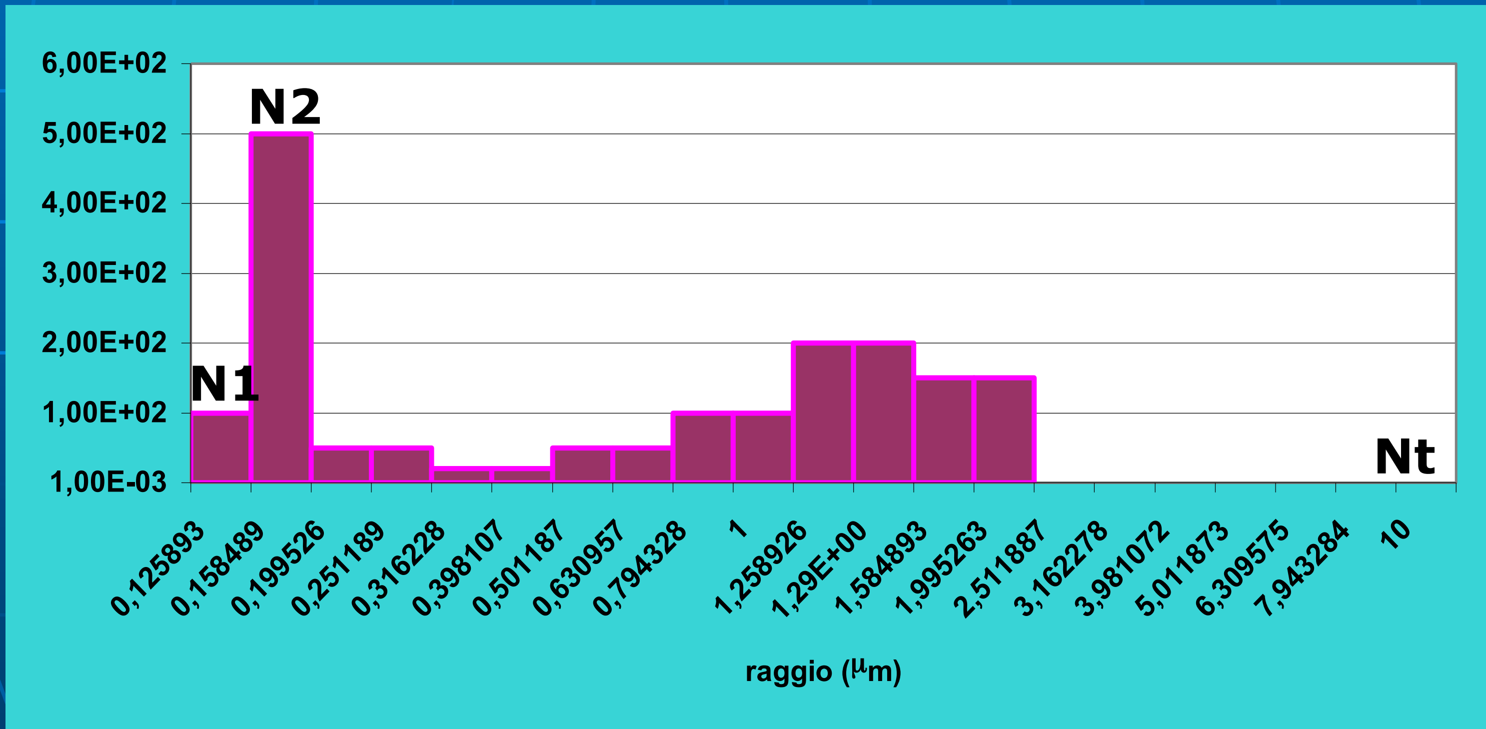


How do we construct the model?

3. Description of particle distribution

Radius(i)=0.001*10$^{(i \times 0.1)}$ i=1,46

4. Initial conditions for the particles



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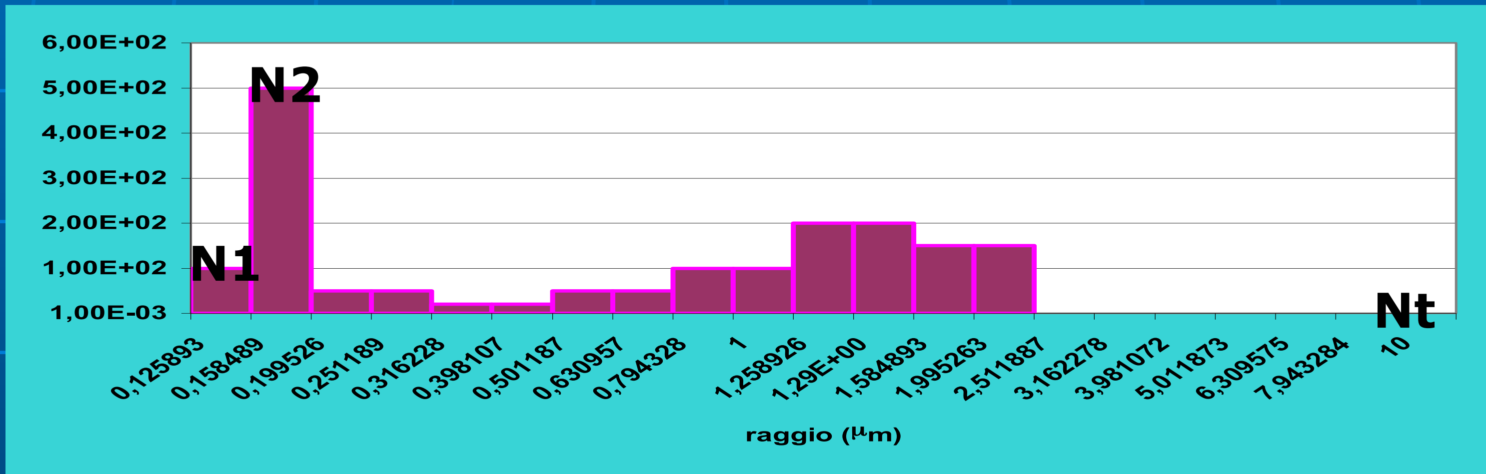
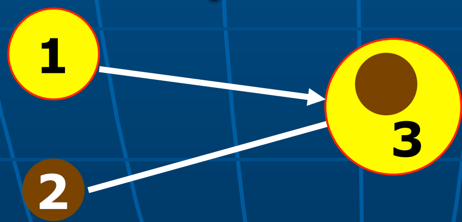


5. Ipothesis on particle coagulation



$$r_1^3 + r_2^3 = r_3^3$$

Processes to be modelled

- Coagulation
- Diluition of the car plume from the exhaust
- Entrainment of background particles already present in the street

6. We write the governing equation

$$\frac{dN_i}{dt} = P_{(i)} - L_{(i)}N_i + \frac{1}{S}\frac{dS}{dt}\left(N_{b(i)} - N_i\right)$$

N_i = particle number in class i
P_i = production of particles in classe i due to coagulation
L_i = loss of particles in class i due to coagulation
$N_{b(i)}$ = background particle number concentration
S = plume section

7. We solve it numerically

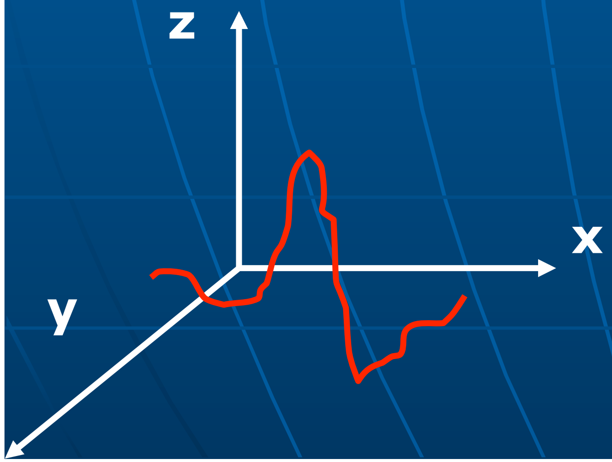
8. We look at the results….

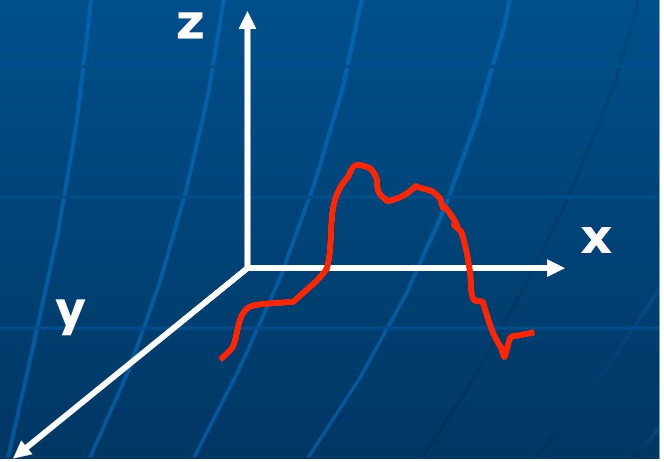
and we have a surprise

- Coagulation alone does not have any effect
- The resulting size distribution is dominated by entrained background particles

Aerosol dynamics in 3-D

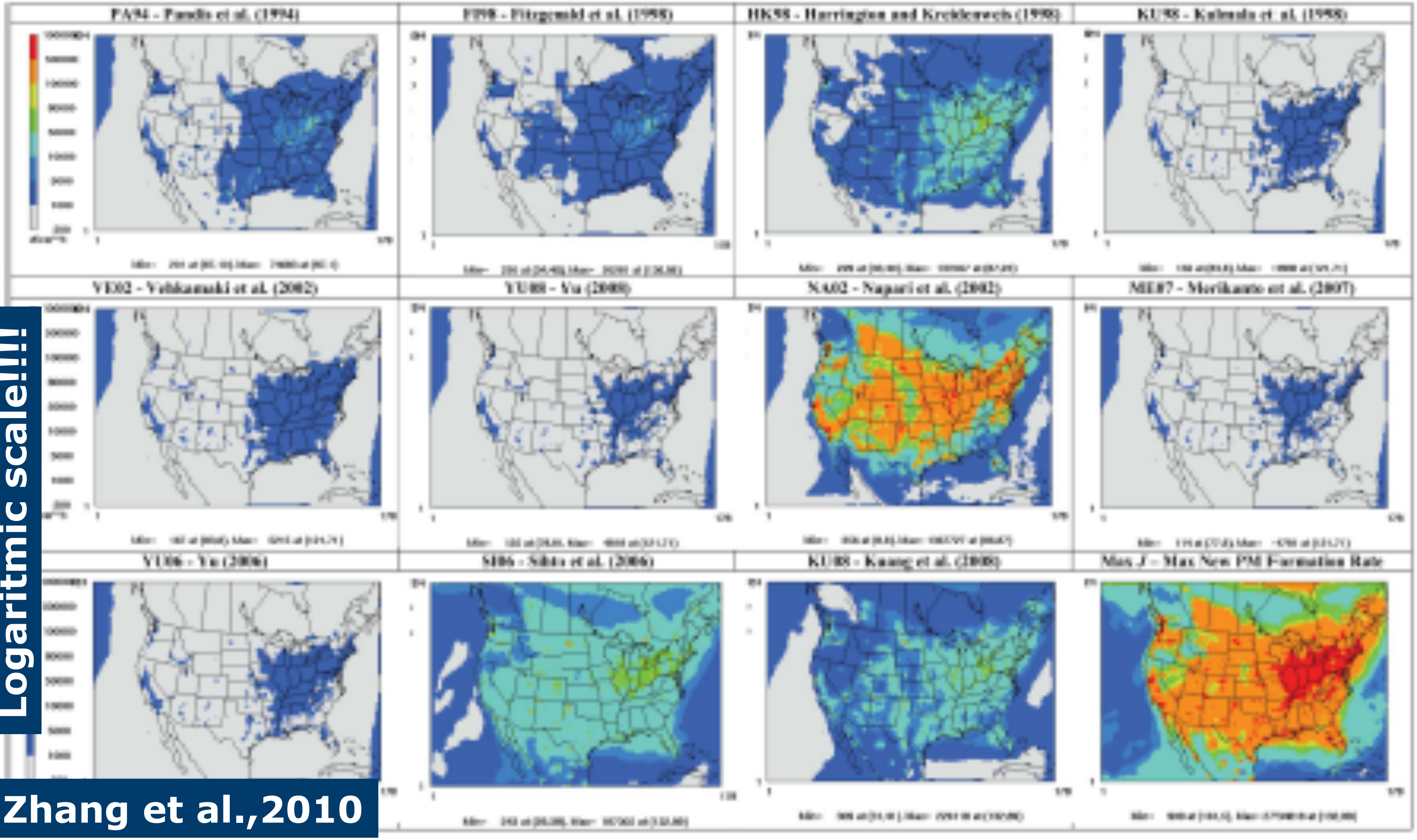
3-D spatial (x, y, z)
and time





Nucleation schemes make a difference!

Particle concentrations in USA, with a regional model and nucl. sch.



Logaritmic scale!!!

Zhang et al.,2010

Trasport of Black Carbon to the Poles

- Produced by incomplete compustion of fossil fuels
- It absorbes solar radiation fwarming the atmosphere
- Depositated on snow it favours the snow warming and caused its rapid melting

Which aerosol chemical composition and size distribution?

- We have a 3-D global chemistry transport model
- We need to include all compounds important for the global scale:

black carbon, organic carbon, sea salt, dust, sulphate → large computer time!

Which aerosol chemical composition and size distribution?

- We have a 3-D global chemistry transport model
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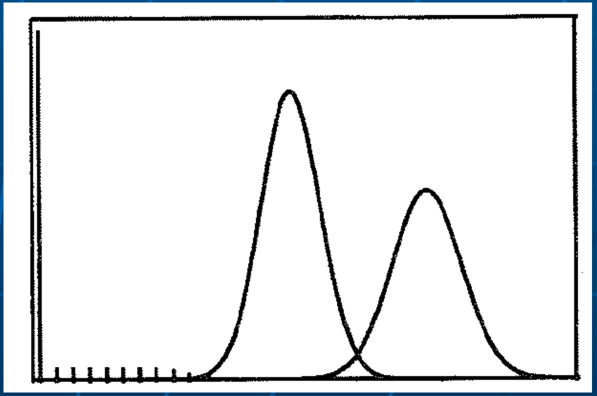
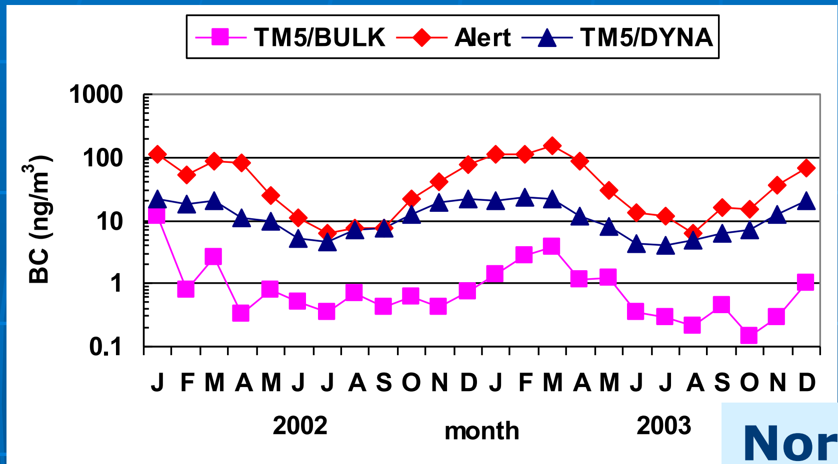
black carbon, organic carbon, sea salt, dust, sulphate → large computer time!

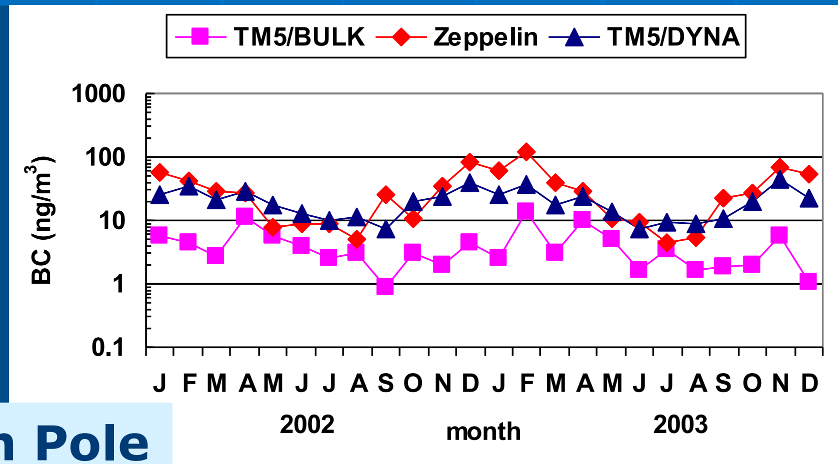
Modal model is the best choice



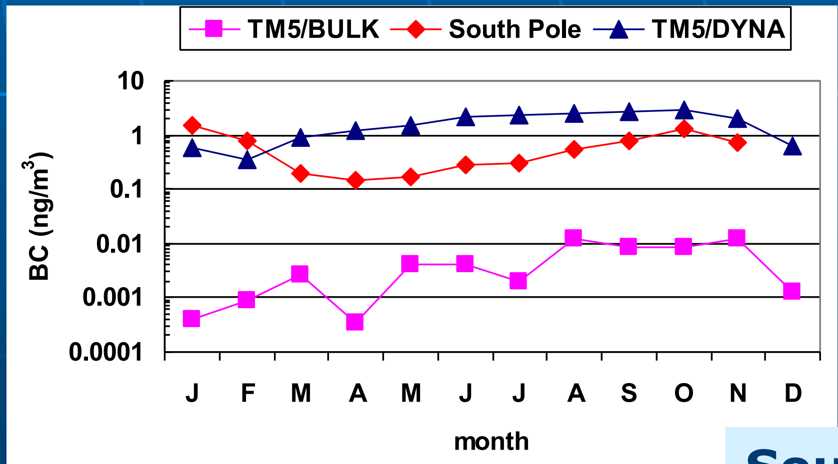
Is dynamics necessary?

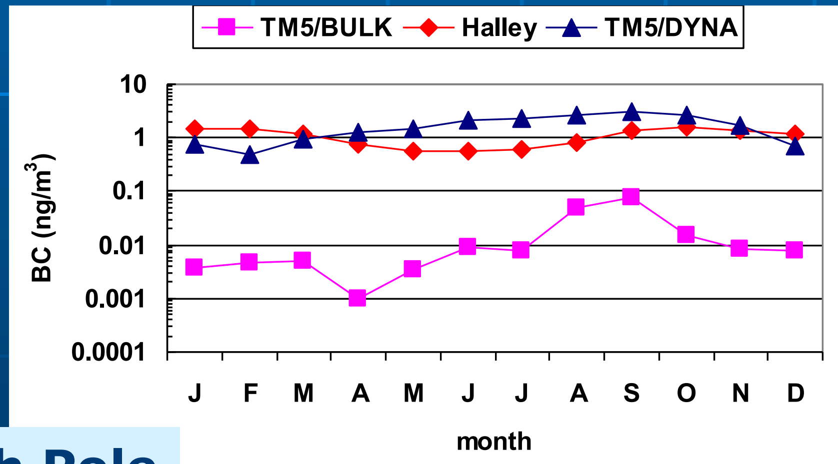
without dinamics △ **with dinamics** ◆ **observations**





North Pole





South Pole

Emissions

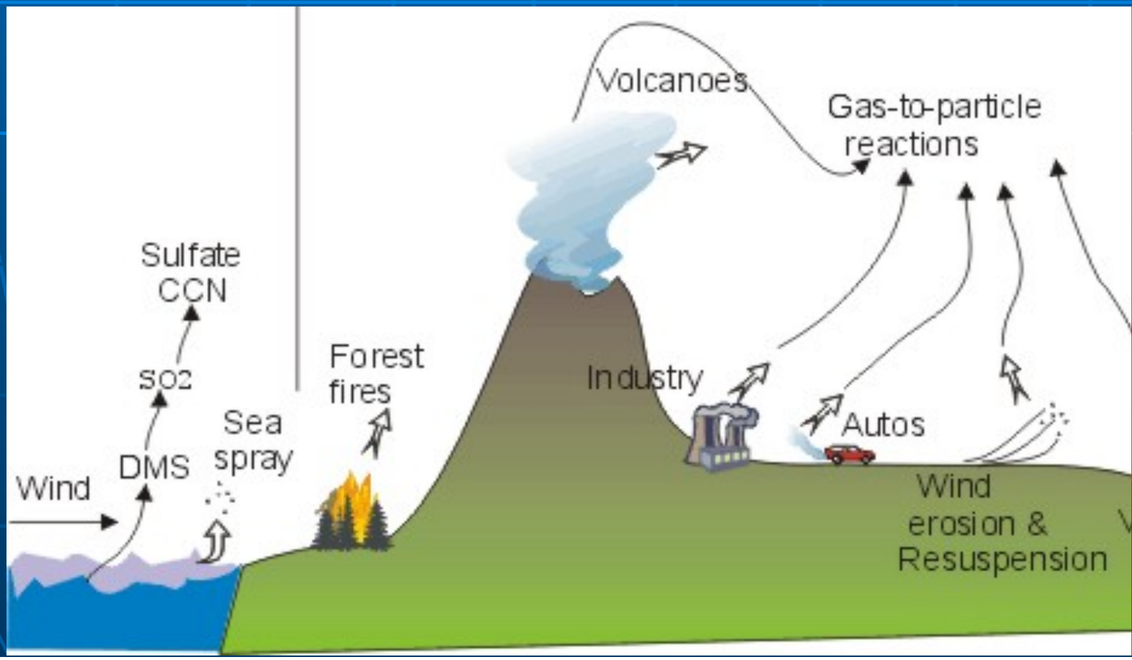
Sources

Primary particles

- Black carbon
- Organic Carbon
- Sea salt
- Dust

Precursours

- SO2, DMS
- NOx
- NH3
- VOCs



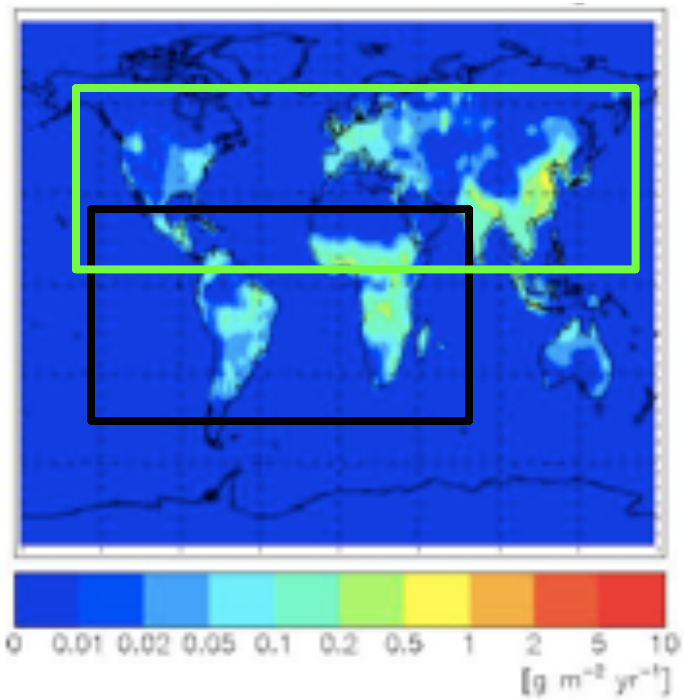
Black carbon

- **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

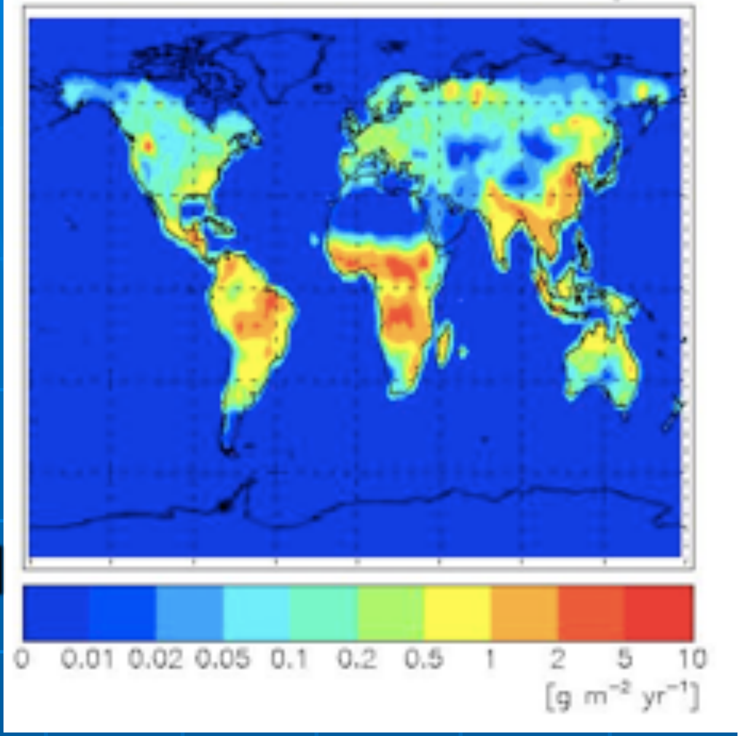
- **Anthropogenic sources (fossil and biofuels)**:

 ≈ 19.1 Tg yr-1

A) Domestic use

B) Road transport

C) Industry

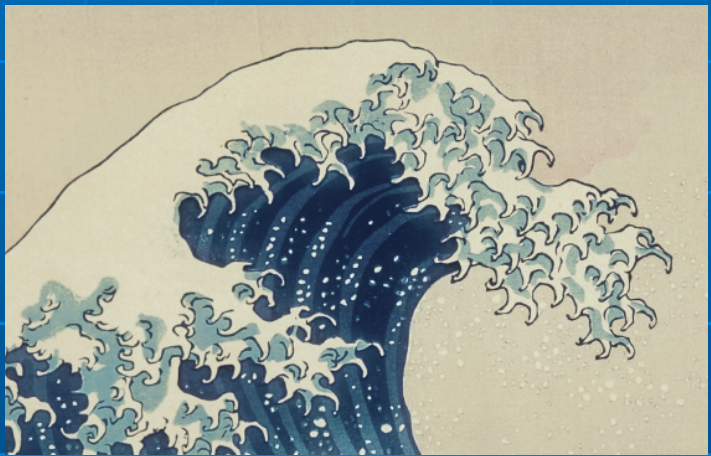


Uncertainty of a factor of 2

Sea Salt

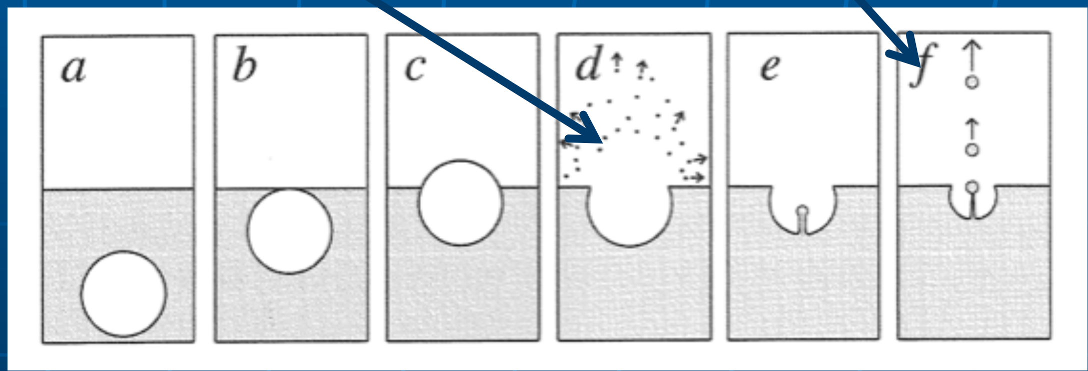
Mechanism of production

Air entrainment

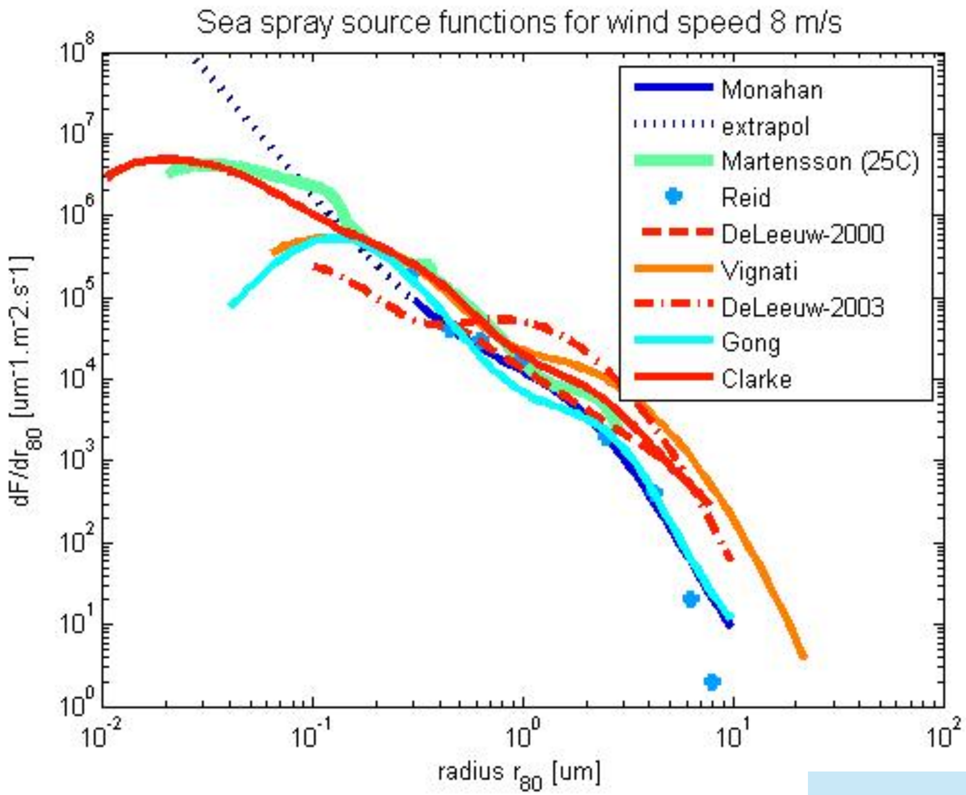


Film droplet injection   Jet droplet injection

Bubble bursting



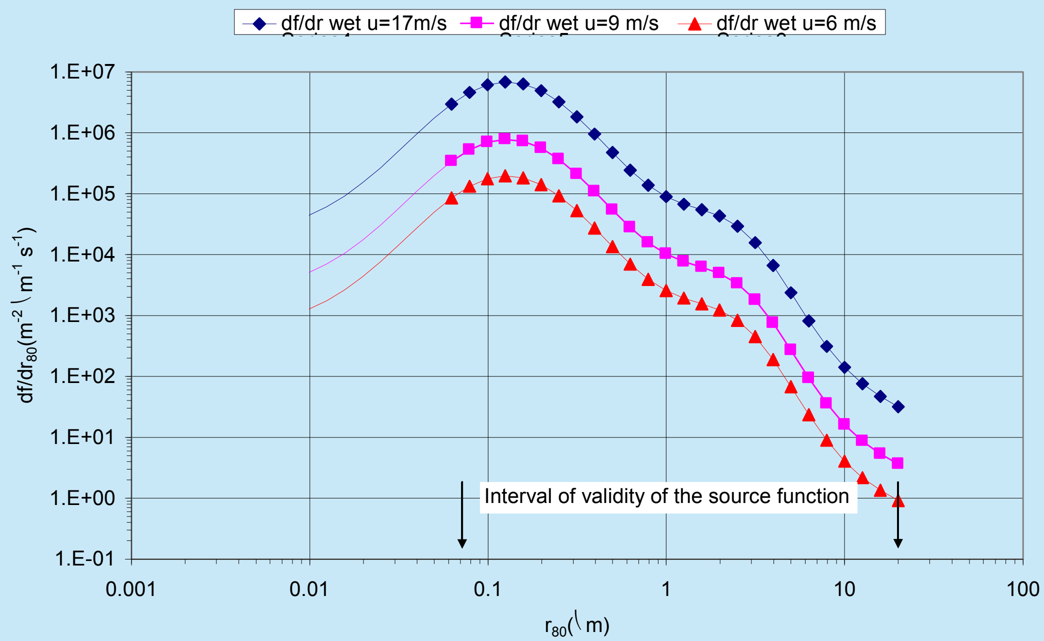
(Schwarz and Lewis, 2004)

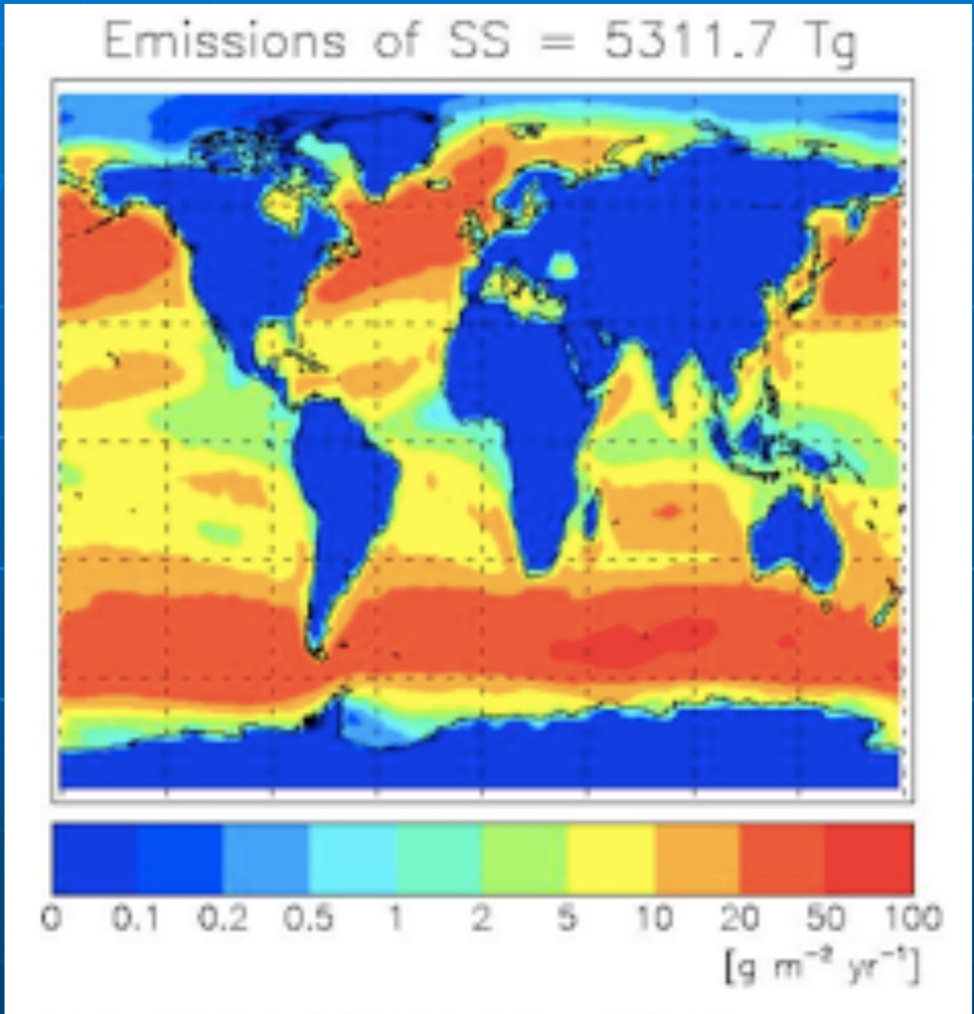


(De Leeuw et al, 2011)

Dependence of wind speed

Gong, 2003





High winds

Low winds

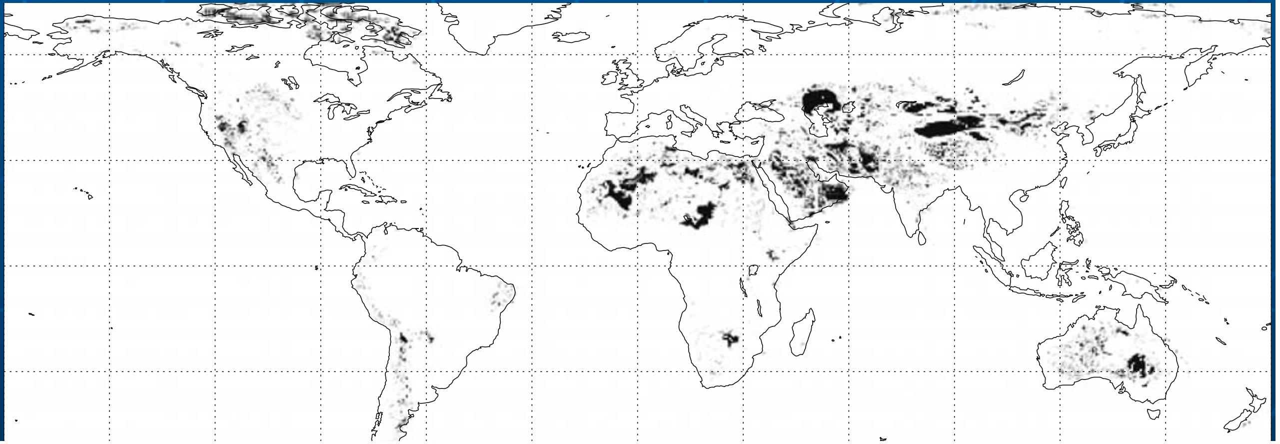
High winds

Dust

- Mechanism of production: soil deflation from bare surface when wind exceeds a certain threshold

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,…)



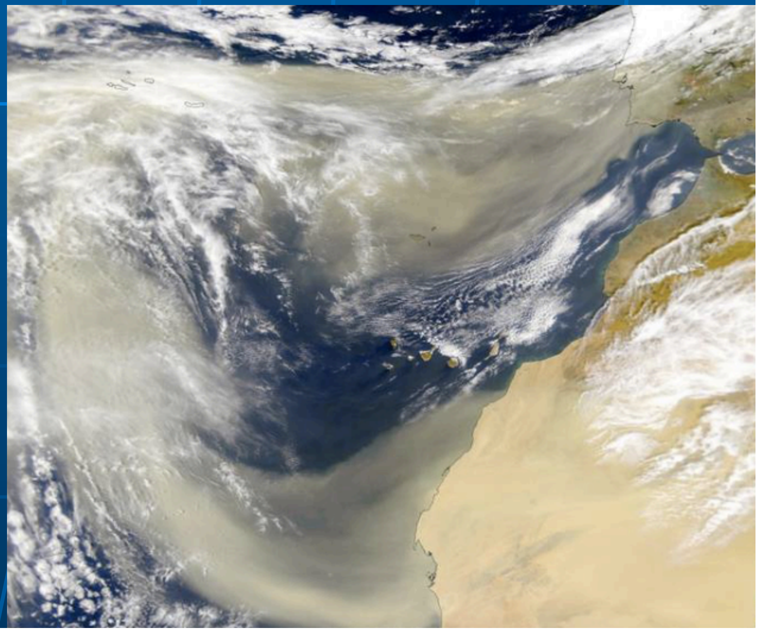
Tegen et al., 2002

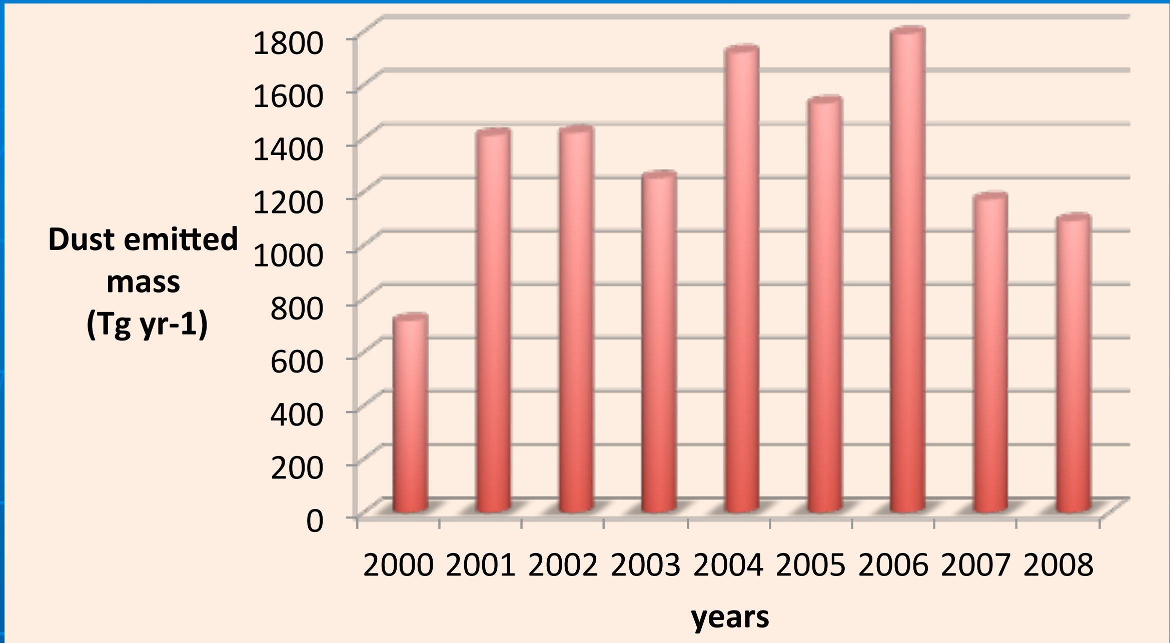
Still quite uncertaint

- High uncertainties: too few data that can constrain the modelled emissions

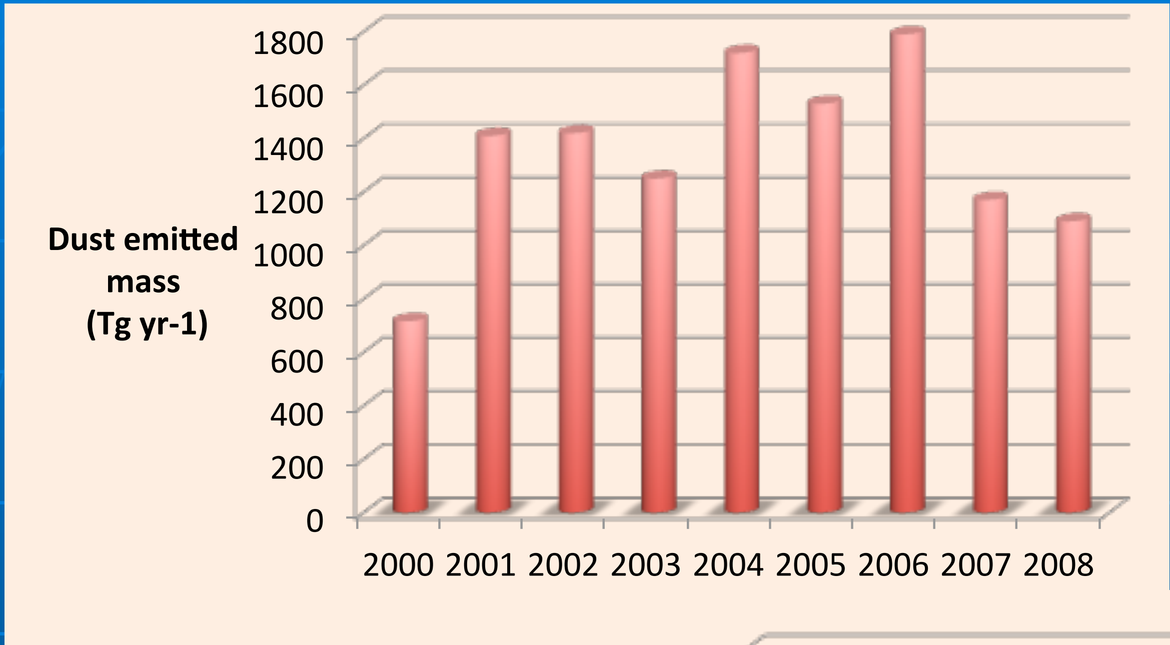
(published range 430-3000 Tg y^{-1})

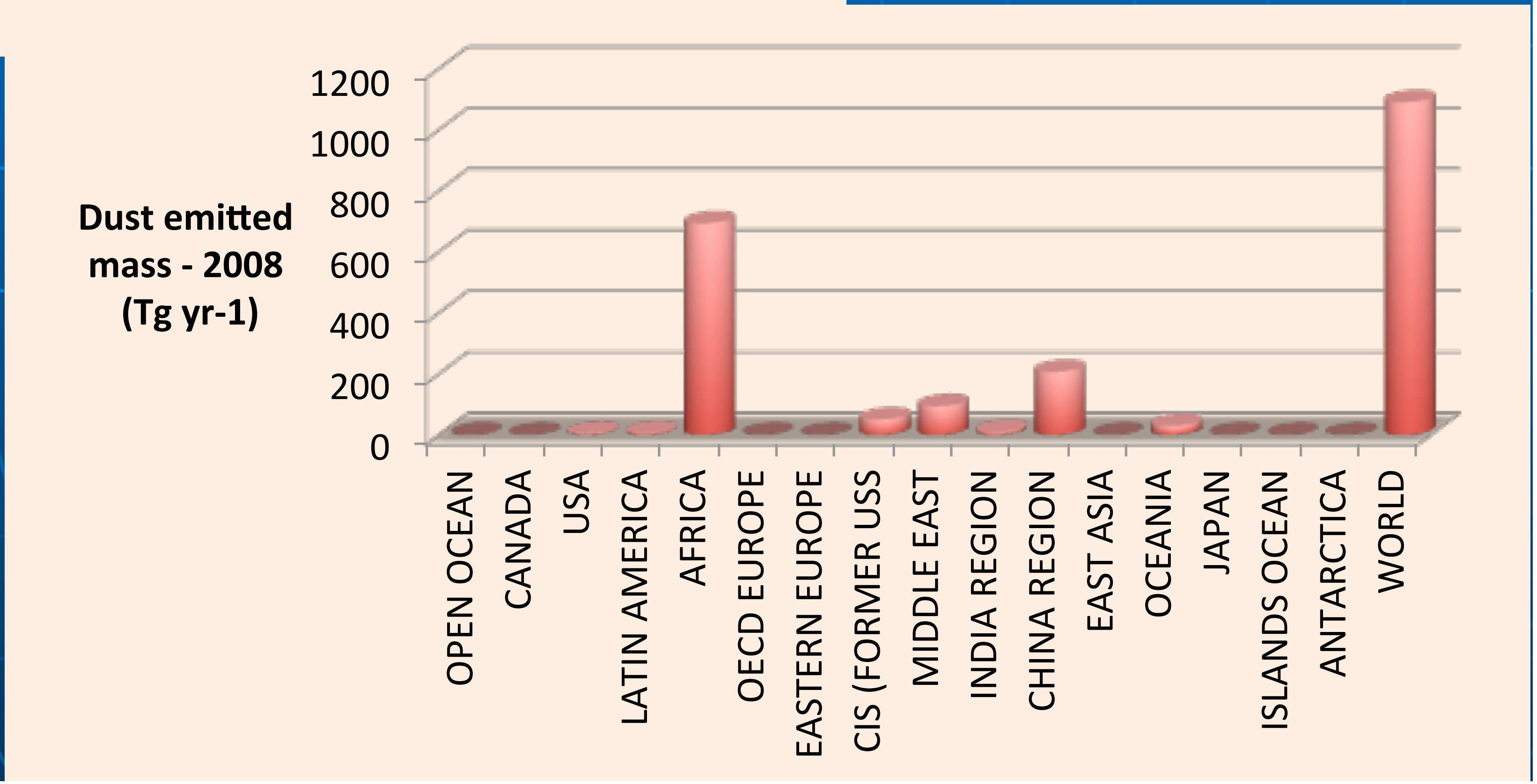
(Tegen et al, 2002)





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
years


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


Dust emitted mass - 2008 (Tg yr-1)
0
200
400
600
800
1000
1200
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