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Aerosol Dynamics

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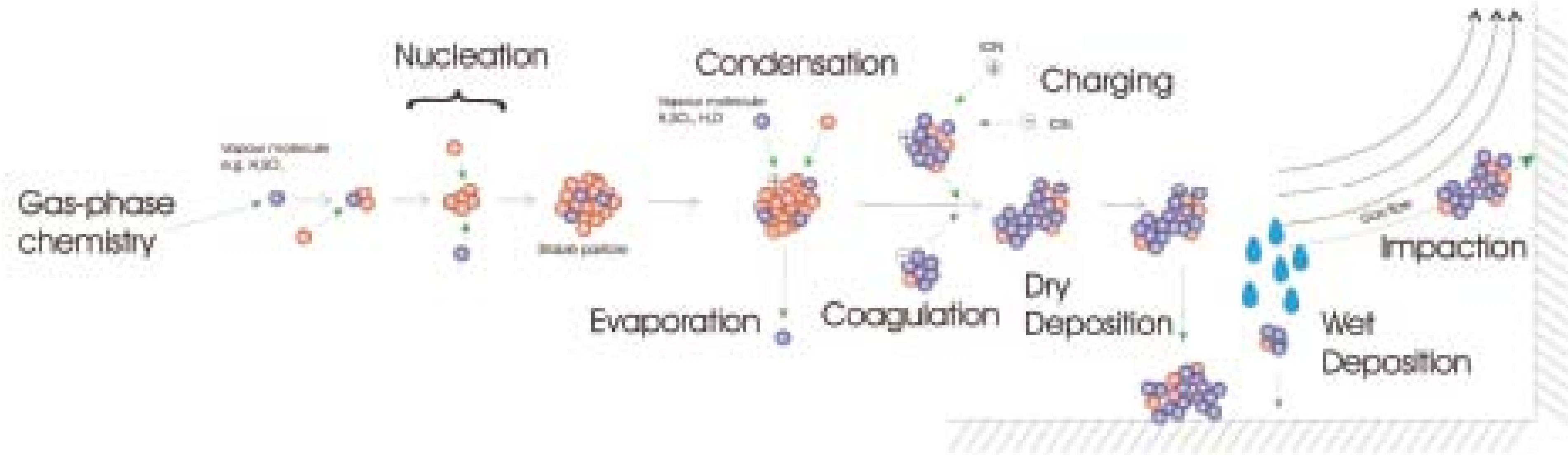
Aerosol Dynamics: What?

- A way to try to understand nature, in this case the behaviour of aerosol particles
- Aerosol Dynamics describes formation, growth and transportation of aerosol particles
- Based on existing theories
- Basic Aerosol Dynamics suitable for process-level model studies
- For atmospheric models, parameterisations are needed

Aerosol Dynamics: Processes



Aerosol dynamic processes

1. Primary emissions
2. Nucleation
3. Activation for Growth
4. Condensational Growth
5. Coagulation
6. Cloud Processes
7. Deposition
8. Connection with atmospheric chemistry and meteorology

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Primary emissions of aerosol particles

- Particles that have been emitted directly to the atmosphere

- Natural
  - Desert dust, pollen, viruses, bacteria, seasalt, …

- Anthropogenic
  - Combustion generated: traffic, power generation, woodburning, …

- Mainly larger particles ($D_p > 1\ \mu m$)

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Nucleation

- Formation of a new phase
- In the atmosphere: vapour $\rightarrow$ liquid, vapour $\rightarrow$ solid (ice nucleation)
- Types of nucleation
  - Homogeneous nucleation: No foreign nuclei or surfaces
  - Heterogeneous nucleation: Nucleation on a foreign substance
    - e.g. nucleation onto surface of aerosol particles
  - Ion induced nucleation: Nucleation on charged particles
- Number of species
  - One: homomolecular or unary nucleation
  - Two or more: heteromolecular or binary, ternary, … nucleation

Homogeneous vs. heterogeneous nucleation

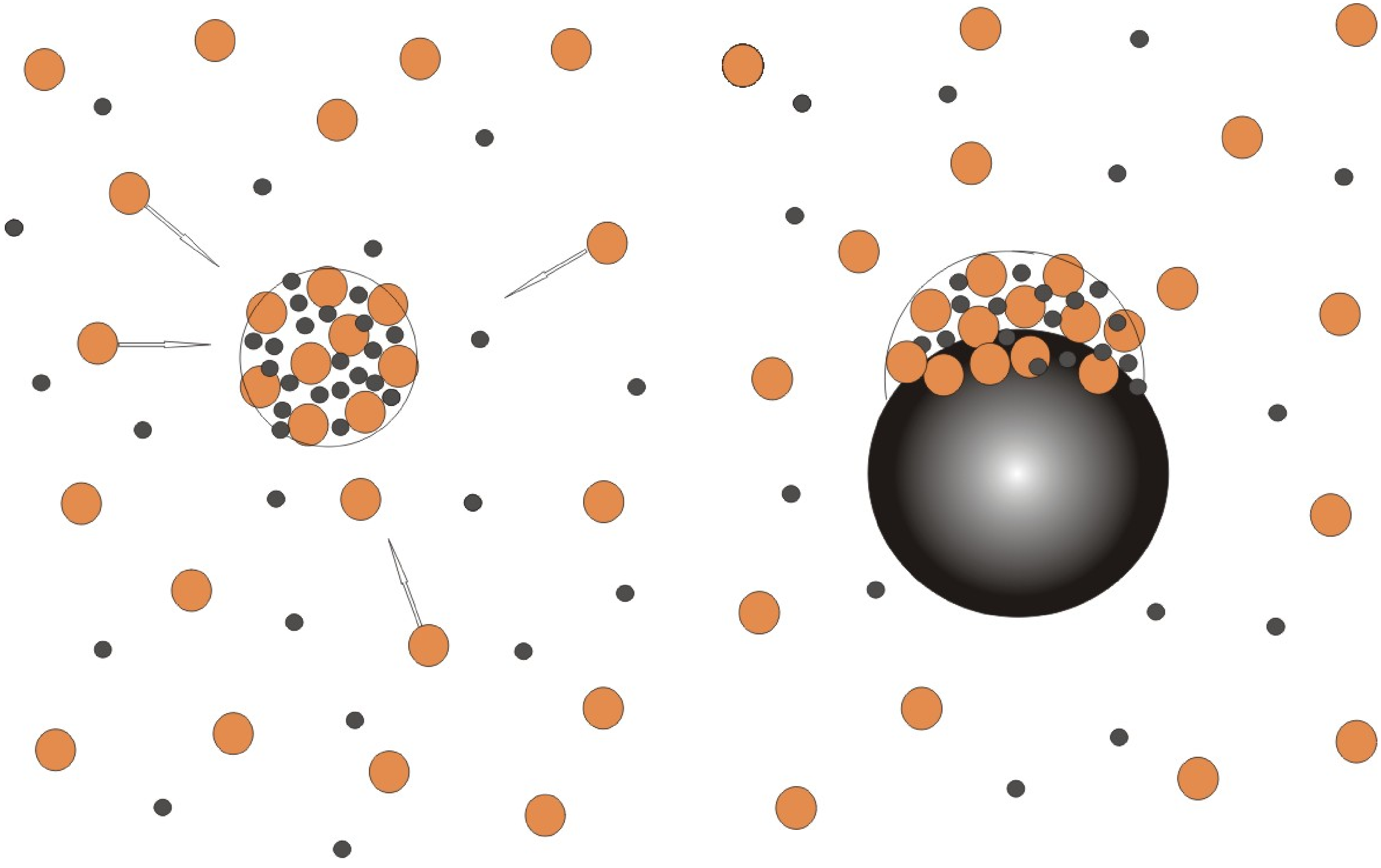


Figure by Hanna Vehkamäki

Homogeneous nucleation in the atmosphere

- formation of new aerosol particles in the atmosphere from gaseous precursors
- the initial size of these particles is typically of the order of one nanometer in diameter
- potential nucleation pathways in the atmosphere:
  - binary water-sulphuric acid nucleation (mainly free troposphere)
  - ternary water-sulphuric acid-ammonia nucleation (lower troposphere)
  - ion-induced nucleation
  - nucleation of some organic compounds
- there are large uncertainties in both calculating and measuring the atmospheric homogeneous nucleation rate

Nucleation rate J

- Number of critical clusters formed per unit volume per unit time

[J]= 1/(cm^{3}s), 1/(m^{3}s)

$$J = K^* \times Z \times \underbrace{C_{monomers} \exp(-\Delta G^* / kT)}_{\text{Number of critical clusters in a supersaturated equilibrium vapour}}$$

Collision rate of monomers to critical cluster

Zeldovich factor:

-½: number of clusters differs from supersaturated equilibrium

-~1/10: part of overcritical clusters break up

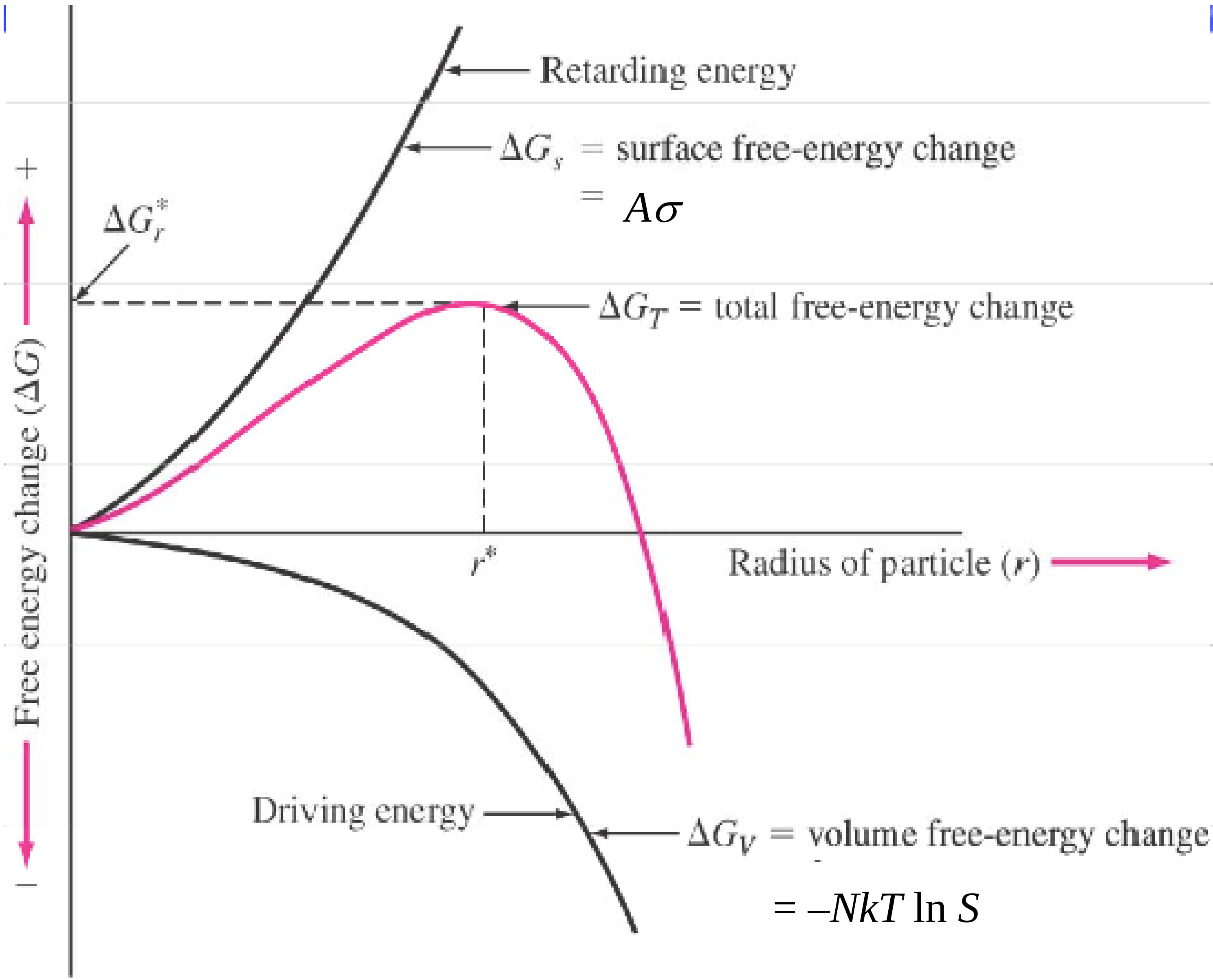
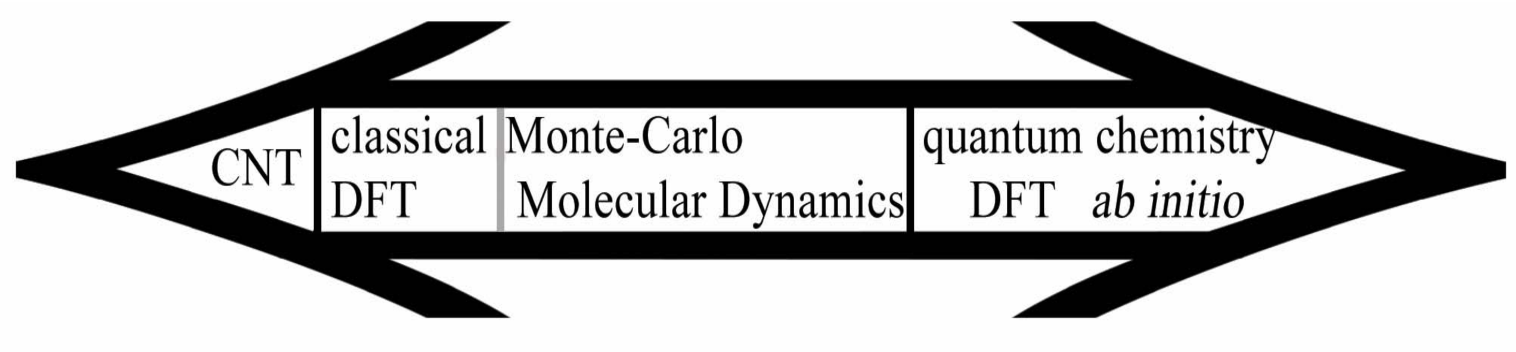


Figure by Hanna Vehkamäki

Comparison of methods for calculating formation free energies for clusters

- Computationally cheap
  - Large clusters
- Inaccurate molecular interaction energies

- Computationally demanding
  - Only small clusters
- Very accurate molecular interaction energies



- Advanced and accurate statistical sampling
- Much empirical data needed
  - System-specific

- Very primitive and approximate statistical sampling
- Little or no empirical data needed
  - Can be used to study any system

Figure by Hanna Vehkamäki

Nucleation treatment in atmospheric models

- Each theoretical approach is way too heavy to be handled in a large-scale model

- Parameterisations available for some substances
  - Water – sulphuric acid
  - Water – sulphuric acid – ammonia

- Parameterisations are based on calculations with one or more of the theories available
  - Input: RH, T, concentrations
  - Output: J

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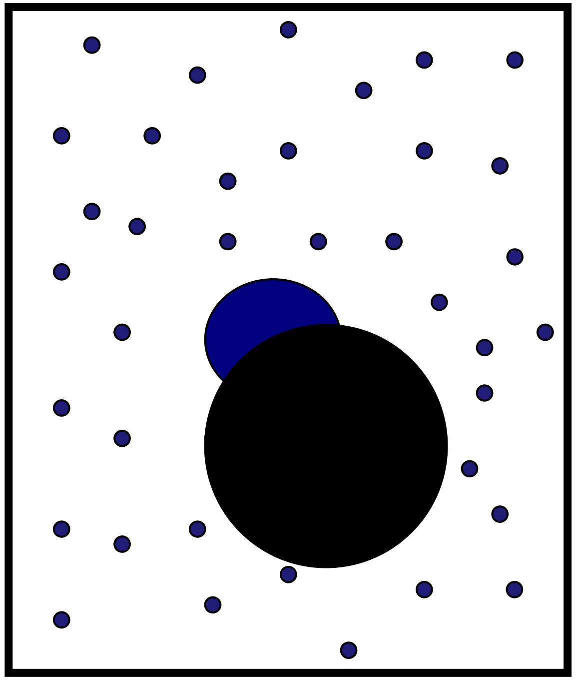
Heterogeneous nucleation

- Nucleation on a pre-existing surface (e.g. aerosol particle)
- Formation of a new phase
- Occurs more likely than homogeneous nucleation



The nano-Köhler mechanism

- Example: Freshly-nucleated thermodynamically stable clusters (TSCs), composed of ammonium bisulfate and water, are activated for condensational growth by an water-soluble organic vapour
- Activation means that the organic vapor starts to condense irreversibly into these particles
- However, this does not occur before TSCs have reached a certain threshold size!

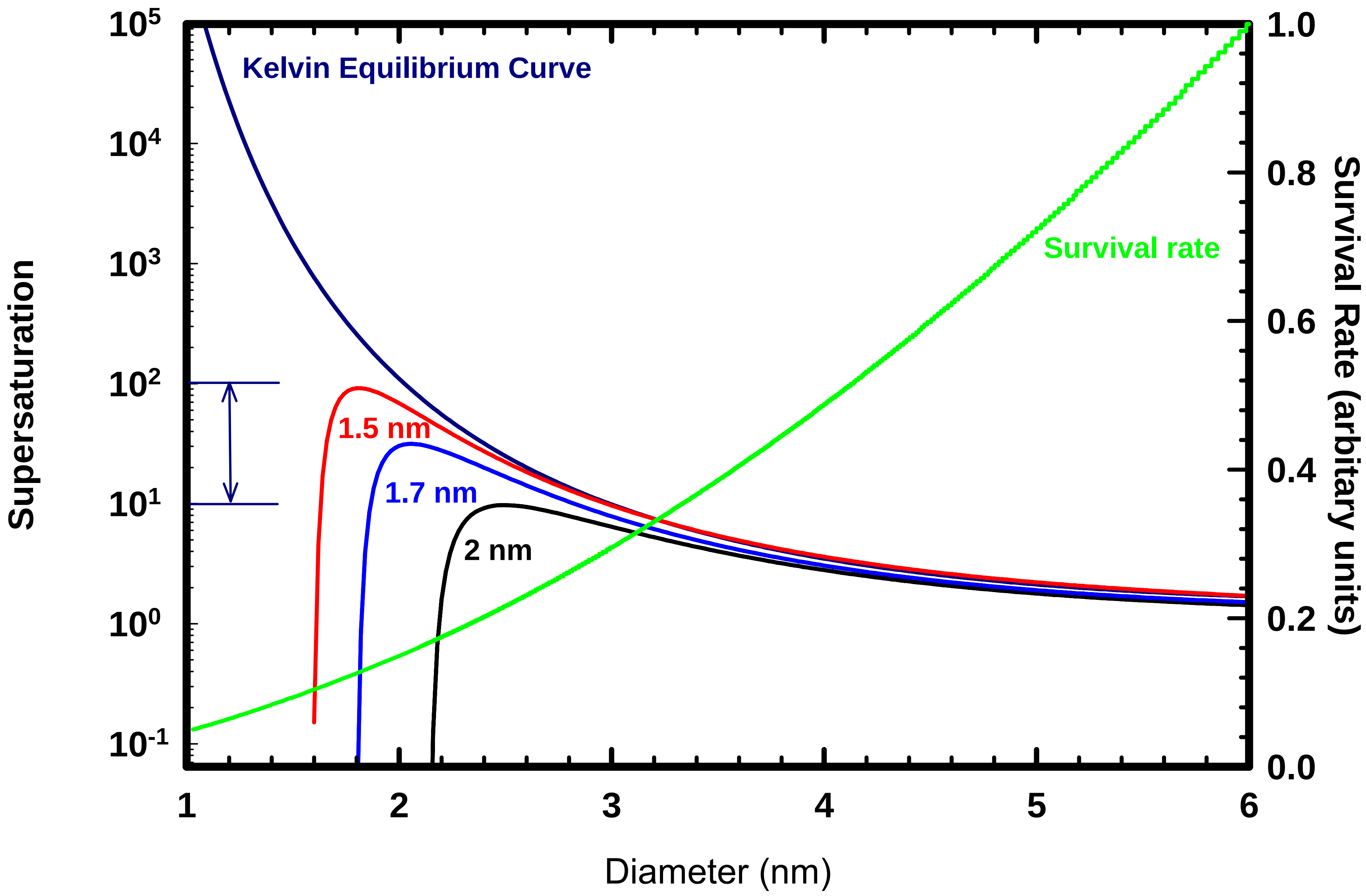
Traditional Köhler theory vs nano-Köhler

Köhler:

- CCN, > 50 nm
- activating vapour: water
  10^{16}-10^{17} molec/cm^3
- saturation ratio < 1.05
- S depends on pre-existing particle size distribution, cooling rate, fluctuations

nano-Köhler:

- Inorganic TSCs 1-3 nm
- activating vapours: soluble organic compounds
  10^{6}-10^{8} molec/cm^3
- saturation ratio not limited
- S depends on condensation sink, vapour source rate and saturation vapour pressure, fluctuations



Kelvin Equilibrium Curve
1.5 nm
1.7 nm
2 nm
Survival rate
Supersaturation
Survival Rate (arbitary units)
Diameter (nm)
10^5
10^4
10^3
10^2
10^1
10^0
10^-1
1
2
3
4
5
6
1.0
0.8
0.6
0.4
0.2
0.0

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Condensation

- Condensation: aerosol particle grows in size by taking up vapours from the gas phase

- The most important mechanism of particle growth in the atmosphere

- Gas – liquid (or gas – solid) phase transition: always accompanied with characteristic energy released (condensation) or absorbed (evaporation)
  → mass and heat transfer to/from droplet coupled by latent heat of evaporation (also enthalpy of vaporization)
  - Condensation processes can be modelled by solving appropriate mass and heat transfer equations

Condensational growth of atmospheric aerosol particles

- condensational growth is most effective in the size range < 0.1 μm
- in the atmosphere, gaseous compounds causing the condensational growth include sulphuric and nitric acid, water, ammonia and numerous organic vapours
- difficulties in estimating the particle condensational growth in the atmosphere:
    - many compounds responsible for atmospheric condensational growth have not been identified yet
    - the saturation vapour pressures of many condensing compounds are not known accurately (or not at all)

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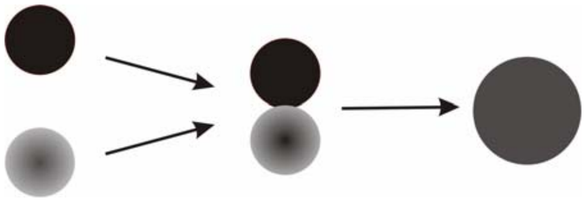
Coagulation

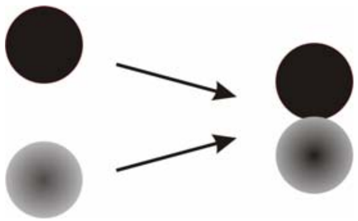
- when two aerosol particles collide with each other in the air, they usually stick together (coagulation)
- in the atmosphere, coagulation is usually caused by the particle Brownian motion (Brownian coagulation)
- the influence of Brownian coagulation on the aerosol particle population is relatively easy to calculate (analytical equations)
- in the atmosphere, the main role of coagulation is to deplete the smallest ($D_p < 10$ nm) aerosol particles (by coagulation into larger particles)

Definitions

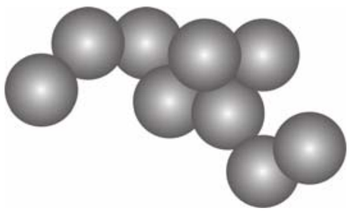
coagulation = collision + coalescence



agglomeration = collision + sticking (no coalescence)

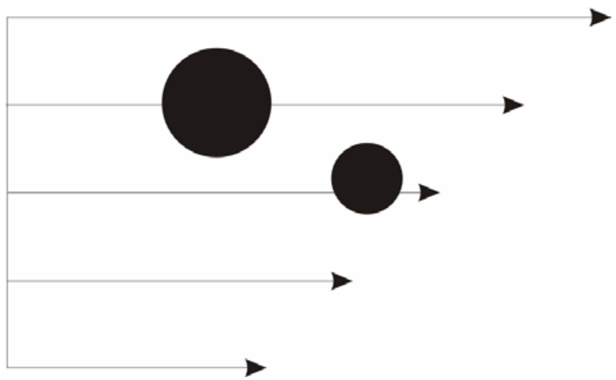


successive agglomeration events result in irregular structures called agglomerates



What causes coagulation?

- Gravitation
- Shear
- Brownian motion
- Turbulence



shear

- In coagulation/agglomeration, the number concentration decreases and the mean size increases

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Cloud processing

- when the ambient relative humidity exceeds 100%, a fraction of aerosol particles (D_p > 50-100 nm) activates to form cloud/for droplets with diameters >10 μm
- activation is a result of water vapour condensation onto the aerosol particles and it occurs within a few minutes
- in cloud droplets, many chemical reactions take place and new compounds are formed
- only about 10% of clouds form rain droplets and precipitate; the rest evaporate and release cloud-processed aerosol particles
- during cloud evaporation, most of the water and a fraction of other material present in the cloud droplets is transferred into the gas-phase

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Deposition

- aerosol particles are removed from the atmosphere by deposition (dry and wet deposition)
- in dry deposition, particles touch/hit a surface (soil, ground, water) and remain there
- dry deposition the most important removal pathway for coarse (2.5 μm < D_p < 10 μm) and ultrafine (D_p < 0.1 μm) particles
- in wet deposition, particles are removed from the atmosphere by rain or fog
- wet deposition is the most important removal pathway for fine particles, especially particles in the size range 0.1-1 μm

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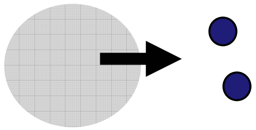
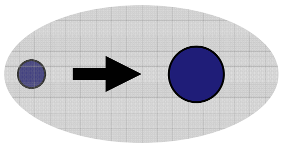
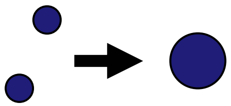
Aerosol-phase reactions

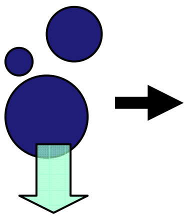
- take place at the surface or inside aerosol particles
- compared to other aerosol dynamical processes, mechanistic understanding of aerosol-phase reactions is still very poor
- extremely important for stratospheric chemistry (formation of ozone hole)
- tropospheric importance largely unknown
  - important for marine sulphur chemistry (SO_2 oxidation in sea salt particles)
  - seems to be important for ageing of secondary organic aerosols
  - indications that takes also place in recently-formed aerosol particles

Dynamical processes and their effects on size distributions









	Particle number	Particle mass & surface
Nucleation	Increase	Increase, Increase
Condensation	No effect	Increase, Increase
Coagulation	Decrease	No effect, Decrease
Deposition	Decrease	Decrease, Decrease