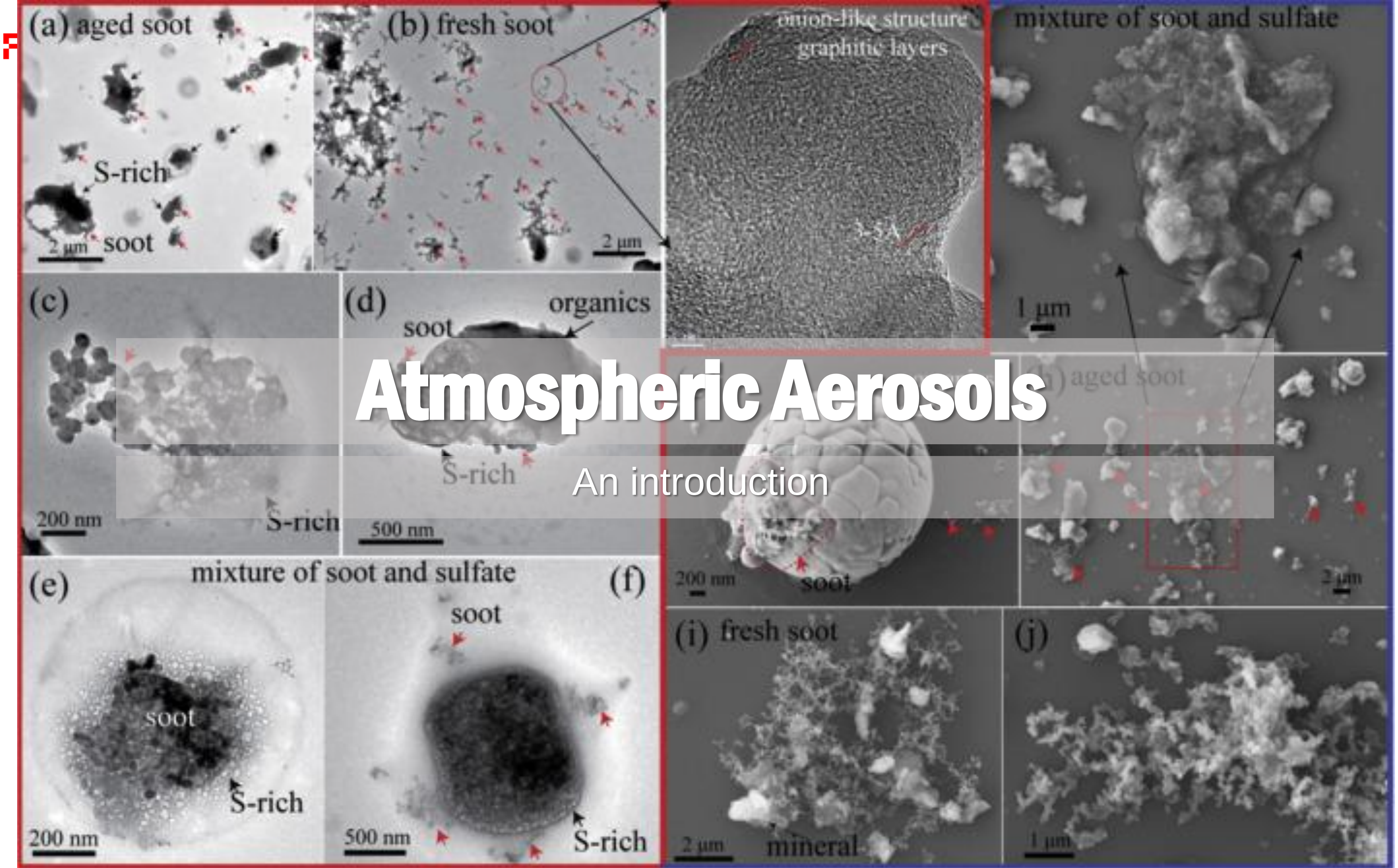
Atmospheric Aerosols

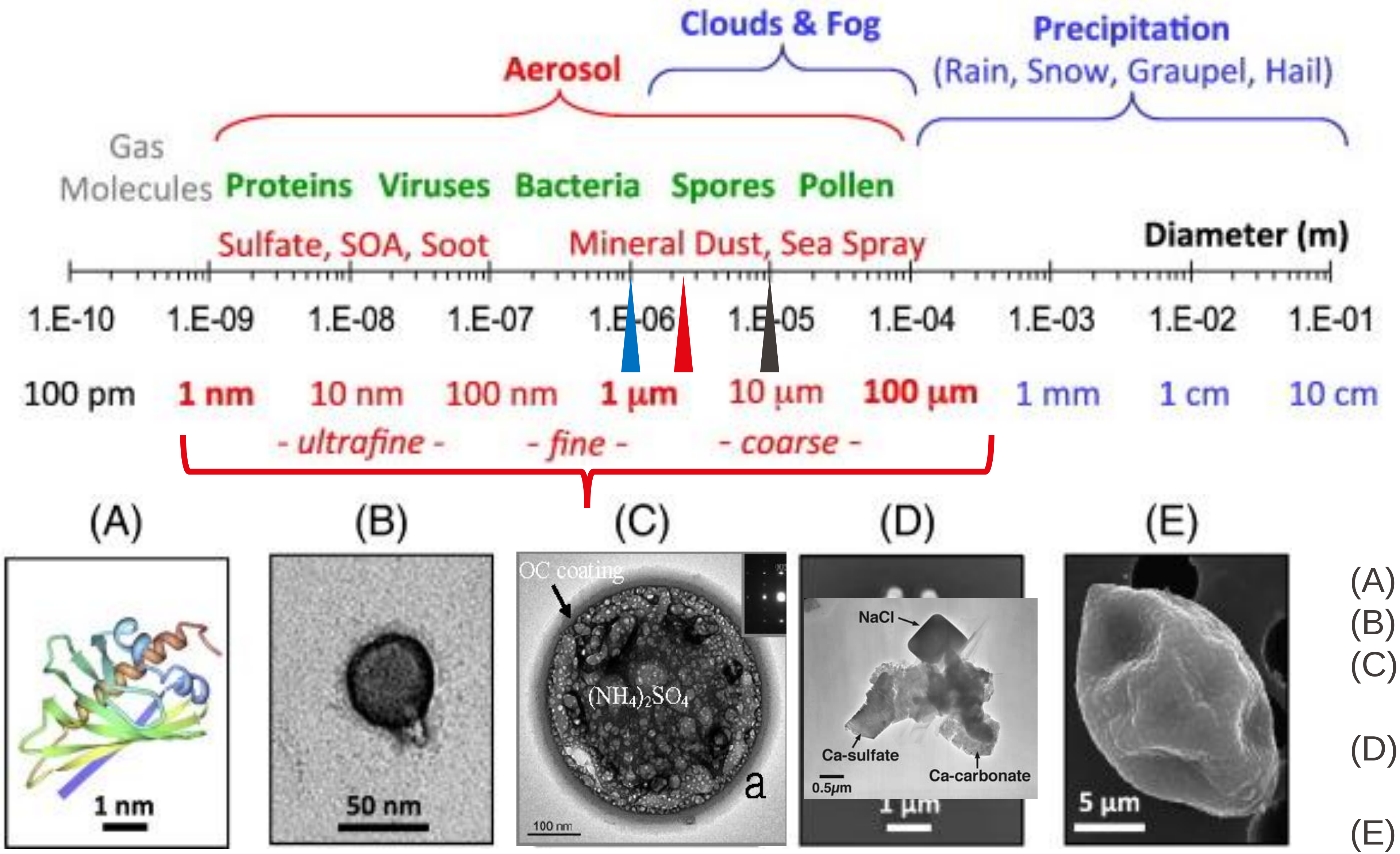
An introduction



Learning outcomes

- Know sources of aerosols and factors determining lifetime
- Distinguish between primary and secondary particles
- Understand the principles of various particle diameters and particle motion
- Be able to calculate aerosol size distributions
  - Number, surface and volume
  - Lognormal size distribution
- Understand the principles of gas / particle partitioning
  - Saturation vapor pressure
  - Gibbs energy
  - Henry’s and Raoult’s laws

Size of aerosols



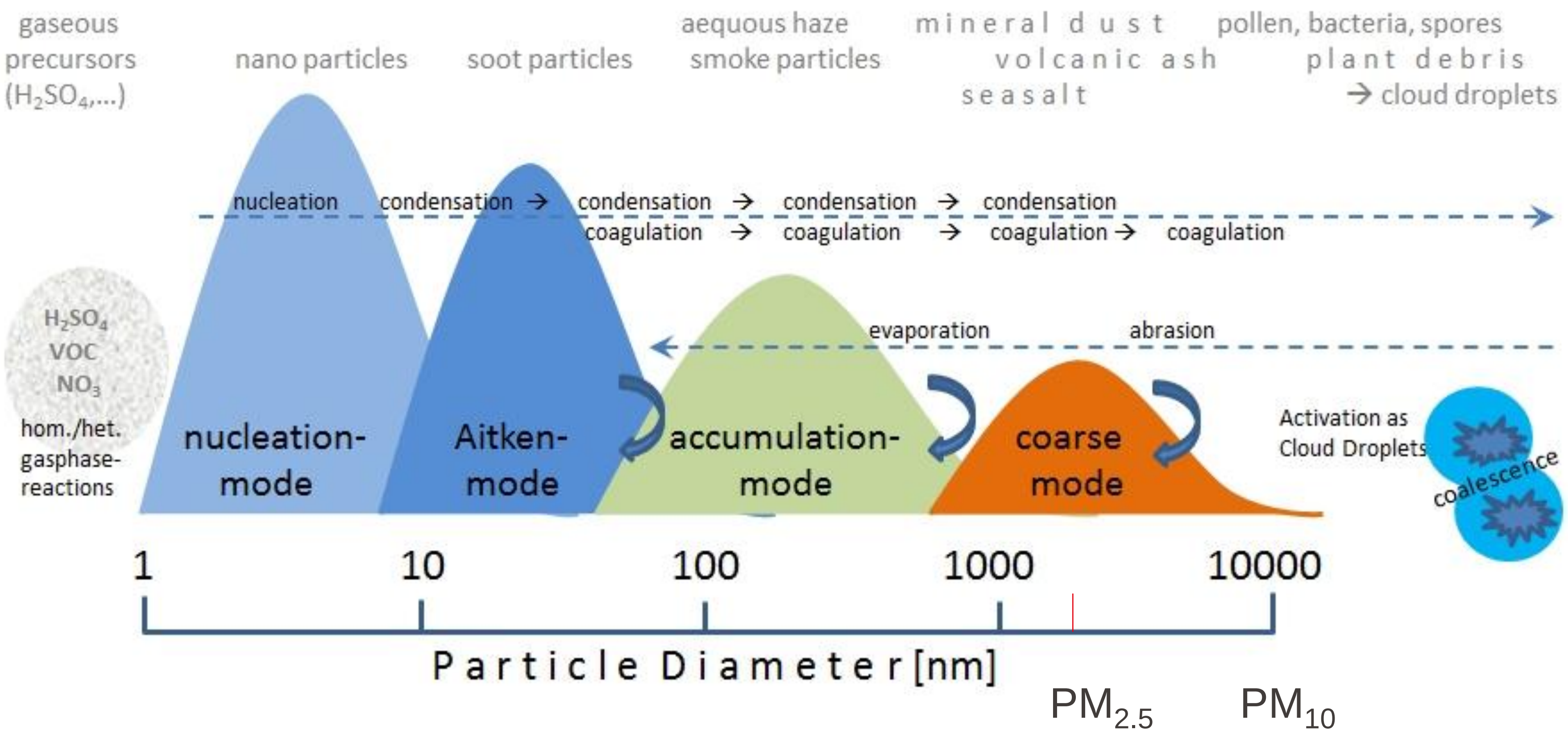
PM$_1$
PM$_{2.5}$
PM$_{10}$

Particulate matter with a diameter equal to or smaller than x µm (air quality)

(A) protein,
(B) virus
(C) Urban particle
(D) Mineral dust
(E) pollen grain

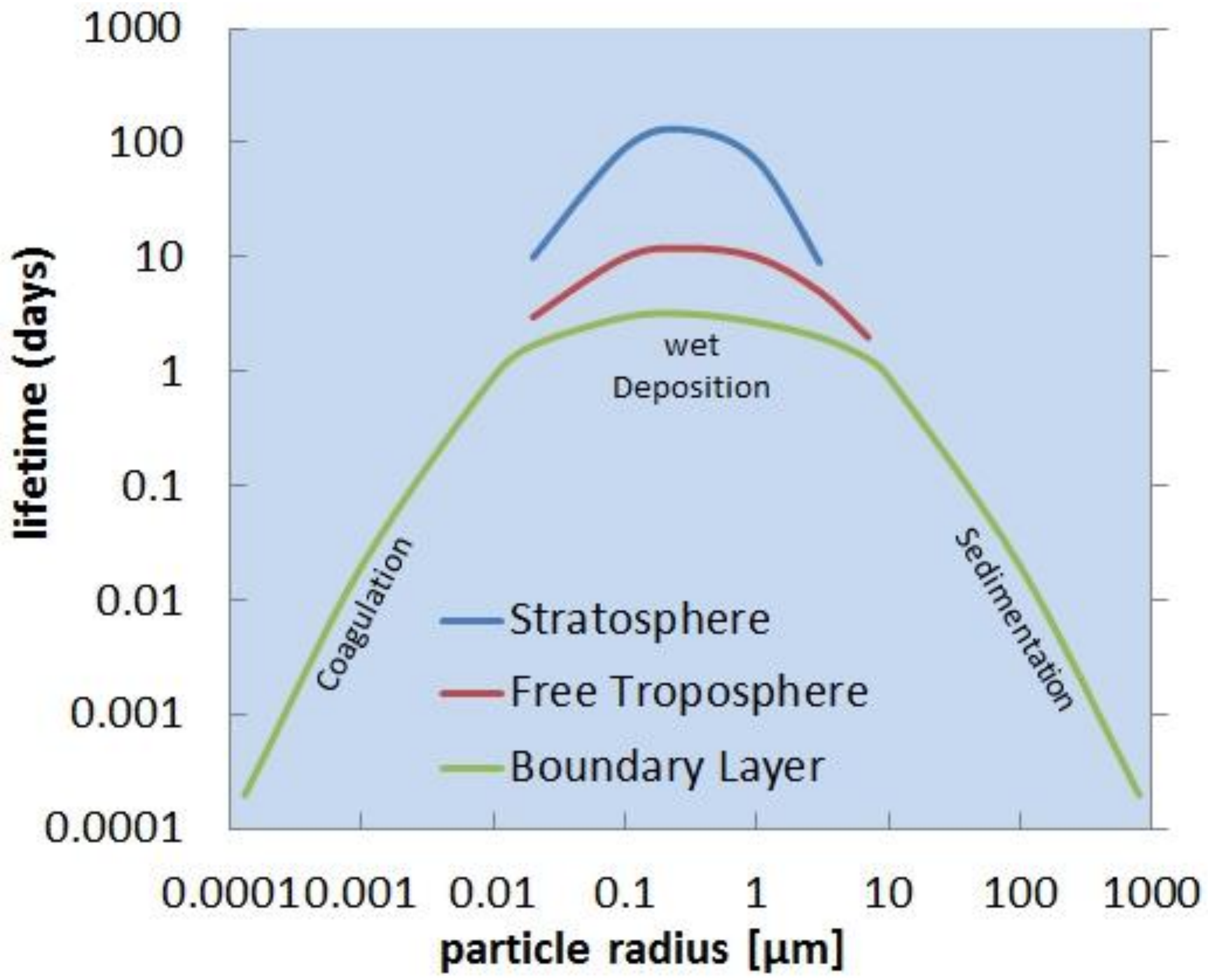
Fröhlich-Nowoisky et al. (2016), https://doi.org/10.1016/j.atmosres.2016.07.018

Aerosol size distributions



https://www.dwd.de/EN/research/observing_atmosphere/composition_atmosphere/aerosol/cont_nav/particle_size_distribution_node.html

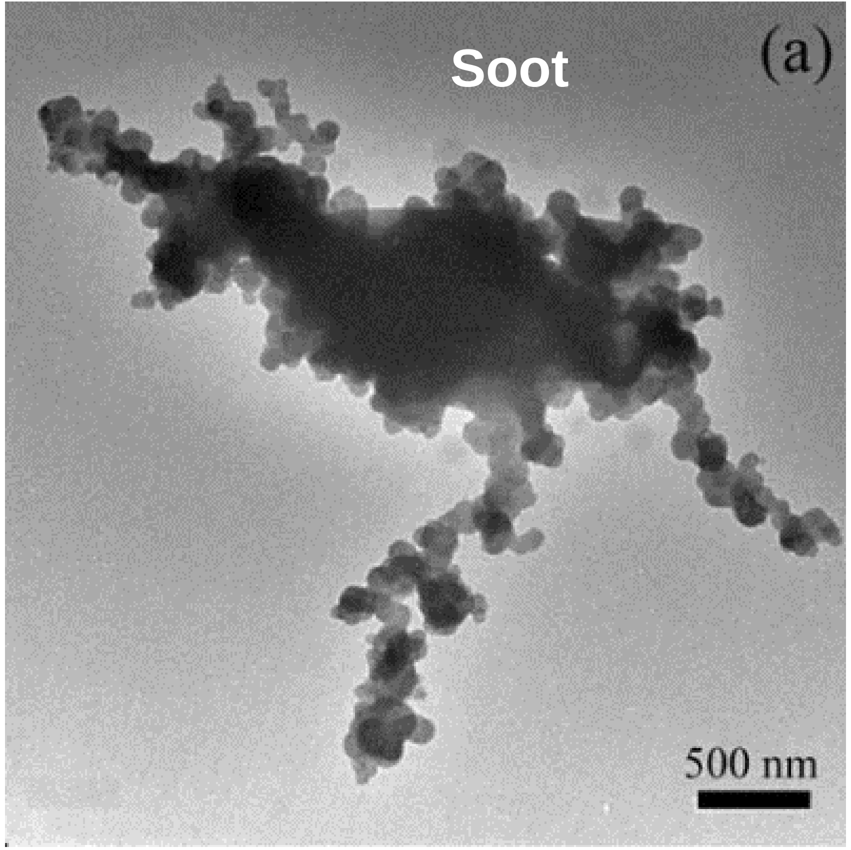
Aerosol lifetime



https://www.dwd.de/EN/research/observing_atmosphere/composition_atmosphere/aerosol/cont_nav/particle_size_distribution_node.html

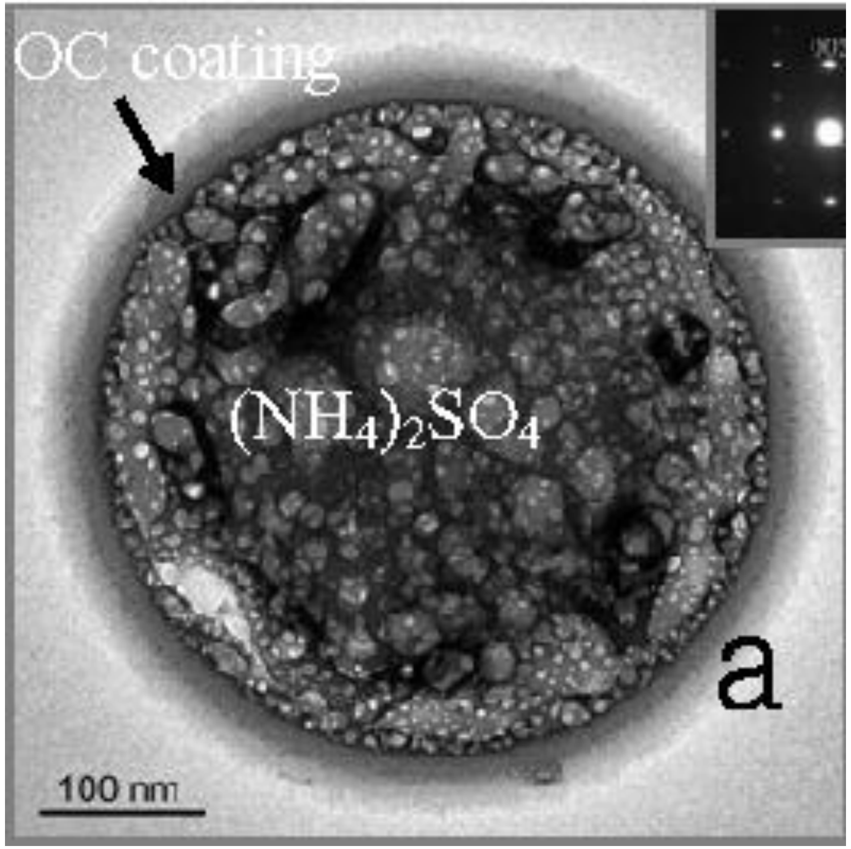
Types of aerosols

Primary



Primary particles are emitted from their source as particles. Examples: soot for combustion, mineral dust from soil.

Secondary



Secondary particles are NOT emitted as particles, but they are formed from gases in the atmosphere through condensation or chemical reactions (in clouds). Examples: Ammoniumsulfate, ammoniumnitrate, secondary organic aerosol

Images are from a Transmission Electron Microscope (TEM).

Links to papers: right, left

Sources of aerosols

Mixed

Natural

Forest fires

Sea spray

Dust

Volcanic eruptions

Traffic / Transport

Domestic activities

Industry

Agriculture

Anthropogenic

Global emission estimates of major aerosol classes

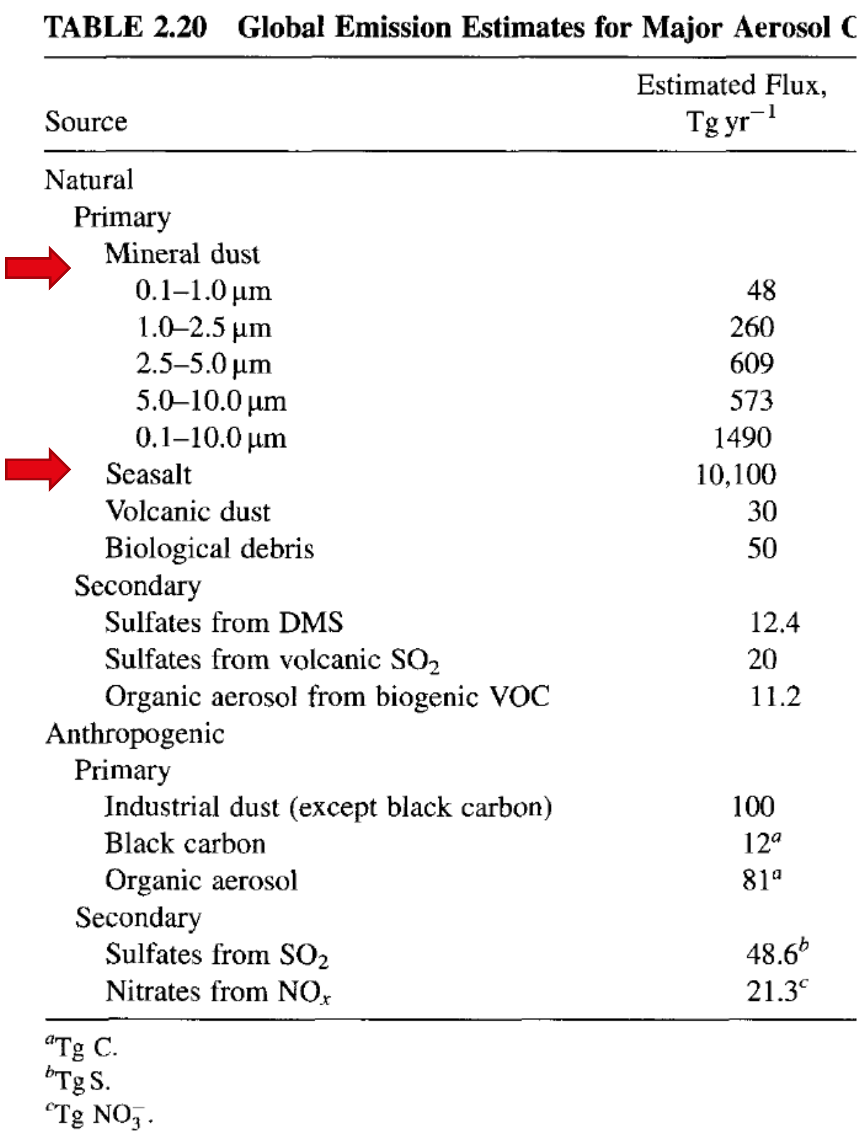


TABLE 2.20 Global Emission Estimates for Major Aerosol C

Source	Estimated Flux, Tg yr^{-1}
Natural	
Primary	
Mineral dust	
0.1–1.0 µm	48
1.0–2.5 µm	260
2.5–5.0 µm	609
5.0–10.0 µm	573
0.1–10.0 µm	1490
Seasalt	10,100
Volcanic dust	30
Biological debris	50
Secondary	
Sulfates from DMS	12.4
Sulfates from volcanic SO_2	20
Organic aerosol from biogenic VOC	11.2
Anthropogenic	
Primary	
Industrial dust (except black carbon)	100
Black carbon	12[a]
Organic aerosol	81[a]
Secondary	
Sulfates from SO_2	48.6[b]
Nitrates from NO_x	21.3[c]

[a] Tg C.

[b] Tg S.

[c] Tg NO_3^-.

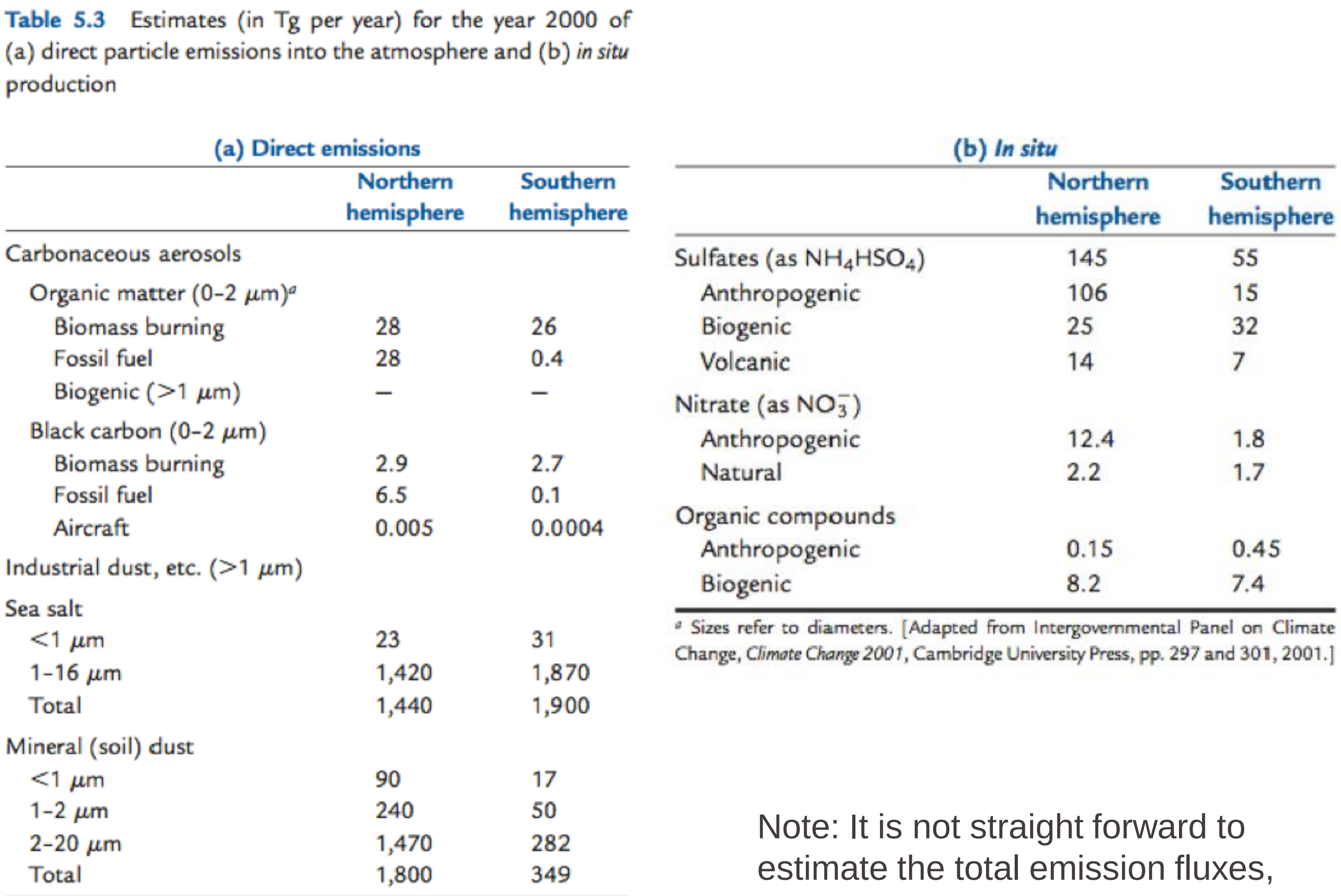


Table 5.3 Estimates (in Tg per year) for the year 2000 of (a) direct particle emissions into the atmosphere and (b) *in situ* production

(a) Direct emissions

	Northern hemisphere	Southern hemisphere
Carbonaceous aerosols		
Organic matter (0–2 µm)[a]		
Biomass burning	28	26
Fossil fuel	28	0.4
Biogenic (>1 µm)	–	–
Black carbon (0–2 µm)		
Biomass burning	2.9	2.7
Fossil fuel	6.5	0.1
Aircraft	0.005	0.0004
Industrial dust, etc. (>1 µm)		
Sea salt		
<1 µm	23	31
1–16 µm	1,420	1,870
Total	1,440	1,900
Mineral (soil) dust		
<1 µm	90	17
1–2 µm	240	50
2–20 µm	1,470	282
Total	1,800	349

(b) *In situ*

	Northern hemisphere	Southern hemisphere
Sulfates (as NH_4HSO_4)	145	55
Anthropogenic	106	15
Biogenic	25	32
Volcanic	14	7
Nitrate (as NO_3^-)		
Anthropogenic	12.4	1.8
Natural	2.2	1.7
Organic compounds		
Anthropogenic	0.15	0.45
Biogenic	8.2	7.4

[a] Sizes refer to diameters. [Adapted from Intergovernmental Panel on Climate Change, *Climate Change 2001*, Cambridge University Press, pp. 297 and 301, 2001.]

Note: It is not straight forward to estimate the total emission fluxes, hence there can be deviations betweens publications.

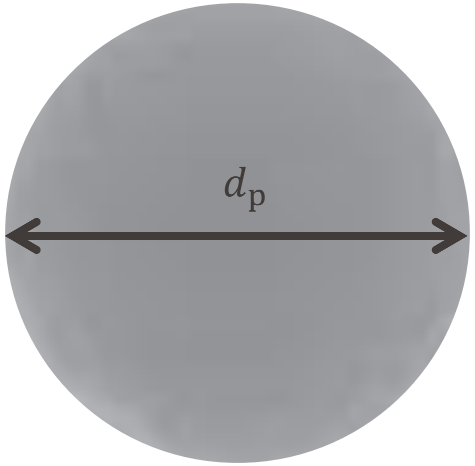
Seinfeld and Pandis, 2006

Wallace and Hobbs, 2006

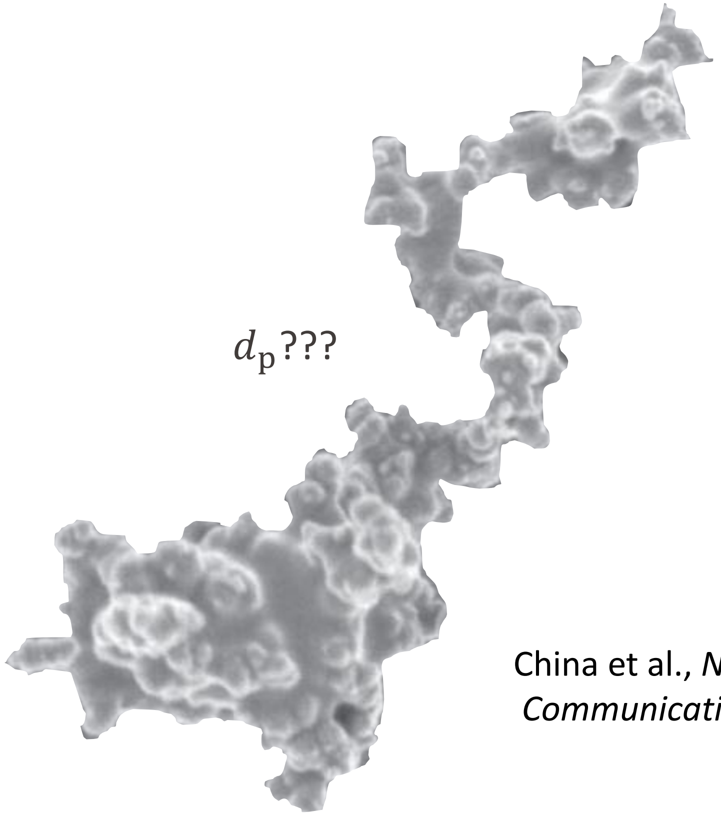
Particle size definitions

Spherical particle

Geometric diameter d_p



Fractal aggregate



China et al., *Nature Communications,* 2013

To define particle sizes precisely we use the concept of an ***equivalent diameter:***
«Diameter of a sphere, having the same value of a particular physical property (that is measurable) as the particle under consideration».

Volume equivalent diameter and mass equivalent diameter

Definition of the ***volume equivalent diameter*** (through «reference particle»):
«Diameter of a sphere, having the same volume as the particle under consideration».

This means:

$$V_{\mathrm{ref}}(d_{\mathrm{geom}}^{\mathrm{ref}}) = V_{\mathrm{particle}} \xRightarrow{\text{use: } d_{\mathrm{ve}} \coloneqq d_{\mathrm{geom}}^{\mathrm{ref}}} \frac{\pi}{6} d_{\mathrm{ve}}^{3} = V_{\mathrm{particle}}$$

$$\Rightarrow \quad d_{\mathrm{ve}} = \left(\frac{6}{\pi} V_{\mathrm{particle}}\right)^{1/3}$$

There are other diameter definitions that mainly depend on the measurement principle (not treated in this lecture), e.g.:

- Optical diameter
- Electrical mobility diameter
- Aerodynamic diameter
- Vacuum aerodynamic diameter

Flow of aerosol particles in the air: Reynolds number

Consider that aerosol particles move in the atmosphere, i.e. a gas. A useful dimensionless parameter to describe the interaction between the particles and gas is the Reynolds number Re, the ratio of ***inertial*** to ***viscous*** forces. For an object of characteristic length scale L,

$$Re = \frac{\rho_g v L}{\eta} \qquad \rightarrow \qquad \frac{inertial\ forces}{viscous\ forces}$$

where
ρ_g: the density of the gas, for air $\rho_{g,air} = 1.2\ \mathrm{kg/m^3}\ (T = 293\ \mathrm{K},\ p = 1\ \mathrm{atm})$
v: the velocity of the gas relative to the object
η: the viscosity of the gas, for air $\eta_{air} = 1.8 \times 10^{-5}\ \mathrm{Pa.}s\ (T = 293\ \mathrm{K},\ p = 1\ \mathrm{atm})$

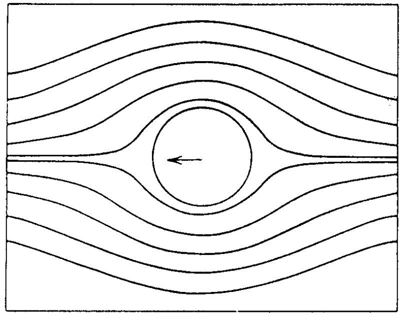
For a particle ‘submerged’ in air L can be considered to be the d_{ve} of the particle (other choices also possible)

Note: Re is also useful when describing aerosol flow in a tube. In our work we use it to characterize particle losses, so we can deliver quantitative results. In this case $L \coloneqq d_{\mathrm{tube}}$

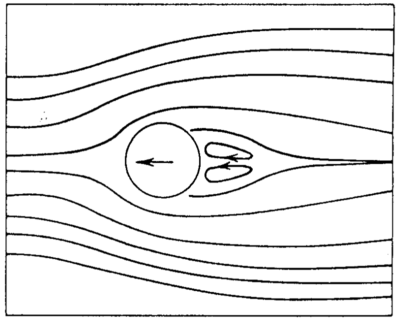
Flow of aerosol particles in the air: Reynolds number

Laminar (smooth) flow for **low Re** (< 1)

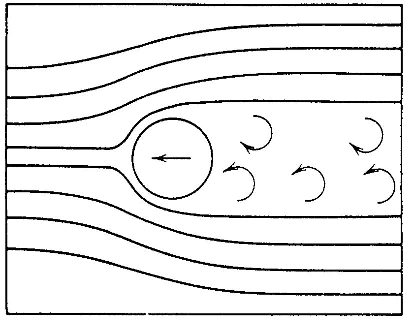
Turbulent flow for **high Re**



$Re = 0.1$



$Re = 2$



$Re = 250$

Hinds, 1999

And which *Re* applies in the atmosphere?

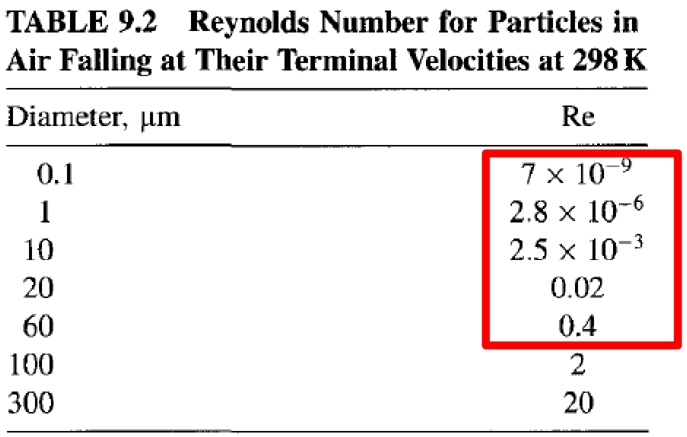


TABLE 9.2 Reynolds Number for Particles in Air Falling at Their Terminal Velocities at 298 K

Diameter, μm	Re
0.1	7×10^{-9}
1	2.8×10^{-6}
10	2.5×10^{-3}
20	0.02
60	0.4
100	2
300	20

In most situations the flow is laminar
Re (< 1) around atmospheric particles

Seinfeld and Pandis, 2006, p. 406

Stokes Law

Stokes Law describes the drag force $F_{\mathrm{drag}}^{\mathrm{p}}$ acting on an individual particle moving in a gas.

$$F_{\mathrm{drag}}^{\mathrm{p}}(v, d_{\mathrm{ve}}) = 3\pi\eta d_{\mathrm{ve}} v$$

η gas viscosity,
v particle velocity relative to the gas
d_{ve} volume equivalent diameter

The aerodynamic drag force in the continuum regime is proportional to:

- particle diameter
- velocity of the particle (relative to the surrounding gas)

The simplifying assumptions required to derive Stokes law from the Navier-Stokes equation are:

- Inertial forces negligibly small relative to viscous forces ➔ $Re < 1$
- Gas velocity at the particle surface is 0 (‘no slip condition’) ➔ not true at small d_{ve}
- Spherical, rigid particle with constant velocity relative to the gas ➔ not always true either
- Incompressible gas and no other particles or boundaries nearby

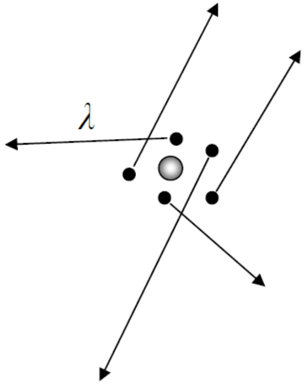
Particle motion in gases: Knudsen number

The behavior of a particle in a gas is characterised by the ratio of the mean free path of the gas molecules to the diameter of the particle. This ratio is called *Knudsen number* (*Kn*):

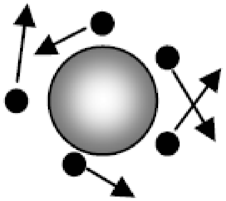
$$Kn = \frac{2\lambda_\mathrm{g}}{d_\mathrm{ve}}$$

λ_g represents the mean distance travelled by a gas (thermal velocity) molecule between collisions with other gas molecules.

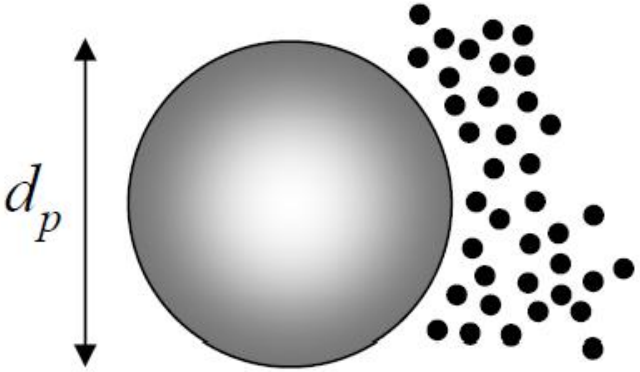
Flow regimes



Free molecular (kinetic): $Kn \gg 1$



Transition: $Kn \sim 1$



Continuum: $Kn \ll 1$ (Stokes Law valid, see next slides)

At $T = 298$ K and p =1 atm, $\lambda_\mathrm{g} = 66$ nm ➔ Kn is 1 for a particle with $d_\mathrm{ve} = 132$ nm.
We typically consider the free molecular regime for particles < 10 nm (nucleation mode), and the continuum regime for particles > 10 µm.

Seinfeld and Pandis, 2006

Cunningham slip correction (Stokes for all regimes)

Stokes’ law, which includes the **boundary condition that the gas velocity at the particle surface is zero** (i.e. drag force caused be shear forces), is **only valid** in the **continuum regime** (i.e. if $K_\mathrm{n} \ll 1$, large particles).

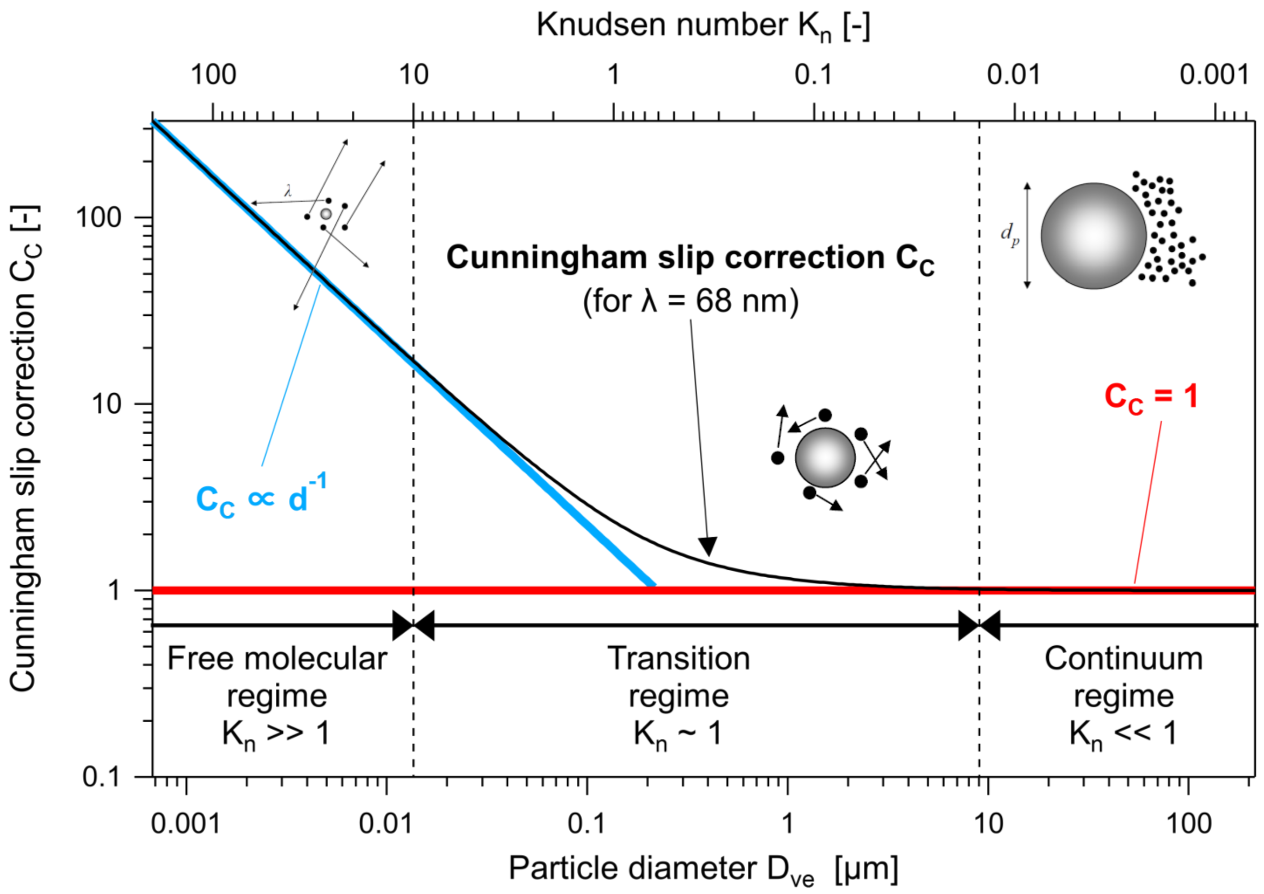
Stokes’ law becomes **invalid in the free molecular regime**, where the mean free path of the molecules is much greater than the particle diameter (i.e. if $K_\mathrm{n} \gg 1$, small particles), the **drag force is fully caused by collisions of individual molecules with the particle** (viscous forces dominate).

This problem is solved by modifying Stokes’ law with the **Cunningham slip correction ($\boldsymbol{C_\mathrm{c}}$)**, which makes it more generally **applicable** for spherical particles **across all size regimes** (and laminar flow):

$$F_\mathrm{drag}^\mathrm{p}(v, d_\mathrm{ve}) = \frac{3\pi\eta d_\mathrm{ve} v}{C_\mathrm{c}(d_\mathrm{ve})}$$

C_c depends on the ratio of mean free path to particle diameter and thereby also on the Knudsen number.

The Cunningham slip correction



C_c is needed to e.g. calculate the terminal settling velocity of a particle (→ see dry deposition from earlier lecture)

Free molecular regime:

$$C_C \propto d^{-1} \iff F^{p}_{\text{drag}} \propto d^2$$

Transition regime

$$F^{p}_{drag} \propto \frac{d}{C_C(d)}$$

Continuum regime:

$$C_C = 1 \iff F^{p}_{\text{drag}} \propto d$$

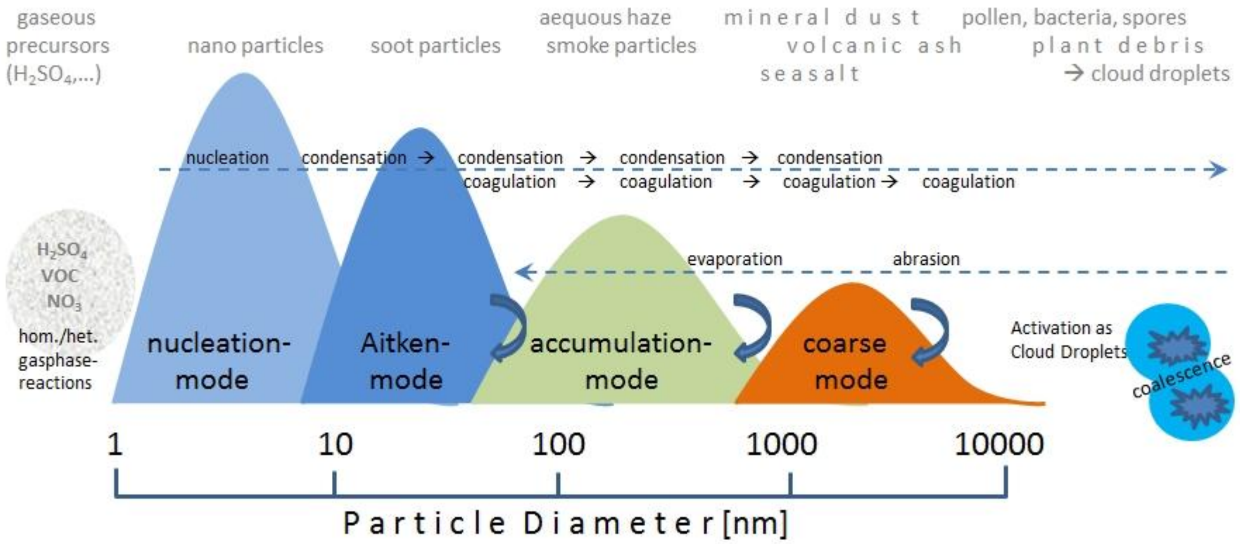
Figure from M. Gysel-Beer

Aerosol size distribution

A monodisperse aerosol (i.e., all particle have the same size) does not exist in the ambient atmosphere; in the laboratory only as an approximation. Hence we have to deal with **polydisperse** aerosol.

Thus, it is necessary to describe the sizes of the aerosol particles with a a size distribution: a distribution that gives the concentration of particles having a certain size (i.e. diameter).

In practice, a number concentration can be determined only in a certain size range
$d_{p(1)} - d_{p(2)} = \Delta d_p$ or dd_p
(i.e. number of particles with diameters between $d_{p(1)}$ and $d_{p(2)}$).



Total particle number, surface area, and volume

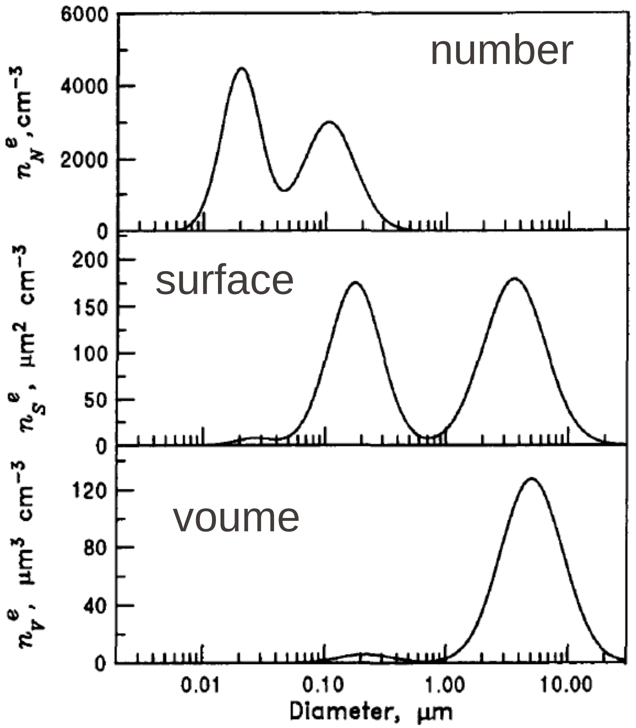


FIGURE 8.6 The same aerosol distribution as in Figures 8.4 and 8.5 expressed as a function of log D_p and plotted against log D_p. Also shown are the surface and volume distributions. The areas below the three curves correspond to the total aerosol number, surface, and volume, respectively.

Seinfeld and Pandis, 2006, p. 357

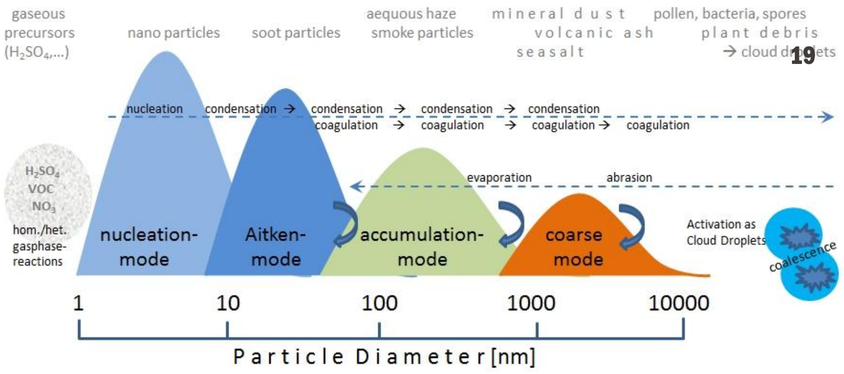
$$\frac{dN}{dlogD_p}$$

Detailed explanation in exercises.

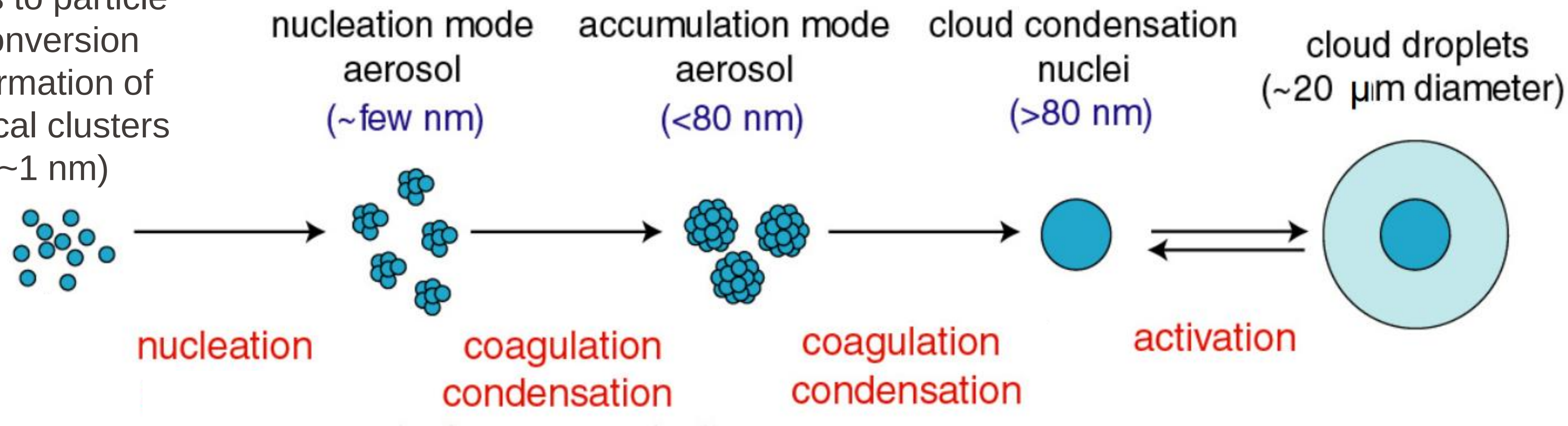
$$\frac{dS}{dlogD_p}$$

$$\frac{dV}{dlogD_p}$$

From gas to particle to cloud droplet



Gas to particle conversion (formation of critical clusters ~1 nm)



Considerations

- Here we consider **equilibrium conditions** (see next slide) of a two phase system (gas and condensed - solid, liquid – phase).
- We consider a **closed system** (the system under consideration and the environment are normally considered as one system, where the environment dictates temperature and pressure).
- We consider **isothermal-isobaric conditions**, i.e. fixed temperature and pressure, which refer to the conditions at the boundary of the system, i.e. temperature and pressure of the system are fixed by its surroundings. This is representative of atmospheric conditions.

- Vapor is defined as gas that can condense.
- In the atmosphere, air is a gas carrier that determines temperature. In the atmospheric boundary layer there are:
  - 10^{19} cm^{-3} air molecules,
  - 10^{17} cm^{-3} water molecules,
  - 10^{10} cm^{-3} sulfuric acid molecules
- When colliding with particles, air molecules do not stick to particles, but substances like sulfuric acid will.

Terminology

Thermodynamic state variables (state functions, state parameters or thermodynamic variables):

T:	Absolute temperature	**intensive** properties (independent of system size)
p:	Pressure	
μ:	Chemical potential	
S:	Entropy	**extensive** properties (scale with system size)
V:	Volume	
n_i:	Number of moles of species i.	

Thermodynamic potentials:

U: Internal energy

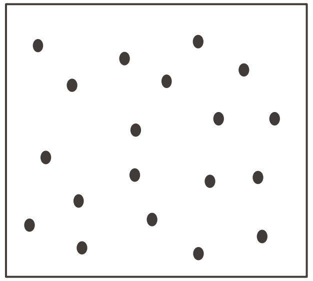
H: Enthalpy

$\boldsymbol{G}$: **Gibbs energy**
(Gibbs function, Gibbs free energy,
or free enthalpy)

μ see following slides
S is associated with a state of disorder, randomness, or uncertainty of the system.
H is the sum of the system’s internal energy.
G see next slides

Extensive and Intensive Thermodynamic State Variables and Potentials

Any thermodynamic **system "a"**:



state variables:

$$T_a \qquad S_a$$
$$p_a \qquad V_a$$
$$\mu_{i,a} \qquad n_{i,a}$$

potentials:

$$U_a$$
$$H_a$$
$$G_a$$

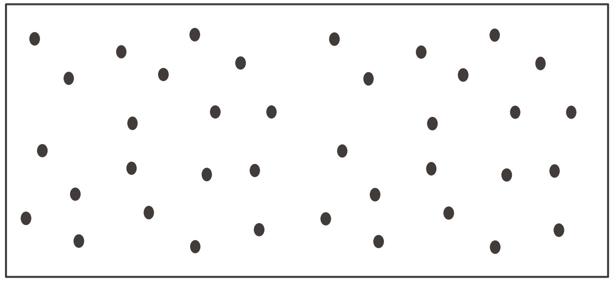
State variables

T:	Absolute temperature
p:	Pressure
μ:	Chemical potential
S:	Entropy
V:	Volume
n_i:	Number of moles of species i.

potentials

U:	Internal energy
H:	Enthalpy
$\boldsymbol{G}$:	**Gibbs energy** (Gibbs function, Gibbs free energy, or free enthalpy)

System "b": exactly equal to system "a" except for scaling the system with factor of 2 (doubled system size and mass):



state variables:

$$T_b = T_a$$
$$p_b = p_a$$
$$\mu_{i,b} = \mu_{i,a}$$

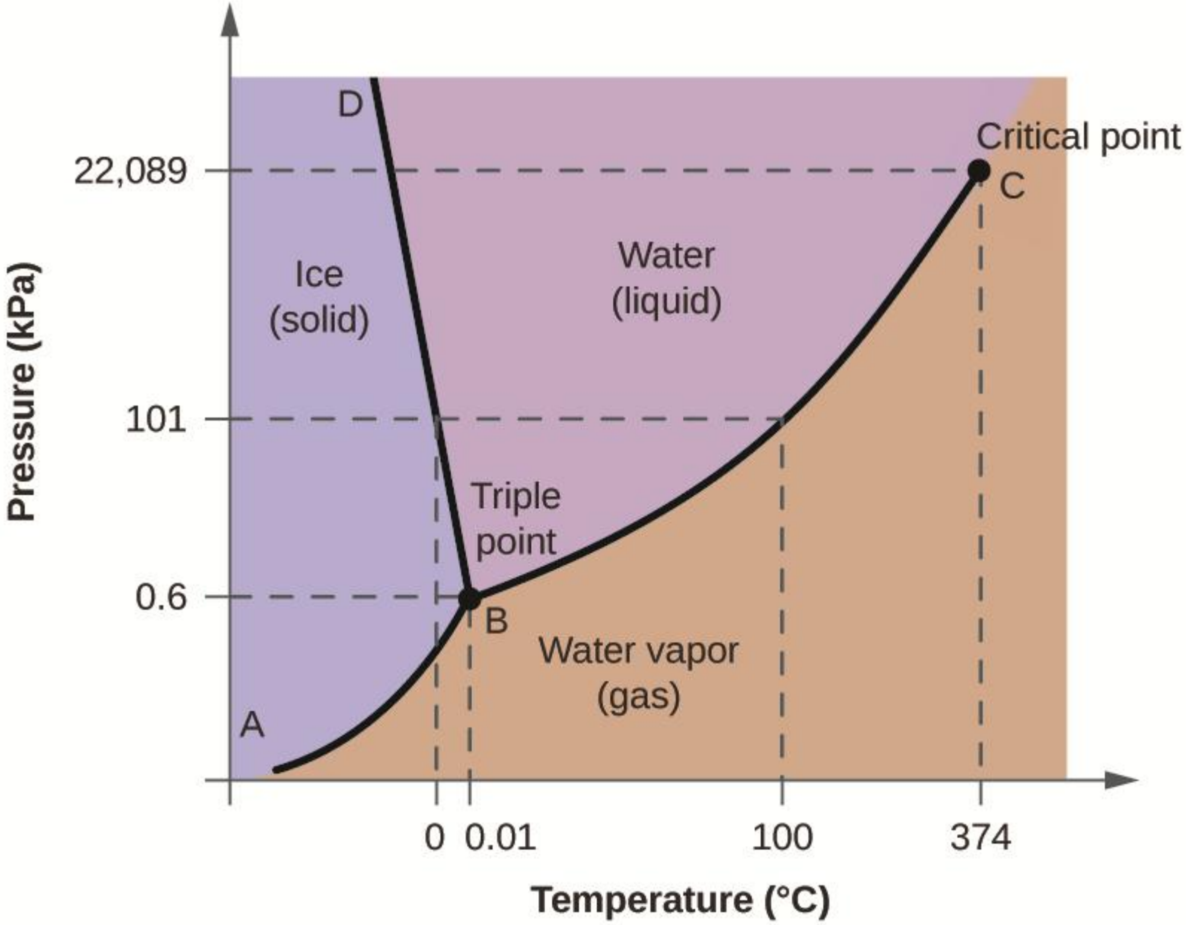
potentials:

$$S_b = 2 \cdot S_a \qquad U_b = 2 \cdot U_a$$
$$V_b = 2 \cdot V_a \qquad G_b = 2 \cdot G_a$$
$$n_{i,a} = 2 \cdot n_{i,a} \qquad H_b = 2 \cdot H_a$$

independent of system scaling
➔ *intensive* properties

proportional to system scaling factor
➔ *extensive* properties

Phase diagram (of H_2O)

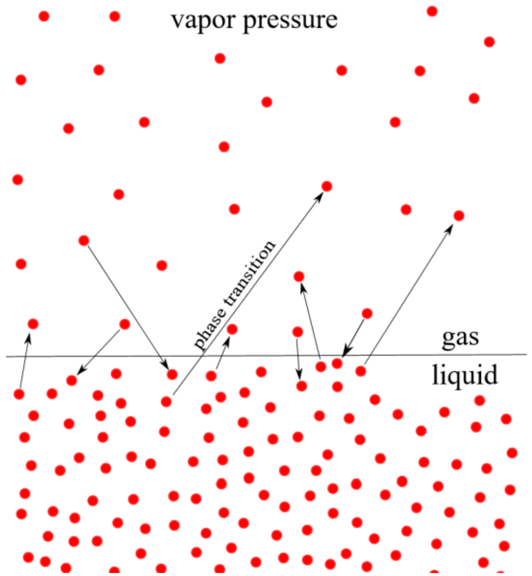


- Solid lines are the phase boundaries
- Critical point: liquid and gas are indistinguishable
- Triple point (273.16 K and a partial vapor pressure of 611.657 Pa): all three phases co-exist

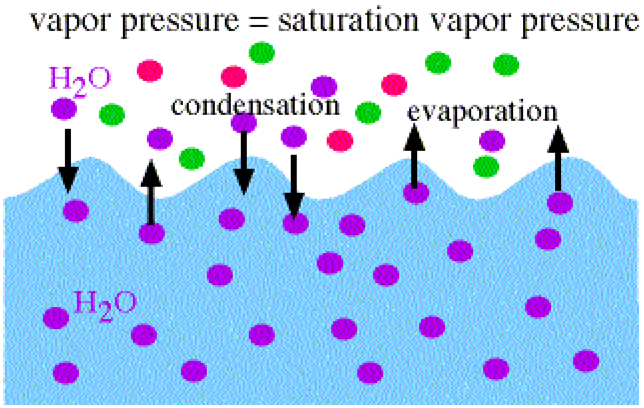
→ Here we are mostly interested in the gas-liquid relationship

https://courses.lumenlearning.com/chemistryformajors/chapter/phase-diagrams-2/

Vapor pressure and Saturation vapor pressure



When the number of molecules that condense and evaporate is the same, the system is in equilibrium and we speak of the saturation vapor pressure.



The vapor pressure of a liquid or solid is the pressure exerted by the vapor in equilibrium with the condensed (solid/liquid) phase.

The **equilibrium vapor pressure $p_{\mathrm{sat,i}}$** for substance *i* is also referred to as its **saturation vapor pressure**, and determines the amount of substance that can be "held" in the gas phase at equilibrium.

The **saturation ratio (S_A)** of a vapour of species *i* is defined as:

$S_\mathrm{A} \coloneqq \frac{p_i}{p_{\mathrm{sat},i}(T)}$, where p_i is the partial pressure and $p_{\mathrm{sat},i}$ the saturation vapor pressure of species *i*.

https://upload.wikimedia.org/wikipedia/commons/6/67/Vapor_pressure.svg

Reminder: 1st law of thermodynamics

The first law of thermodynamics (conservation of energy) can be written as:

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i$$

The internal energy U is the corresponding thermodynamic potential with its natural extensive state variables S, V and $n_1, \ldots, n_k$:

$$U\,(S, V, n_1, \ldots, n_k) = TS - pV + \sum_{i=1}^{k} \mu_i n_i$$

Total kinetic energy

Potential energy tied to volume expansion work

Potential energy associated with latent heat and chemical bonds

Thermodynamic Equilibrium / 2nd law of thermodynamics

2nd law of thermodynamics: «in a closed system, entropy increases in all spontaneous reactions, arriving at a state of thermodynamic equilibrium, which means minimizing the free energy of the system under consideration» → Gibbs energy: $dG = 0$

The Gibbs energy is defined as:

$$G \coloneqq U + pV - TS \tag{1}$$

Inserting “$U = TS - pV + \sum_{i=1}^{k} \mu_i n_i$” (from previous slide) directly provides:

$$G = \sum_{i=1}^{k} \mu_i n_i \tag{2}$$

The total differential of Equation 1 is:

$$\mathrm{d}G = \mathrm{d}U + V\mathrm{d}p + p\mathrm{d}V - T\mathrm{d}S - S\mathrm{d}T \tag{3}$$

Inserting the 1st law of thermodynamics ($\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i$) provides the exact differential of the Gibbs energy:

$$\boldsymbol{dG = Vdp - SdT + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i} \tag{4}$$

Note: the natural variables of the Gibbs energy are p, T and $n_1, \ldots, n_k$.

Gibbs Energy

$$\boldsymbol{dG = Vdp - SdT + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i}$$

simplifies under **isothermal-isobaric** conditions (i.e. $\mathrm{d}T = 0$, $\mathrm{d}p = 0$):

$$\mathrm{d}G = \sum_{i=1}^{k} \mu_i \mathrm{d}n_i$$

And the condition for **thermodynamic equilibrium under isothermal-isobaric conditions** eventually becomes:

$$\mathrm{d}G = 0 \xRightarrow{\boldsymbol{(2^{nd}\ law)}} \sum_{i=1}^{k} \mu_i \mathrm{d}n_i = 0$$

Chemical Potential of an Ideal Gas

The chemical potential (μ_i) of substance i is the partial molar Gibbs energy, i.e. the change of the Gibbs free energy if one mole of substance i is added to a system under isothermal-isobaric conditions (and otherwise constant composition). **Lowering pressure of a pure gas lowers its chemical potential.**

$$\mu(T,p) = \mu^{o}(T,p^{o}) + RT\ln\frac{p}{p^{o}}$$

$$pV = nRT$$

(ideal gas law)

Symbols:

T: temperature

n: Number of moles

V: Volume

p: Pressure

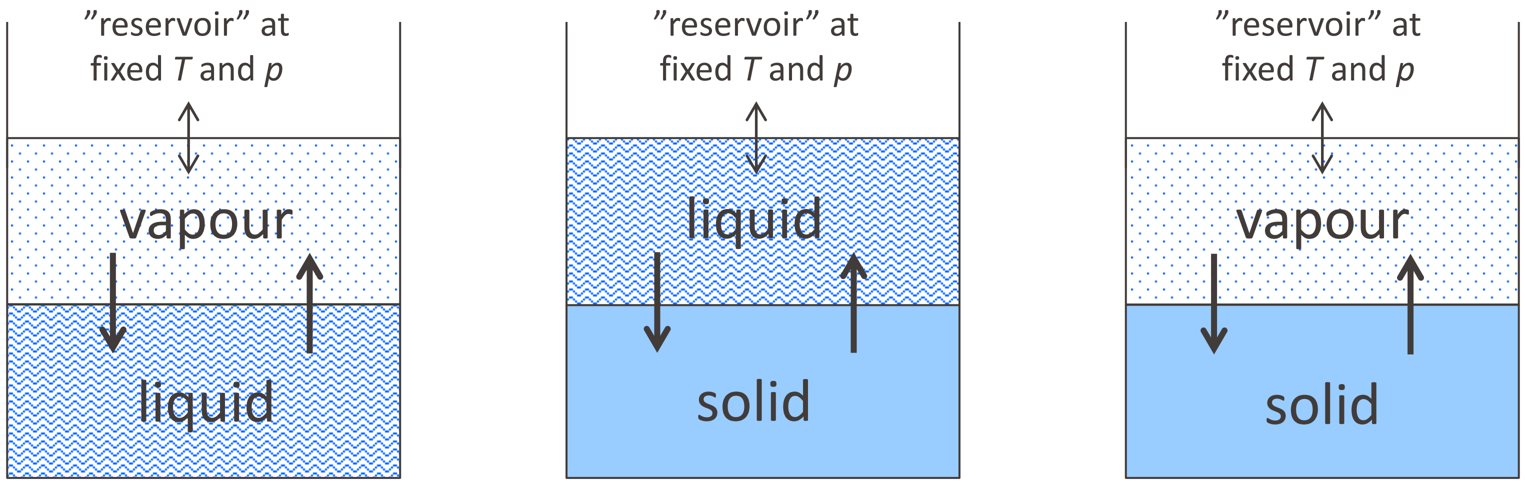
p^{o} : Pressure of the standard state (1 atm)

μ: Chemical potential

μ^{o}: Chemical potential of the standard state

Note: we don’t derive above equation here fully, this might be treated in another class in the future.

Equilibrium Between Two Phases of a Substance



The condition for equilibrium under isothermal-isobaric conditions is:

$$\mathrm{d}G = \sum_i \mu_i \mathrm{d}n_i = 0$$

G: Gibbs free energy
μ: Chemical potential
n: Number of moles

For transitions of species *i* between two phases applies:

$\mathrm{d}n_{i,\mathrm{phase1}} = -\mathrm{d}n_{i,\mathrm{phase2}}$ and $\text{total number of molecules doesn't change}$

and we directly obtain:

$\mu_{i,\mathrm{phase1}} = \mu_{i,\mathrm{phase2}}$ (for phase transitions of a species)

$\Rightarrow$ **The chemical potentials of a species in two different phases are equal in equilibrium.**

Chemical Potential of a Liquid/Solid

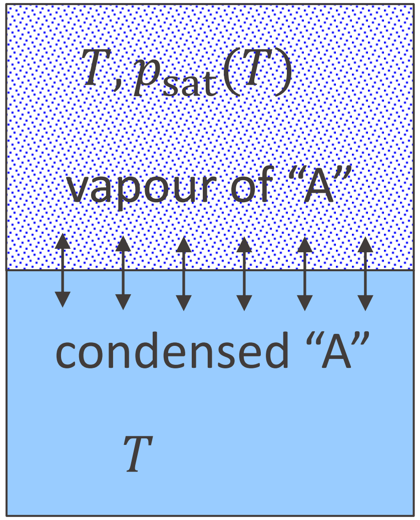
The chemical potentials of a species in two different phases are equal in equilibrium:

$$\mu_{i,\text{phase1}} = \mu_{i,\text{phase2}}$$

For a pure condensed phase (liquid or solid) in equilibrium with its saturated vapor follows:

$$\mu^*_{\text{cond}}(T) = \mu_{\text{vap}}(T, p_{\text{sat}}(T))$$

➔ **The chemical potential of the pure condensed phase is constrained by its saturation vapour pressure.**



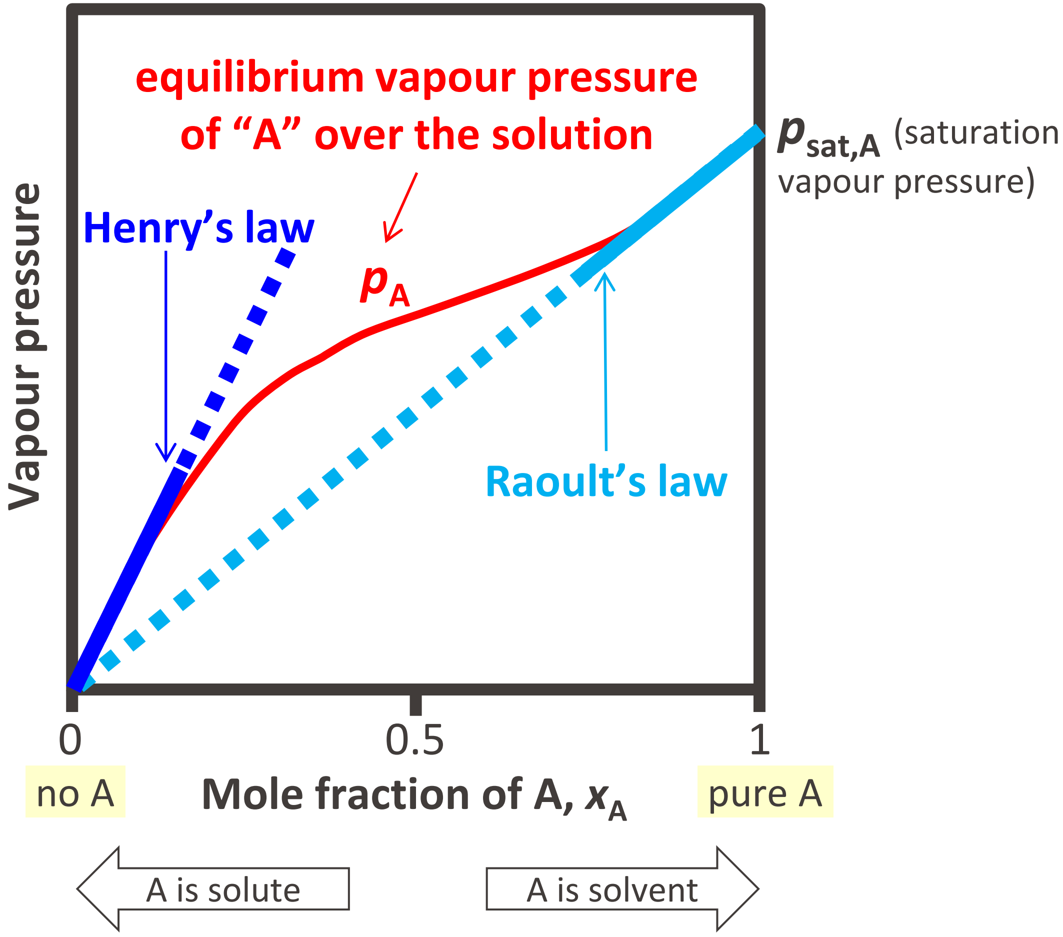
The two phases can be **mixtures**, as long as species *i* can change between the two phases independently of all other species

Symbols:

μ_{vap}:	Chemical potential of the vapour phase
μ^{o}:	Chemical potential of the standard state of a gas
μ^*_{cond}:	Chemical potential of the pure condensed phase (solid or liquid)
p^{o}:	Pressure of the standard state of a gas (1 atm)
p_{sat}:	Saturation vapour pressure of the pure liquid/solid

Two types of mixtures: Raoult's and Henry's law

- **Raoult's** law applies when x_A → 1 (ideal solution)
  - $p_A(T) = p_{sat,A}(T) x_A$
  - Raoult's law states that the equilibrium partial pressure of species A over an **ideal solution** is equal to the saturation vapour pressure of this species in pure form times its mole fraction in the solution.
- **Henry's** law applies when x_A → 0 (ideal-dilute solution)
  - $p_A = H'_A x_A$
  - Henry's law denotes the non-reactive absorption of gases in aqueous solution.
  - The equilibrium vapour pressure of A over an aqueous solution containing small amounts of A.



p_A vapor pressure
$p_{sat,A}$ saturation vapor pressure
x_A mole fraction of substance A
H'_A Henry constant for A

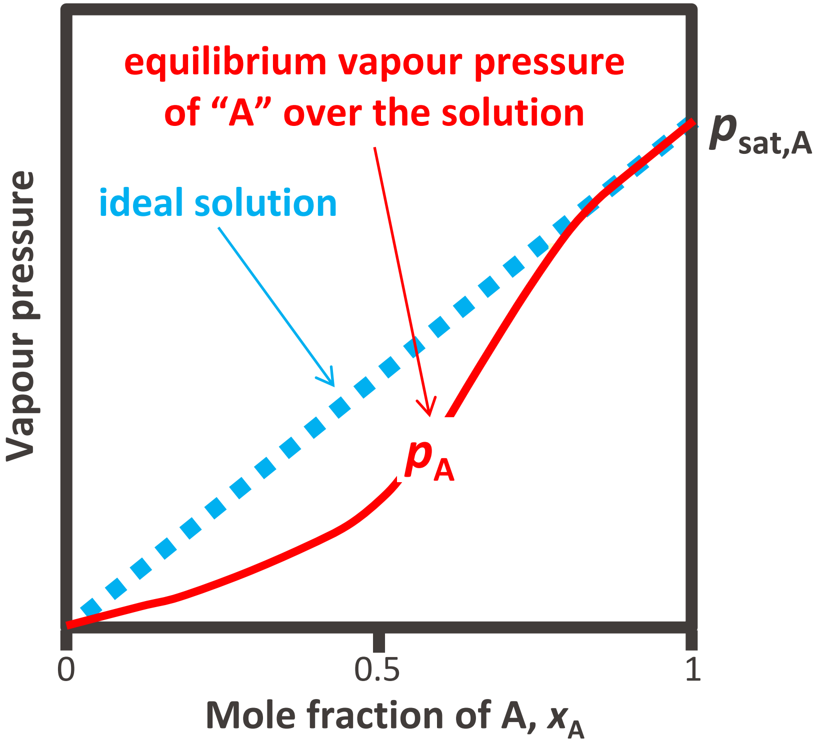
Equilibrium Vapour Pressure over Non-Ideal Solutions

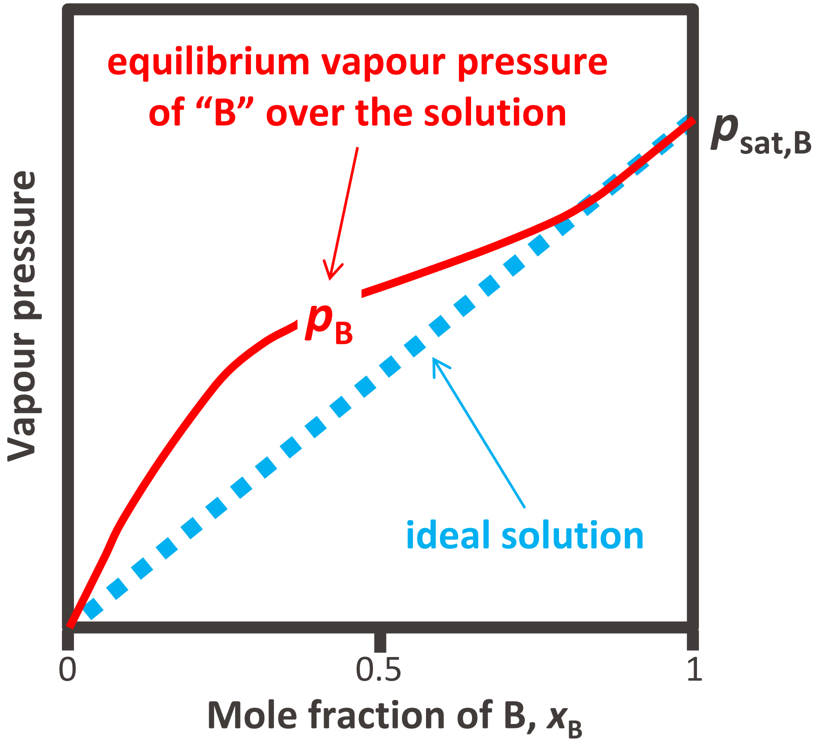
Example: Species A is experiencing
positive/attractive interactions
in the solution

➔ **decreased vapour pressure**

Example: Species B is experiencing
negative/repelling interactions
in the solution

➔ **increased vapour pressure**





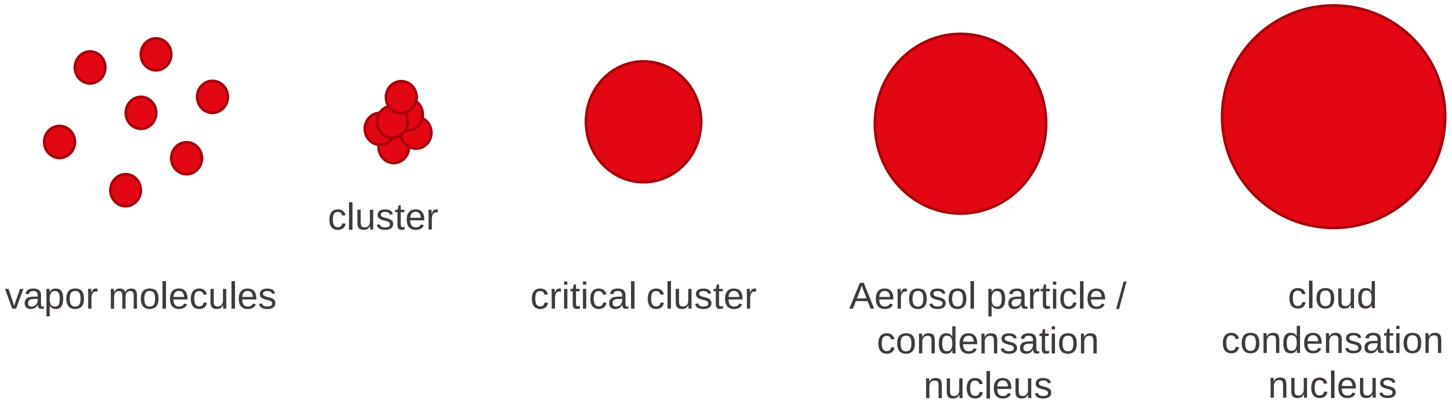
Thought experiment

- We now understand the saturation ratio (***S***) of a gas over the condensed phase.
- When ***S*** < 1 there is vapor undersaturation and the liquid evaporates until we reach equilibrium.
- When ***S*** > 1, the vapor is supersaturated and condenses, provided there is already a planar liquid surface.
- If such a liquid does not exist, the vapor faces a dilemma, because the state that minimizes the Gibbs energy (2nd law!) is the bulk liquid rather than supersaturated gas.
- However, to form a liquid, the interface between gas and liquid must be created first, which costs free energy ($dG \neq 0$).

→ The stochastic, kinetic process through which supersaturated vapors form clusters that overcome this energy barrier is called **nucleation**.

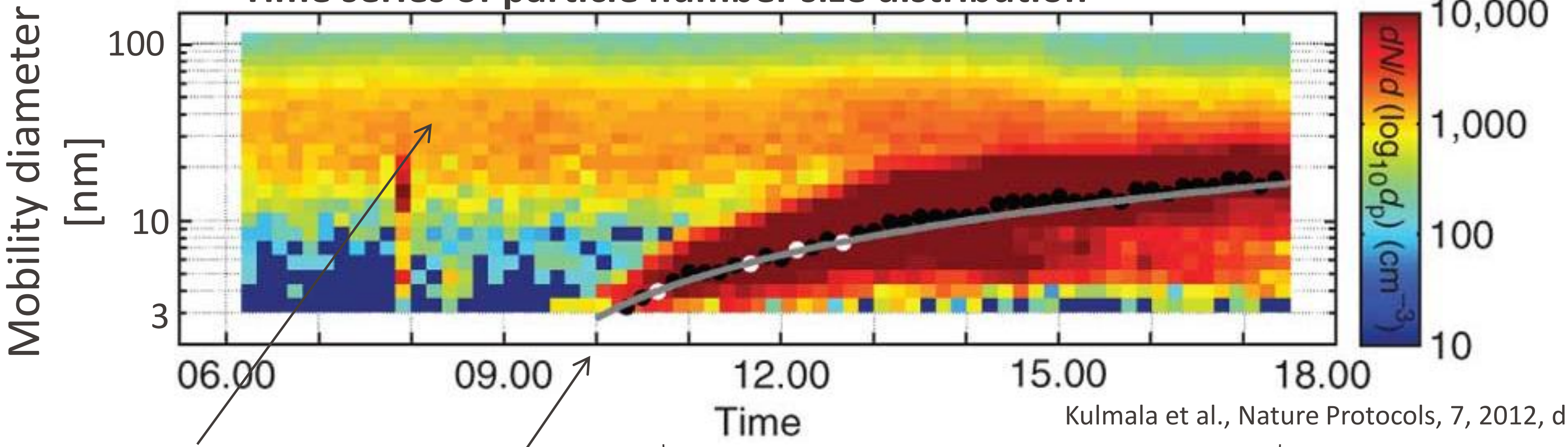
Mind map of a liquid drop model for nucleation

- We describe the cluster formation (nucleation) process as if they were liquid droplets with bulk liquid density and surface tension.
- The gas phase is treated as an ideal mixture of ideal gases.
- This results in the **classical nucleation theory** (CNT).
  (Extensions exist, which we will not treat in this lecture.)
- In CNT we look at the change in the Gibbs free energy (dG/dt).



«Banana-Type» Nucleation Event in the Atmosphere

Time series of particle number size distribution



Kulmala et al., Nature Protocols, 7, 2012, doi:10.1038/nprot.2012.091

background aerosol

nucleation event
(some species are sufficiently supersaturated to trigger new particle formation)

growth by condensation
(coagulation also results in growth but it is a loss in terms of particle number!)

photochemistry produces low volatility vapours that drive nucleation and condensation (previous lecture)

- **Nucleation events are frequently observed in the atmosphere.**
- **Secondary particles from nucleation give a substantial contribution to the total number of cloud condensation nuclei (see lectures by Thanos Nenes).**

Take home messages / aerosols

- There are natural and anthropogenic sources of aerosols. Global quantification is a challenge, particularly for natural sources.
- Primary particles are emitted as particles, secondary particles are formed in the atmosphere from vapors.
- Aerosol lifetime is a function of particle size and removal by precipitation.
- Particle diameters are a matter of definition.
- With Stoke’s law we can describe the movement of particles through air.
- Particles occur in polydisperse manner and form a size distribution. Size distributions can be characterized by modes
  - Nucleation
  - Aitken
  - Accumulation
  - Coarse
- The equilibrium vapor pressure, Gibbs energy and the 2nd law of thermodynamics help us understand the partitioning between gas and particle.
- Henry’s and Raoult’s laws define the equilibrium vapor pressure over a solution.