

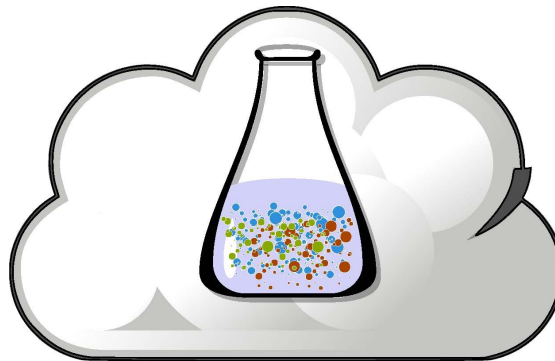
NUCLEATION AND ACTIVATION OF CLOUD DROPLETS



UNIVERSITY
OF WARSAW



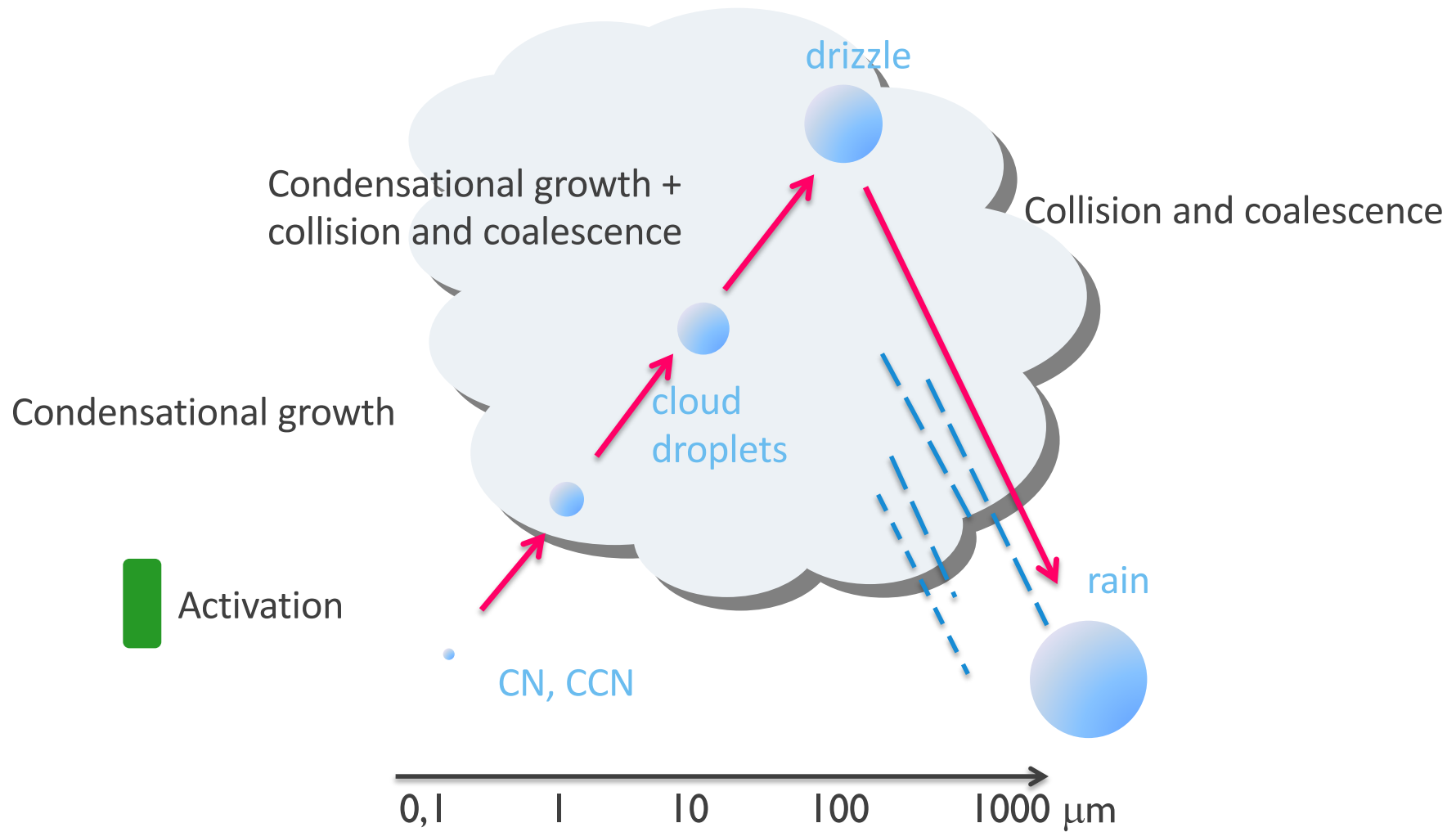
Heterogeneous
nucleation
Cloud Condensation
Nuclei (CCN)
activation



Diffusional growth
Condensational growth
Collision/coalescence
Drizzle formation



Rain
CCN washout



LECTURE OUTLINE

1. Equilibrium conditions over a curved surface (the Kelvin effect)
2. Equilibrium conditions in the presence of soluble matter (the Raoult effect)
3. Köhler curve
4. κ -Köhler theory



UNIVERSITY
OF WARSAW

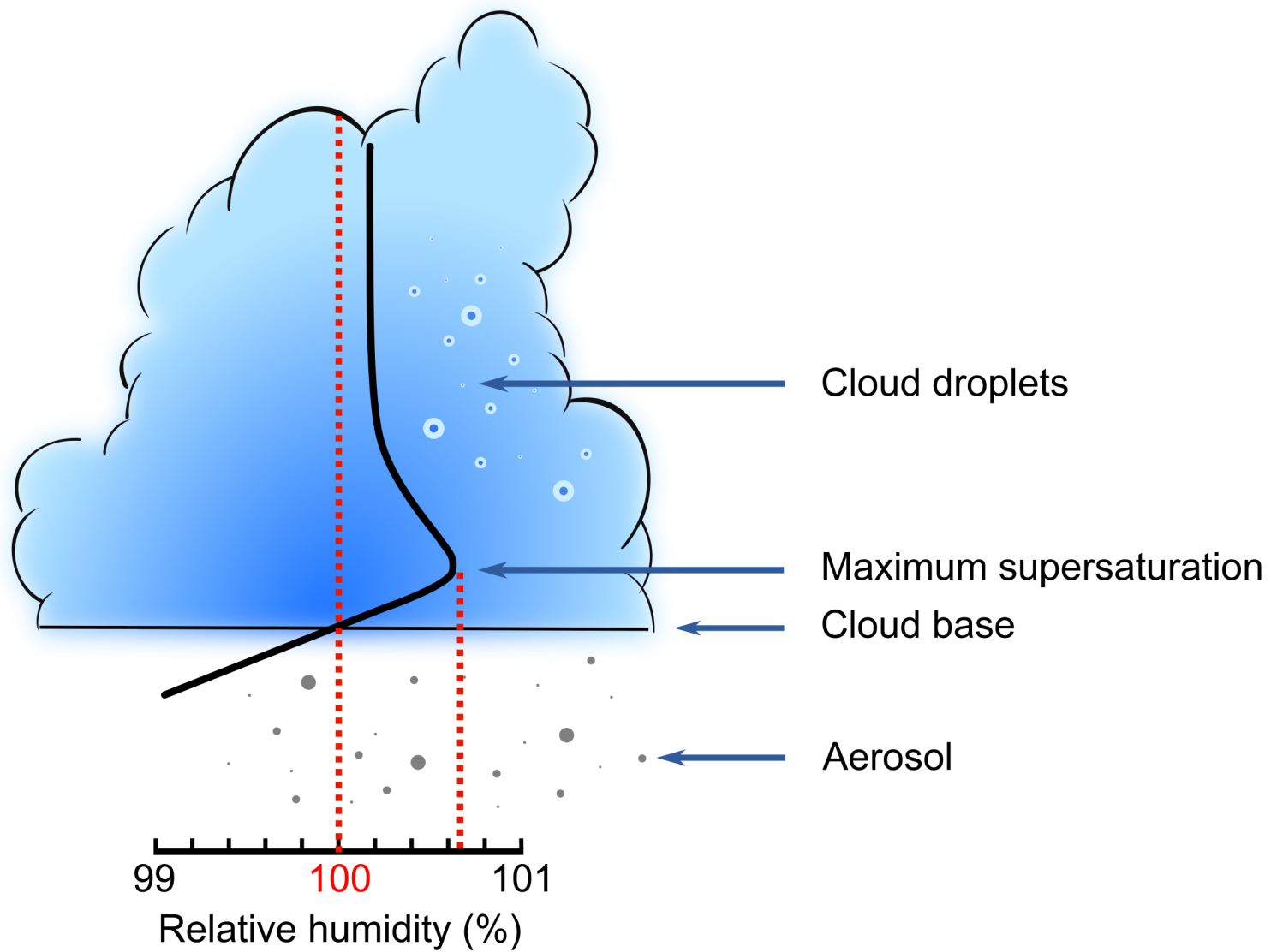


Figure credit: Katarzyna Nurowska

NUCLEATION

- **Nucleation** is a process whereby a stable embryo of a new phase forms within the initial or 'parent' phase (e.g., a water droplet in a field of water vapor)
- Phase transitions do not occur strictly at thermodynamic equilibrium:
 - An energy barrier must be surmounted for a new phase to nucleate.
 - The energy barrier arises because an interface must be formed between the two phases (surface tension/energy).
- **Homogeneous nucleation** refers to nucleation occurring in a pure, single-component system (without foreign surfaces).
- **Heterogeneous nucleation** refers to nucleation that occurs in the presence of a foreign substance or surface, which reduces the energy barrier.

SATURATION CONDITIONS OVER A CURVED SURFACE



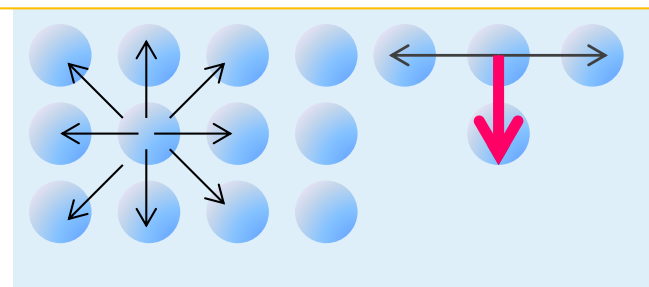
UNIVERSITY
OF WARSAW

We can extend the thermodynamic equations to include surface effects with the introduction of *surface tension work*

$$dW_{st} = \sigma \cdot d\Omega$$

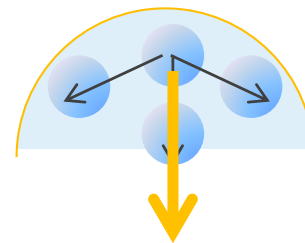
σ - the surface tension between two phases

$d\Omega$ – the change in surface area



$$\sum F = 0$$

$$\sum F > 0$$



$$\sum F > \sum F > 0$$

Surface tension over curved surface is proportional to $1/r$

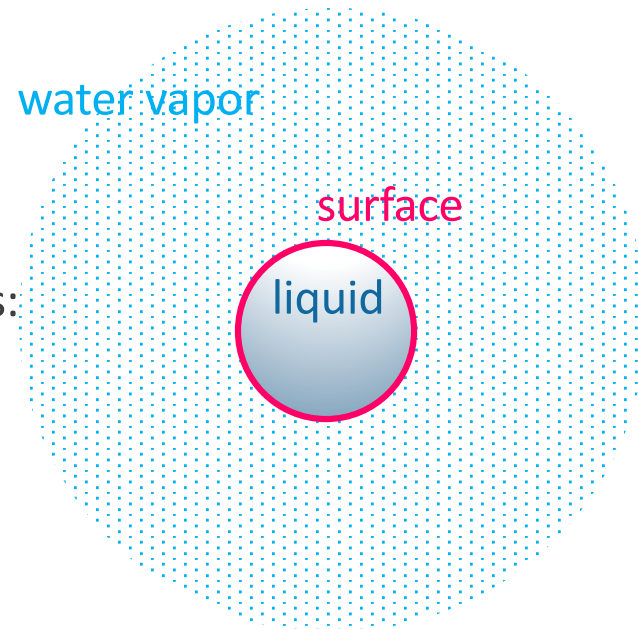
When modeling surface effects, it is useful to treat the surface as a distinct phase.

Doing so describes the combined liquid-surface-vapor system as a composition of three subsystems:

- vapor; v
- surface; σ
- liquid, l

Each property is the sum of the subsystem contributions:

- internal energy : $U = U_v + U_\sigma + U_l$
- entropy: $S = S_v + S_\sigma + S_l$
- number of molecules: $N = N_v + N_\sigma + N_l$



The systems differ in their extensive spatial parameters: the surface is characterized by its area, Ω , whereas that the bulk phases (vapor and liquid) are characterized by their volume, V .

$$U = U_v(S_v, V_v, N_v) + U_\sigma(S_\sigma, \Omega, N_\sigma) + U_l(S_l, V_l, N_l)$$

$$\begin{aligned} dU &= dU_v + dU_\sigma + dU_l \\ &= T_v dS_v + T_\sigma dS_\sigma + T_l dS_l - e dV_v + \sigma d\Omega - p_l dV_l + \mu_v dN_v + \mu_\sigma dN_\sigma + \mu_l dN_l \end{aligned}$$

This expression implicitly introduces a new intensive variable, σ , defined as **surface tension**

$$\sigma \equiv \left. \frac{\partial U_\sigma}{\partial \Omega} \right|_{S_\sigma, N_\sigma}$$

σ has units of force per unit length, or energy per unit area, by analogy with pressure, which is energy per unit volume (or force per unit area).

$\sigma d\Omega$ is positive because the surface is part of the system; thus, work done to expand the surface increases the internal energy of the system.

At equilibrium, state variables take values that minimize the internal energy, i.e., $dU = 0$.

$$0 = T_v dS_v + T_\sigma dS_\sigma + T_l dS_l - e dV_v + \sigma d\Omega - p_l dV_l + \mu_v dN_v + \mu_\sigma dN_\sigma + \mu_l dN_l$$

For a closed system: $dS = dN = dV = 0$

$$dS = 0 \Rightarrow dS_\sigma = -dS_v - dS_l$$

$$dN = 0 \Rightarrow dN_\sigma = -dN_v - dN_l$$

$$dV = 0 \Rightarrow dV_l = -dV_v$$

Consider a surface Ω bounding a sphere of radius r : $d\Omega = (2/r)dV_l$

$$(T_v - T_\sigma)dS_v + (T_l - T_\sigma)dS_l - \left(e + 2\frac{\sigma}{r} - p_l\right)dV_v + (\mu_v - \mu_\sigma)dN_v + (\mu_l - \mu_\sigma)dN_l = 0$$

The equation can only be satisfied in general (i.e., for arbitrary variations of S, V, and N) if the prefactors themselves are identically zero.

$$(T_v - T_\sigma)dS_v + (T_l - T_\sigma)dS_l - \left(e + 2\frac{\sigma}{r} - p_l\right)dV_v + (\mu_v - \mu_\sigma)dN_v + (\mu_l - \mu_\sigma)dN_l = 0$$

The conditions for thermal, chemical, and mechanical equilibrium are:

$$T_v = T_l = T_\sigma = T$$

$$\mu_v = \mu_l = \mu_\sigma = \mu$$

$$e + 2\frac{\sigma}{r} = p_l$$

How does the surface tension modify phase equilibrium and the Clapeyron equation (chemical equilibrium)?

$$-s_vdT + v_vde = -s_ldT + v_ldp_l$$

We employ the mechanical equilibrium constraint to relate dp_l to de :

$$(s_v - s_l)dT = (v_v - v_l)de + \frac{2\sigma}{r^2}v_ldr$$

The Clausius-Clapeyron equation for liquid – water vapor equilibrium

$$(s_v - s_l)dT = (v_v - v_l)de + \frac{2\sigma}{r^2}v_l dr \quad v_v \gg v_l$$

$$(s_v - s_l)dT = v_v de + \frac{2\sigma}{r^2}v_l dr$$

To isolate the effect of droplet radius, the temperature is held constant (i.e.; $dT=0$)

$$0 = v_v de + \frac{2\sigma}{r^2}v_l dr \quad v_v = \frac{1}{\rho_v}, \quad v_l = \frac{1}{\rho_l}$$

$$de = -\frac{2\sigma}{r^2} \frac{\rho_v}{\rho_l} dr \quad e = R_v T \rho_v$$

$$de = -\frac{2\sigma}{r^2} \frac{1}{\rho_l} \frac{p_v}{R_v T} dr$$

How does e change as we integrate $de = -\frac{2\sigma}{r^2} \frac{1}{\rho_l} \frac{e}{R_v T} dr$

- from an infinite radius $r \rightarrow \infty$ (where surface tension effects vanish by definition)
- to a given radius r

Notation:

- saturation vapor pressure over a curved droplet $e_s(r, T)$,
- saturation vapor pressure over a flat (plane) surface $e_s(\infty, T)$.

$$\int_{e_s(\infty, T)}^{e_s(r, T)} \frac{de}{e} = - \int_{\infty}^r \frac{2\sigma}{\rho_l R_v T} \frac{1}{r^2} dr$$

$$\ln e_s(r, T) - \ln e_s(\infty, T) = \left. \frac{2\sigma}{\rho_l R_v T r} \right|_r - \overbrace{\left. \frac{2\sigma}{\rho_l R_v T r} \right|_{\infty}}^{=0}$$

$$e_s(r, T) = e_s(\infty, T) \exp\left(\frac{A(T)}{r}\right) \quad A(T) = \frac{2\sigma}{\rho_l R_v T}$$

CLAUSIUS-CLAPEYRON EQUATION

SATURATION VAPOR PRESSURE OVER A FLAT SURFACE

$$\frac{de_s(\infty, T)}{dT} = \frac{L_{lv}e_s(\infty, T)}{R_v T^2}$$

- $L_v = \text{const} = L_v(T_0) = L_{v0}$ $e_s(\infty, T) = e_{s0} \exp \left[-\frac{L_{v0}}{R_v} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]$
- $L_v = L_{v0} + \Delta c(T - T_0)$ $e_s(\infty, T) = e_{s0} \left(\frac{T}{T_0} \right)^{\Delta c/R_v} \exp \left[-\frac{L_{v0} - \Delta c T_0}{R_v} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]$

$$T_0 = 273.15 \text{ K}$$

$$L_{v0} = 2.5 \cdot 10^6 \text{ J} \cdot \text{kg}^{-1}$$

$$e_{s0} = 611 \text{ Pa}$$

$$\Delta c = c_{pv} - c_l = -2317 \text{ J} \cdot \text{kg}^{-1} \text{ K}^{-1}$$

- **Bolton formula**

Bolton, D., The computation of equivalent potential temperature, Monthly Weather Review, 108, 1046-1053, 1980

$$e_s(\infty, T) = e_{s0} \exp \left[\frac{17.67(T - T_0)}{(T - T_0) + 243.5} \right]$$

KELVIN TERM – LINEAR APPROXIMATION

$$e_s(r, T) = e_s(\infty, T) \exp\left(\frac{A(T)}{r}\right) \quad A(T) = \frac{2\sigma}{\rho_l R_v T}$$

For T=273 K

$$A(T) = 1.202 \cdot 10^{-9} m = 1.202 \cdot 10^{-3} \mu m$$

$$\frac{A(T)}{r} \approx 0.12 \quad \text{for } r \geq 0.01 \mu m$$

$$e_s(r, T) \approx e_s(\infty, T) \cdot \left(1 + \frac{A(T)}{r}\right)$$

SATURATION OVER A DROPLET

Saturation $S(r, T) = \frac{e_s(r, T)}{e_s(\infty, T)} = \exp\left(\frac{2\sigma}{r\rho_l R_v T}\right)$ Kelvin effect

Supersaturation: $S(r, T) - 1$

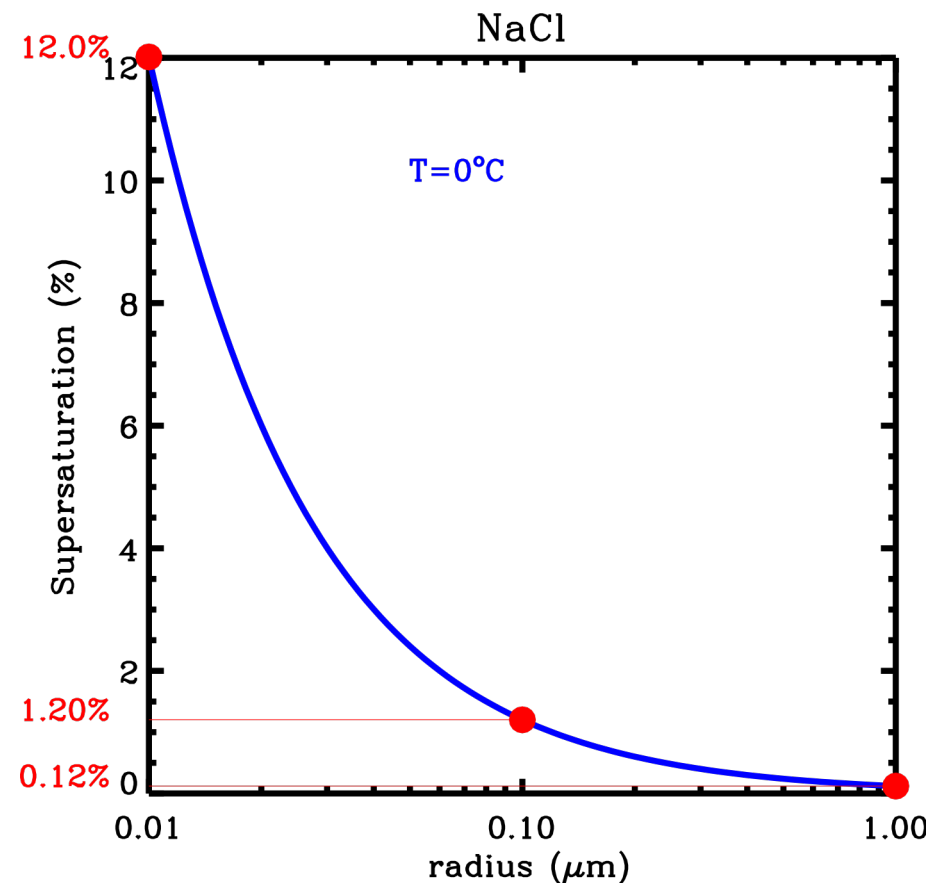
Equilibrium radius (critical radius)

$$r_c = \frac{2\sigma}{\rho_l R_v T \ln S}$$

$$r_c = 0.01\mu m \quad S - 1 = 12\%$$

$$r_c = 0.1\mu m \quad S - 1 = 1.2\%$$

$$r_c = 1\mu m \quad S - 1 = 0.12\%$$



EQUILIBRIUM RADIUS AT 0°C

HOMOGENEOUS NUCLEATION????

$$r_c = \frac{2\sigma}{\rho_l R_v T \ln S}$$

Supersaturation, (S-1);%	Critical radius (μm)	Number of molecules
0	∞	∞
1	1.208x10 ⁻¹	2.468x10 ⁸
10	1.261x10 ⁻²	2.807x10 ⁵
50	2.964x10 ⁻³	3.645x10 ³
100	1.734x10 ⁻³	730
200	5.221x10 ⁻⁴	20

SATURATION EQUILIBRIUM OVER A SOLUTION. RAOULT EFFECT.



UNIVERSITY
OF WARSAW

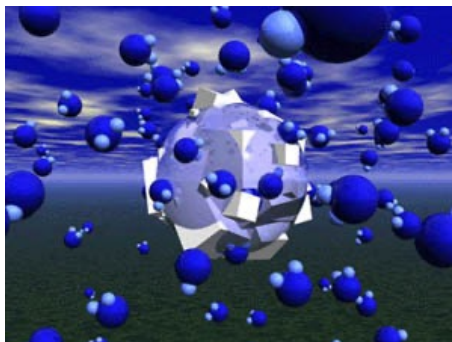
HETEROGENEOUS NUCLEATION

- In the atmosphere, cloud droplets form by **heterogeneous nucleation**.

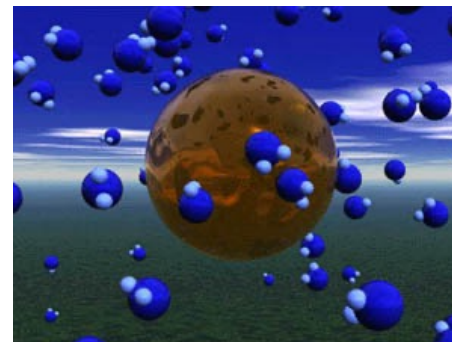
However, referring to this process as 'nucleation' can be misleading: true nucleation of the liquid phase is often unnecessary because a liquid solution already exists on soluble aerosol particles that have undergone deliquescence and hygroscopic growth under subsaturated conditions.

- Some aerosol particles are **hygroscopic**; that is, they attract water vapor molecules to their surfaces through chemical interactions or physical forces, such as dipole-dipole interactions.
- Nucleation of droplets occurs in the presence of an aerosol particle known as a **condensation nucleus (CN)**.
- Soluble condensation nuclei lower the equilibrium saturation vapor pressure over the liquid phase.

HYDROPHOBIC PARTICLE



HYGROSCOPIC PARTICLE



HETEROGENEOUS NUCLEATION

- A hygroscopic aerosol particle can undergo **deliquescence**—the formation of a solution through the absorption of atmospheric moisture—into a saturated aqueous solution at relative humidity (RH) levels well below 100%.

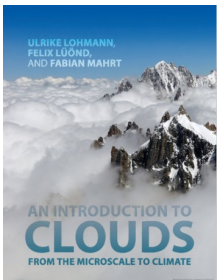
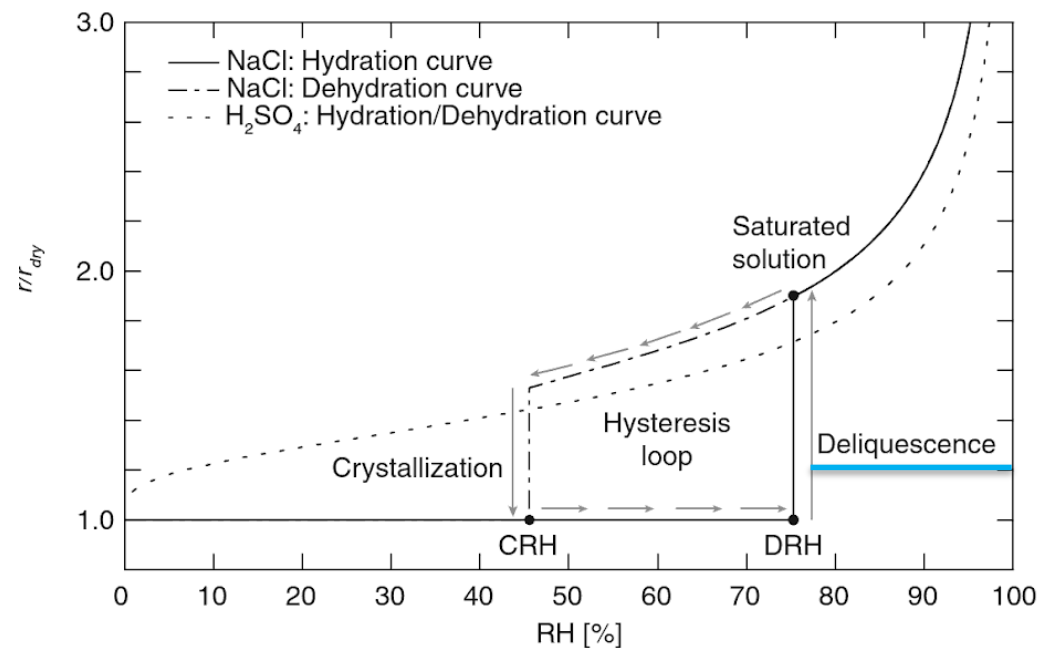


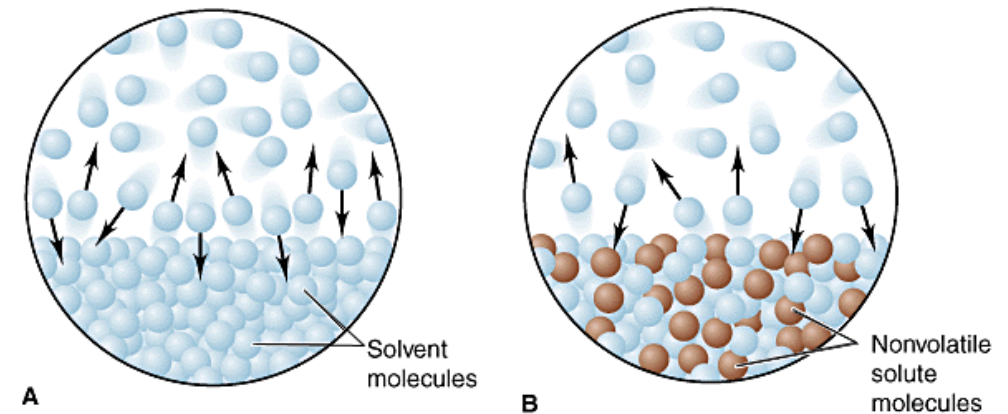
Fig. 6.5

Growth factor as a function of RH for sulfuric acid (H₂SO₄) and sodium chloride (NaCl) particles, expressed as the ratio of the actual radius r and the radius at 0% RH, r_{dry} . The solid line denotes stable equilibrium, the broken-and-dotted line metastable equilibrium, CRH the crystallization RH and DRH the deliquescence RH. The arrows indicate the hysteresis loop.

RAOULT'S LAW

For a flat water Surface, the reduction in saturation vapor pressure due to a **nonvolatile** solute is governed by Raoult's law and quantified by the mole fraction of water:

$$x_s = \frac{e_s(\infty, x_s)}{e_s(\infty)} = \frac{n_l}{n_s + n_l}$$



$e_s(\infty, x_s)$ is the equilibrium vapor pressure over a solution consisting of :

- n_l molecules of water and n_s molecules of solute ;
- $e_s(\infty)$ – the saturation vapor pressure over bulk water.

A solution that obeys Raoult's law is defined as an **ideal solution**, conceptually analogous to the thermodynamic model of an **ideal gas**.

For dilute solutions $n_s \ll n_l$:

$$\frac{e_s(\infty, x_s)}{e_s(\infty)} = \frac{n_l}{n_s + n_l} = \frac{1}{\frac{n_s}{n_l} + 1} \approx 1 - \frac{n_s}{n_l}$$

Experimental evaluations of Raoult's law reveal critical limitations when applied to real atmospheric aerosols:

1. Electrolyte Dissociation: Solute moles (n_s) must be adjusted by the **van 't Hoff factor** (i): $n_s \rightarrow i \cdot n_s$
2. Baseline Approximation: For NaCl, complete dissociation into constituent ions (Na^+ and Cl^-) yields $i \approx 2$.
3. Activity Correction: Precise values of i depend on concentration and are derived from ionic activity coefficients.
4. Even with this correction, Raoult's law remains an approximation that can substantially deviate from experimental measurements, even at moderate solute concentrations.

These discrepancies represent departures from thermodynamic ideality. Because real solutions deviate significantly from Raoult's law, cloud microphysics relies on a more empirical formulation based on the effective mole fraction of water, known as **water activity** (a_w).

Instead of tabulating activity coefficients, non-ideality is represented via the **practical osmotic coefficient** (Φ_i):

$$a_w \equiv \exp\left(-i\Phi_i \frac{n_s}{n_l}\right) \cong 1 - i \frac{n_s}{n_l} \Phi_i$$

Φ_i is usually less than 1.

i is the dissociativity (in the case of NaCl $i=2$).

Water activity (a_w) depends on both the water mole fraction and the chemical identity of the solute.

ACTIVITY (RAOULT'S LAW)

For $n_s \ll n_l$: $a_w \equiv 1 - i \frac{n_s}{n_l} \Phi_s$

$$\frac{n_s}{n_l} = \frac{m_s}{m_l} \quad m_s = \frac{4}{3} \pi r_s^3 \rho_s$$

m_s – mass of the solute, M_s – molar mass

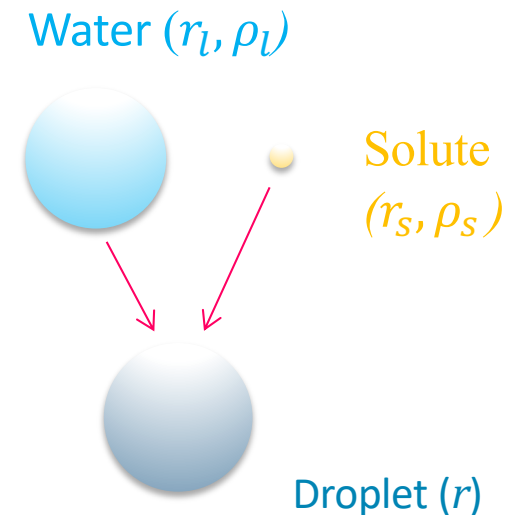
$$\frac{n_l}{n_l} = \frac{m_l}{m_l} \quad m_l = \frac{4}{3} \pi (r^3 - r_s^3) \rho_l$$

m_l – mass of water, M_l – water molar mass

$$\frac{n_s}{n_l} = \frac{m_s}{m_l} \cdot \frac{M_l}{M_s}$$

$$\frac{m_s}{m_l} = \frac{r_s^3}{r^3 - r_s^3} \cdot \frac{\rho_s}{\rho_l} = \frac{\left(\frac{r_s}{r}\right)^3}{1 - \left(\frac{r_s}{r}\right)^3} \cdot \frac{\rho_s}{\rho_l}$$

$$\frac{m_s}{m_l} \approx \left(\frac{r_s}{r}\right)^3 \left(1 + \left(\frac{r_s}{r}\right)^3\right) \cdot \frac{\rho_s}{\rho_l} \approx \left(\frac{r_s}{r}\right)^3 \cdot \frac{\rho_s}{\rho_l}$$



$r^3 \gg r_s^3$

ACTIVITY (RAOULT'S LAW)

$$a_w \equiv 1 - i \frac{n_s}{n_l} \Phi_s$$

$$\frac{n_s}{n_l} = \frac{m_s}{m_l} \cdot \frac{M_l}{M_s} = \left(\frac{r_s}{r}\right)^3 \cdot \frac{\rho_s}{\rho_l} \cdot \frac{M_l}{M_s}$$

$$a_w = 1 - \frac{B_s}{r^3}$$

$$B_s = i \Phi_s r_s^3 \frac{\rho_s}{\rho_l} \frac{M_l}{M_s} = i \Phi_s \frac{3m_s}{4\pi\rho_l} \frac{M_l}{M_s}$$

DESCRIPTION OF ACTIVITY

Determining water activity requires four parameters:

- i - number of ions of dissociated molecule
- Φ_s – osmotic coefficient (usually put to 1)
- M_s – molecular mass of solute substance
- ρ_s – density of solute

$$a_w = \frac{n_l}{n_l + n_s} = f(r, B_s)$$

$$B_s = i \cdot \Phi_s r_s^3 \frac{\rho_s M_l}{\rho_l M_s}$$

The κ -Köhler parameterization allows for the description of the saturation state using a smaller number of parameters.

κ - KÖHLER THEORY

In the κ -Köhler parameterization, the single **hygroscopicity parameter (κ)** is defined by its effect on the water activity of the solution:

$$a_w = \frac{V_l}{V_l + \kappa \cdot V_s}$$

$$a_w = \frac{r^3 - r_s^3}{r^3 - (1 - \kappa)r_s^3}$$

κ – the hygroscopicity parameter

V_s – volume of dry particle $V_s = \frac{4}{3}\pi r_s^3$

V_l – volume of water droplet $V_l = \frac{4}{3}\pi(r^3 - r_s^3)$

r_s is often called a 'dry radius', r_d

For multicomponent aerosol particles containing multiple solute species, a simple linear volume-weighted mixing rule applies:

$$\kappa = \sum_j \varepsilon_j \kappa_i$$

ε_i is the volume fraction of component i in the dry particle, and κ_i is the hygroscopicity parameter of the individual pure component.

κ - KÖHLER THEORY VS. RAOULT LAW

For $\kappa > 0.2$ and critical supersaturation $< 1\%$ a linear approximation is valid:

$$a_w = \frac{r^3 - r_s^3}{r^3 - (1 - \kappa)r_s^3} \approx 1 - \kappa \frac{r_s^3}{r^3}$$

$$a_w = 1 - \frac{B_s}{r^3}$$

$$\kappa r_s^3 = B_s$$

Atmospheric particulate matter is typically characterized by $\kappa > 0.2$, with lower values sometimes observed for particular locations and periods.

In this lecture the κ -Köhler formulation of activity will be used.

We will use the DRY RADIUS, r_d , to describe the amount of solute in the droplet ($r_d = r_s$).

KÖHLER CURVE



UNIVERSITY
OF WARSAW

COMBINING KELVIN AND SOLUTE EFFECTS

- The original Kelvin derivation for surface curvature operates independently of solute presence.
- The curvature term $e_s(r)$ refers strictly to pure water and carries no solute dependence.
- Assuming the solute does not modify the surface tension of the solution:

$$\frac{e_s(r)}{e_s(\infty)} = \frac{e_s(r, x_s)}{e_s(\infty, x_s)}$$

$$a_w = \frac{e_s(\infty, x_s)}{e_s(\infty)} = \frac{e_s(r, x_s)}{e_s(r)} \quad \rightarrow \quad e_s(r, x_s) = a_w e_s(r)$$

$$e_s(r, x_s) = a_w e_s(\infty) \exp\left(\frac{A(T)}{r}\right)$$

$$S_{eq} = \frac{e_s(r, x_s)}{e_s(\infty)}$$

Equilibrium saturation over a droplet with solute

κ -KÖHLER CURVE

$$S_{eq}(r, r_d, \kappa, T) = \frac{r^3 - r_d^3}{r^3 - (1 - \kappa)r_d^3} \exp\left(\frac{A(T)}{r}\right)$$

LINEAR APPROXIMATION

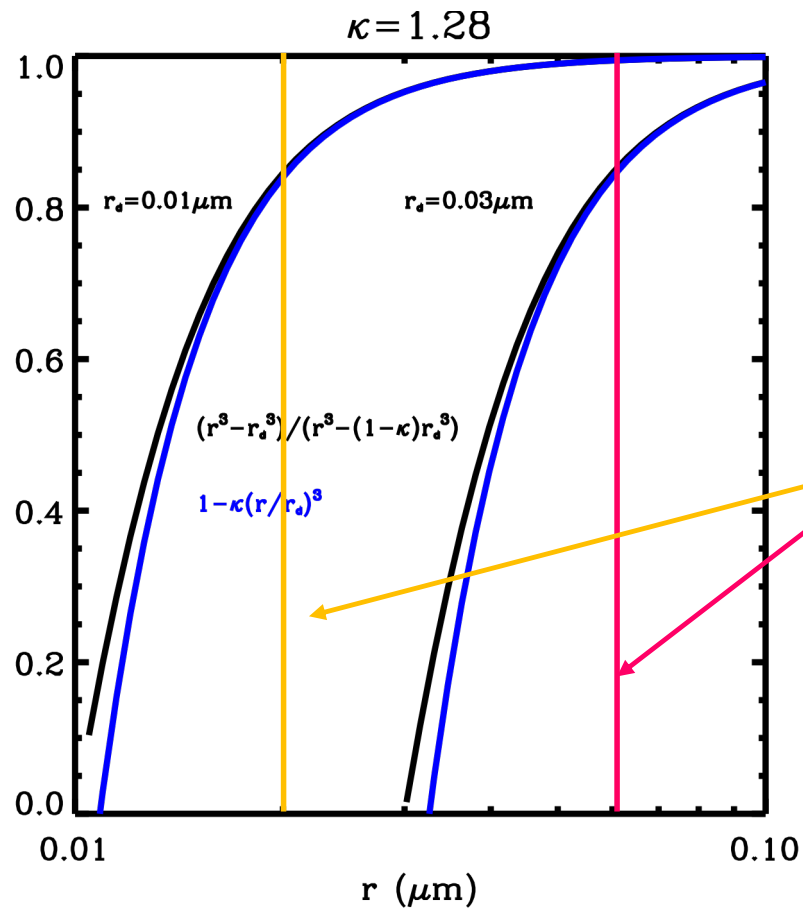
$$\frac{r^3 - r_d^3}{r^3 - (1 - \kappa)r_d^3} \approx 1 - \kappa \frac{r_d^3}{r^3} \quad \exp\left(\frac{A(T)}{r}\right) \approx 1 + \frac{A(T)}{r}$$

$$S_{eq}(r, r_d, \kappa, T) \approx 1 + \frac{A(T)}{r} - \frac{\kappa r_d^3}{r^3}$$

curvature term
Kelvin term

activity term

ACTIVITY TERM



$$a_w = \frac{r^3 - r_d^3}{r^3 - (1 - \kappa)r_d^3} \approx 1 - \kappa \frac{r_d^3}{r^3}$$

$$\frac{r_d}{r} = 0.5 \quad \frac{r_d^3}{r^3} = 0.125$$

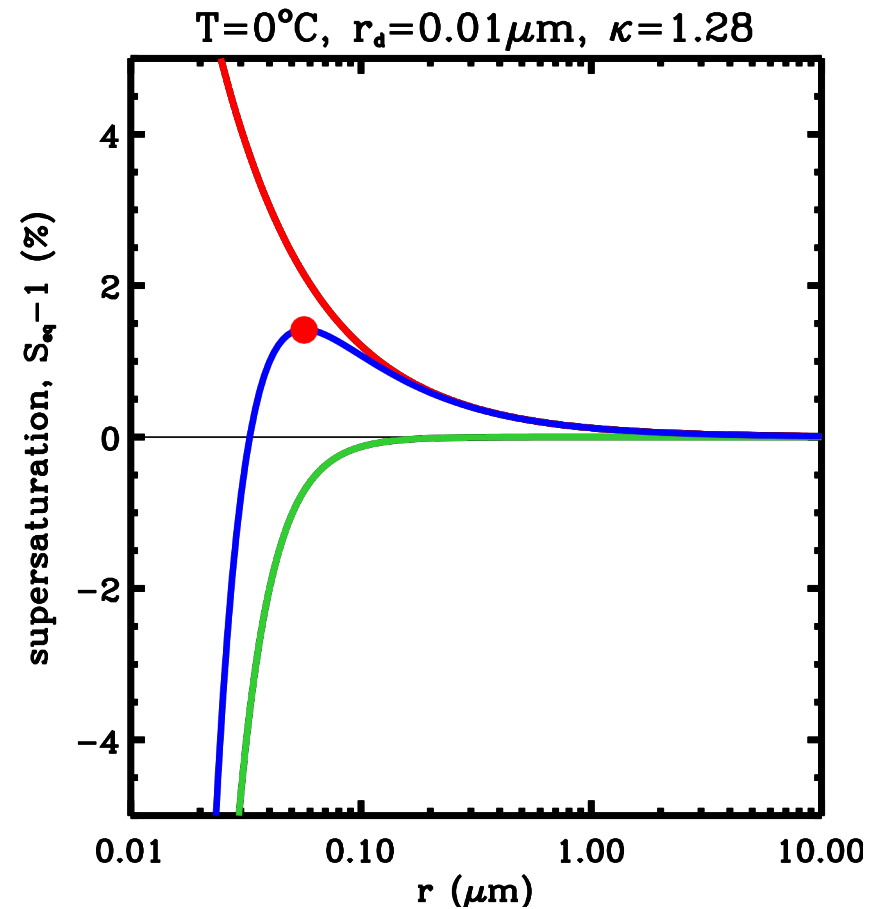
$$r = 0.02 \mu\text{m}$$

$$r = 0.06 \mu\text{m}$$

supersaturation:

$$S_{eq}(r, r_d, \kappa, T) - 1 = \frac{A(T)}{r} - \frac{\kappa r_d^3}{r^3}$$

Supersaturation over
plain surface equals 0



Curvature term $\frac{A(T)}{r}$
Kelvin term

activity term $-\frac{\kappa r_d^3}{r^3}$

CRITICAL SUPERSATURATION ACTIVATION PARAMETERS

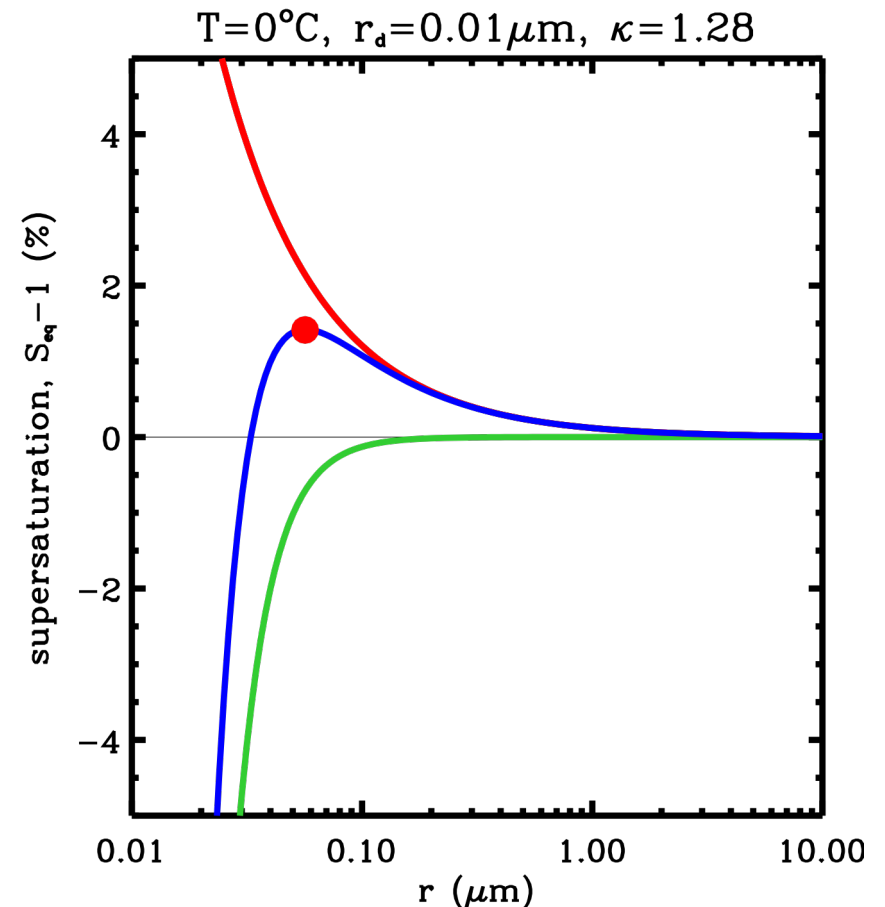
- Critical radius r^* and critical supersaturation S^* denote the maximum of the Köhler curve.

Also called: activation parameters

$$\frac{\partial(S-1)}{\partial r} = 0$$

$$r^* = \sqrt{3 \kappa r_d^3 / A}$$

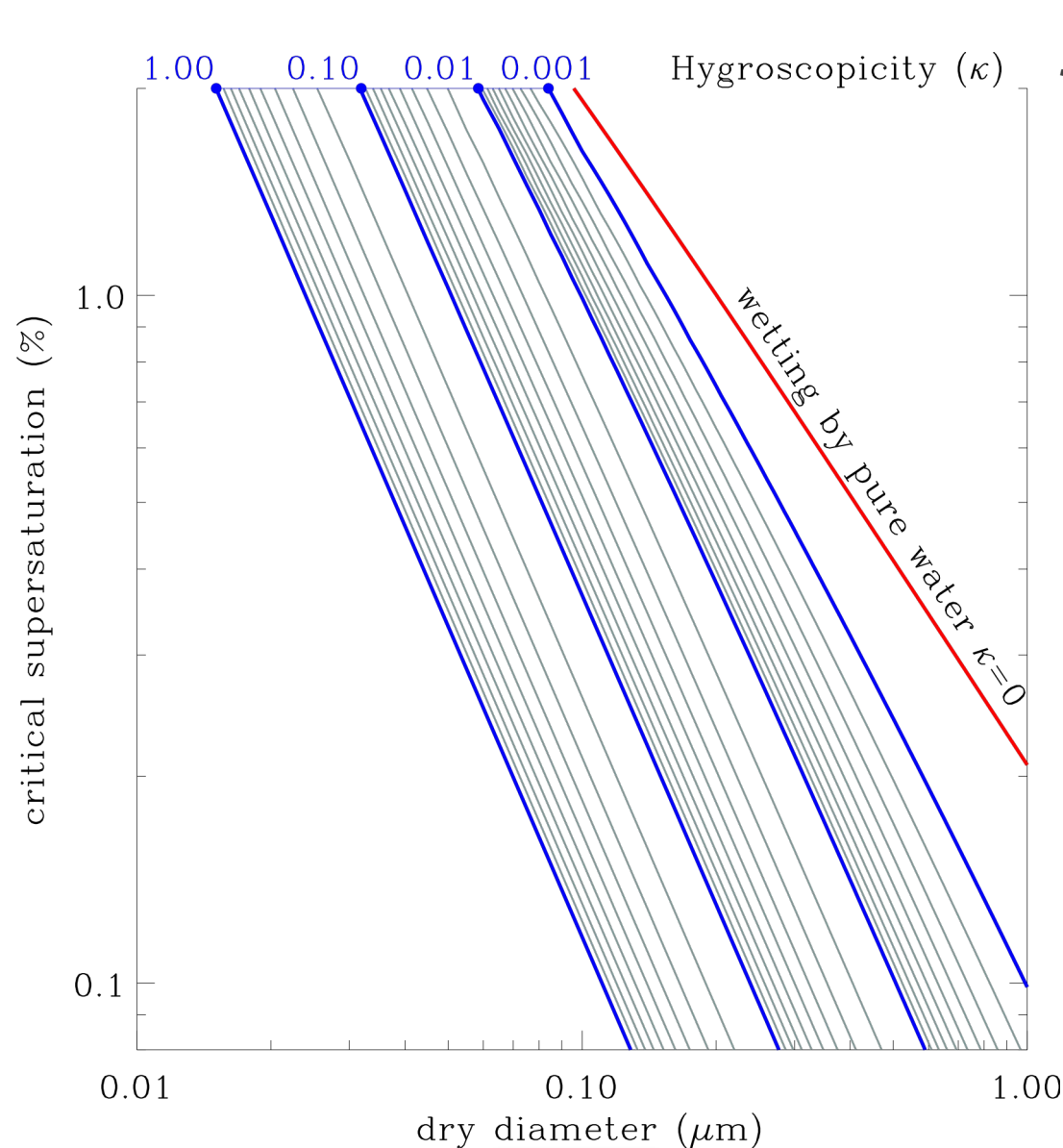
$$S^* - 1 = \sqrt{4A^3 / 27 \kappa r_d^3}$$



In this figure: $r^* = 0.06\mu\text{m}$, $S^* - 1 = 1.38\%$

35 / 40

CRITICAL SUPERSATURATION VERSUS DRY DIAMETER AND κ



$$S_{eq}(r, r_d, \kappa, T) = \frac{r^3 - r_d^3}{r^3 - (1 - \kappa)r_d^3} \exp\left(\frac{A(T)}{r}\right)$$

-3/2 slope in $\log S_c - \log D_d$ for $\kappa > 0.2$

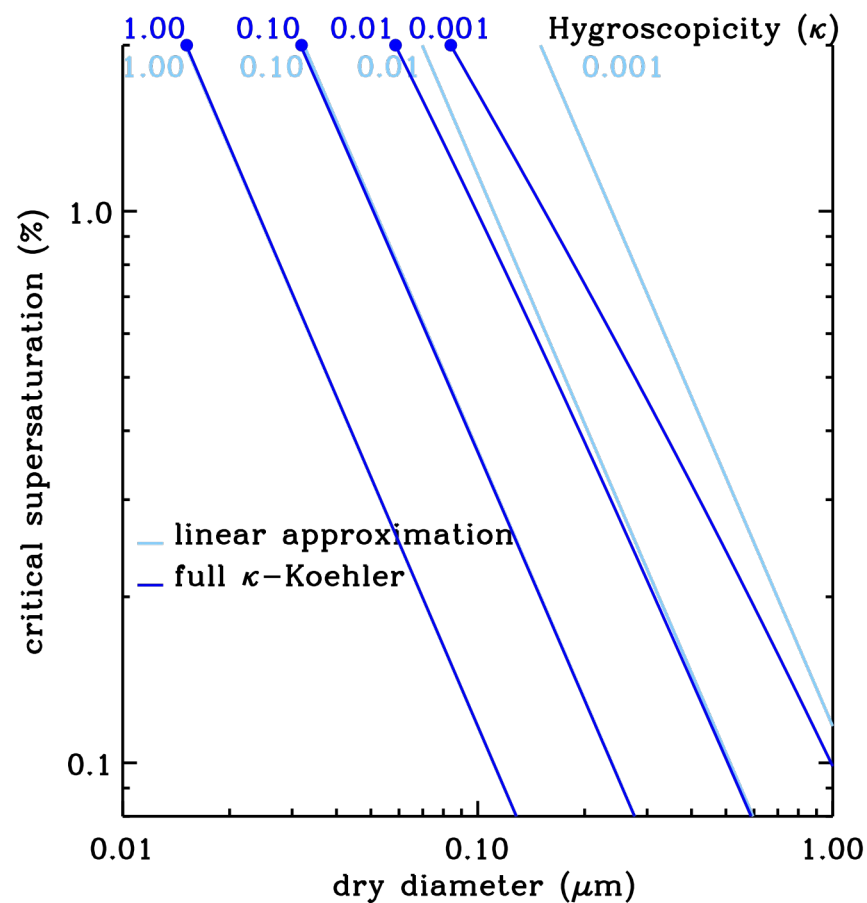
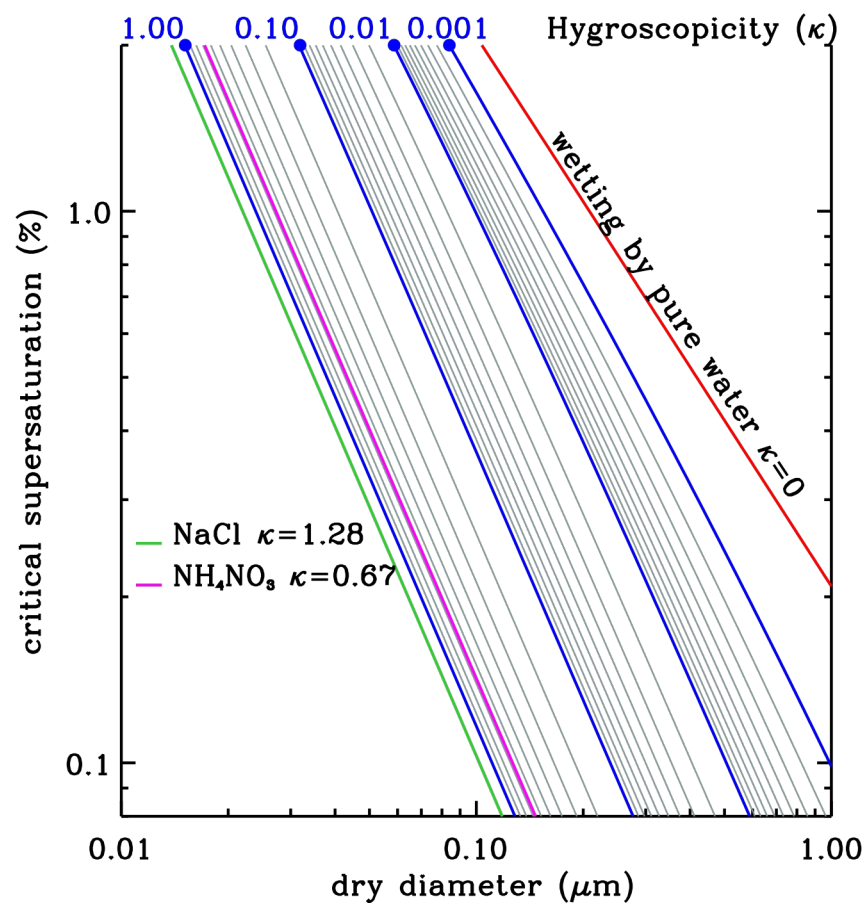
Equation

$$S_{eq}(r, r_d, \kappa, T) - 1 = \frac{A(T)}{r} - \frac{\kappa r_d^3}{r^3}$$

leads to -3/2 slope in
 $\log S_c - \log D_d$ for all choices of $\kappa > 0$

$$S^* - 1 = \sqrt{4A^3/27\kappa r_d^3}$$

$$\rightarrow \log(S^* - 1) \sim -\frac{3}{2} \log r_d$$



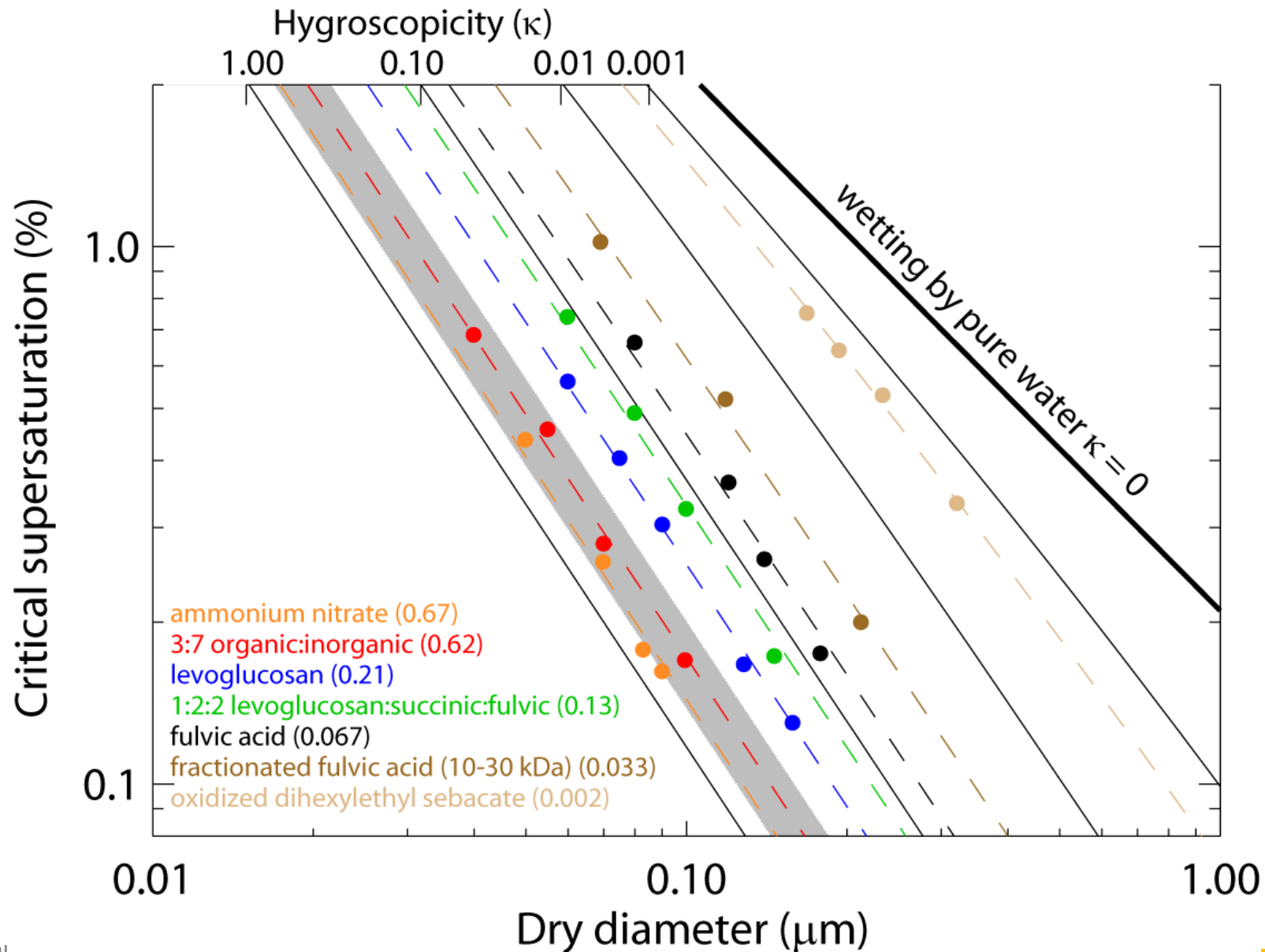
Equation

$$S_{eq}(r, r_d, \kappa, T) = \frac{r^3 - r_d^3}{r^3 - (1 - \kappa)r_d^3} \exp\left(\frac{A(T)}{r}\right)$$

$$S_{eq}(r, r_d, \kappa, T) - 1 = \frac{A(T)}{r} - \frac{\kappa r_d^3}{r^3}$$

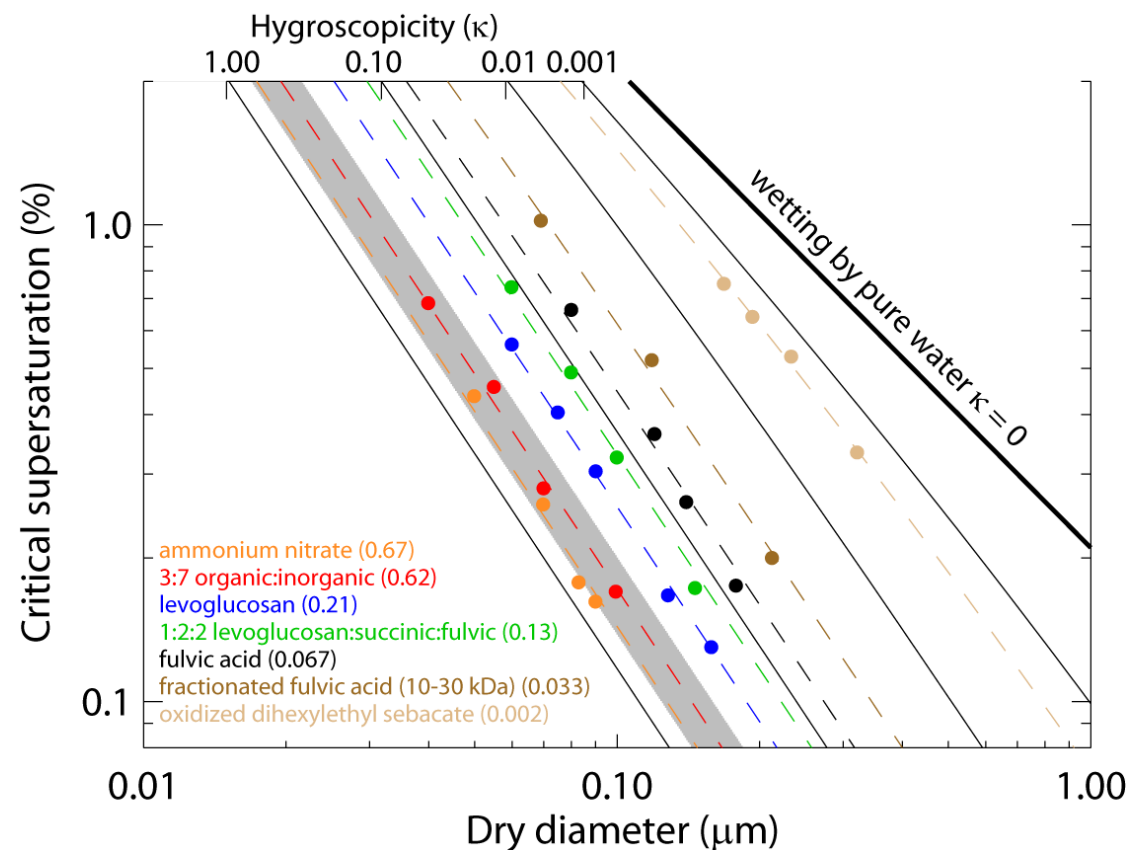
leads to -3/2 slope in
 $\log S^* - \log D_d$ for all choices of $\kappa > 0$

FROM MEASURED CCN DATA WE CAN INFER THE HYGROSCOPICITY, κ , OF THE AEROSOL



Petters and Kreidenweis, ACP 2007 (Fig. 2)

- $S_c - D_d$ data for pure compounds, organic mixtures and organic-inorganic mixtures.
- Dashed lines indicate best-fit κ values for each particle type, as shown in the legend.
- Shaded area indicates range of values for ammonium sulfate.
- κ values were computed for
- $\sigma=0.072 \text{ J m}^{-2}$ and $T=298.15\text{K}$.



RANKED HYGROSCOPICITY BASED ON CCN MEASUREMENTS FOR ATMOSPHERIC AEROSOLS

