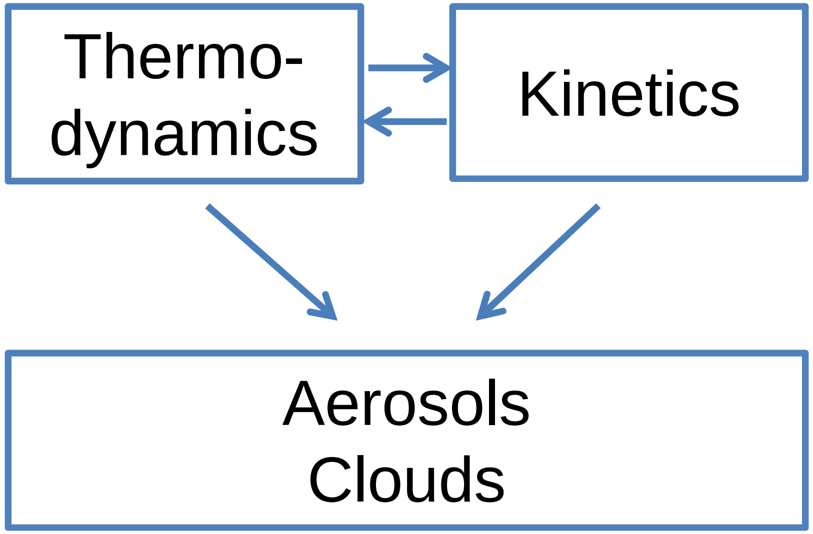
Atmospheric Water Vapour
in the Climate System

(WaVaCS)

Microphysics

Tom Peter, ETH Zurich

- Observations
- Modelling

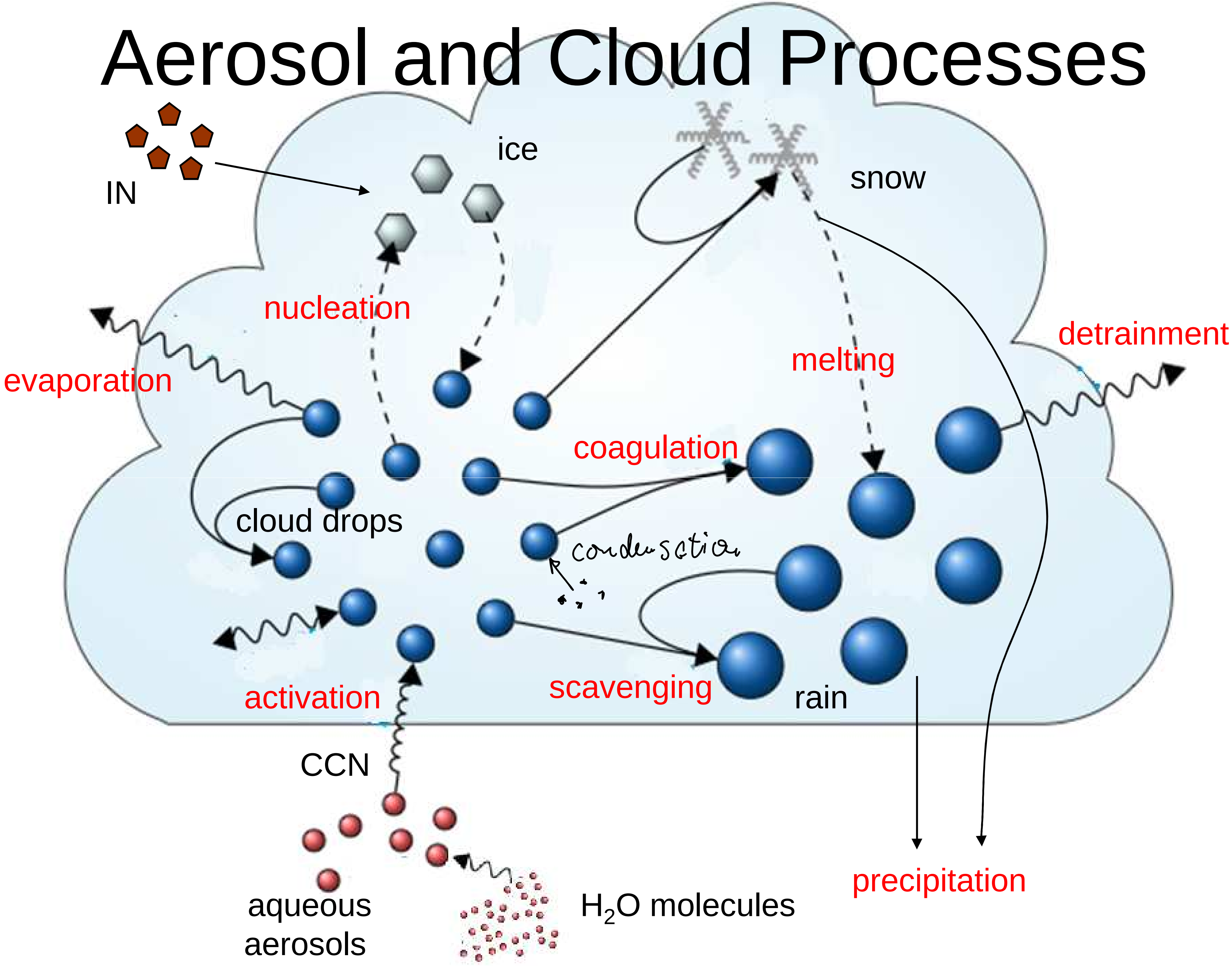


Thermo-
dynamics

Kinetics

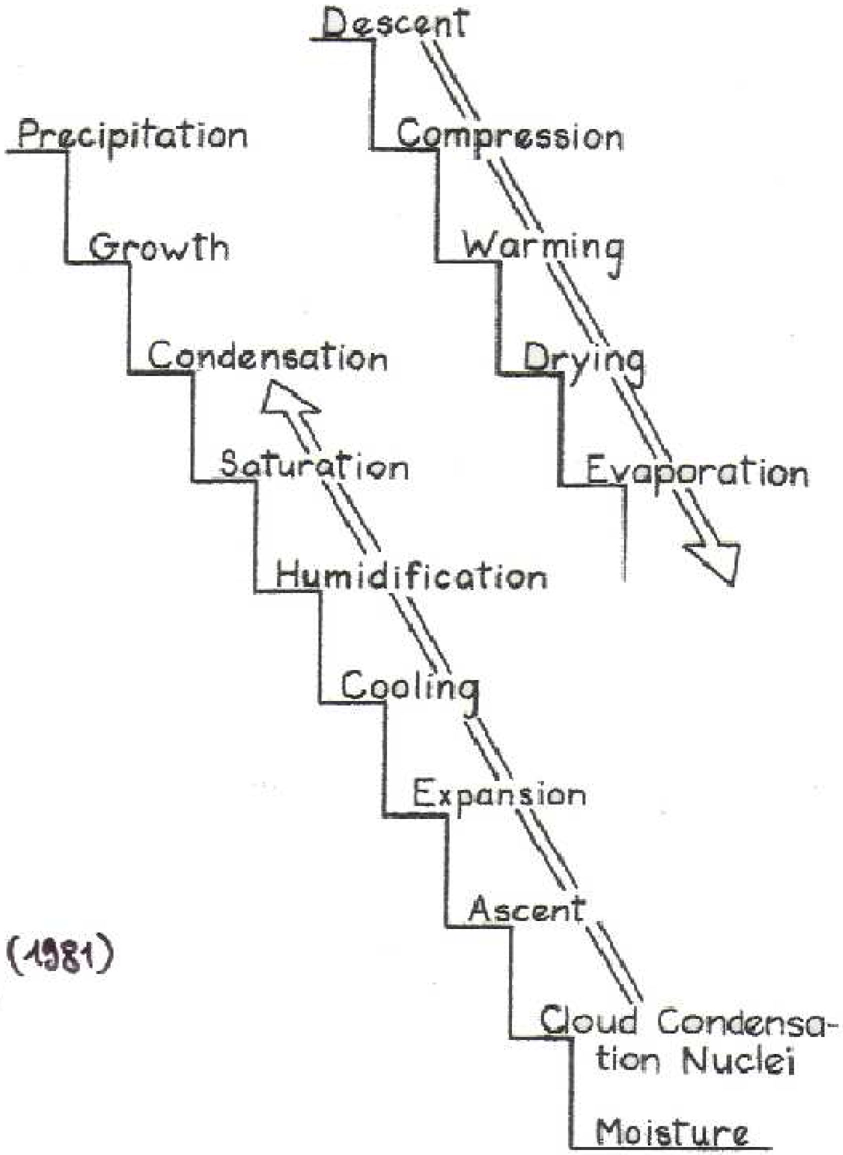
Aerosols
Clouds

Aerosol and Cloud Processes



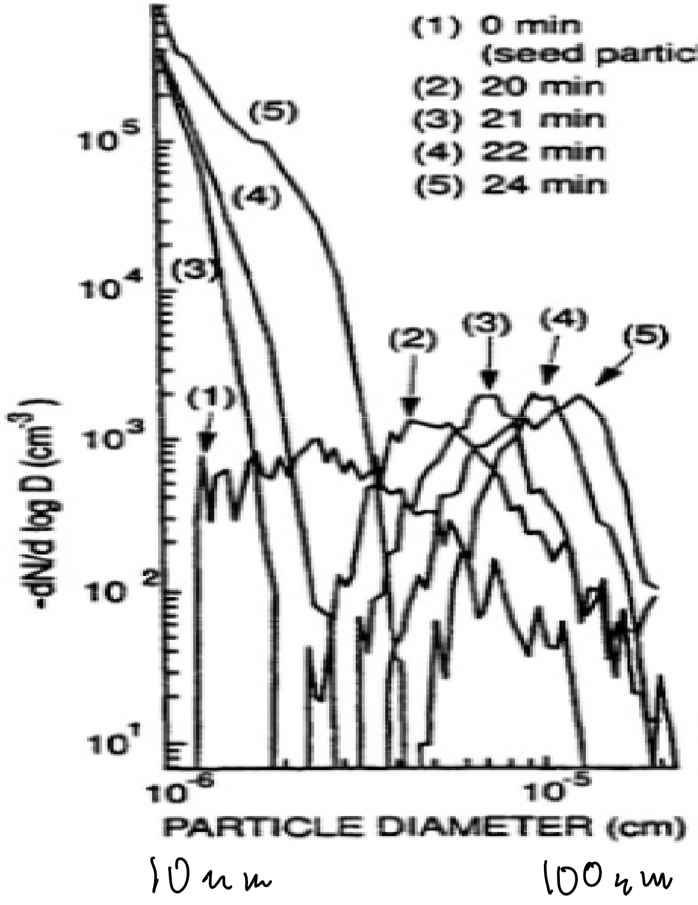
Precipitation staircase

Prerequisites for cloud formation:
- water
- low T
- supersaturation
- Cloud Condensation Nuclei (CCN) or Ice Nuclei (IN)

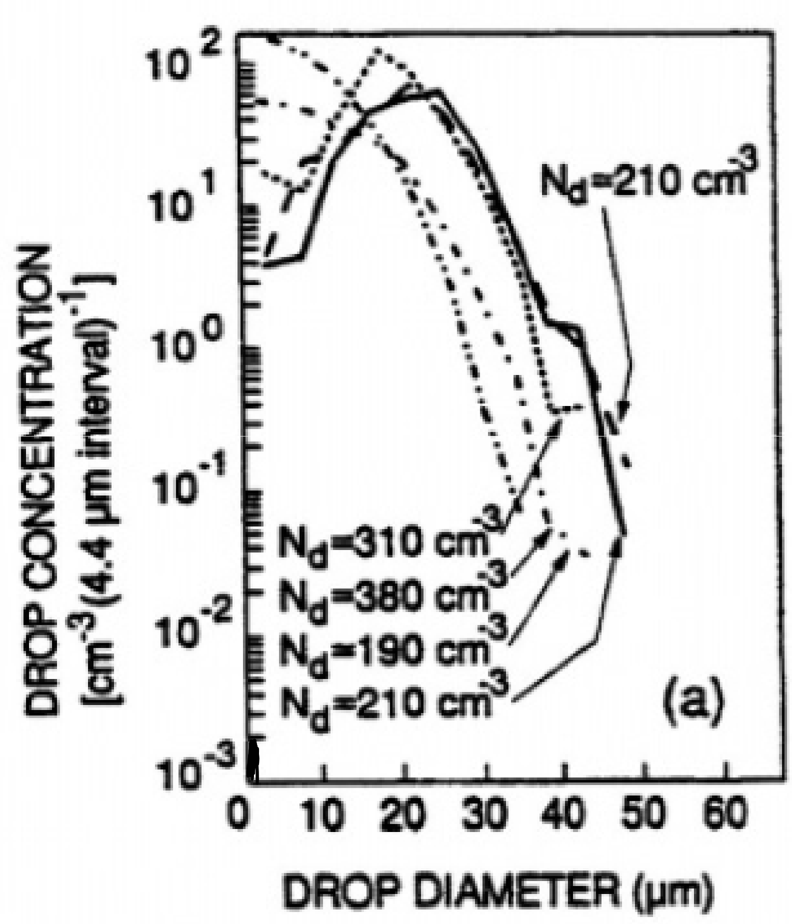


Schaefer & Day (1981)

Particle size distributions:
The result of the interplay of thermodynamics and kinetics in response to outer forcings (*T*, $h\nu$, *g*)



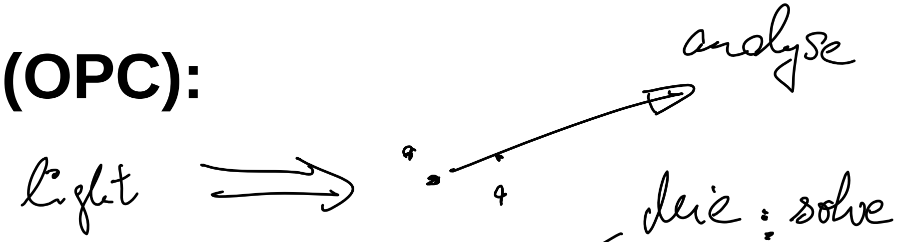
Size distribution of aerosol particles from photooxidaton of a methylcyclohexane-propane-NO_x mixture (Seinfeld,1994)



Size distribution of cloud particles near the top of young continental cumuli (Hobbs et al., 1980)

Example of instrument:

Optical particle counter (OPC):



- “White light counter”
- Aerosol forward scattering single particle counter
- Mie theory to determine aerosol size [Mie, 1908]
- Scattered light amplified by photomultiplier tube
- Pulse height detection
- Prior to each flight calibration with polystyrene latex spheres

Mie: solve Maxwell Eq. for spherical ptcls with $n = Re(n) + i\,Im(n)$

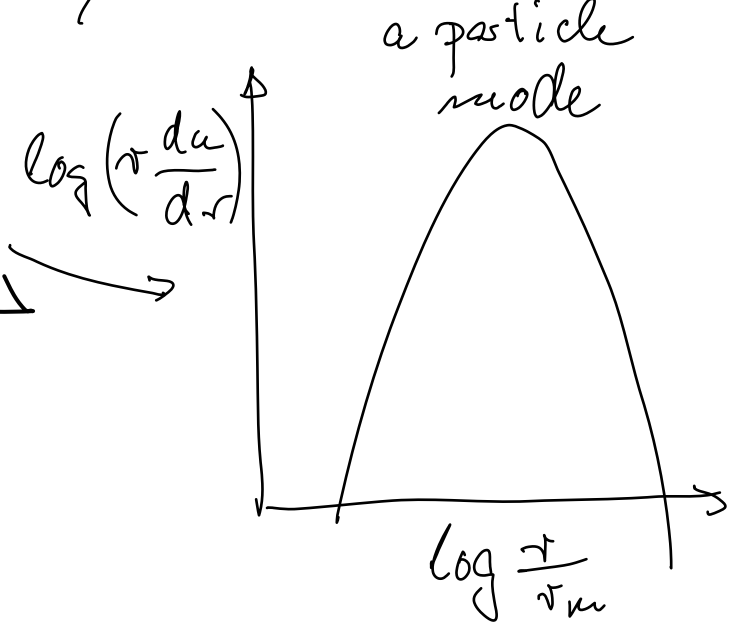
All OPC channels measure particles larger than a certain size

The differential particle size distribution

$$\underset{\text{diameter}}{\frac{dn}{d\log D}}(\vec{x},D,t)=\underset{\text{radius}}{\frac{dn}{d\log r}}(\vec{x},r,t)=r\underbrace{\frac{dn}{dr}(\vec{x},r,t)}_{\frac{\#\,\text{ptcls}}{\text{cm}^{+3}\,\mu\text{m}}}\equiv r\,n_r(\vec{x},r,t)$$

Lognormal distribution :

$$\boxed{\frac{dn}{dr}=\frac{n_t}{\sqrt{2\pi}\;r\,\ln\sigma}\,e^{-\frac{\ln^2(r/r_m)}{2\ln^2\sigma}}}$$



r_m = mode radius

σ = width

Lognormal distribution :

$$\boxed{\frac{dn}{dr} = \frac{n_t}{\sqrt{2\pi}\, r \ln\sigma}\, e^{-\frac{\ln^2(r/r_m)}{2\ln^2\sigma}}}$$

r_m = mode radius

α-th moment :

$$\langle r^\alpha \rangle = \frac{1}{n_t}\int_0^\infty dr\, \frac{dn}{dr}\, r^\alpha = r_m^\alpha \exp\left(\frac{\alpha^2}{2}\ln^2\sigma\right)$$

Thus:

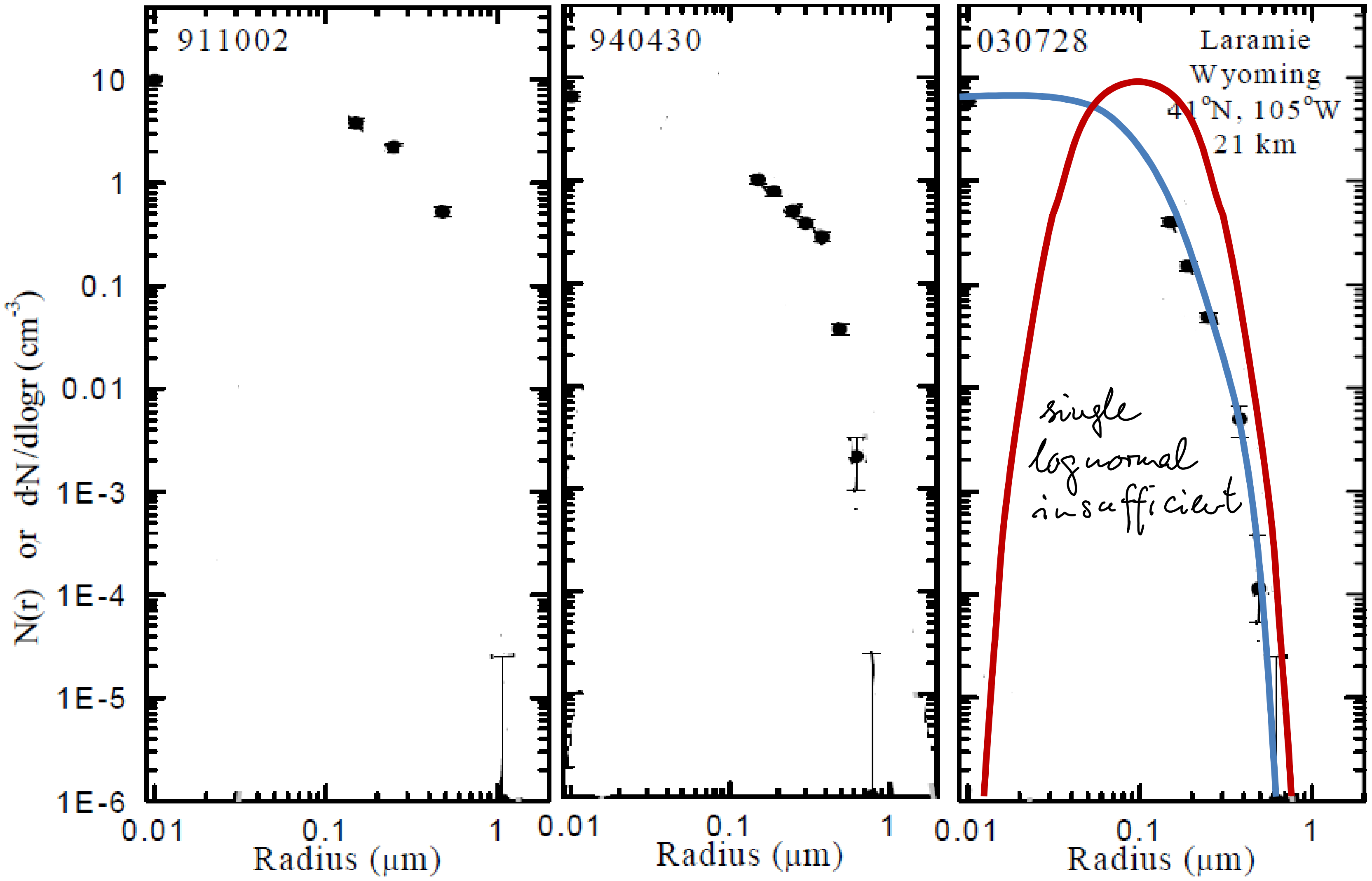
$$\int_0^\infty dr\, \frac{dn}{dr} = n_t = \text{total number density}$$

$$\boxed{\langle r \rangle = r_m \exp\left(\frac{1}{2}\ln^2\sigma\right) = \text{mean radius}}$$

Size distribution of stratospheric aerosols

OPC measurement in strat.

Diffusional growth: $\mathrm{OCS} \xrightarrow{\mathrm{ox}} \mathrm{SO_2} \xrightarrow{\mathrm{ox}} \mathrm{H_2SO_4} \xrightarrow{\mathrm{cond}}$ aerosol



single lognormal insufficient

Size distribution of stratospheric aerosols

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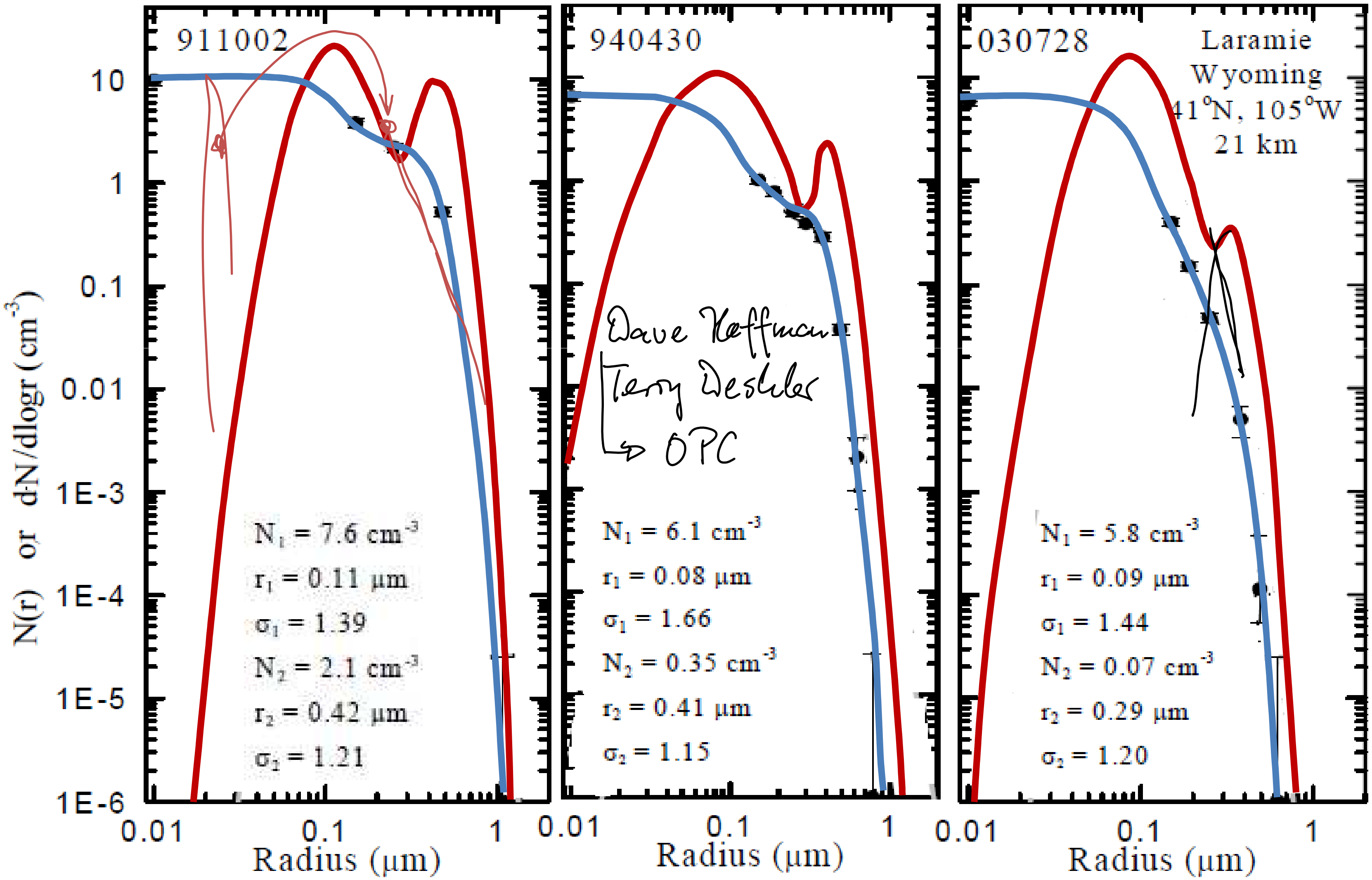


Dave Hoffman

Terry Deshler

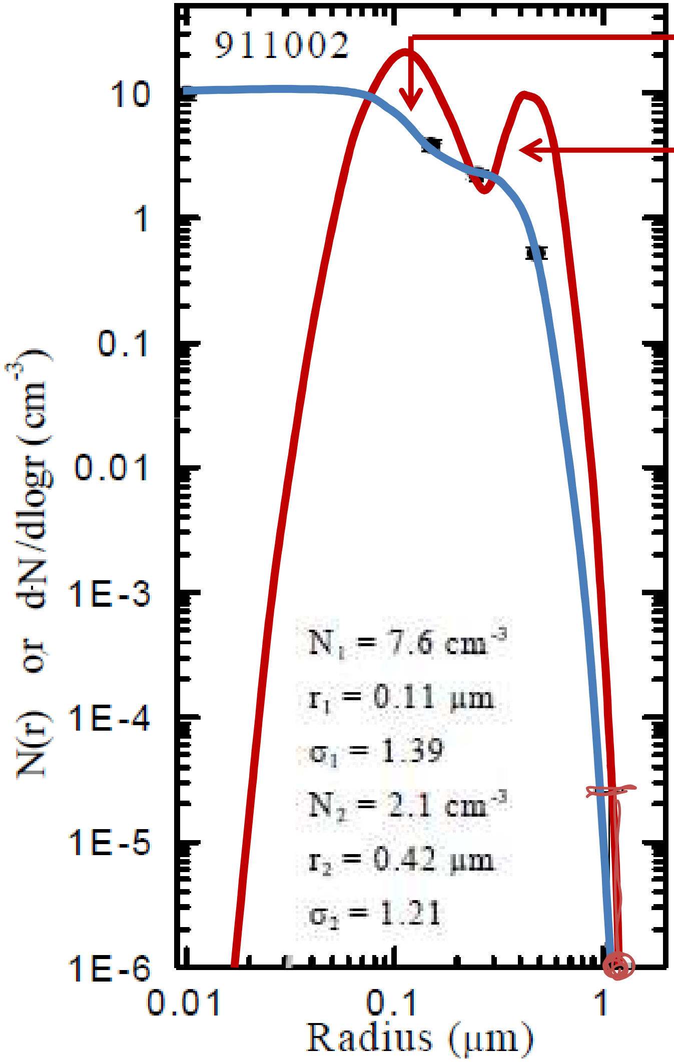
↳ OPC

Thomason and Peter, 2006

Size distribution of stratospheric aerosols

Diffusional growth: $OCS \xrightarrow{ox} \boxed{SO_2} \xrightarrow{ox} H_2SO_4 \xrightarrow{cond}$ aerosol

volcanic



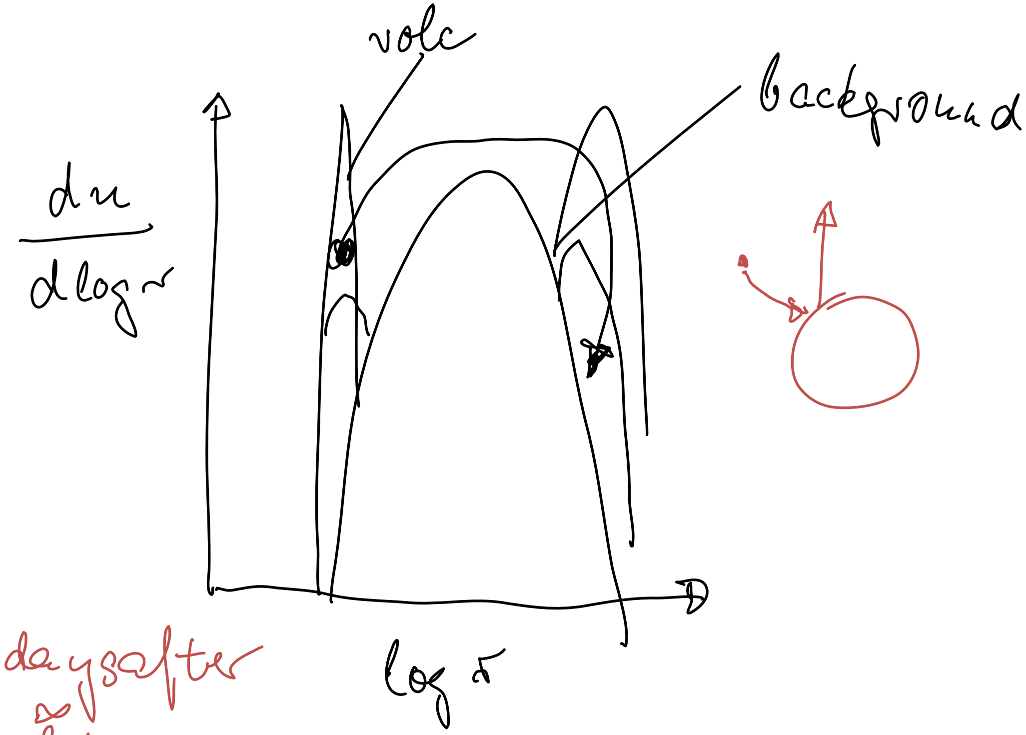
Background mode

Volcanic mode:

Pinatubo, 15°N, June 1991: coagulation of freshly nucleated with largest background particles

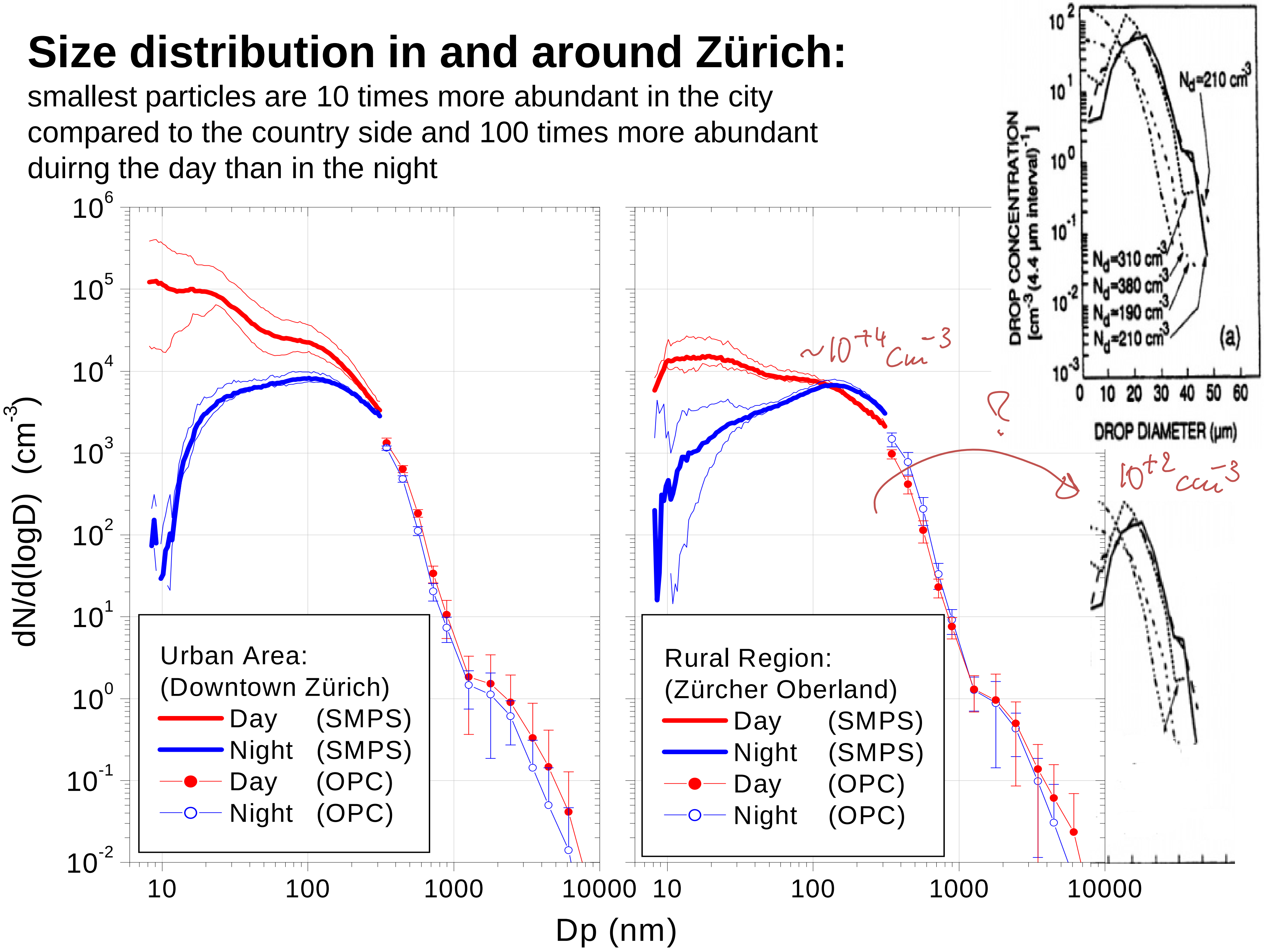
14 days after

$$\int_0^\infty \frac{dn}{dr}\,dr = \text{thousands per cc}$$



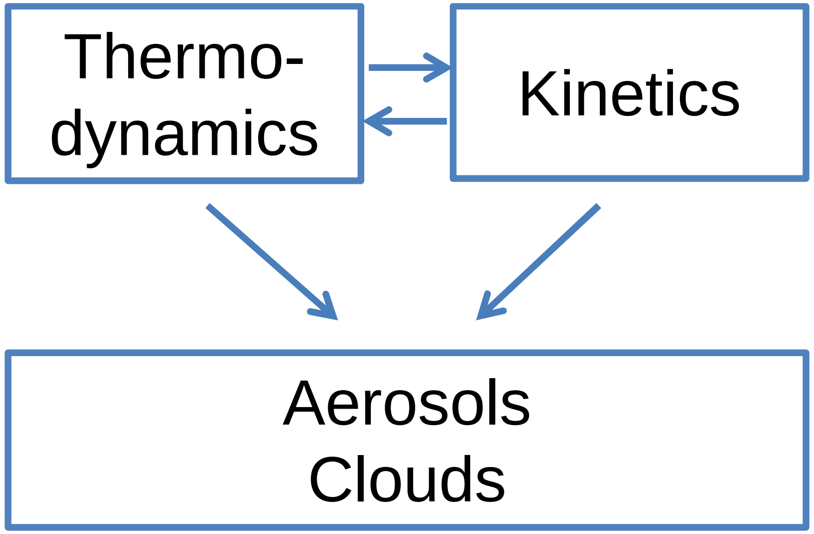
Size distribution in and around Zürich:

smallest particles are 10 times more abundant in the city compared to the country side and 100 times more abundant duirng the day than in the night



Bukowiecki et al., 2002

Formation of water clouds



Thermo-dynamics

Kinetics

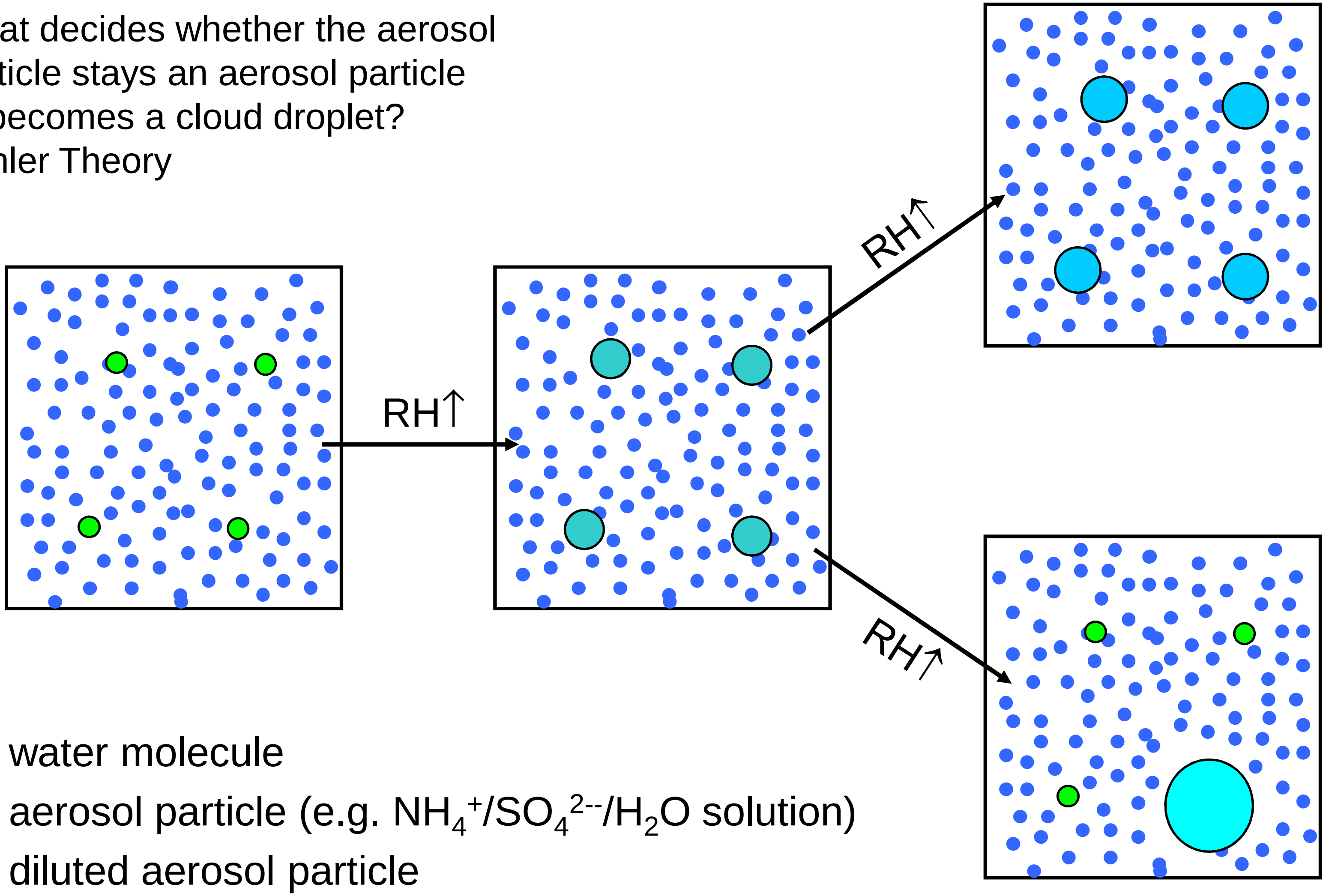
Aerosols
Clouds

How far do we get with thermodynamics in explaining cloud formation?

Cloud droplet formation

A fierce competition without which precipitation would be massively impeded!

What decides whether the aerosol
particle stays an aerosol particle
or becomes a cloud droplet?
Köhler Theory



- ● water molecule
- ● aerosol particle (e.g. $NH_4^+/SO_4^{2-}/H_2O$ solution)
- ● diluted aerosol particle
- ● cloud droplet

3 big names: Raoult, Kelvin, Köhler

- Raoult’s law (1870)

  small droplets have higher solute concentrations (salts, acids) and this reduces the H_2O vapor pressure
  → advantage for small droplets

- Kelvin effect (1879)

  small droplets have a higher H_2O vapor pressure (curvature effect)
  → disadvantage for small droplets

- Köhler equation (1921)

  balance between Kelvin and Raoult terms
  → quantitative understanding

Clapeyron’s equation

(applies to any phase transition of a pure substance)

$\Delta V_m \, dp = \Delta S_m \, dT$

ΔS_m = change of molar entropy during phase transition

ΔV_m = change of molar volume during phase transition

Clausius-Clapeyron equation

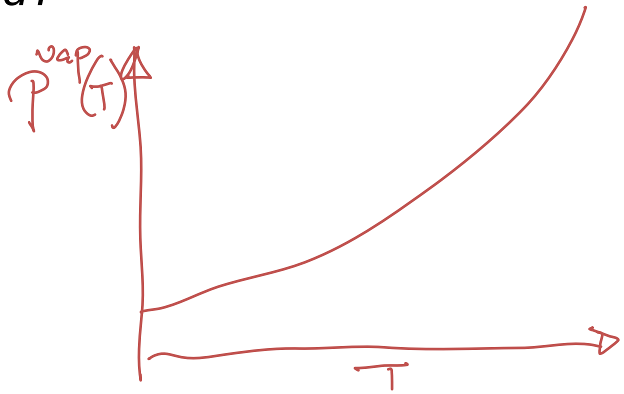
(valid for solid-gas and liquid-gas phase transitions)

Gibbs free energy: $\Delta G_{vap} = \mu dn = \Delta H_{vap} - T\Delta S_{vap} = 0$

ΔH_{vap}: molar enthalpy change during vaporization

→ $\Delta S_{vap} = \Delta H_{vap}/T$ at equilibrium of two phases

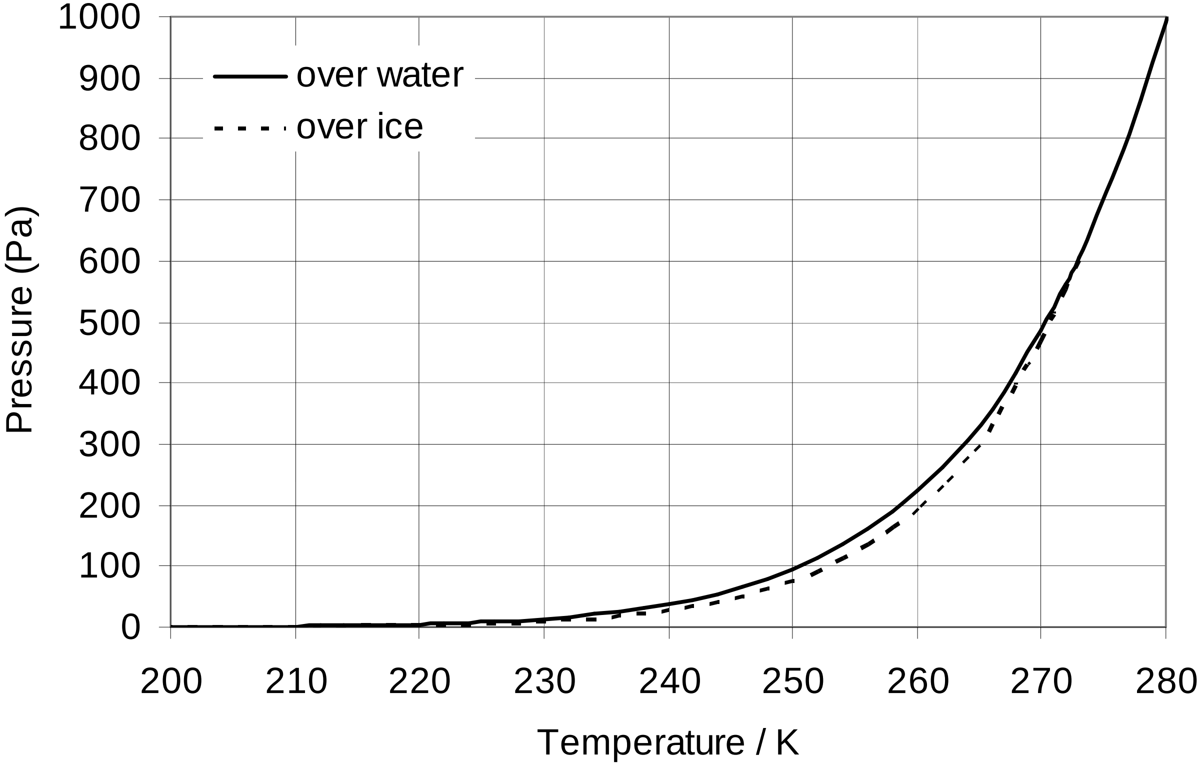
$$\rightarrow \frac{dp}{dT} = \frac{\Delta H_{vap}}{\Delta V_{vap} T} = \frac{\Delta H_{vap} p}{RT^2} \quad \rightarrow \frac{dp}{p} = d\ln p = \frac{\Delta H_{vap}}{RT^2} dT$$



$$\rightarrow \boxed{\ln \frac{p(T)}{p_0} = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_0}\right)}$$

assumes ΔH_{vap} to be T-independent

Vapor pressure of liquid water and ice



Murphy & Koop 2005, Q. J. R. Meteorol. Soc. 131, 1539–1565:

***p* over water in Pa:**

$$\ln(p_{\mathrm{water}}) \approx 54.842763 - 6763.22/T - 4.210\ln(T) + 0.000367T + \tanh\{0.0415(T - 218.8)\} \times (53.878 - 1331.22/T - 9.44523\ln(T) + 0.014025T)$$

***p* over ice in Pa:**

$$\ln(p_{\mathrm{ice}}) = 9.550426 - 5723.265/T + 3.53068\ln(T) - 0.00728332T\ ; \quad T > 110\ \mathrm{K}$$

Vapor pressure of liquid mixtures: Raoult's law

Mixture of two liquids A und B:

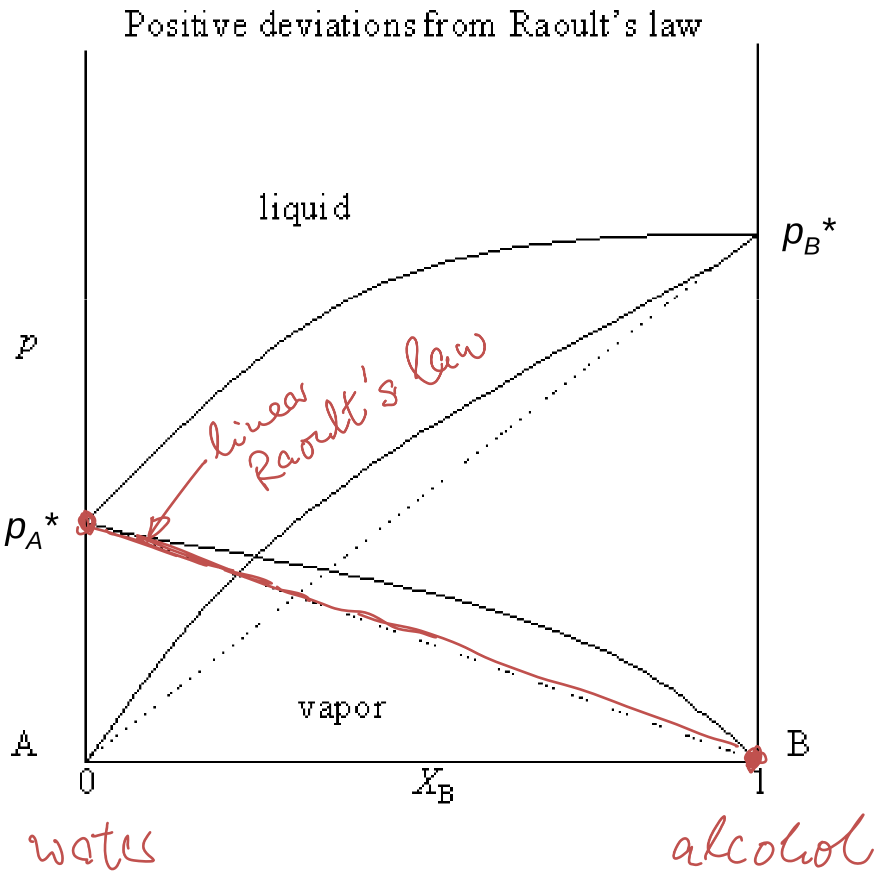
$p_A = x_A p_A^*,\ p_B = x_B p_B^*$

$P = p_A + p_B$

P = total pressure
p = partial pressure
p^* = pressure of pure substance

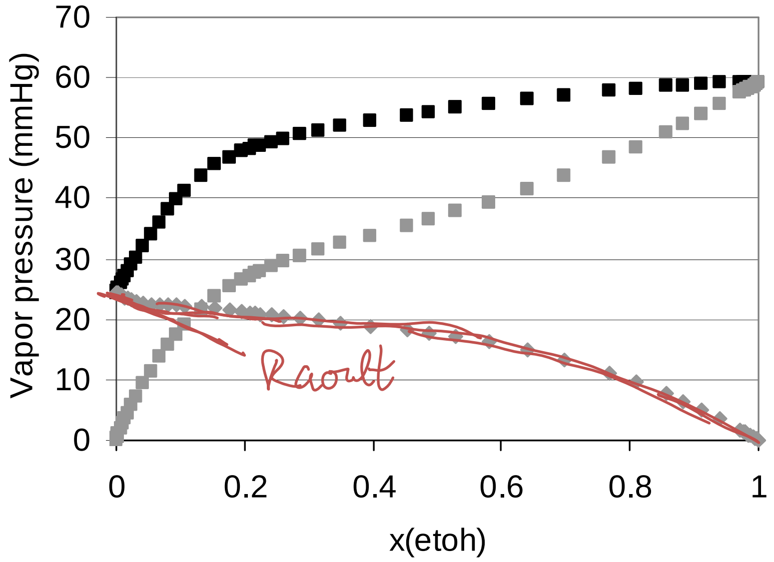
x = mole fraction: $x_1 = \frac{n_1}{\sum n_i}$

n = mole number

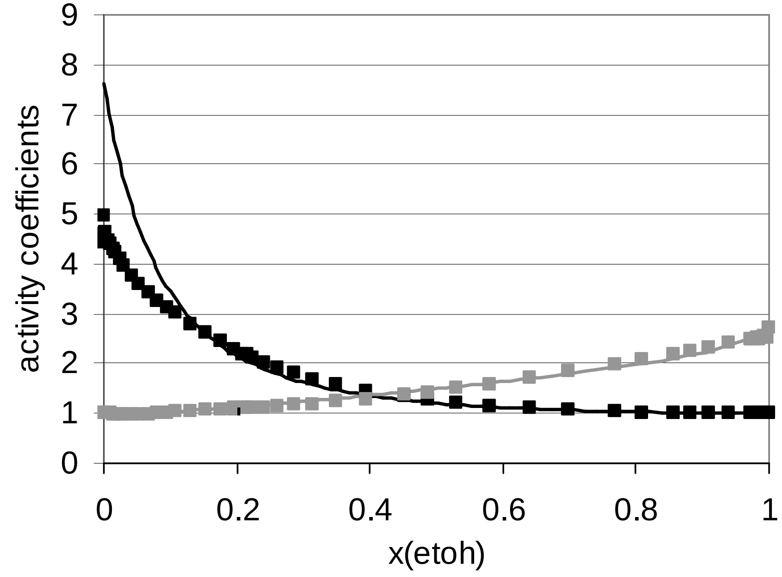


Water / ethanol – mixtures at 25.13°C

Measurement of the vapor-liquid-equilibrium (VLE) of ethanol (etOH) / water mixtures



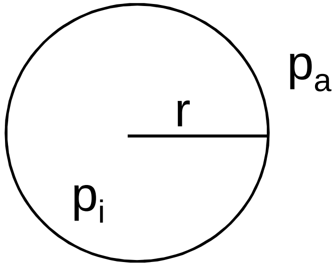
- ■ total vapor pressure P
- ■ partial vapor pressure of etOH = C_2H_5OH
- ◆ partial vapor pressure of H_2O



Activity coefficients γ of ethanol / water mixtures

- — γ(etOH) from UNIFAC model calculation
- — γ(H_2O) from UNIFAC model calculation
- ■ γ(etOH) from VLE data
- ■ γ(H_2O) from VLE data

Kelvin effect

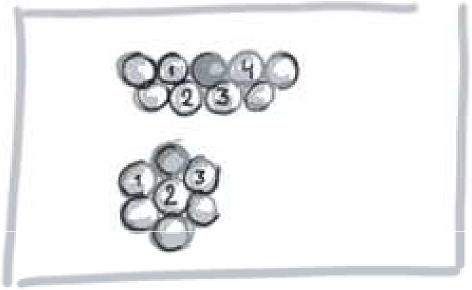


Work required to increase the surface area A of the liquid-vapor interface:

$dW = \sigma dA$

σ = surface tension

A = $4\pi r^2$ = surface area



$$dW = \sigma dA$$

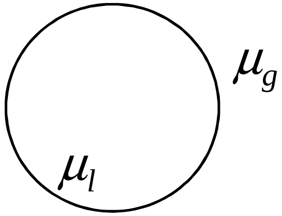
$$4\pi r^2 (p_i - p_a) = A\, dp = \sigma\, d(4\pi r^2) = 8\pi r\, \sigma dr$$

→ $p_i = p_a + 2\,\sigma / r$ Laplace equation (valid for bubble or droplet)

↳ important for $r < 50$nm

↳ 5-10% effect

What is the influence of the higher pressure inside a curved surface on the vapor pressure of a droplet?

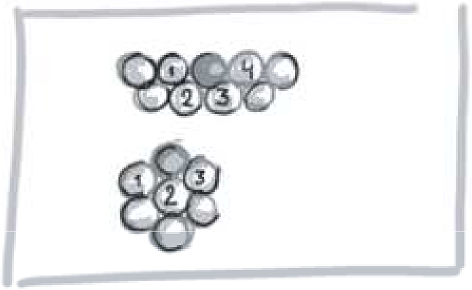


In equilibrium: $\mu_g = \mu_l$ and $d\mu_g = d\mu_l$

Chemical potential depends on pressure: $(\partial\mu/\partial p)_T = V_m$,

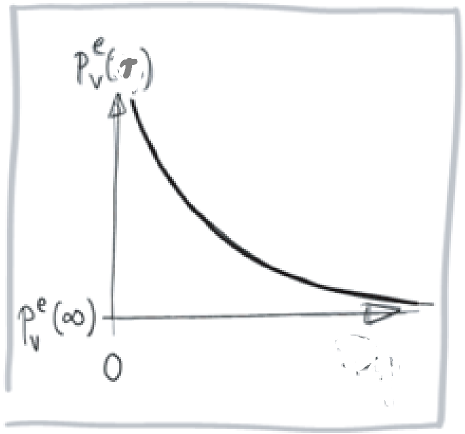
V_m: molar volume

$$\rightarrow \quad V_{m,l}\, dp_l = V_{m,g}\, dp_g = \frac{RT}{p_g} dp_g$$



$$\Rightarrow \quad \int_{p(\infty)}^{p} \frac{1}{p_g} dp_g = \frac{1}{RT} \int_{p(\infty)}^{p^*+\Delta p} V_{m,l}\, dp_l \approx \frac{V_{m,l}}{RT} \Delta p$$

$$\Rightarrow \quad \ln\left(\frac{p(r)}{p(\infty)}\right) = \frac{V_{m,l}\,\Delta p}{RT}$$



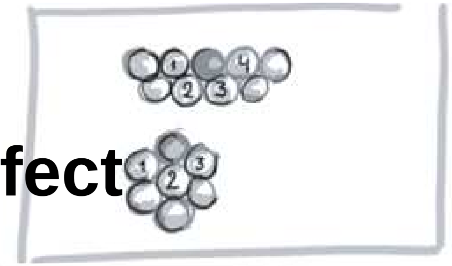
For curved surfaces: $\Delta p = 2\sigma / r$

$$\boxed{p(r) = p(\infty) \times e^{2\sigma V_{m,l}/rRT} \qquad \text{Kelvin Equation}}$$

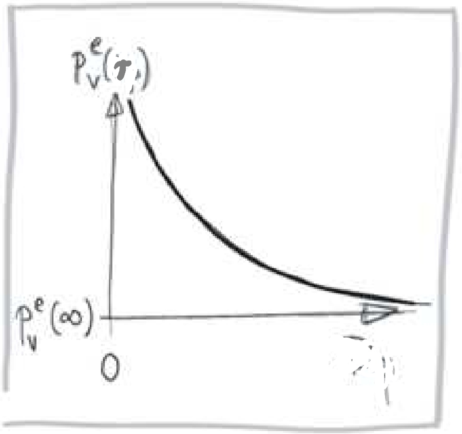
$p(\infty)$ = vapor pressure over flat surface, r = ptcl radius, R = gas constant,

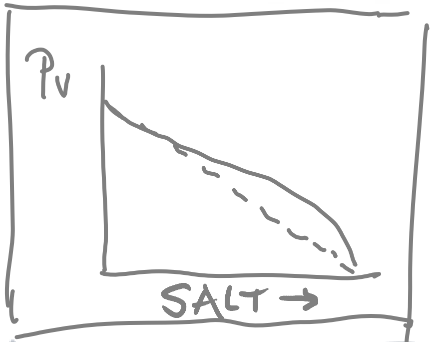
$V_{m.l}$ = liquid molar volume, e.g. of H_2O, σ = surface tension

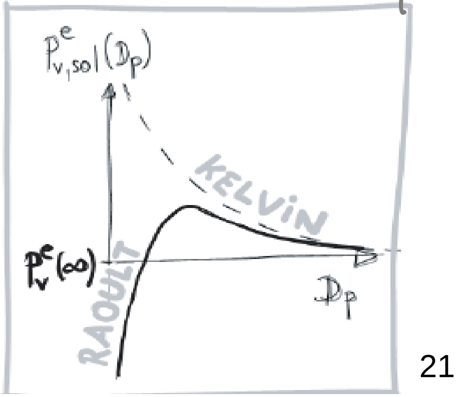
Köhler theory = Raoult’s law + Kelvin Effect



$$
\begin{aligned}
p_w(r) &= p(\infty)\times e^{2\sigma V_{m,w}/rRT} \\
&= x_w p_w(\infty)\times e^{2\sigma V_{m,w}/rRT} \\
&= \frac{n_w}{n_w+n_s}\, p_w(\infty)\times e^{2\sigma V_{m,l}/rRT} \\
&= \frac{1}{1+n_s V_{m,w}/(4\pi r^3/3-n_s V_s)}\, p_w(\infty)\times e^{2\sigma V_{m,l}/rRT} \\
&\approx \frac{1}{1+3n_s V_{m,w}/(4\pi r^3)}\, p_w(\infty)\times e^{2\sigma V_{m,w}/rRT} \\
&\approx p_w(\infty)\times \exp\left(\frac{2\sigma V_{m,w}}{rRT}-\frac{3n_s V_{m,w}}{4\pi r^3}\right)
\end{aligned}
$$



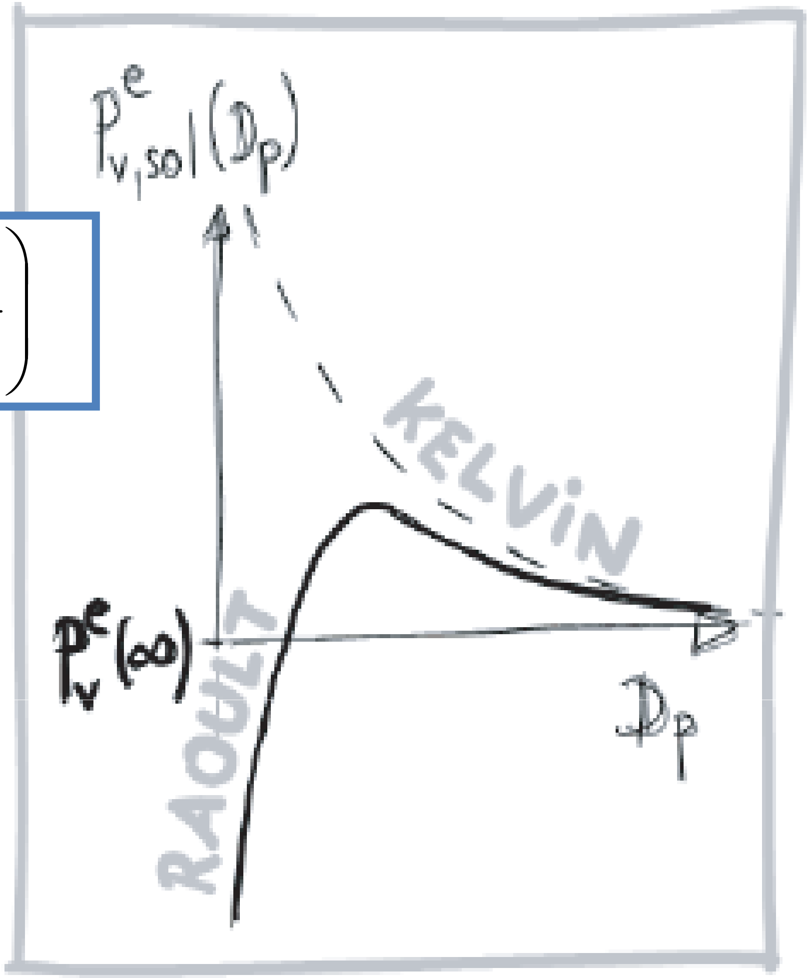


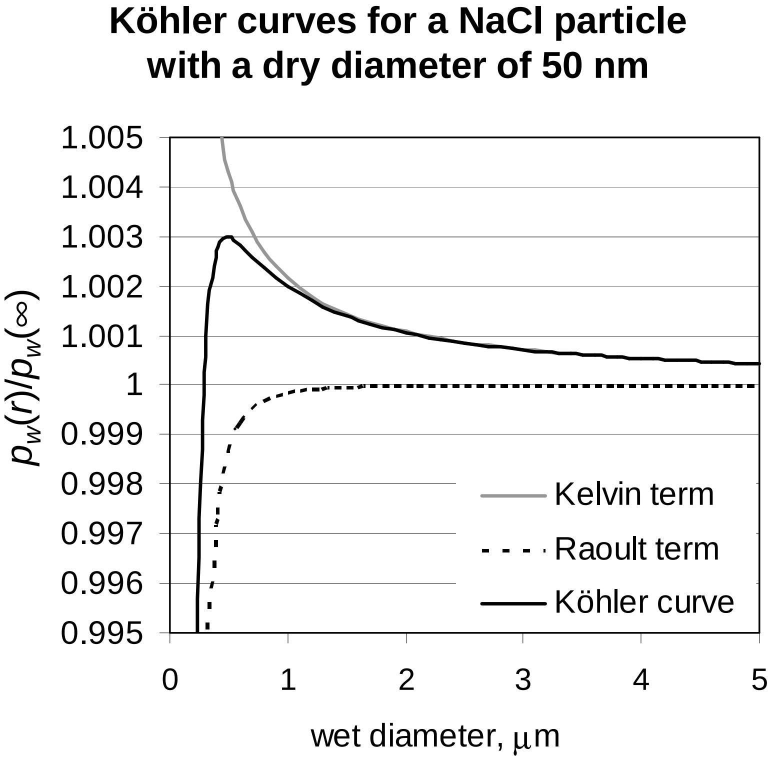


The last two steps assume the solution to be dilute, and make a Taylor expansion;
$p_w(\infty)$ = H_2O vapor pressure over pure liquid bulk water, σ = surface tension of solution,
r = particle radius, $V_{m.w}$ = liquid molar volume of H_2O, n_s = molar density of solute

Köhler theory

$$p_w(D_p) \approx p_w(\infty) \times \exp\left(\frac{4\sigma V_{m,w}}{D_p RT} - \frac{6 n_s V_{m,w}}{\pi D_p^3}\right)$$

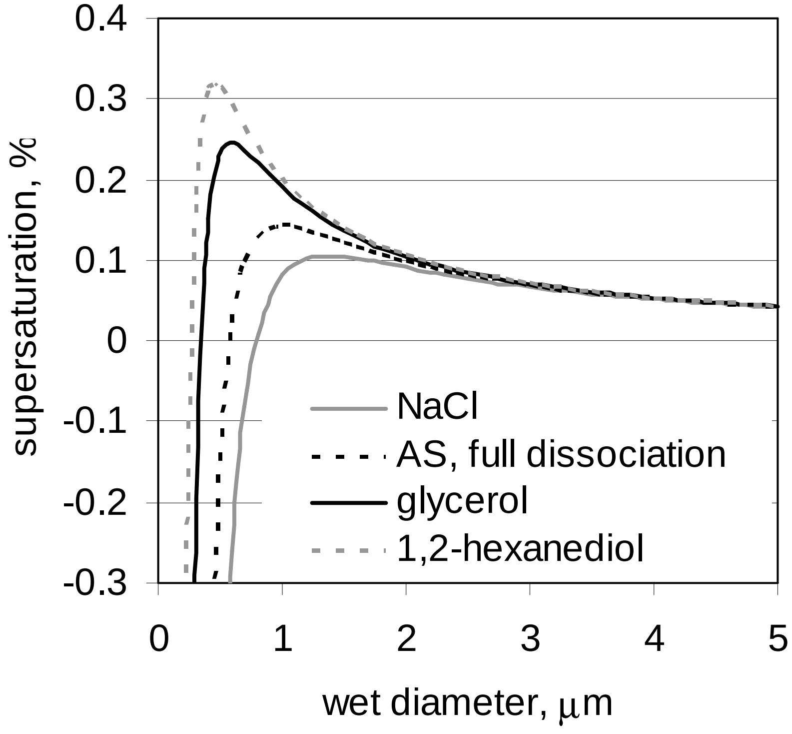




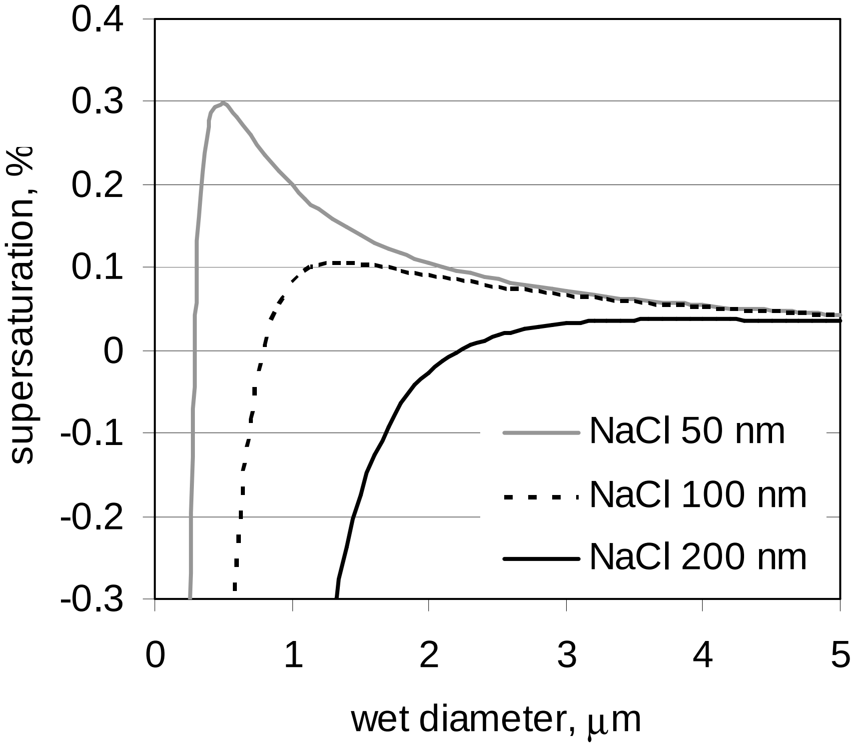
$p_w(\infty)$ = H_2O vapor pressure over pure liquid bulk water, σ = surface tension of solution, D_p = particle radius, $V_{m.w}$ = liquid molar volume of H_2O, n_s = molar density of solute

$$S_w = \frac{p_w(D_p)}{p_w(\infty)} \approx \exp\left(\frac{4\sigma V_{m,w}}{D_p RT} - \frac{6 n_s V_{m,w}}{\pi D_p^3}\right)$$

Köhler curves for particles (with dry diameters of 100 nm) of different compositions



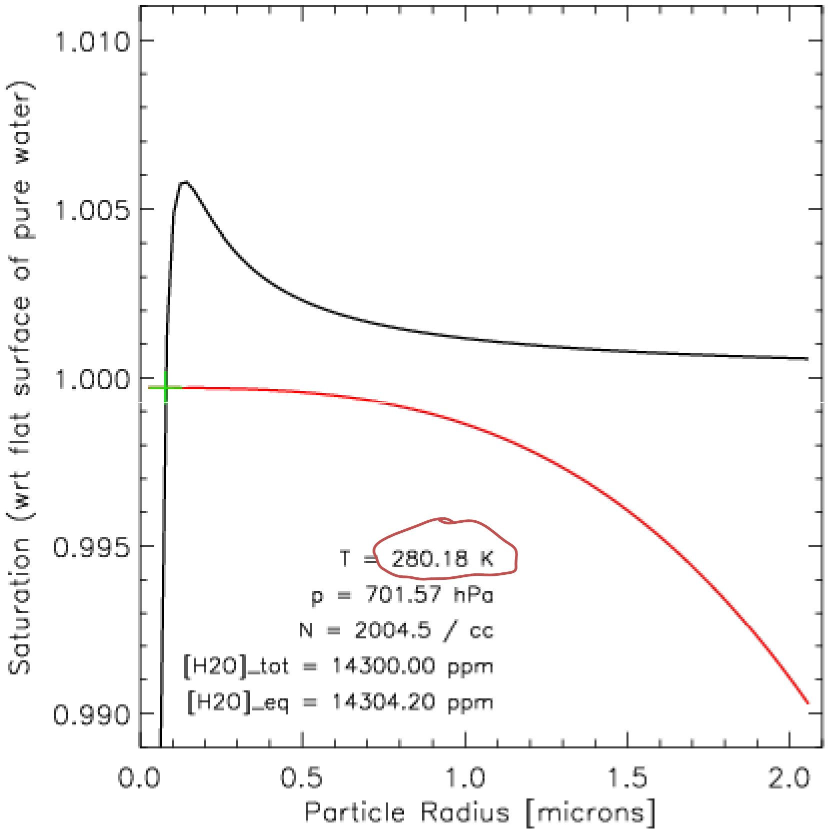
Köhler curves for NaCl particles of different dry diameters



The Köhler curve describes the equilibrium vapor pressure of a droplet with a specified dry diameter as it takes up or loses water.

Adiabatic cooling of an air parcel

701.57 hPa → 700.00 hPa
280.18 K → 280.00 K
(Lift of ~17 m)



χ^{tot} = 14300 ppm
= 1.43 %

Monodisperse salt particles:

Number density: 2000 cm^{-3}

Salt mass: $2{\times}10^{-16}$g $(NH_4)_2SO_4$

Mass balance:

$$p_w = n_w kT = \left(n_w^{tot} - N \frac{4\pi}{3} \frac{r^3}{\upsilon_w} \right) kT \quad \Rightarrow \quad S = \frac{p_w}{p_w^{vap}(T)} = \frac{p_w^{tot}}{p_w^{vap}(T)} - \frac{NkT}{p_w^{vap}(T)} \left(\frac{r}{r_w} \right)^3$$

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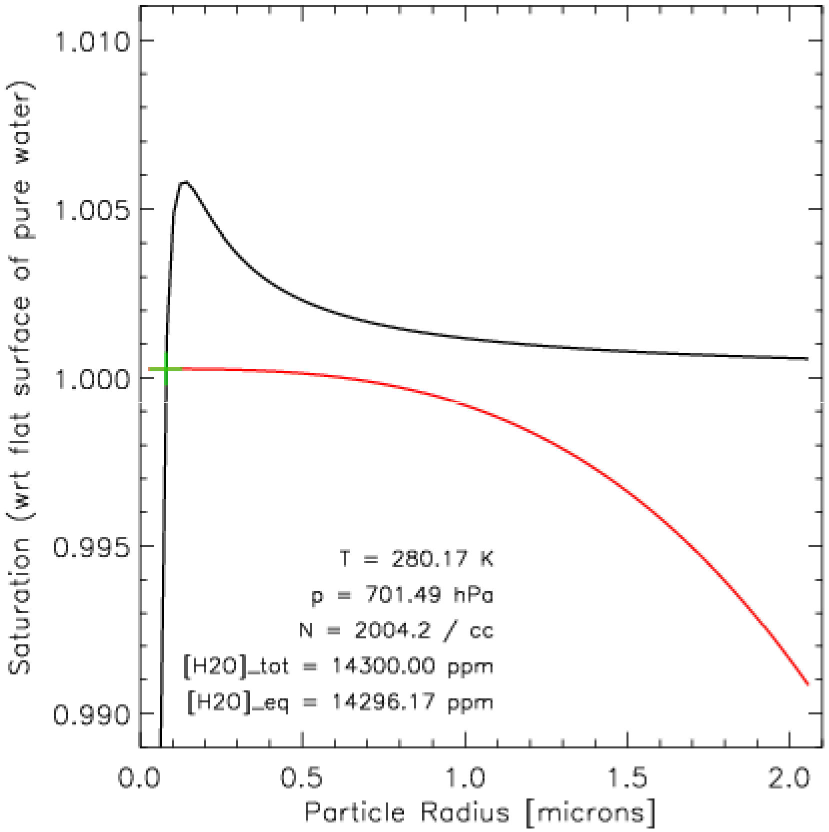

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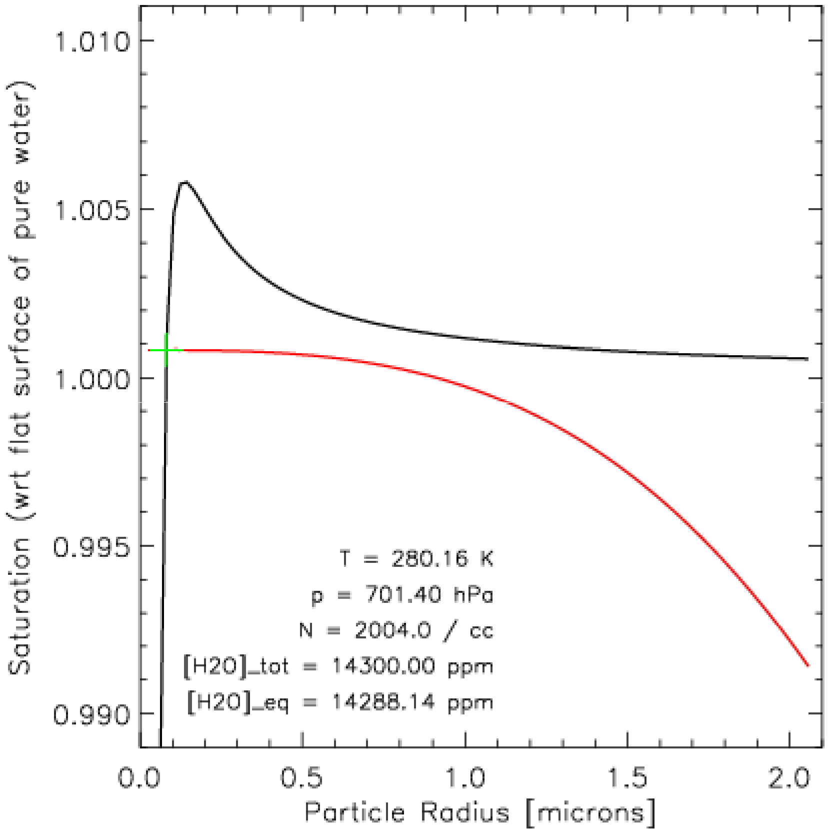

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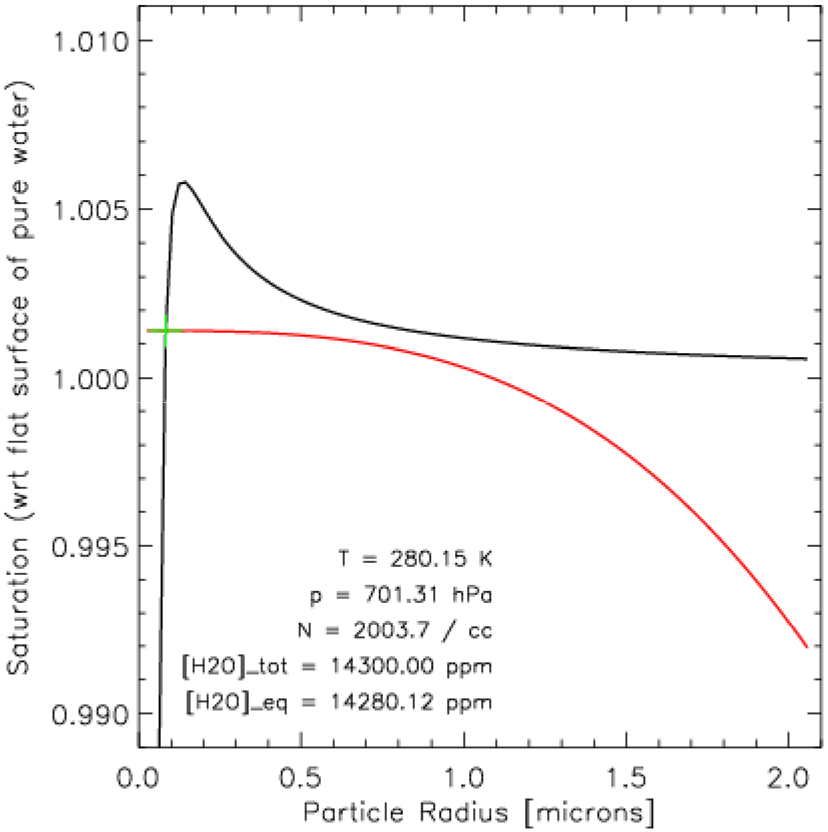

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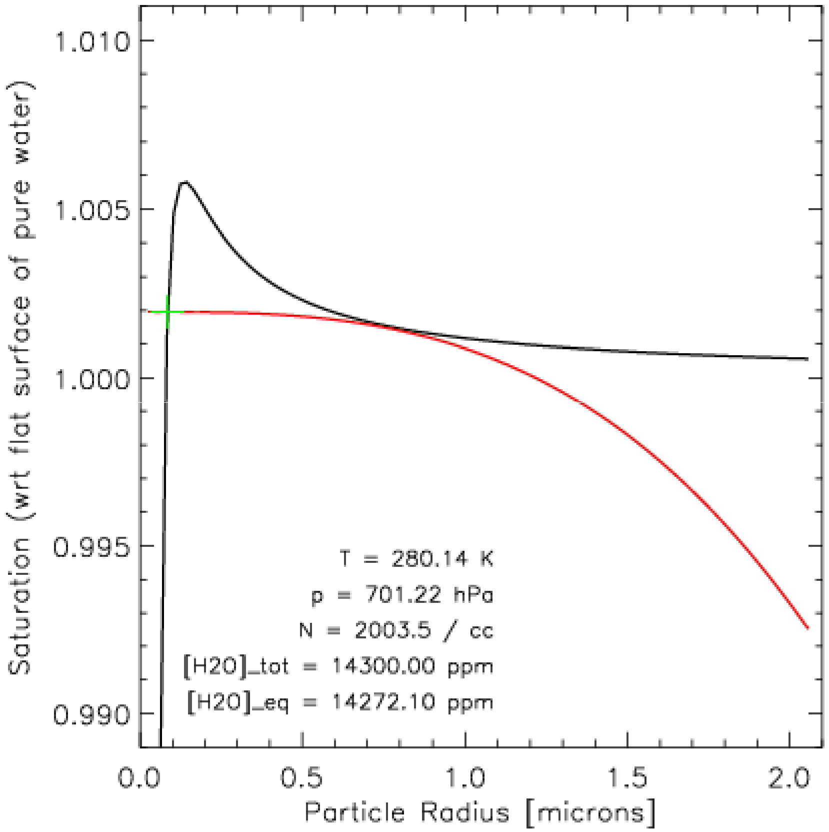

χ^{tot} = 14300 ppm
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Number density: 2000 cm^{-3}

Salt mass: 2×10^{-16}g $(NH_4)_2SO_4$

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Adiabatic cooling of an air parcel

701.57 hPa → 700.00 hPa

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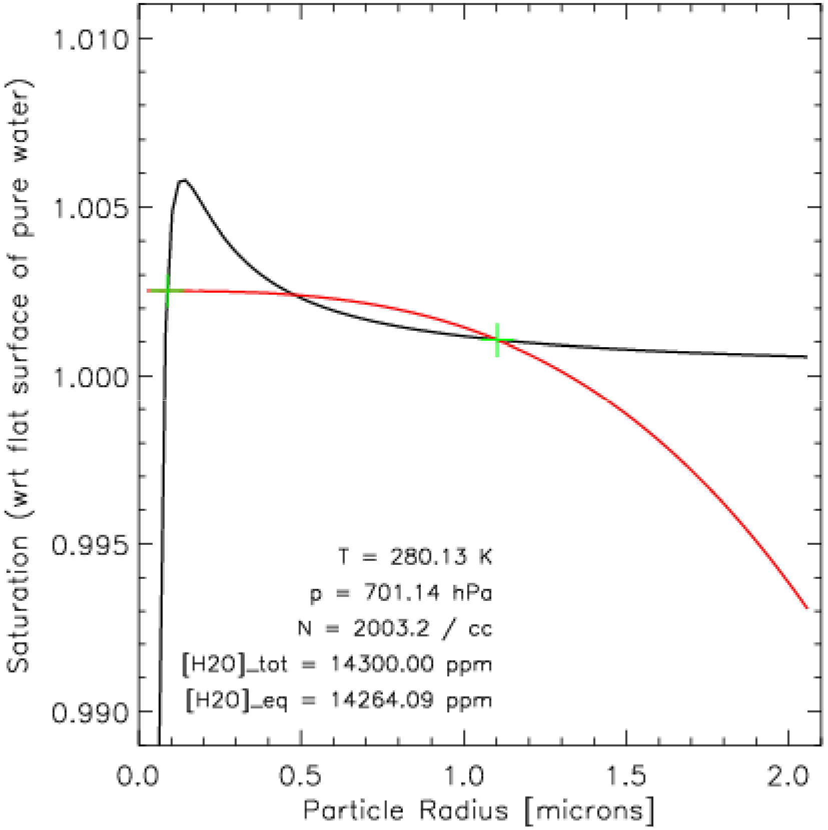

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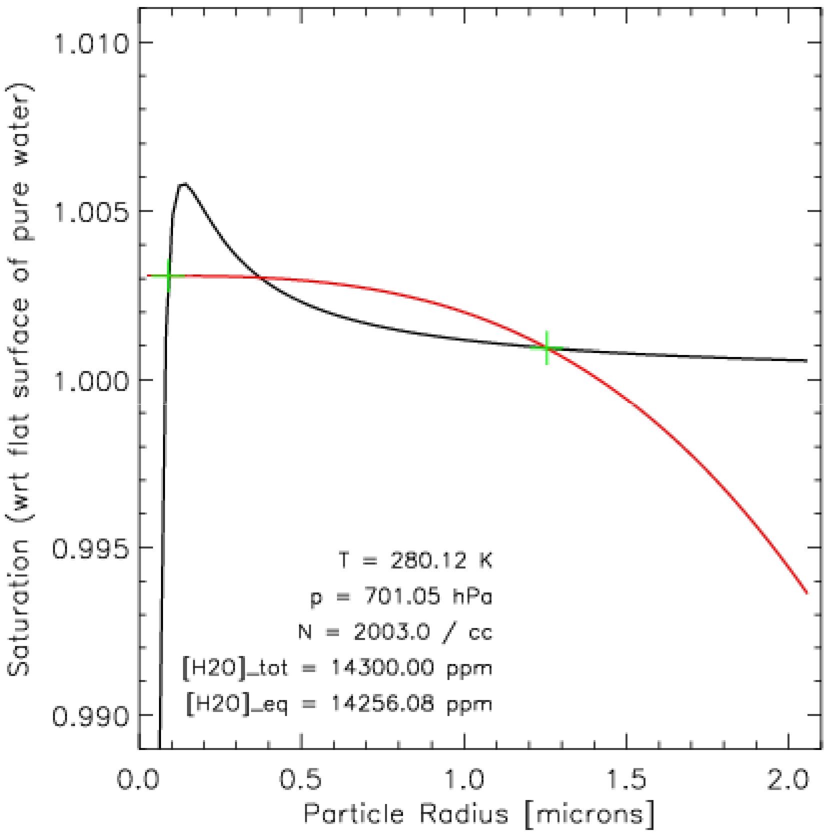

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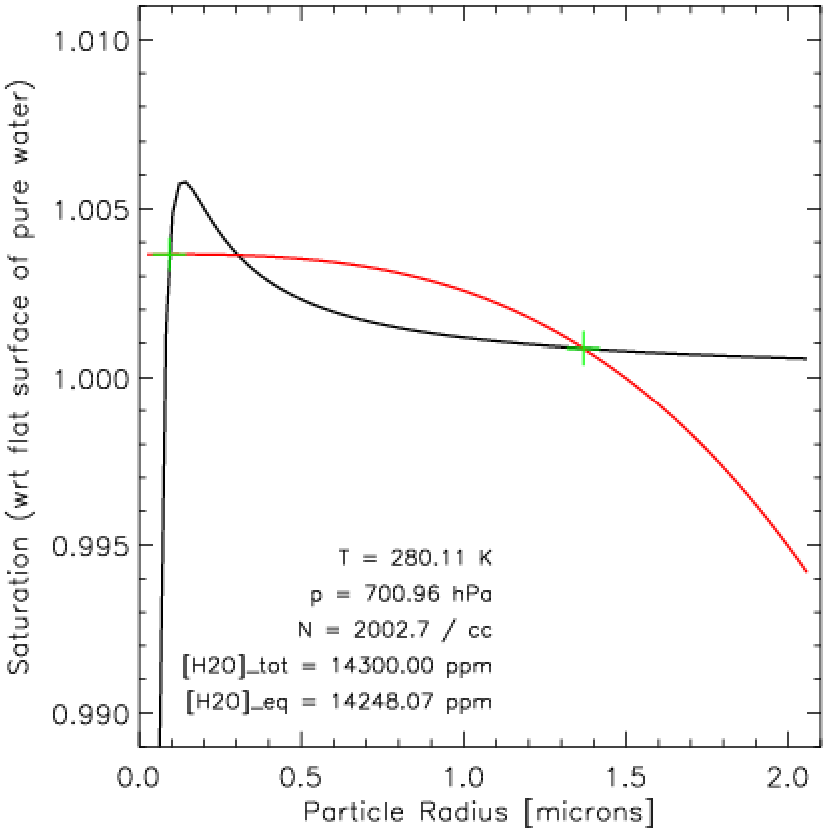

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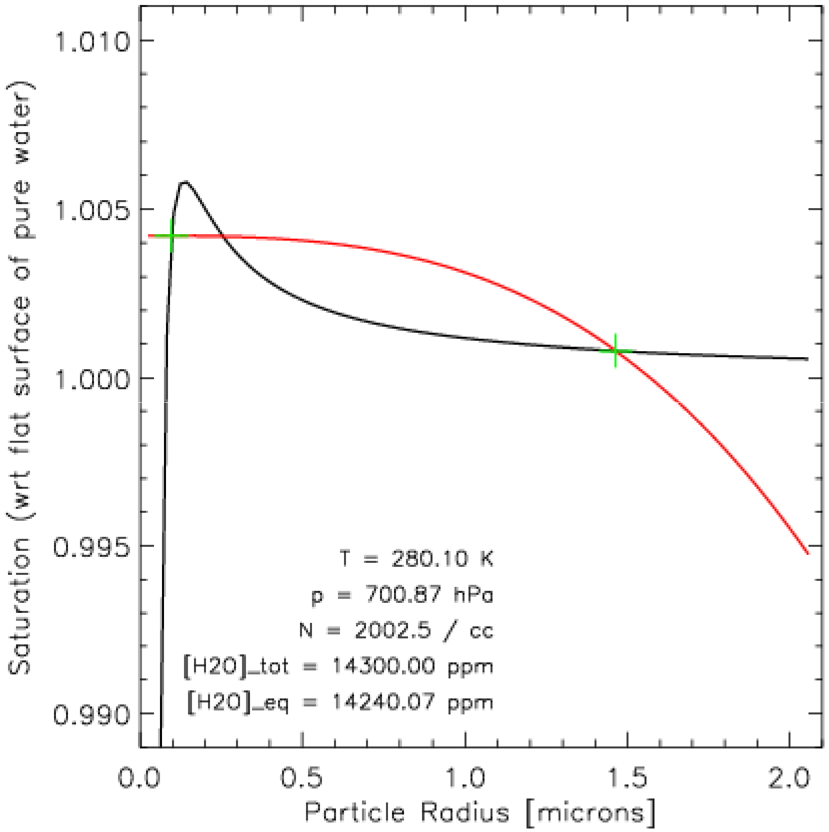

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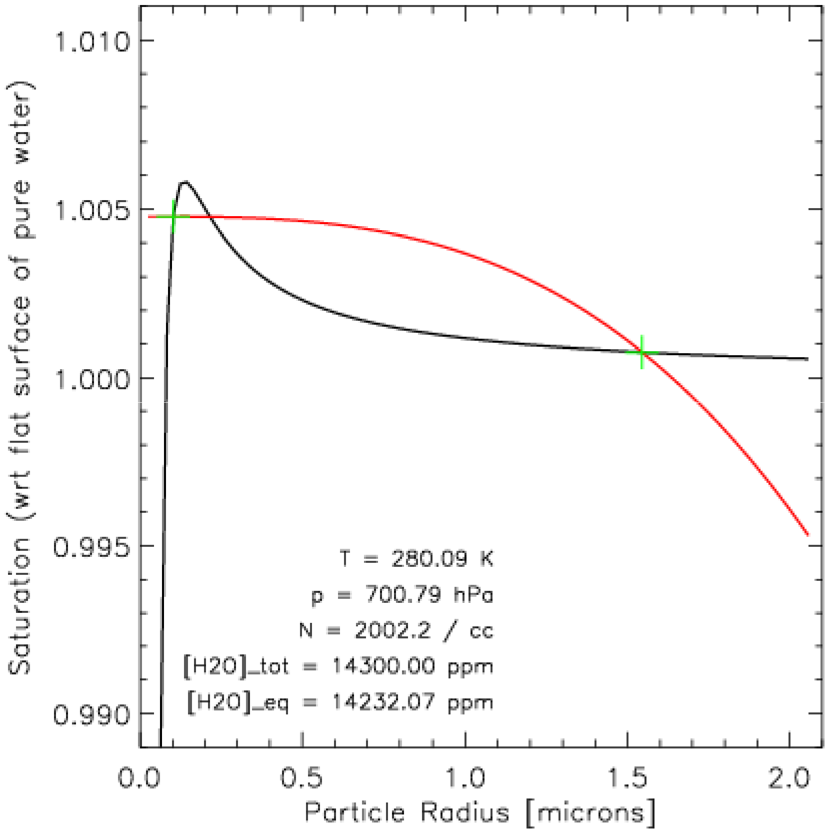

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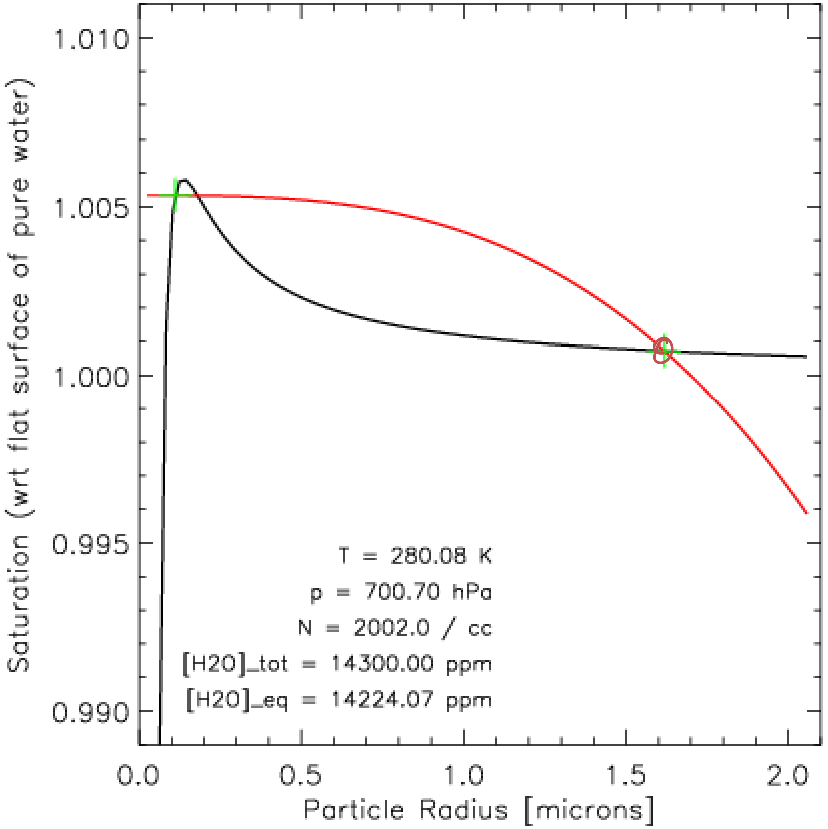

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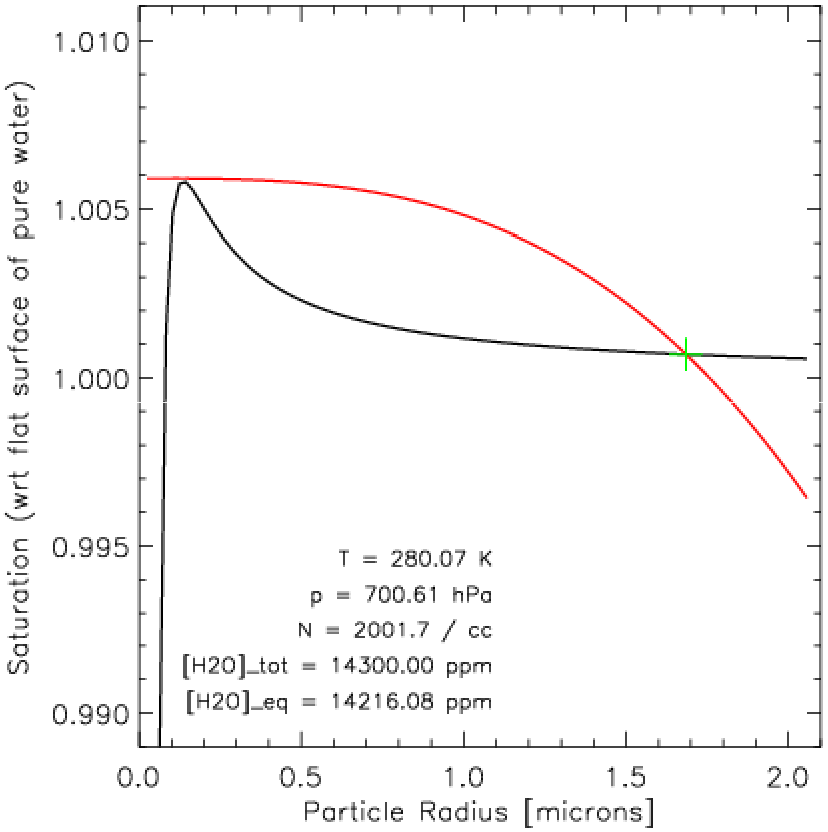

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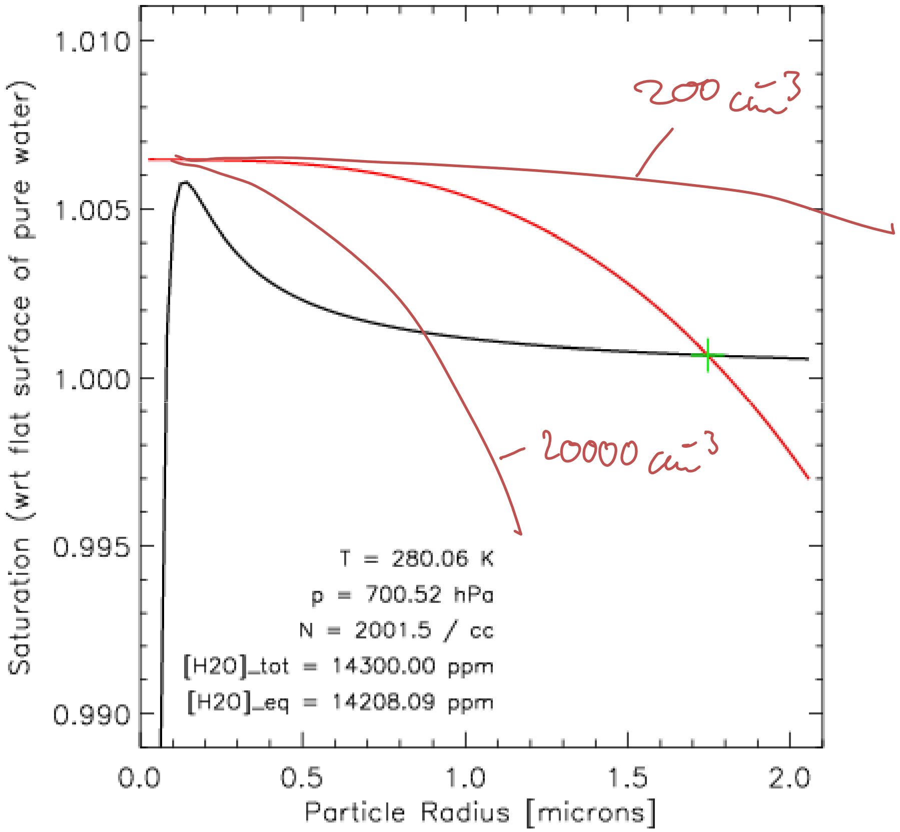

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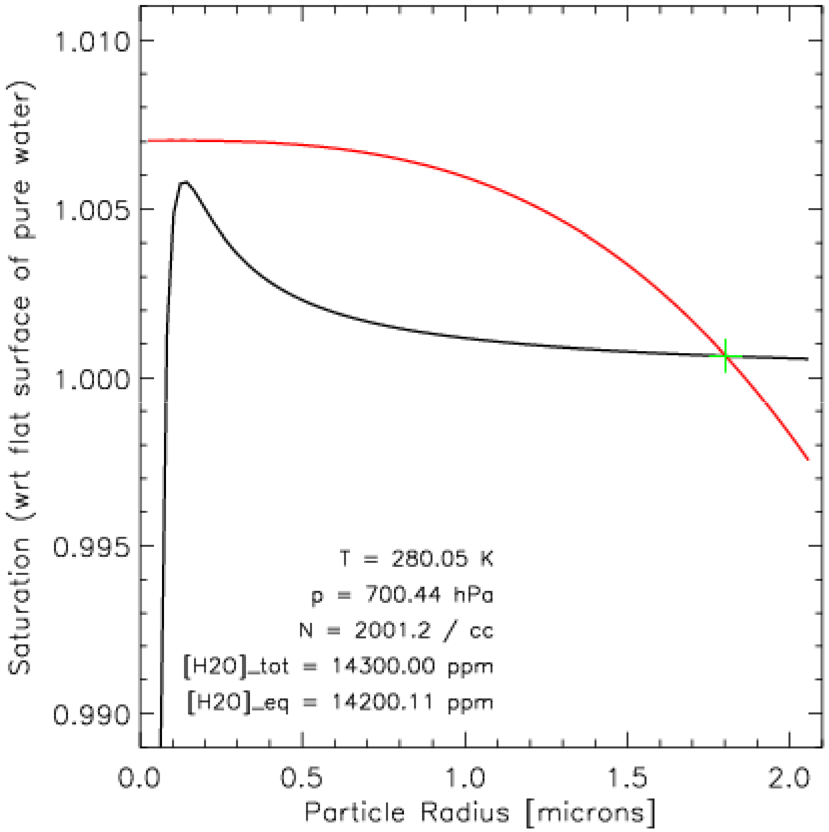

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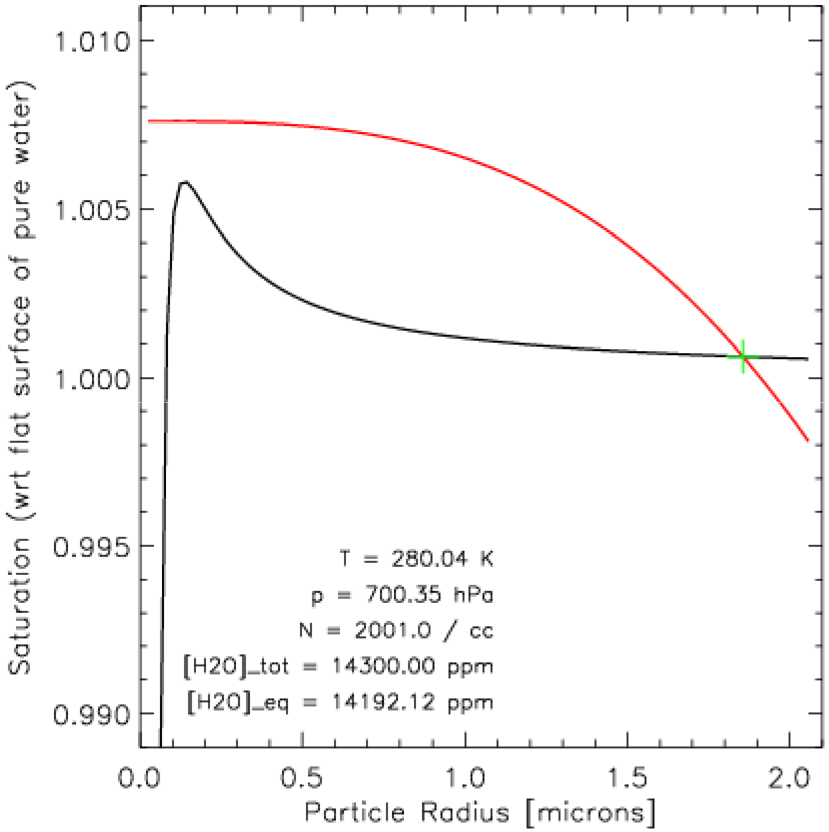

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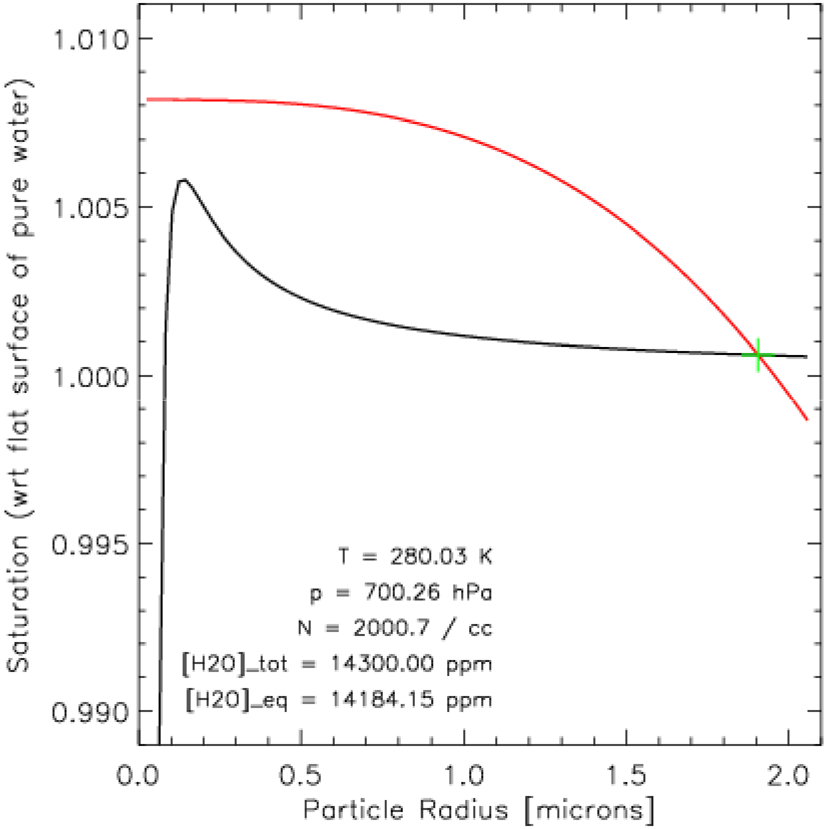

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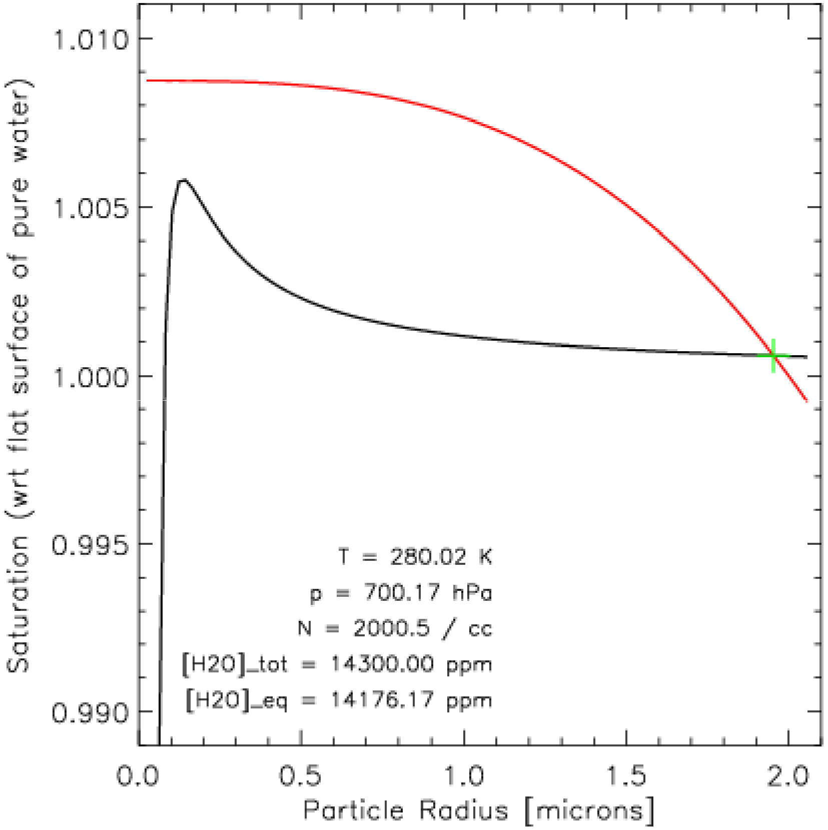

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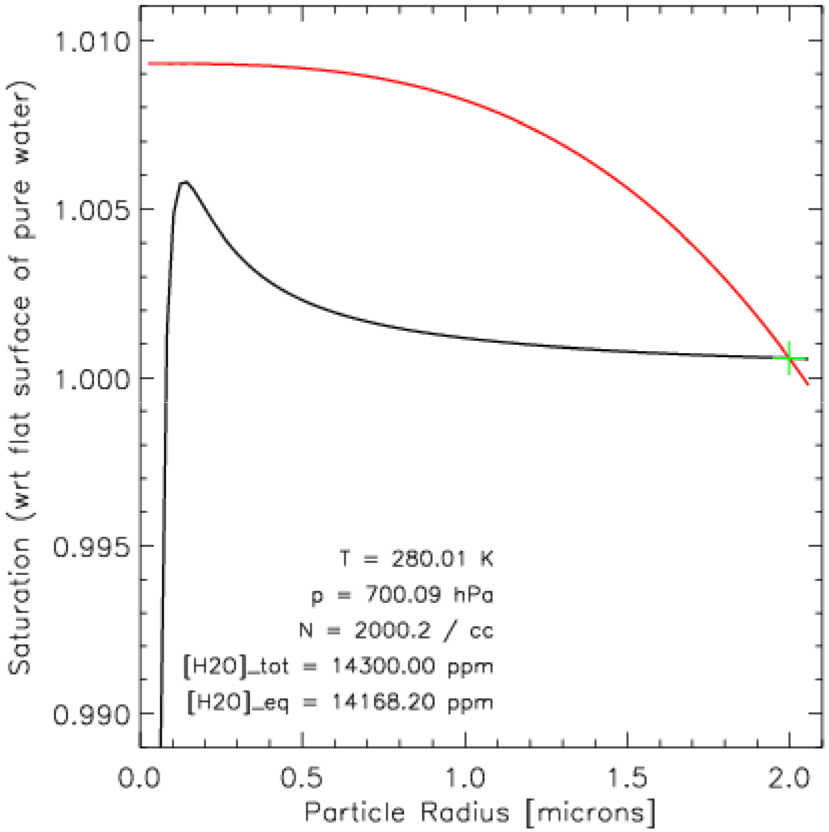

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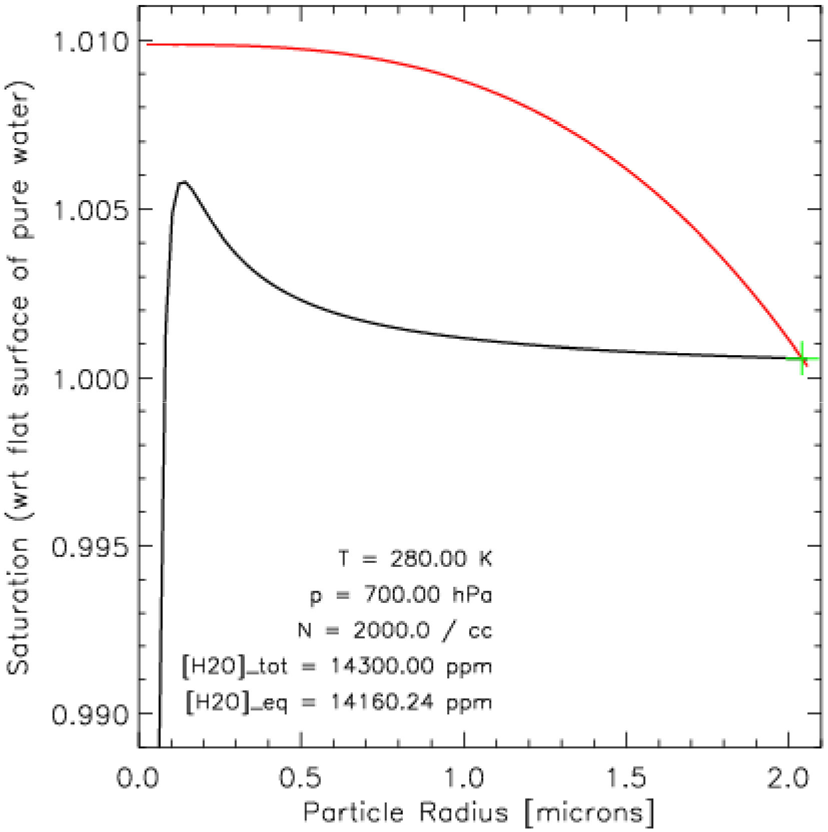

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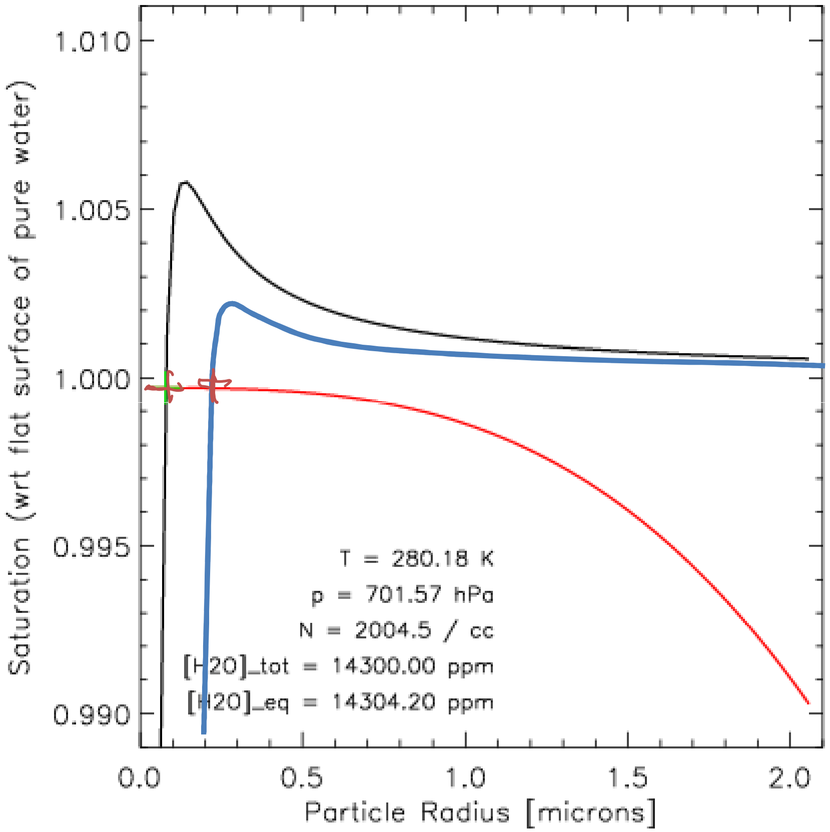

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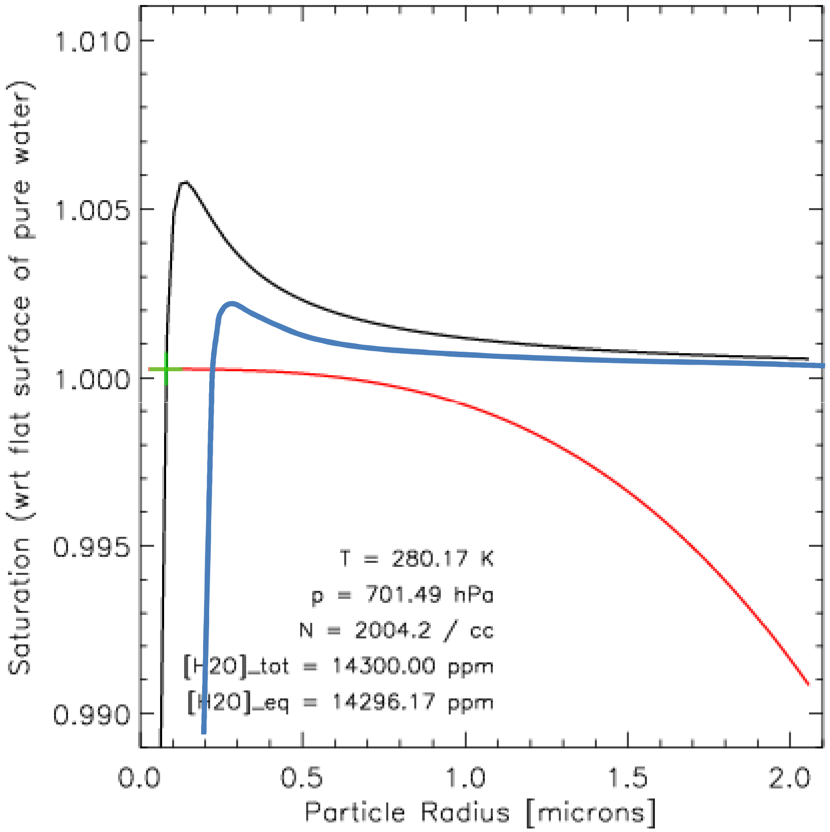

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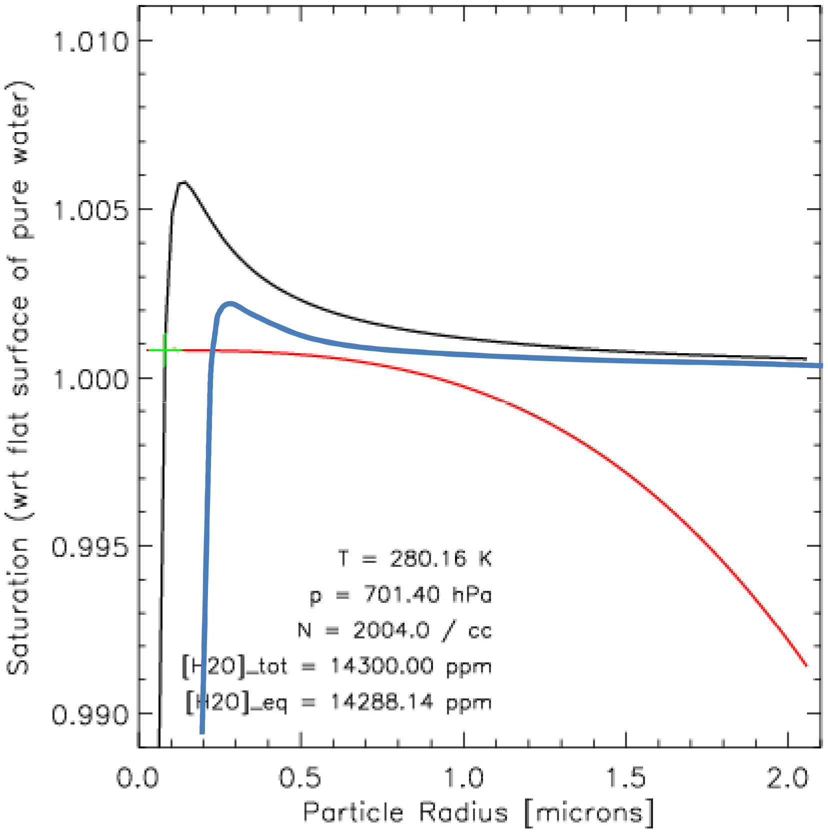

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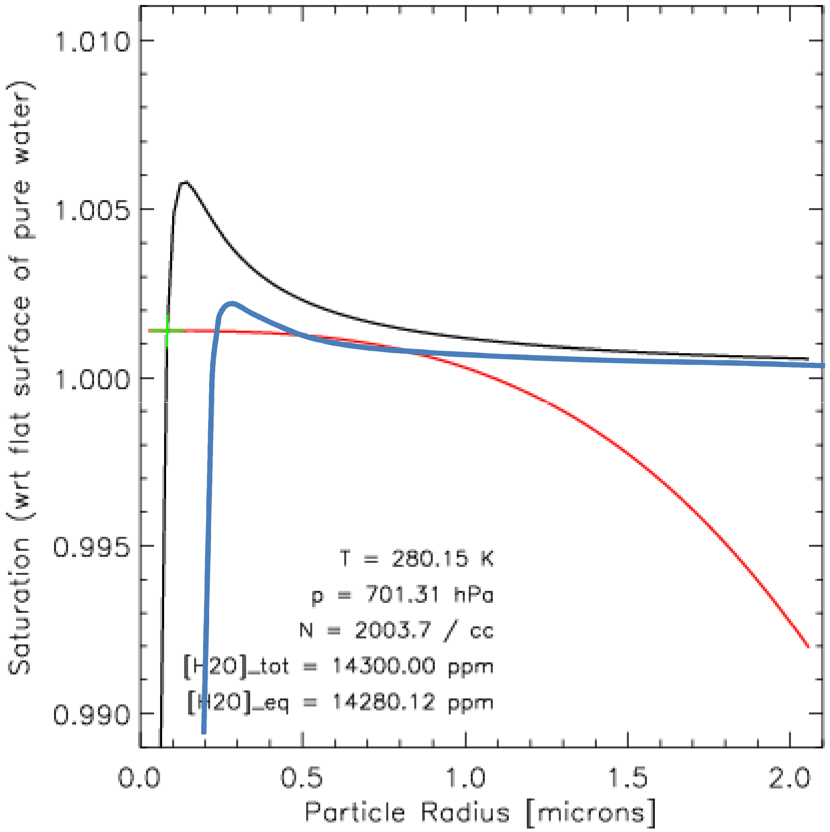

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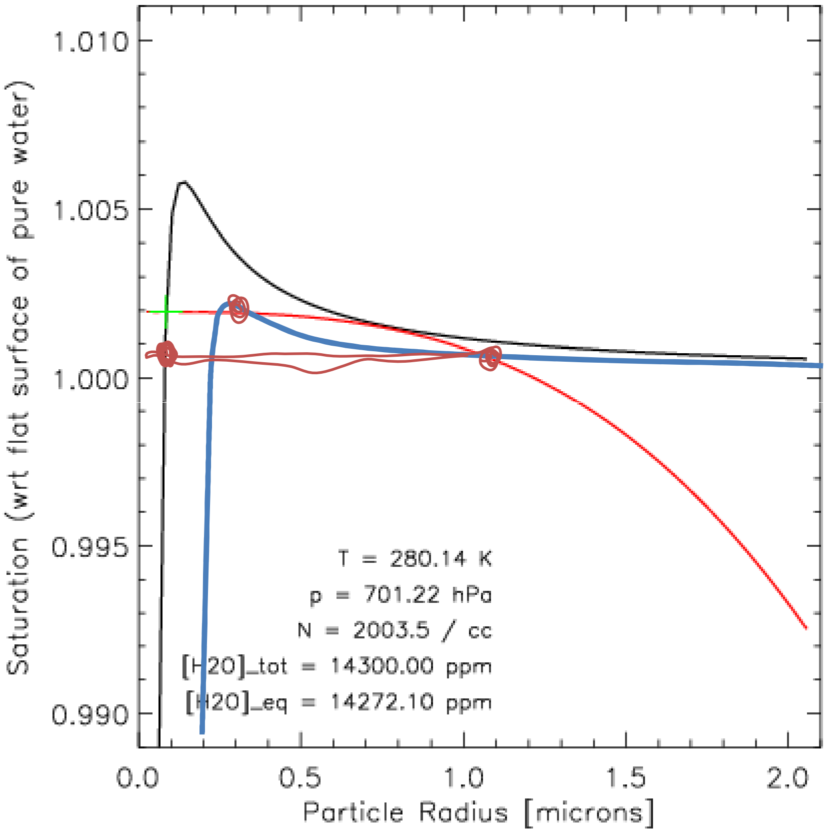

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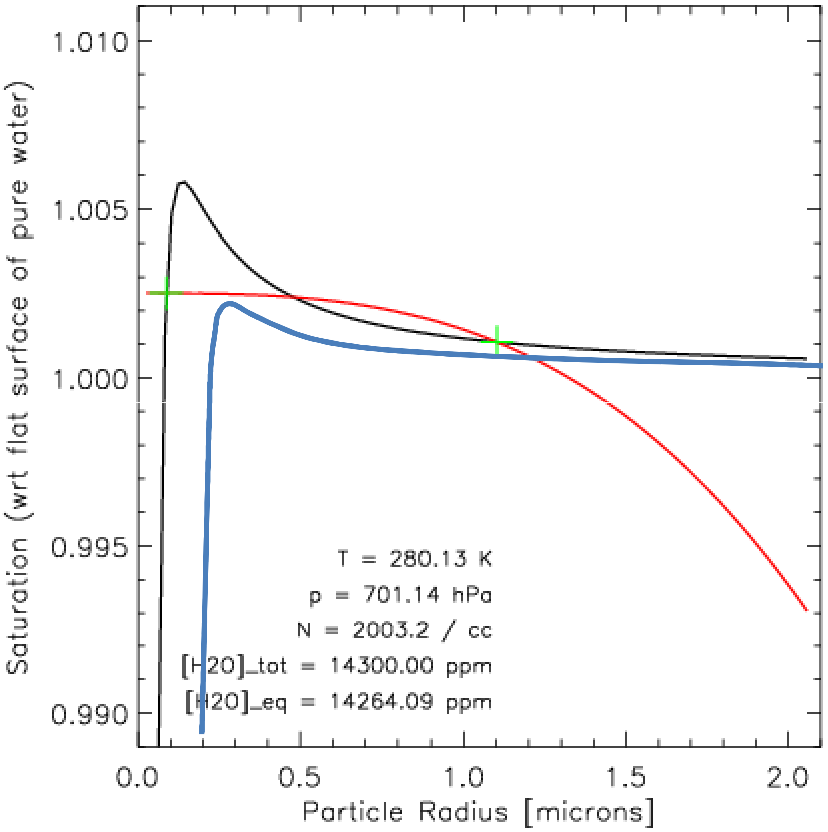

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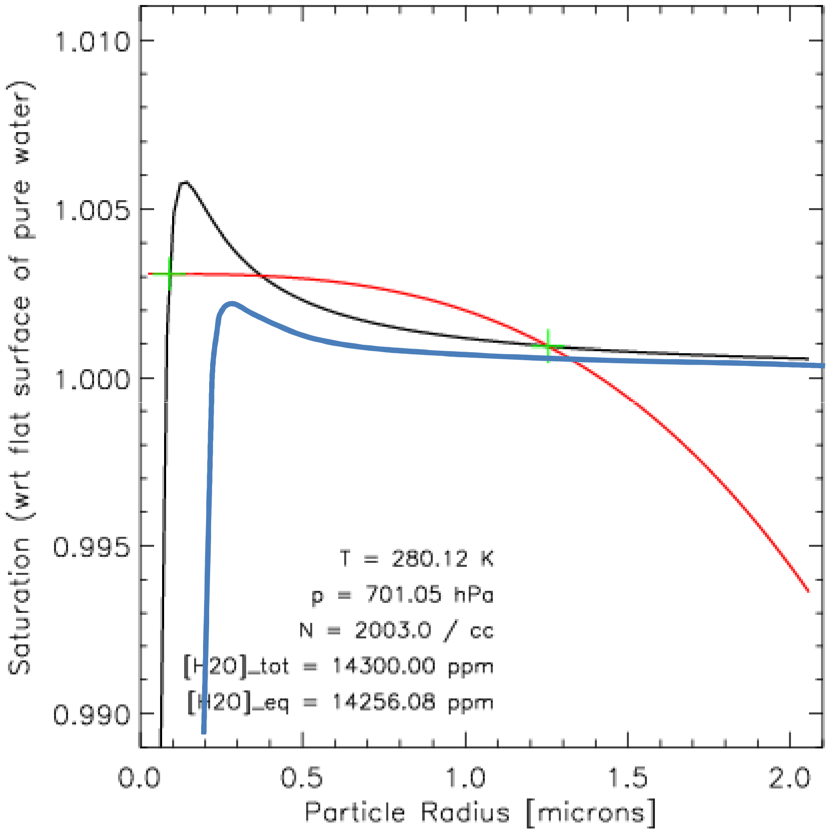

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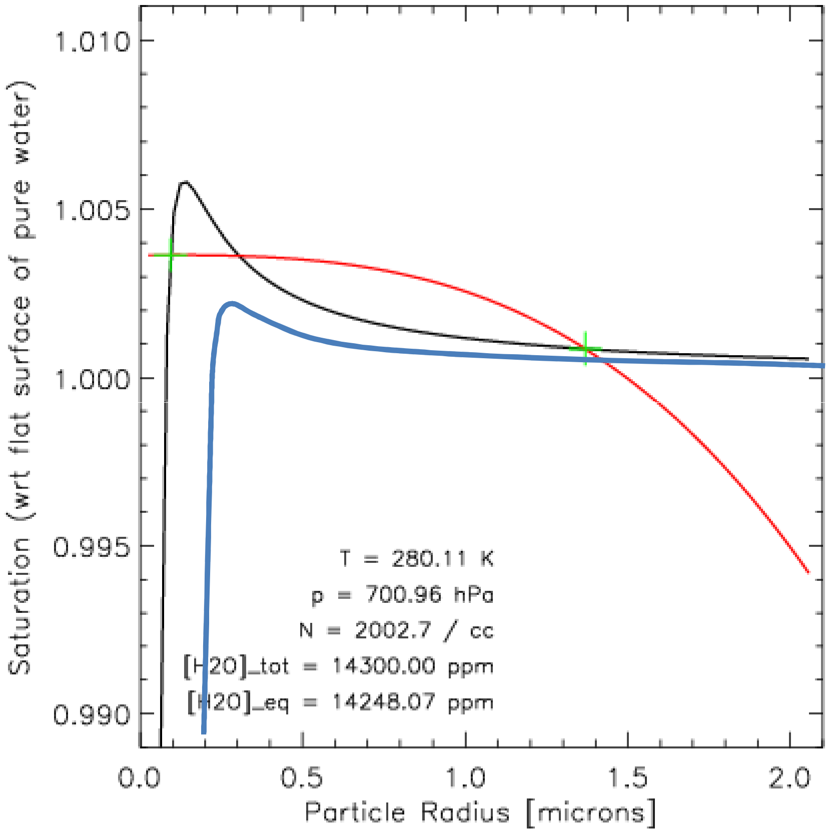

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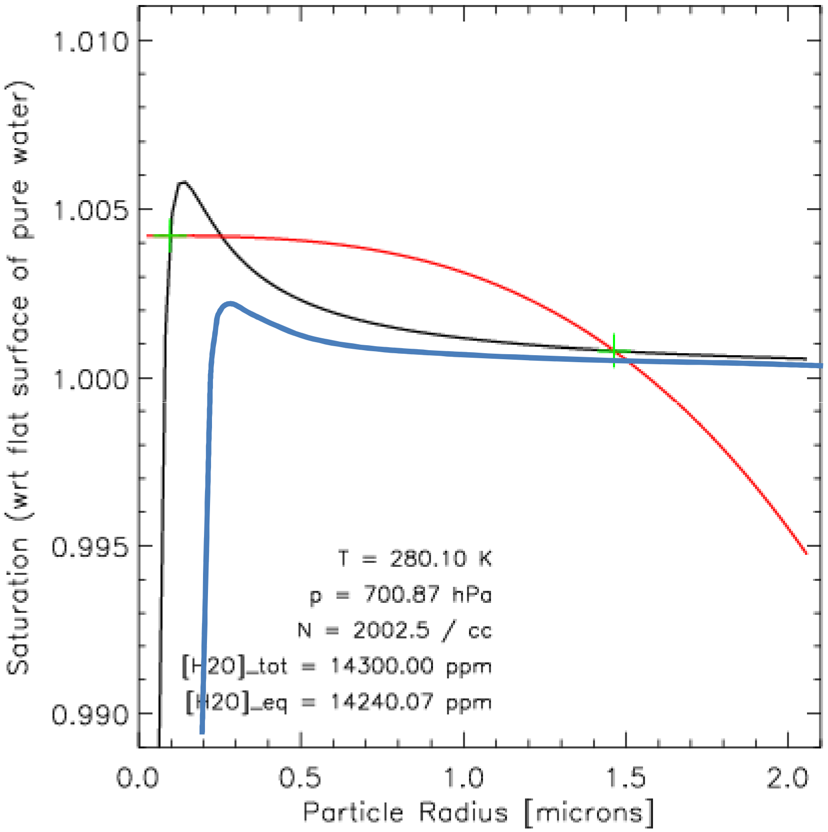

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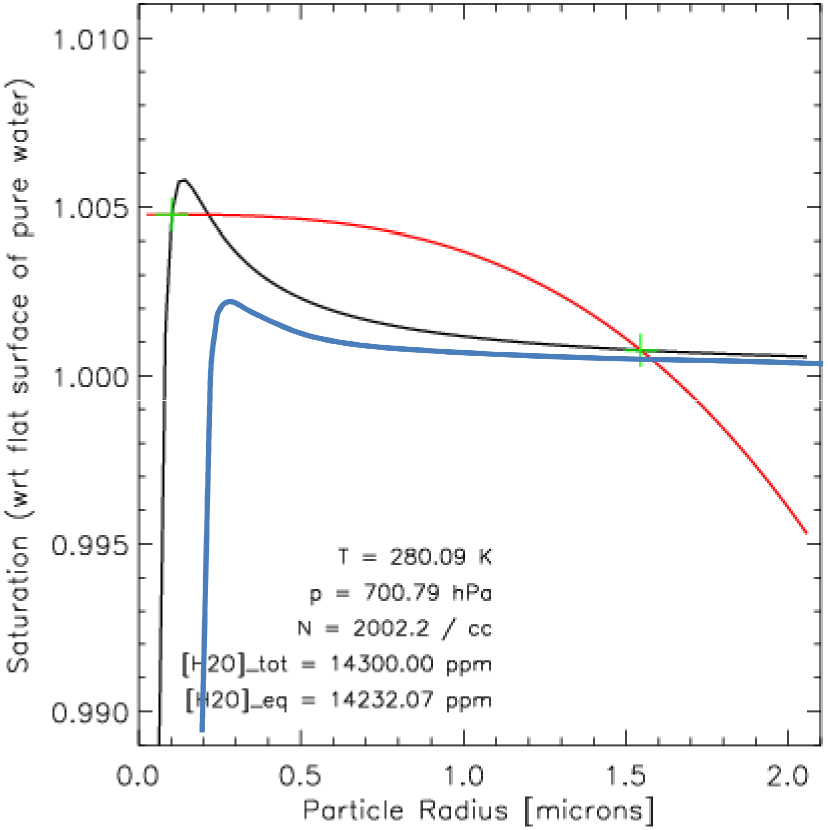
Adiabatic cooling of an air parcel

701.57 hPa → 700.00 hPa
280.18 K → 280.00 K
(Lift of ~17 m)



χ^{tot} = 14300 ppm
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Minority with
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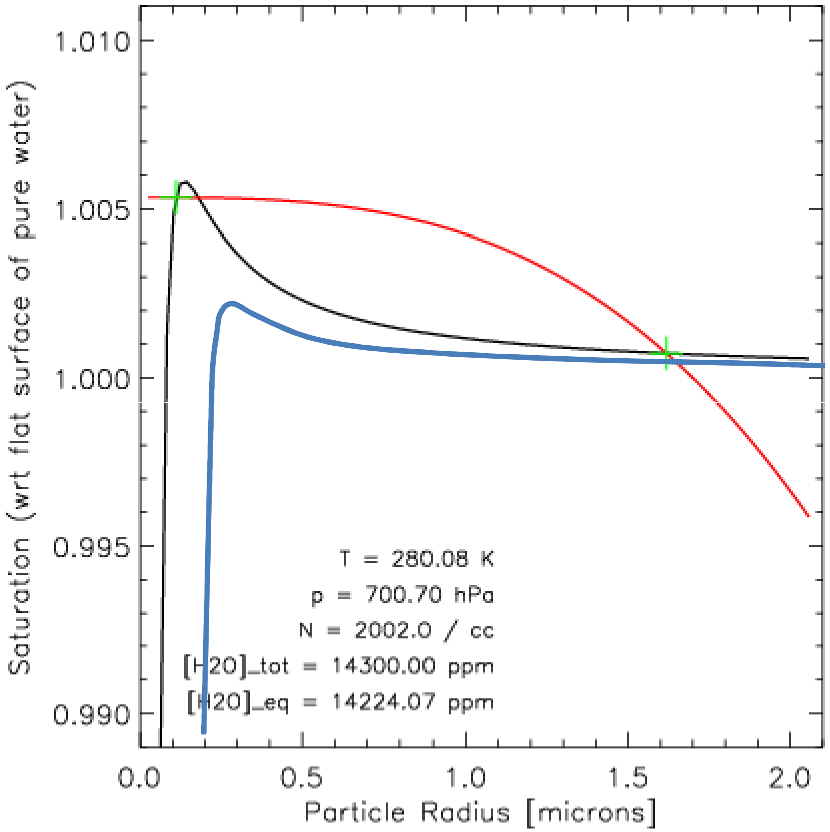

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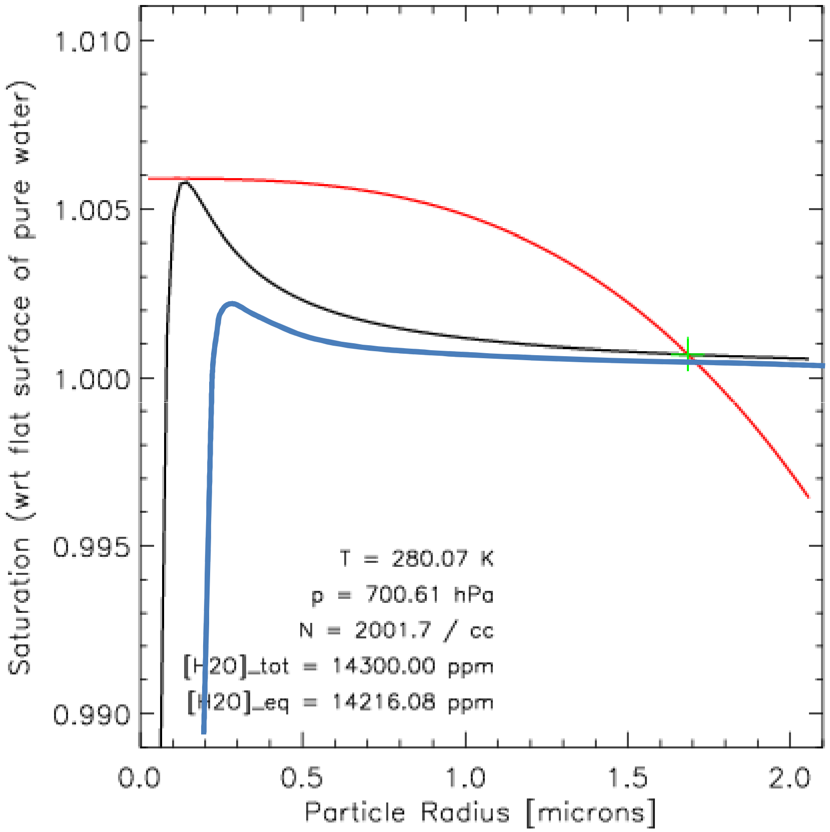

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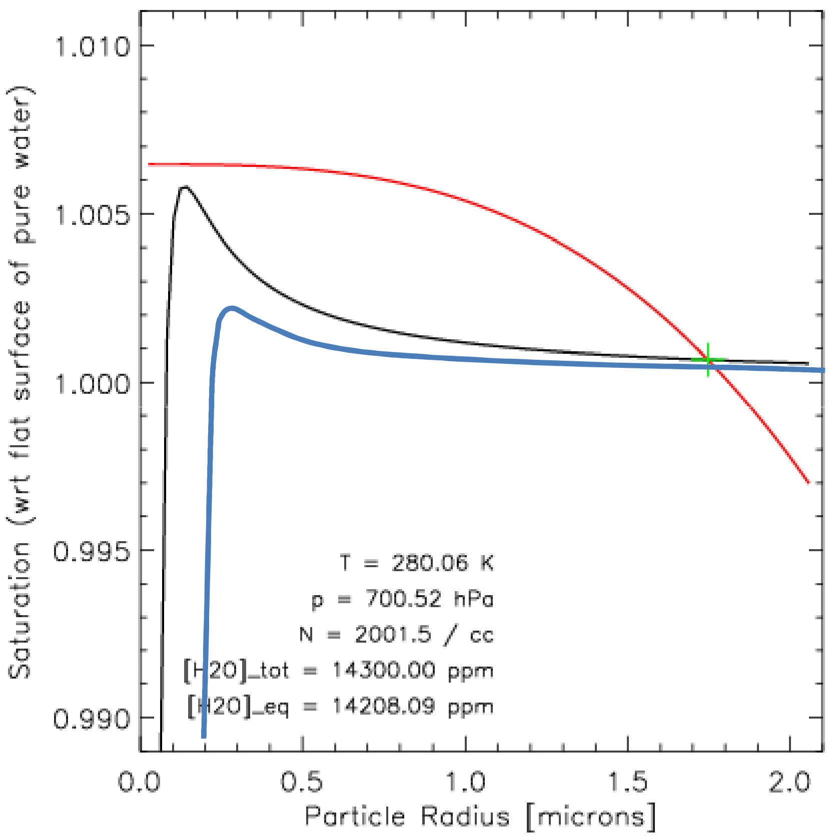

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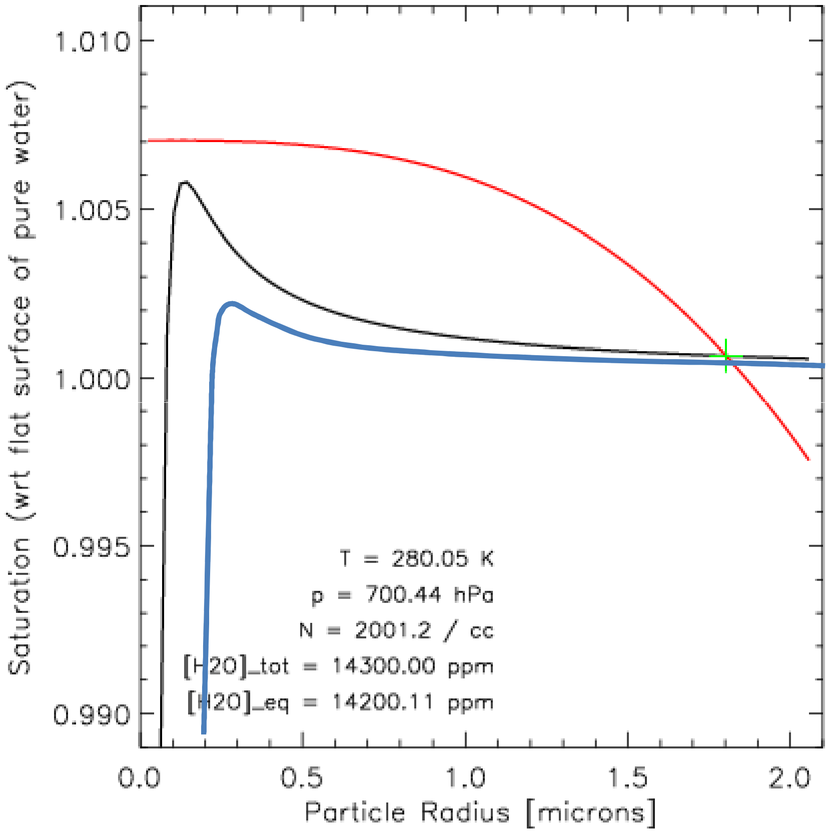

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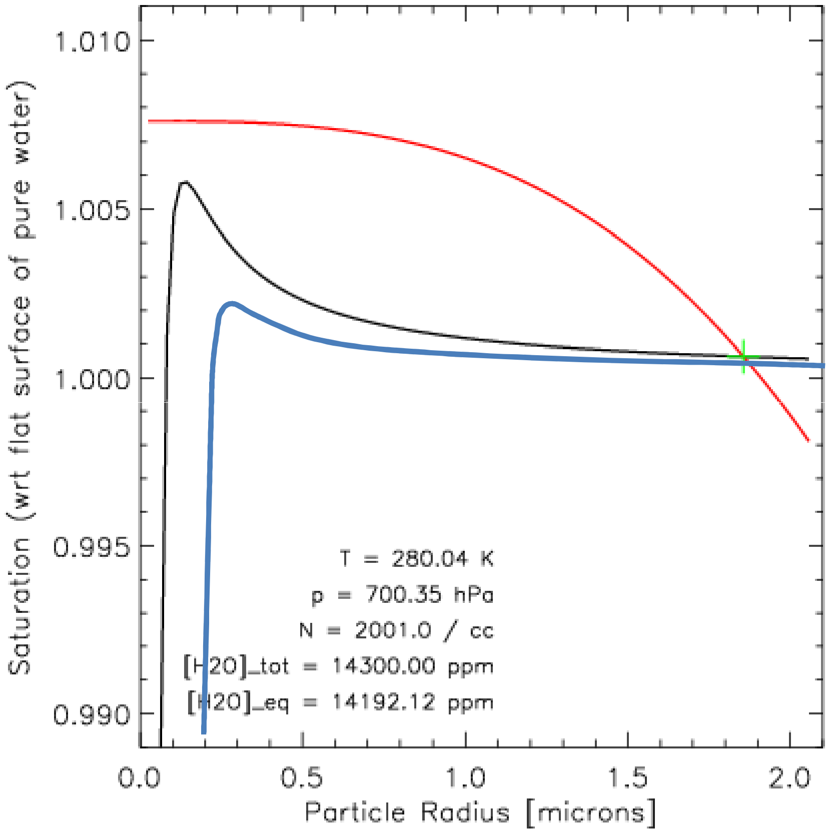

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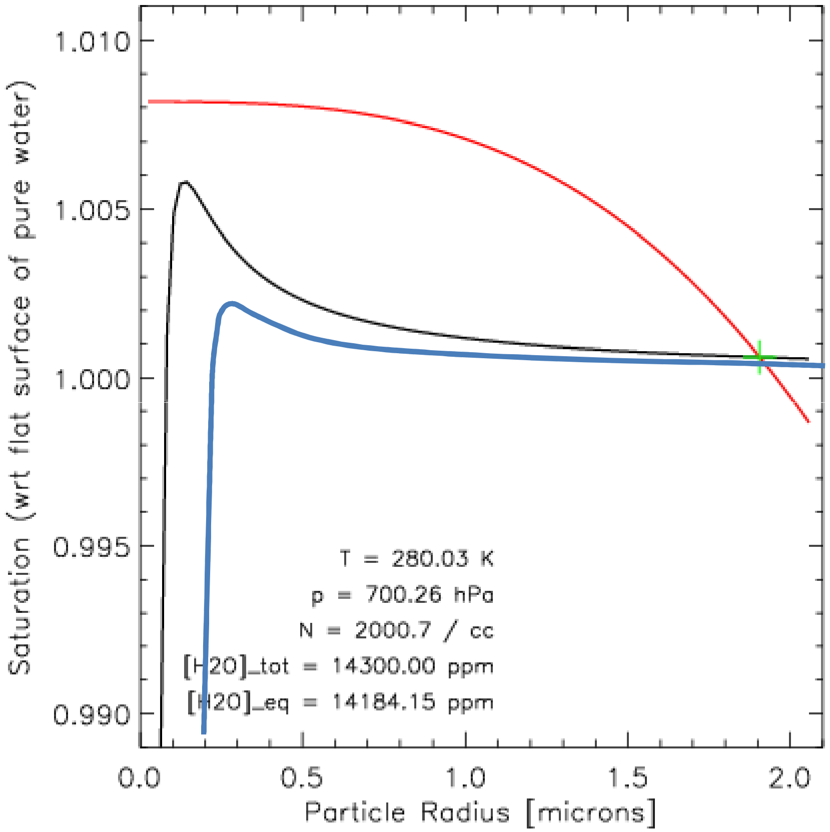

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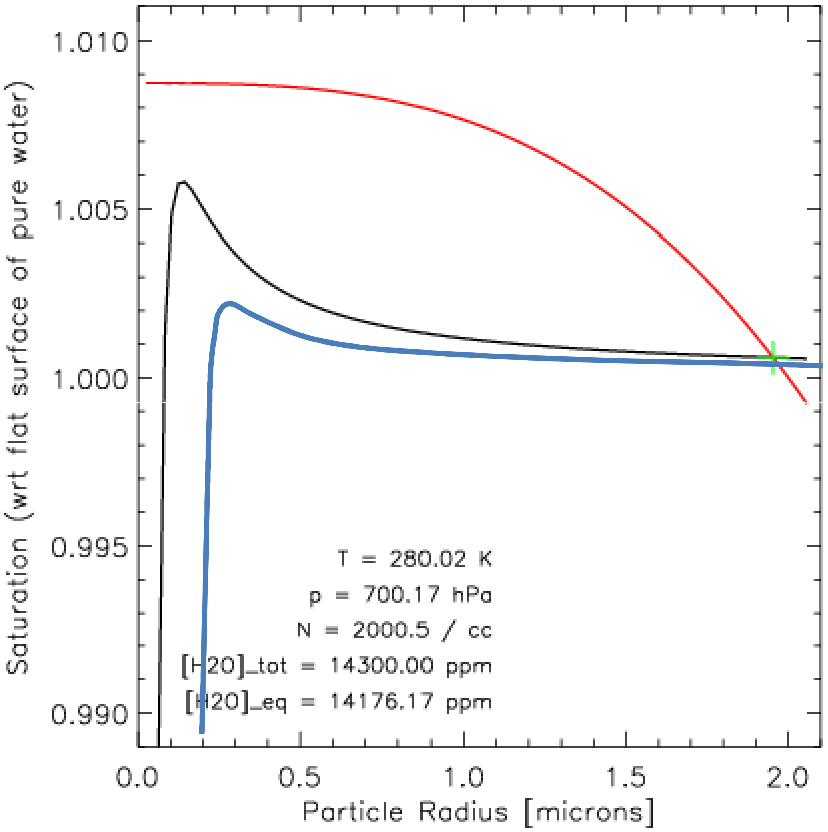

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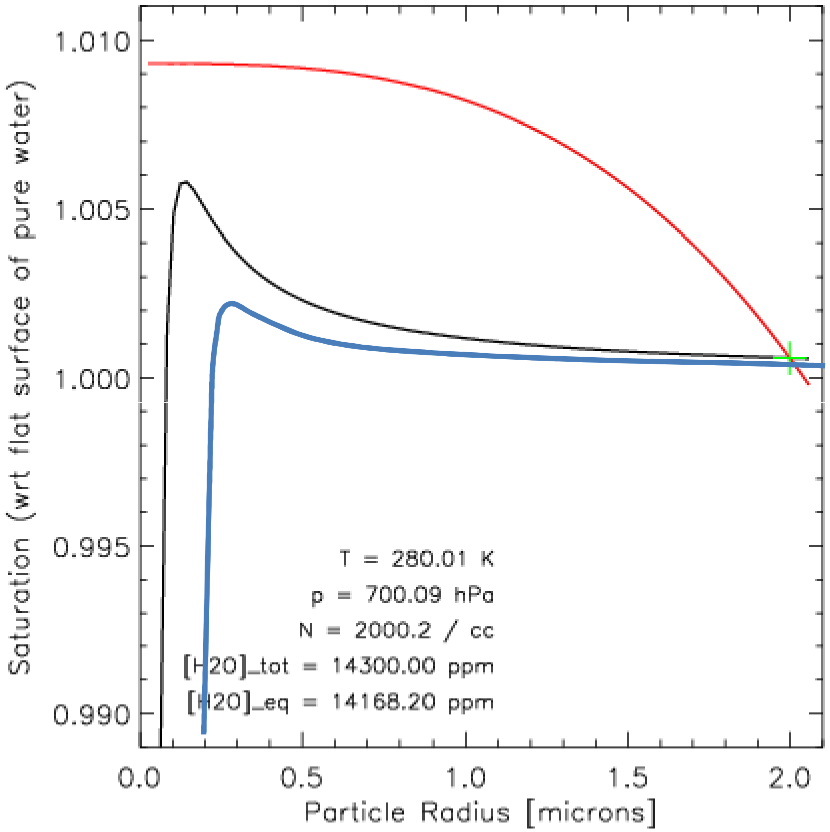

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Adiabatic cooling of an air parcel

Note: other processes, e.g. coalescence, also lead to large ptcle. formation

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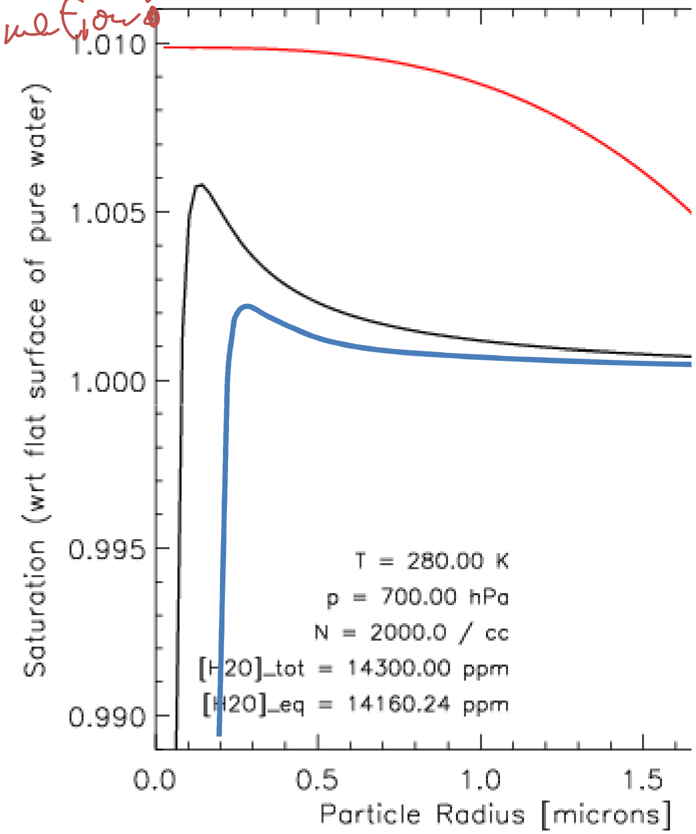


→ The minority has the “size advantage”. But whether it loses or wins the battle depends on the cooling rate, i.e. on kinetics.

For everyone who has will be given more, and he will have an abundance. Whoever does not have, even what he has will be taken from him.

Denn wer hat, dem wird gegeben, und er wird im Überfluss haben; wer aber nicht hat, dem wird auch noch weggenommen, was er hat.

Car à celui qui a, on donnera, et il aura encore davantage; mais à celui qui n'a pas, on ôtera même ce qu'il a.

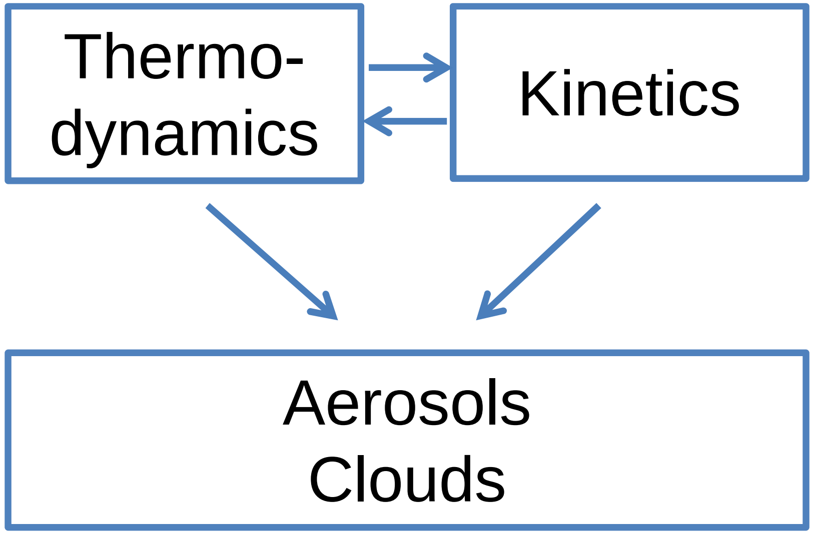
(Mt 25,29)

Mass balance:

$$p_w = n_w kT = \left(n_w^{tot} - N \frac{4\pi}{3} \frac{r^3}{\upsilon_w} \right) kT \quad \Rightarrow \quad S = \frac{p_w}{p_w^{vap}(T)} =$$

Formation of water clouds

Formation of Polar Stratospheric Clouds



Thermo-dynamics

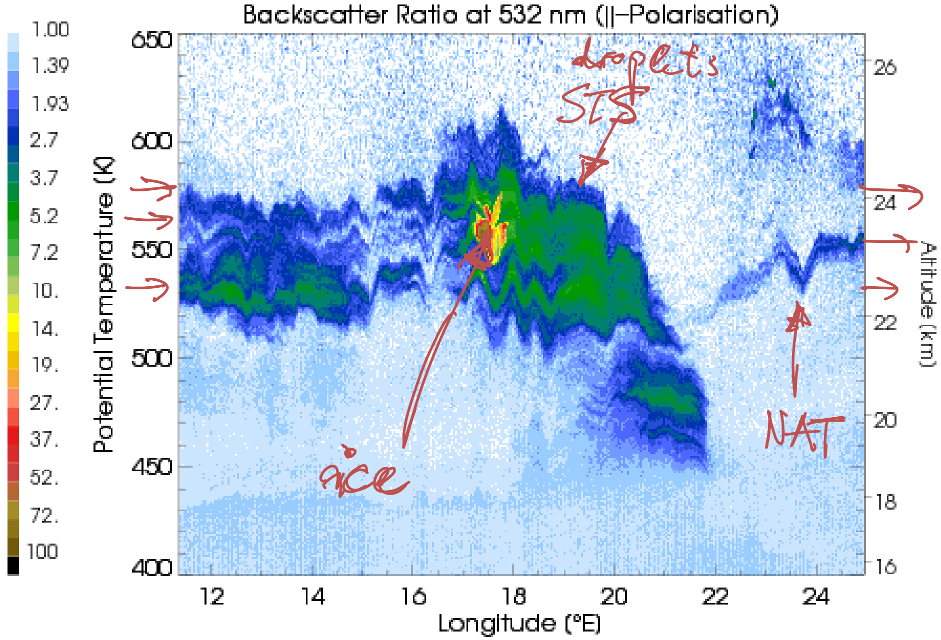
Kinetics

Aerosols
Clouds

How far do we get with thermodynamics in explaining cloud formation?

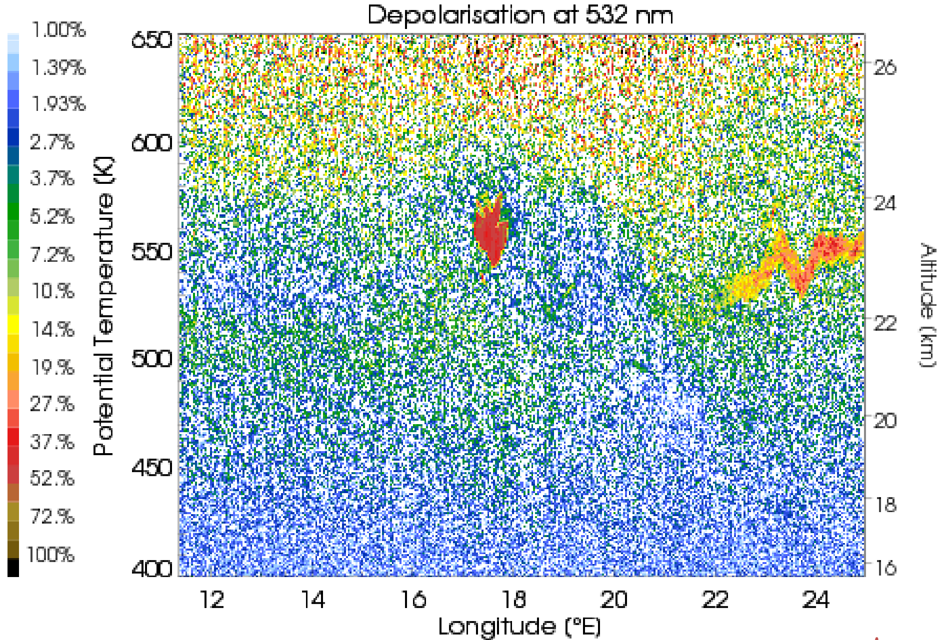
3 Types of
Polar Stratospheric Clouds (PSCs)

(1) Ice
(2) NAT (nitic acid trihydrate
= $HNO_3 \cdot 3H_2O$, crystalline)
(3) STS (supercooled ternary
solutions, $H_2SO_4/HNO_3/H_2O$)



Lidar observations
PSCs over the Norwegian Alps
Wirth et al. (1994)

sphericity
of scatterers



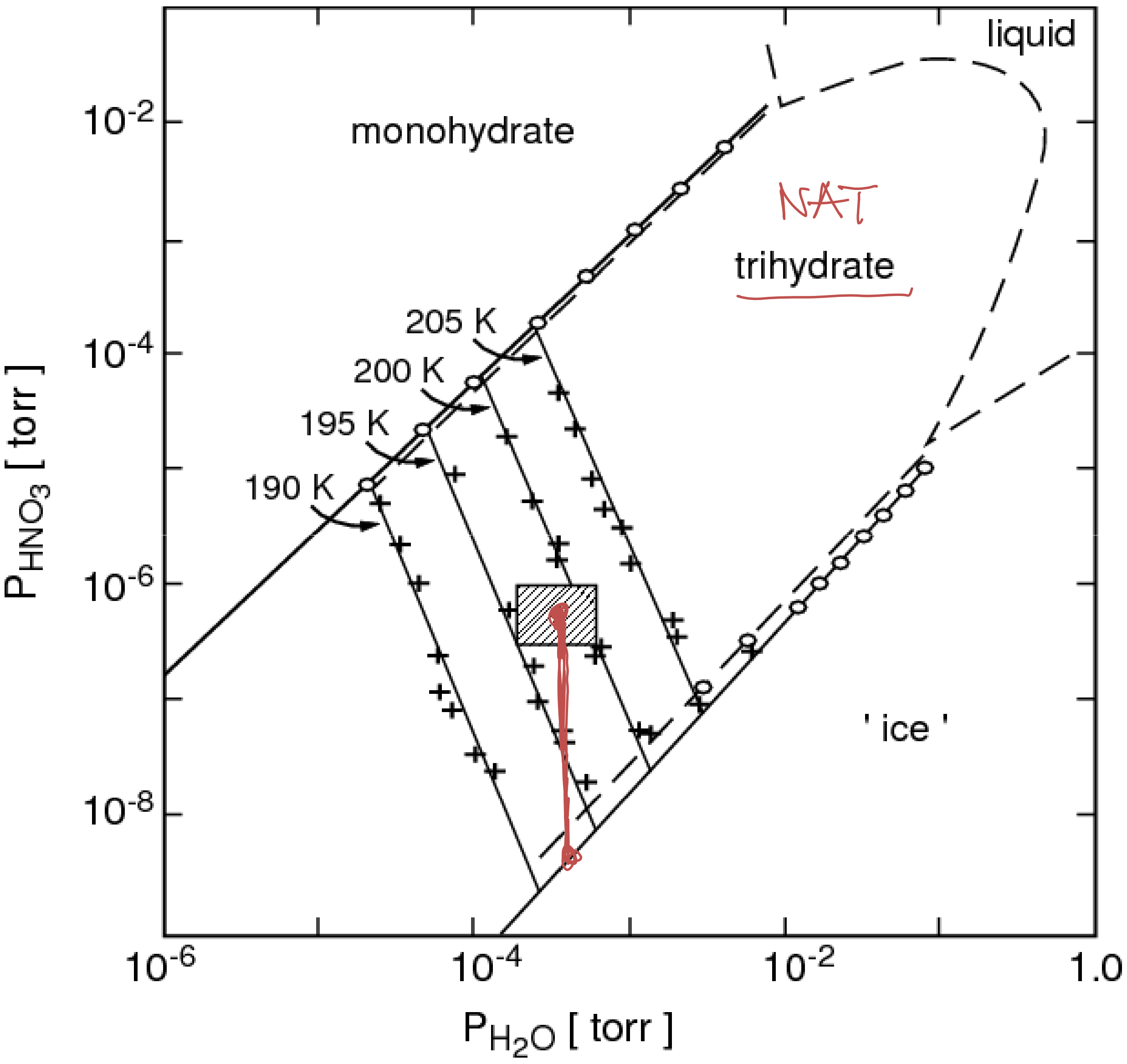
Scandinavian Alps

Hanson and Mauersberger (1986):

Mass spectrometric measurements
Formation of NAT PSCs

$T_{ice} \simeq 188$ K

$T_{NAT} \simeq 195$ K



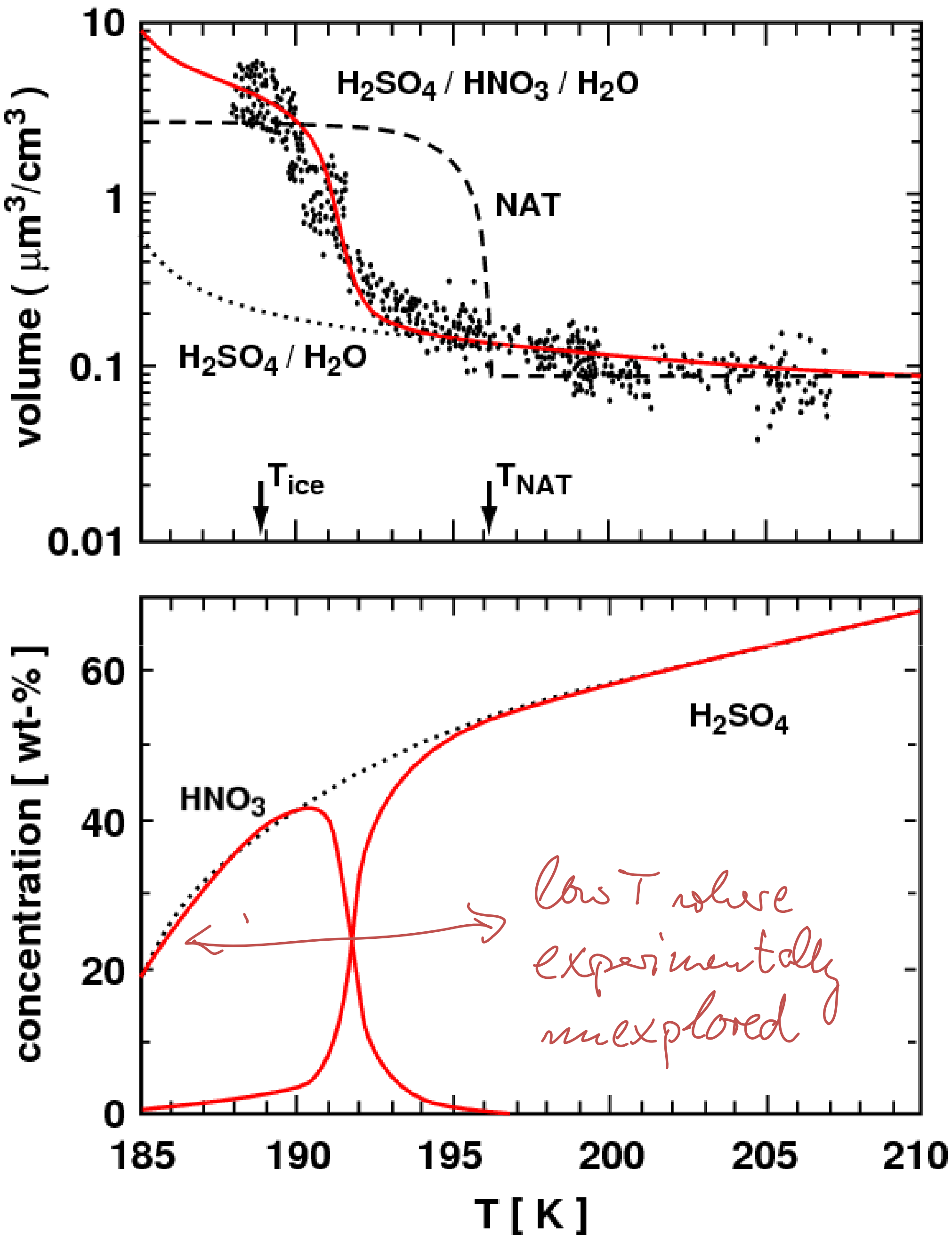
Carslaw et al. (1994):

Thermodynamic modeling of STS (supercooled ternary solutions, $H_2SO_4/HNO_3/H_2O$)

measurements

ER-2

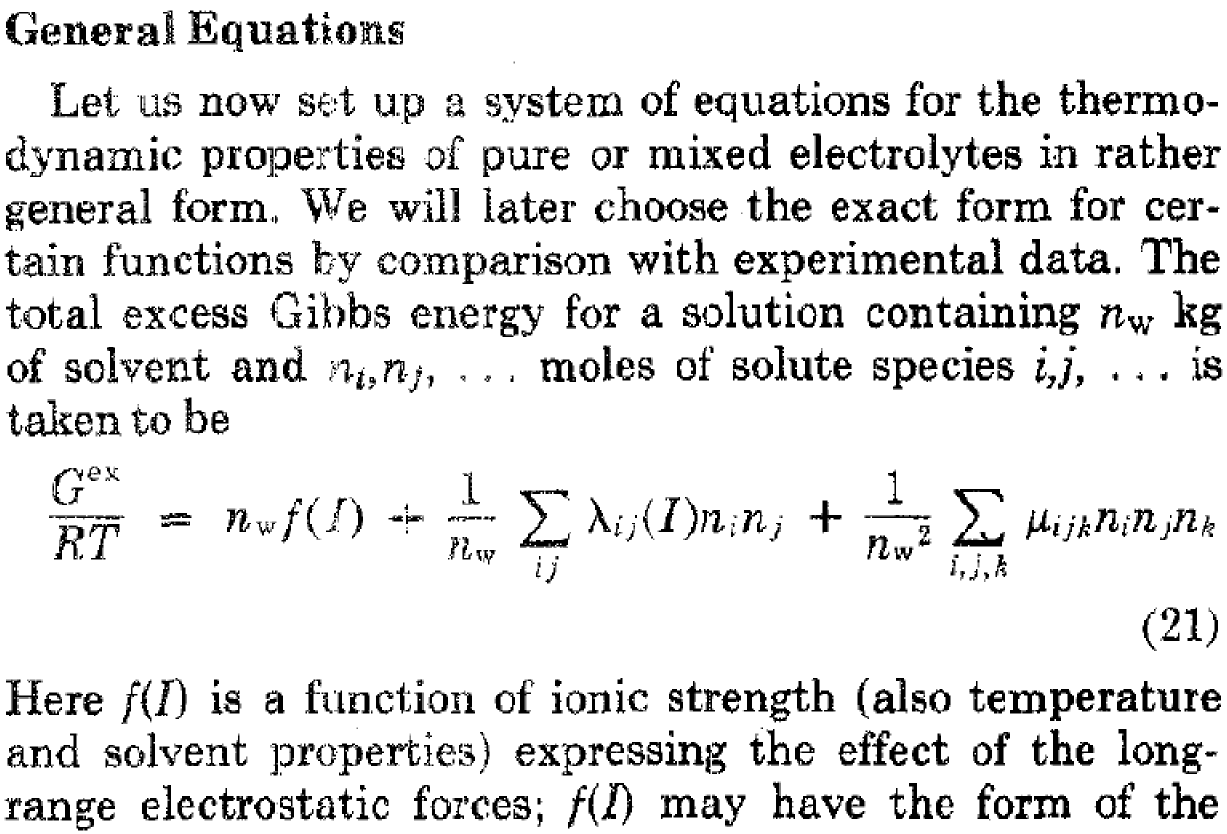
Norway → North Pole



low T where experimentally unexplored

Thermodynamics of Electrolytes.
I. Theoretical Basis and General Equations

Kenneth S. Pitzer, J. Phys. Chem., 77, 268 - 277, 1973:



General Equations

Let us now set up a system of equations for the thermodynamic properties of pure or mixed electrolytes in rather general form. We will later choose the exact form for certain functions by comparison with experimental data. The total excess Gibbs energy for a solution containing n_w kg of solvent and $n_i, n_j, \ldots$ moles of solute species $i, j, \ldots$ is taken to be

$$\frac{G^{ex}}{RT} = n_w f(I) + \frac{1}{n_w} \sum_{ij} \lambda_{ij}(I) n_i n_j + \frac{1}{n_w^2} \sum_{i,j,k} \mu_{ijk} n_i n_j n_k \qquad (21)$$

Here $f(I)$ is a function of ionic strength (also temperature and solvent properties) expressing the effect of the long-range electrostatic forces; $f(I)$ may have the form of the

Pitzer Ion-Interaction Model:

$$\frac{G^{ex}}{RT} = n_w f(I) + \frac{1}{n_w}\sum_{ij}\lambda_{ij} n_i n_j + \frac{1}{n_w^2}\sum_{ijk}\mu_{ijk} n_i n_j n_k + \ldots..$$

long range ionic
interaction potential
(I = ion strength)

short range
2-body interactions
of species (*i, j, k, w*)

short range
3-body interactions
of species (*i, j, k, w*)

neglect
higher order
terms

Activities: $\ln a_i = \frac{1}{RT} \times \frac{\partial G}{\partial n_i}$

Theoretical decription for *f*(*I*): Debye-Hückel theory (1928)

Data used to parameterize the ineraction potentials λ_{ij} , μ_{ijk} :

(1) p^{vap} measurements: for water $p_w = p_w^0 \times a_w$; $\ln a_w = \frac{1}{RT} \times \frac{\partial G}{\partial n_w}$

for solutes,
e.g. HCl ↔ H^+ + Cl^- $p_{HCl} = \frac{a_{H^+} a_{Cl^-}}{K_H}$; $\ln a_{HCl} = \frac{1}{RT} \times \frac{\partial G}{\partial n_i}$

(2) Electromotive force measurements: $E = E_0 + \frac{F}{RT} \times \ln(a_{H^+} a_{Cl^-})$

(3) Enthalpy measurements: $\Delta H = \frac{\partial(\Delta G / T)}{\partial(1/T)}$

(4) Measurements of heat capacities.
(5) Measurements of solubilities.
(6) Measurements of dissociation coefficients

Pitzer Ion-Interaction Model:

$$\frac{G^{ex}}{RT} = n_w f(I) + \frac{1}{n_w}\sum_{ij}\lambda_{ij} n_i n_j + \frac{1}{n_w^2}\sum_{ijk}\mu_{ijk} n_i n_j n_k$$

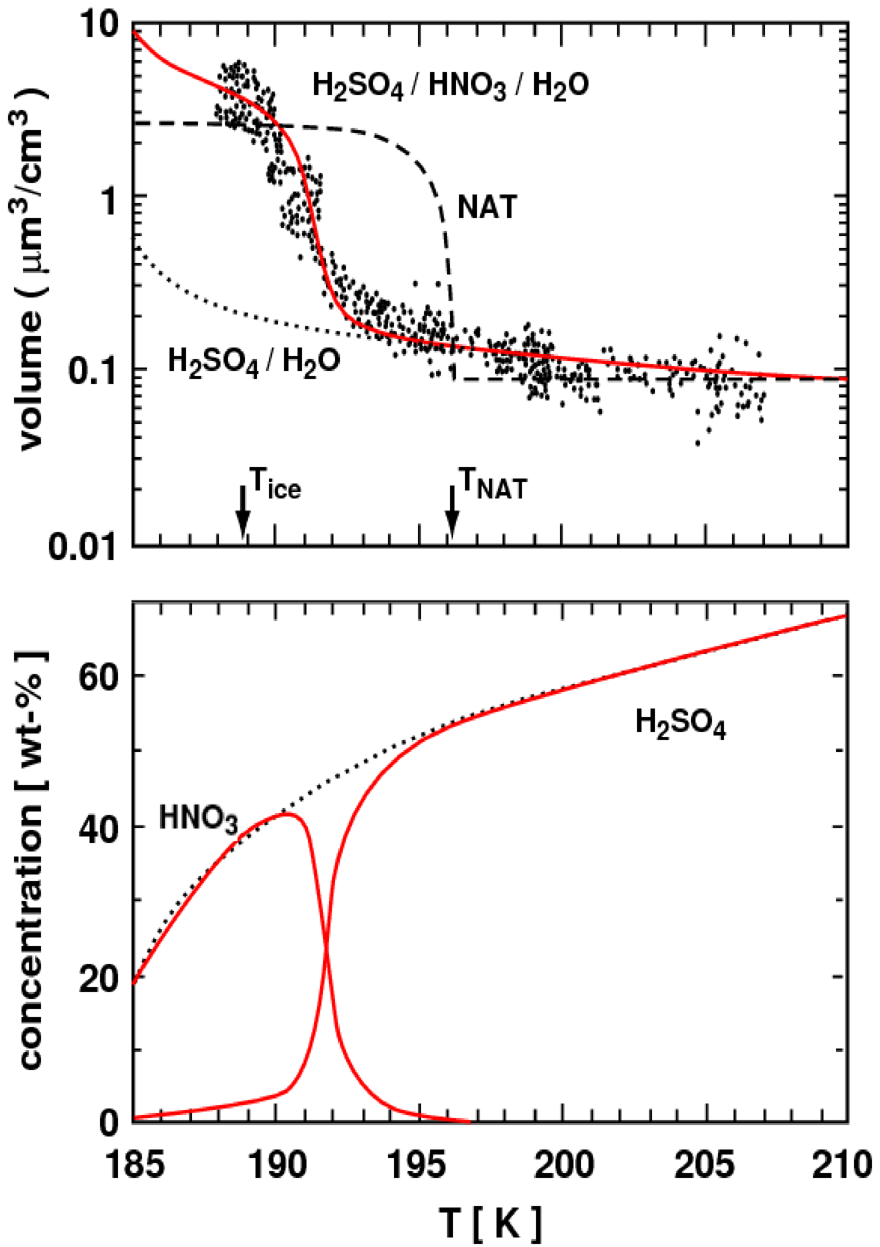
Activities: $\ln a_i = \frac{1}{RT} \times \frac{\partial G}{\partial n_i}$

p^{vap} for H_2O

→ $p_w = p_w^0 \times a_w$; $\ln a_w = \frac{1}{RT} \times \frac{\partial G}{\partial n_w}$

p^{vap} for HNO_3

→ $p_{HNO_3} = \frac{a_{H^+} a_{NO_3^-}}{K_H}$; $\ln a_{HNO_3} = \frac{1}{RT} \times \frac{\partial G}{\partial n_i}$



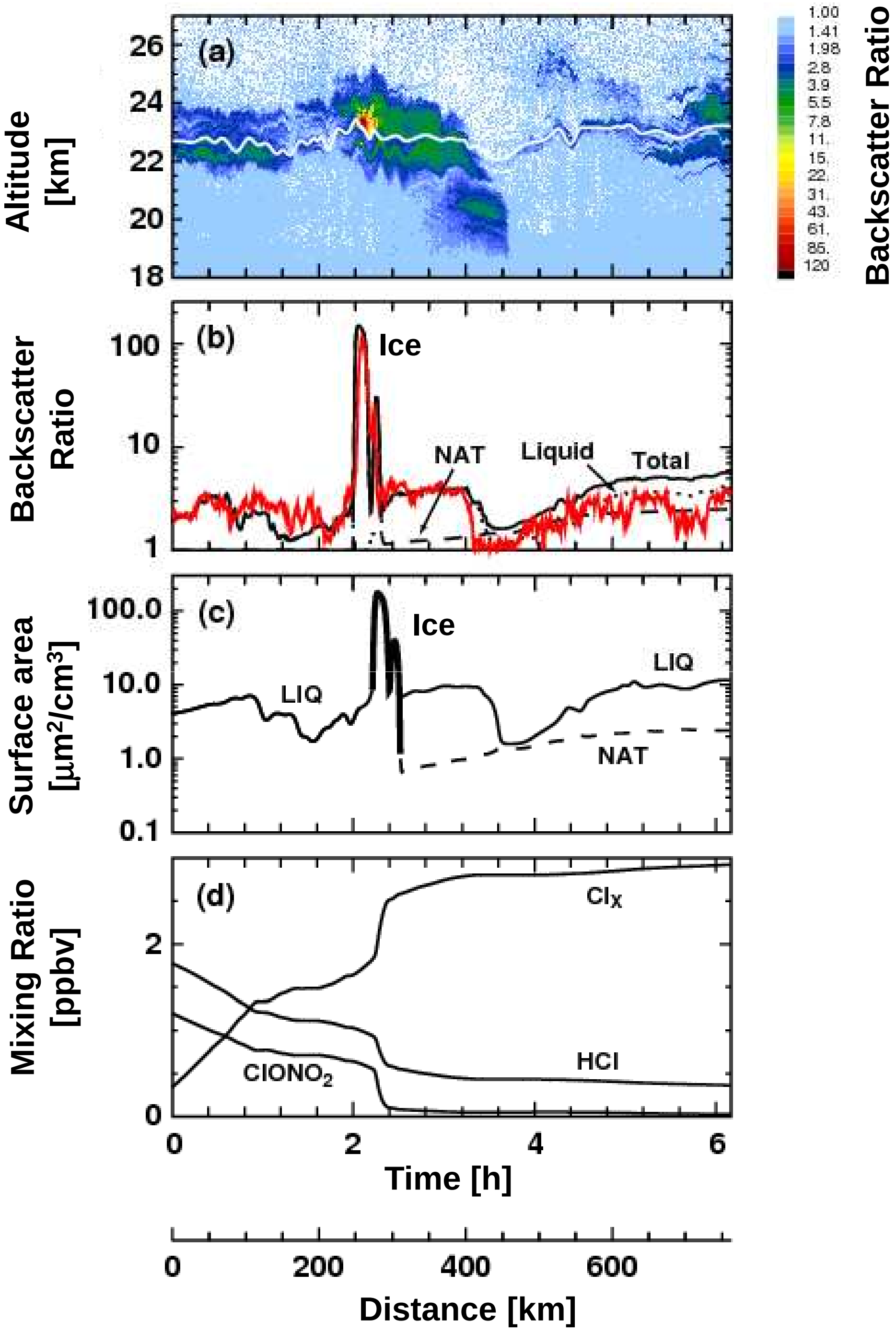
Box modeling of PSCs

(a) Lidar backscatter ratio

(b) Backscatter along trajectory of ice, NAT and STS
Red: measured, black: calc.

(c) Calculated surface area densities

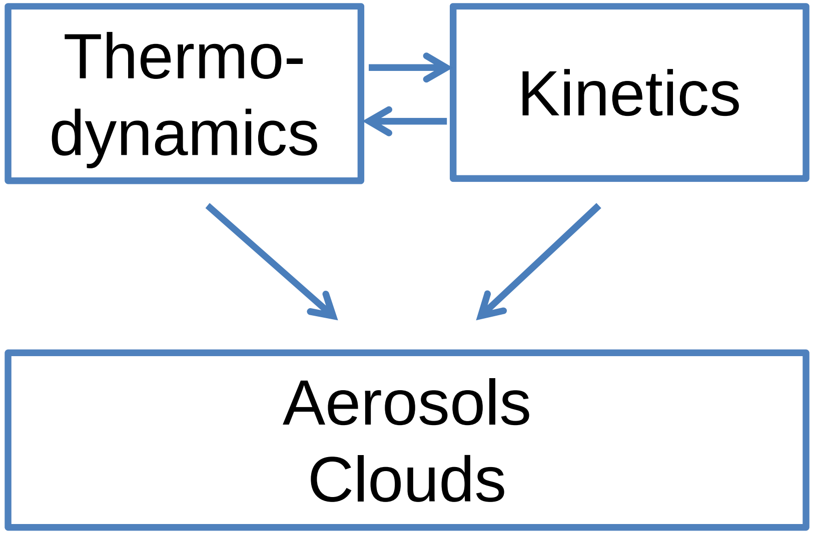
(d) Calculated chemical effects, mainly due to
$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$



Formation of water clouds

Formation of Polar Stratospheric Clouds

Deliquescence of aerosols



Thermo-dynamics

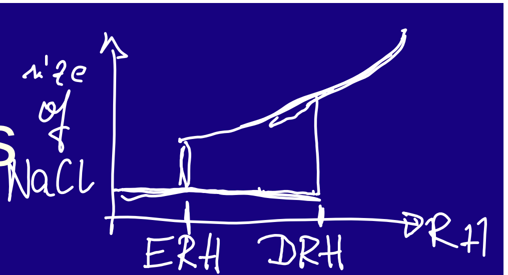
Kinetics

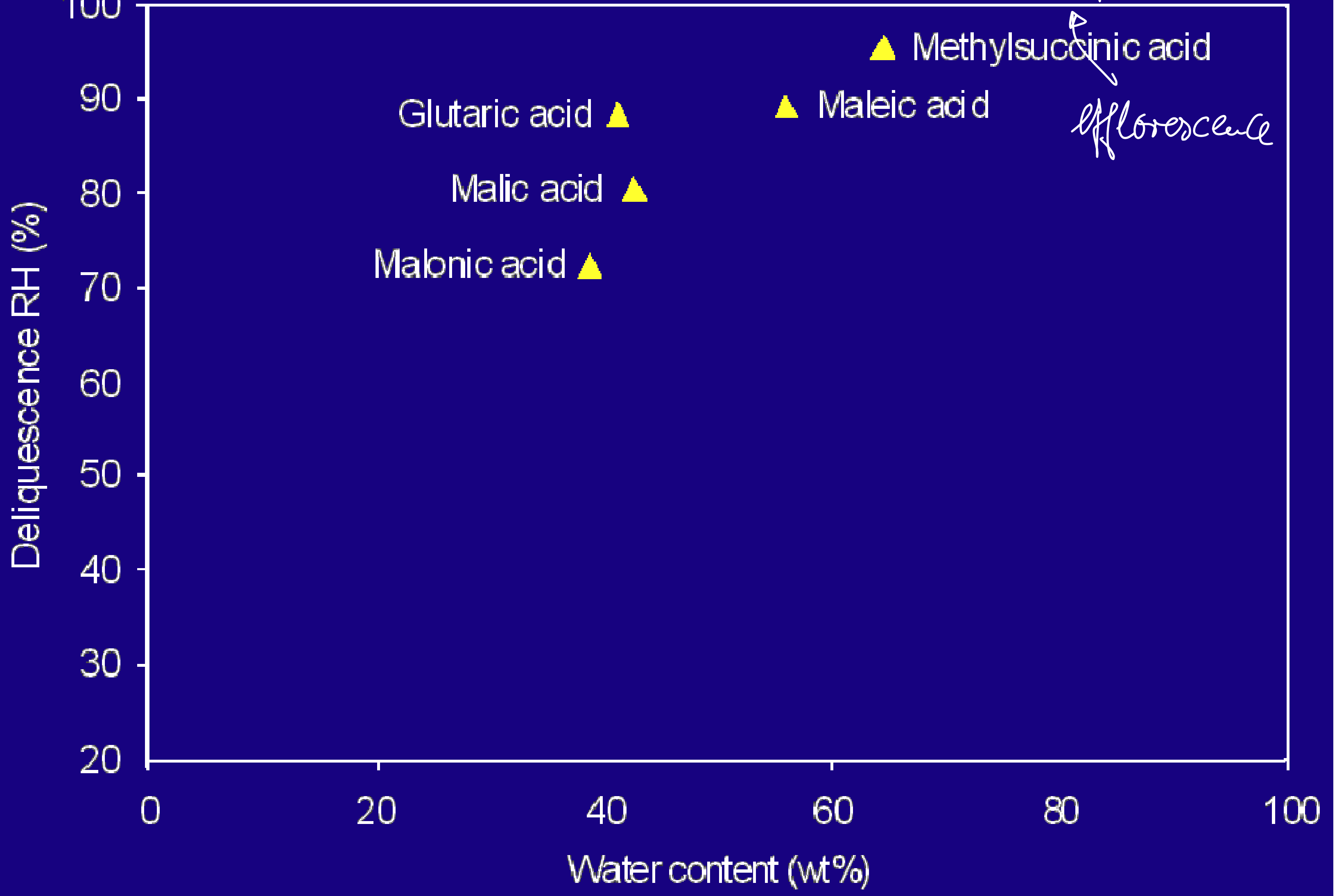
Aerosols
Clouds

How far do we get with thermodynamics in explaining cloud formation?

Deliquescence RH of organic mixtures

DRH



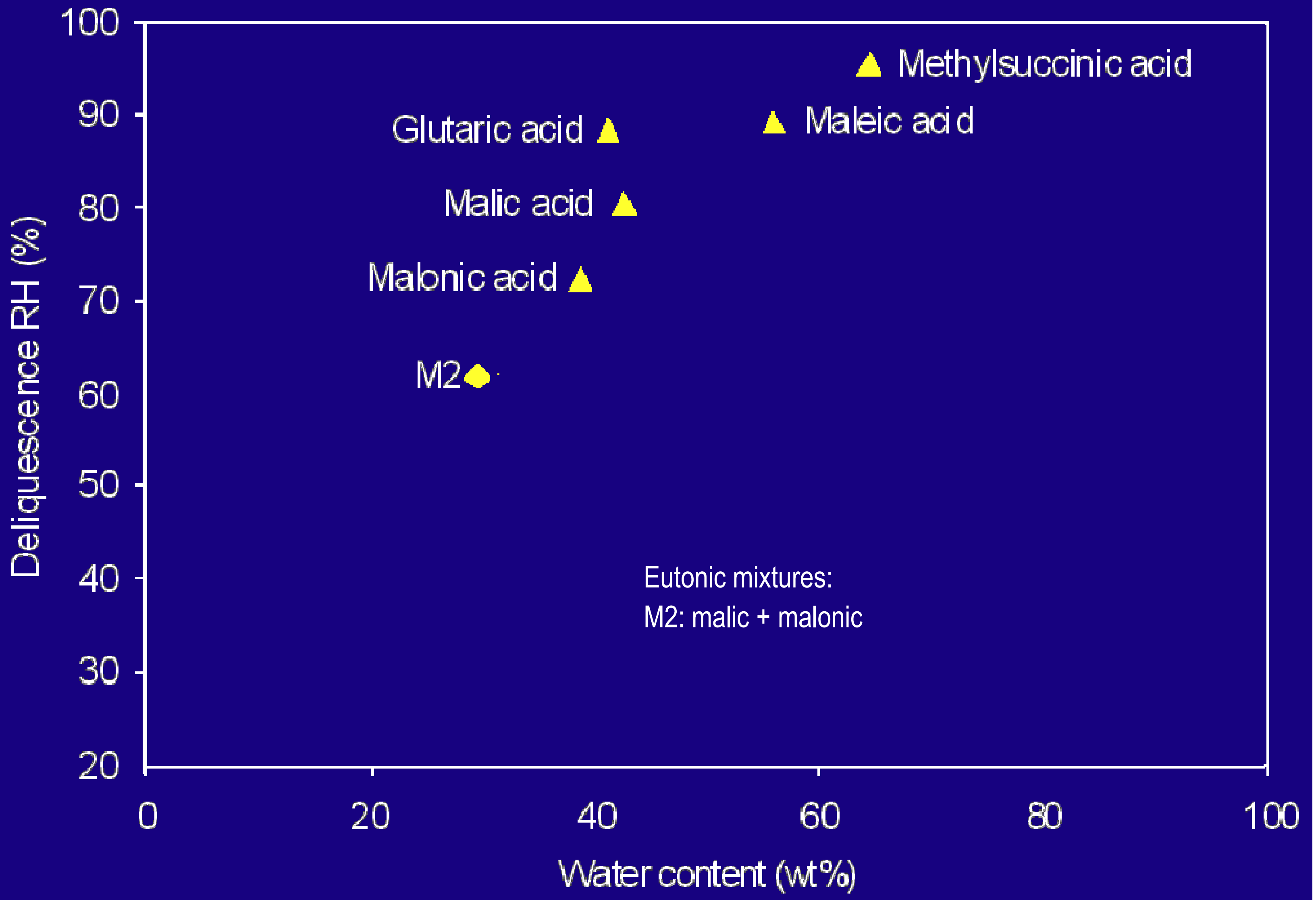


efflorescence

T = 25°C

Marcolli et al. (2004)

Deliquescence RH of organic mixtures

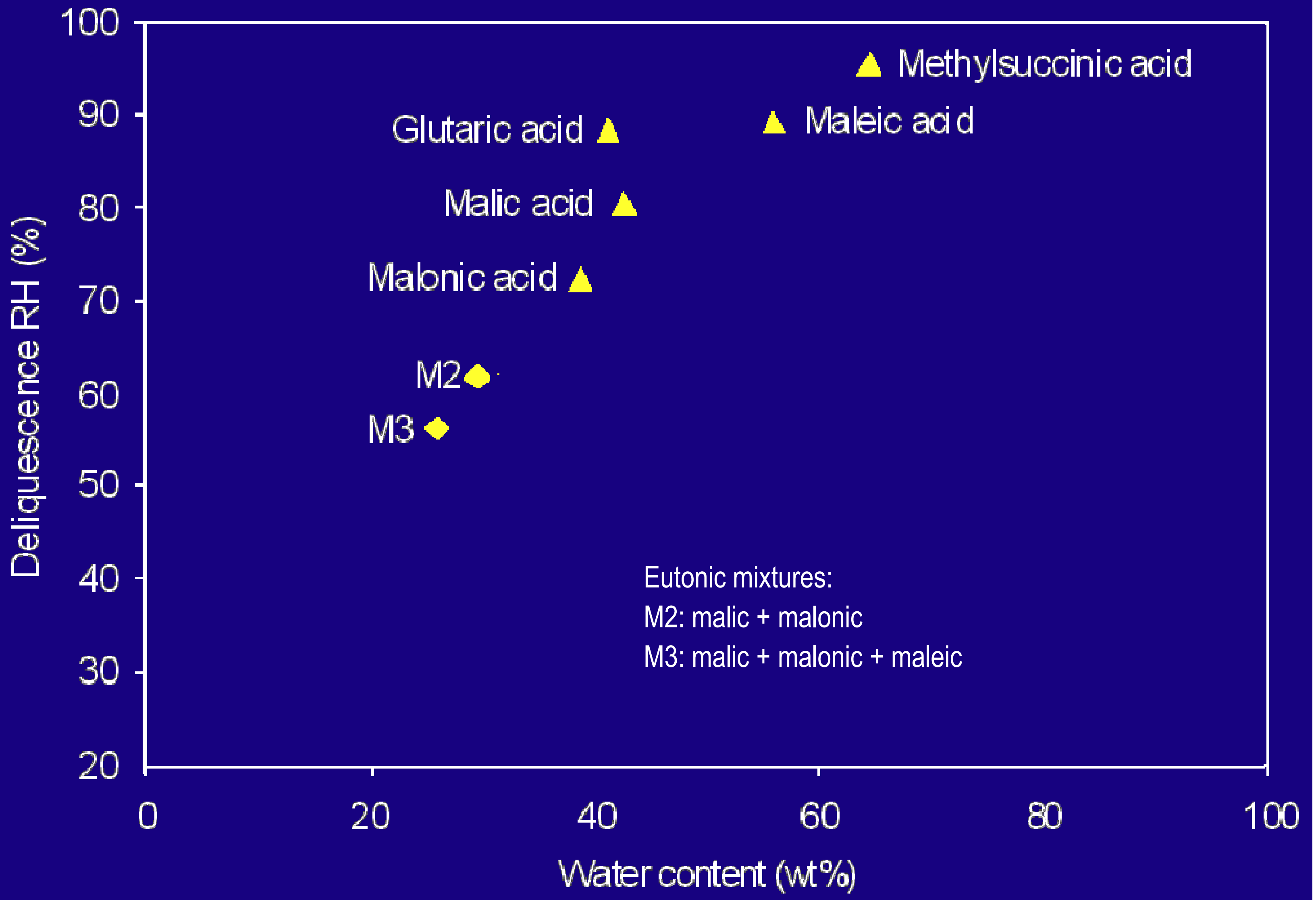


Eutonic mixtures:
M2: malic + malonic

T = 25°C

Marcolli et al. (2004)

Deliquescence RH of organic mixtures

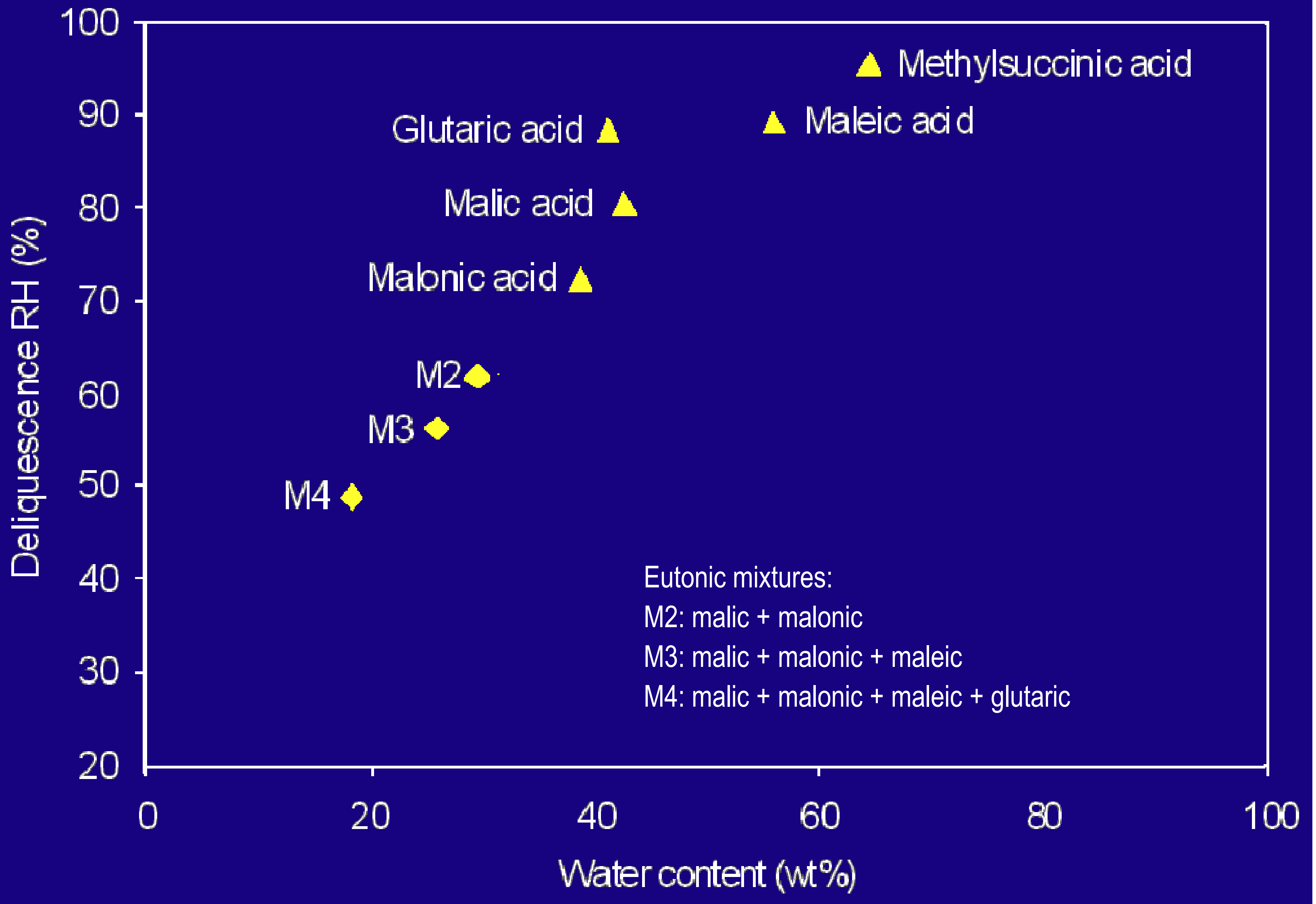


Eutonic mixtures:
M2: malic + malonic
M3: malic + malonic + maleic

T = 25°C

Marcolli et al. (2004)

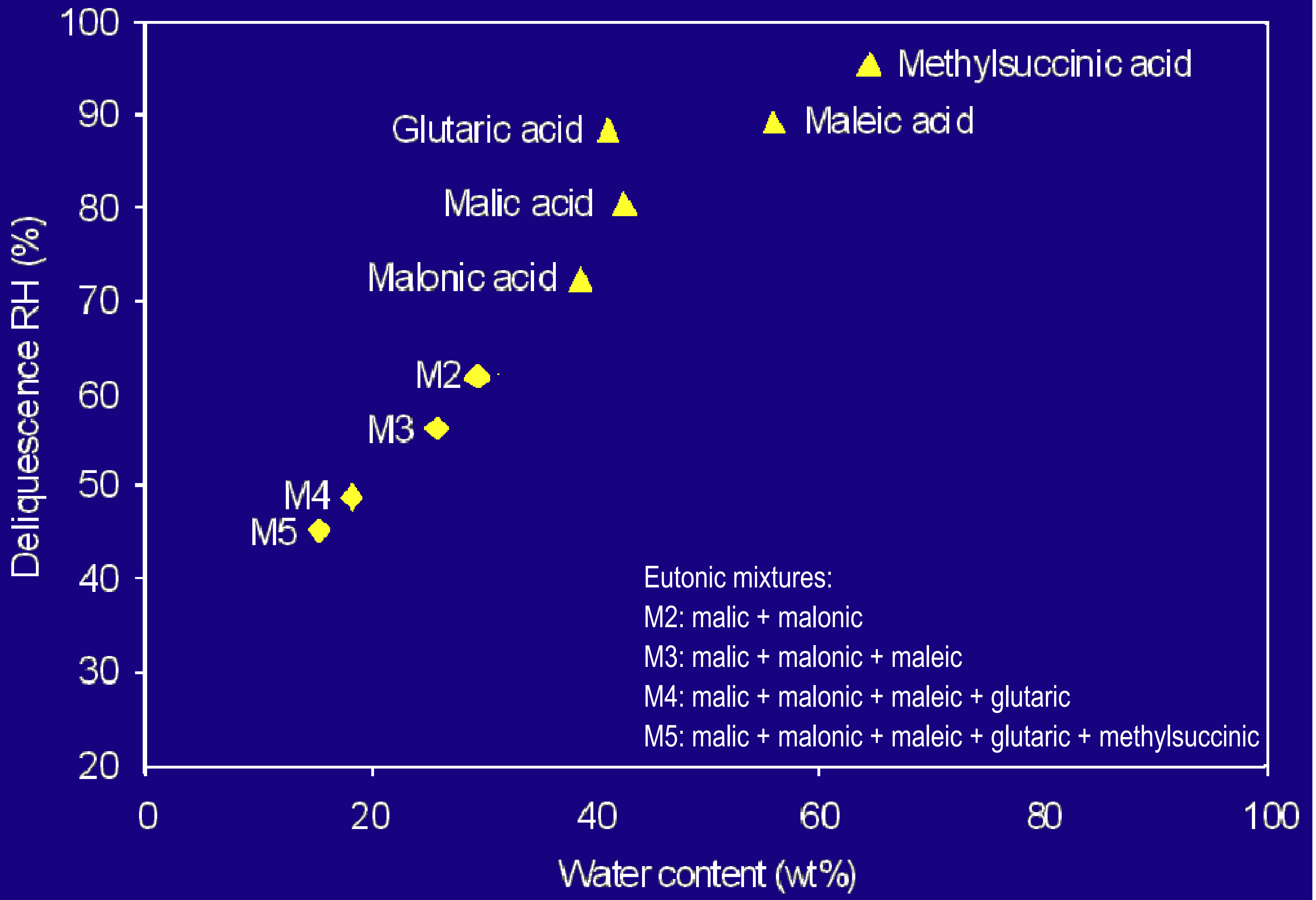
Deliquescence RH of organic mixtures



T = 25°C

Marcolli et al. (2004)

Deliquescence RH of organic mixtures

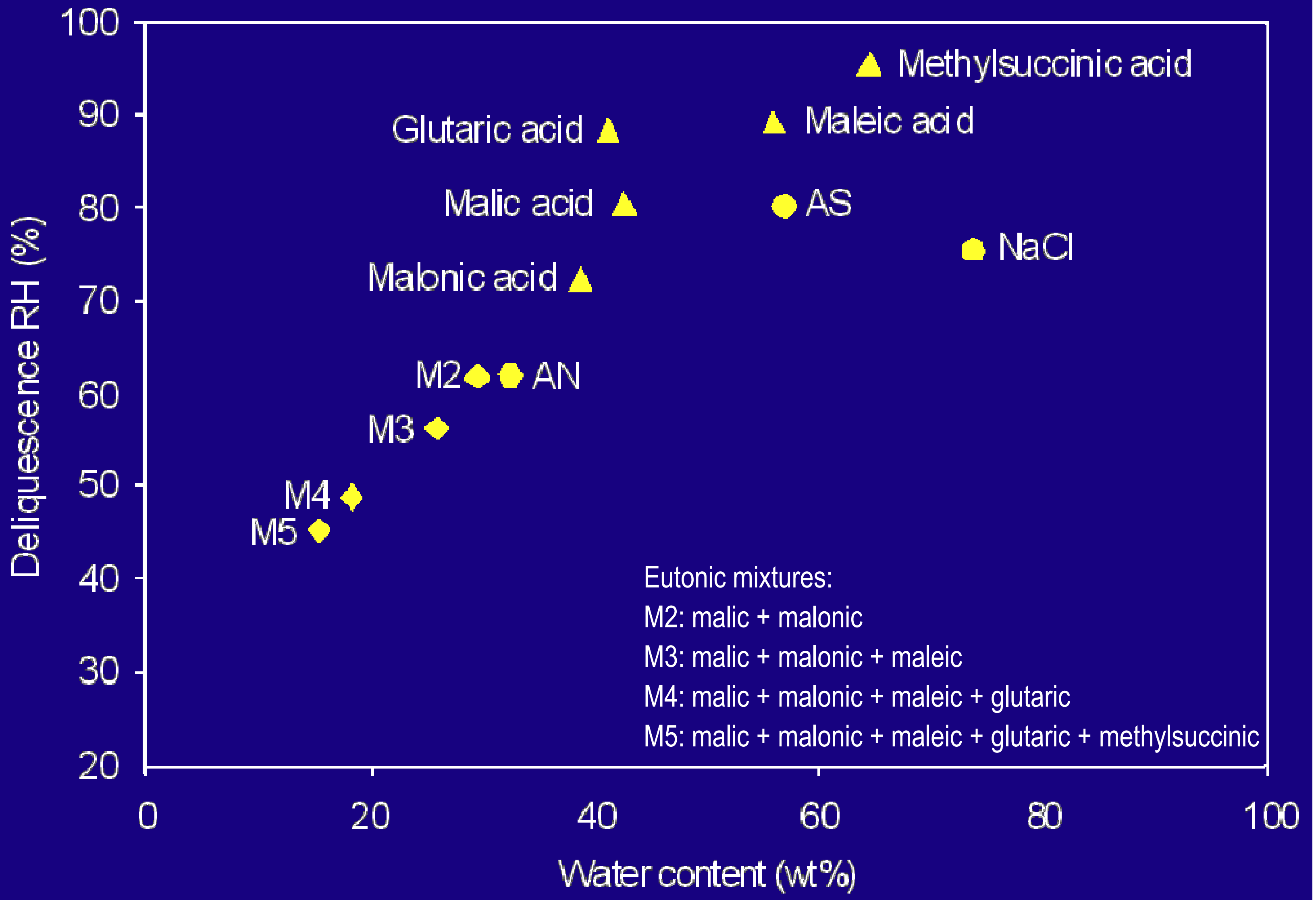


Eutonic mixtures:
M2: malic + malonic
M3: malic + malonic + maleic
M4: malic + malonic + maleic + glutaric
M5: malic + malonic + maleic + glutaric + methylsuccinic

T = 25°C

Marcolli et al. (2004)

Deliquescence RH of organic mixtures



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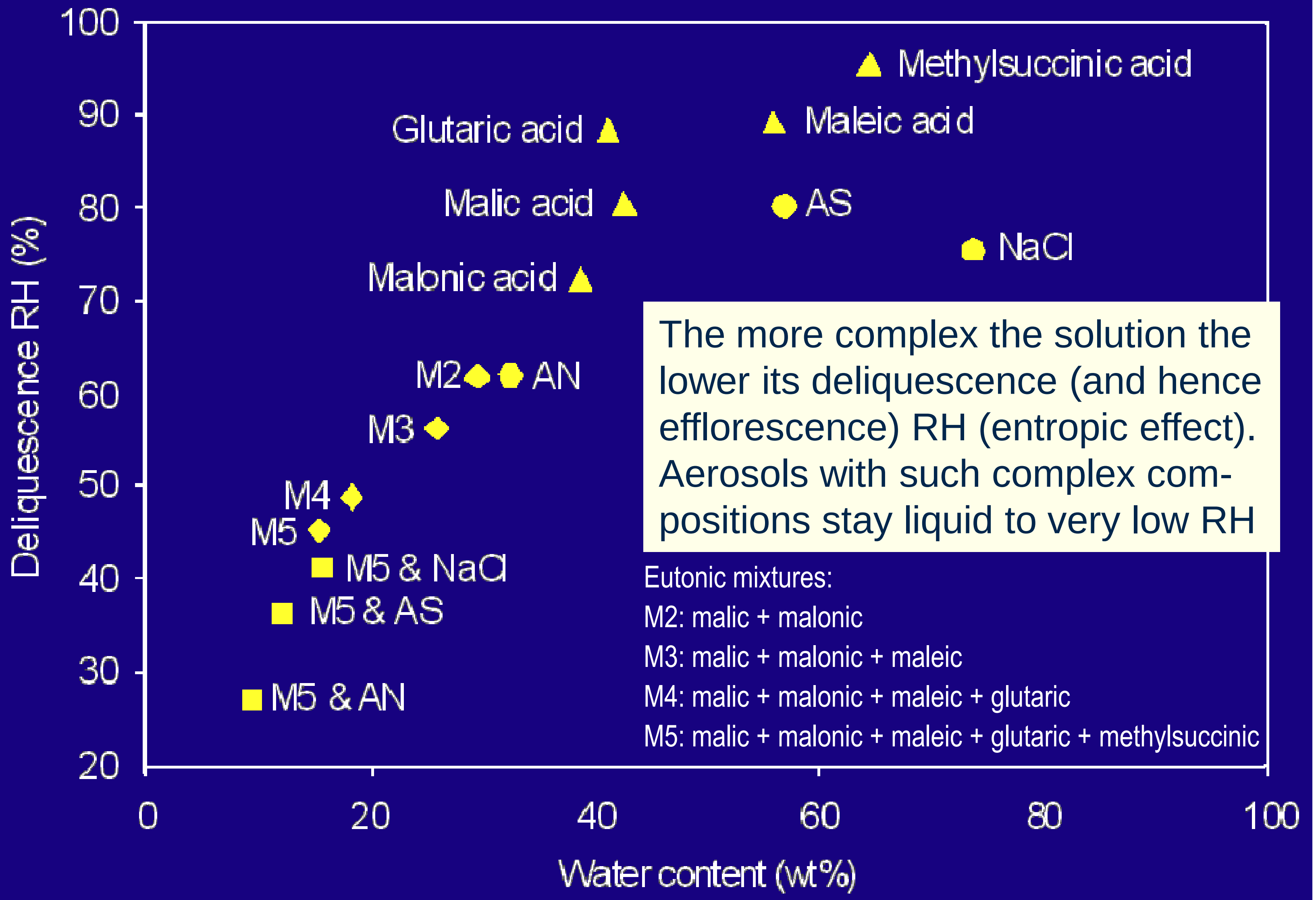

The more complex the solution the lower its deliquescence (and hence efflorescence) RH (entropic effect). Aerosols with such complex compositions stay liquid to very low RH

Eutonic mixtures:
M2: malic + malonic
M3: malic + malonic + maleic
M4: malic + malonic + maleic + glutaric
M5: malic + malonic + maleic + glutaric + methylsuccinic

T = 25°C

Marcolli et al. (2004)

Formation of water clouds

Formation of Polar Stratospheric Clouds

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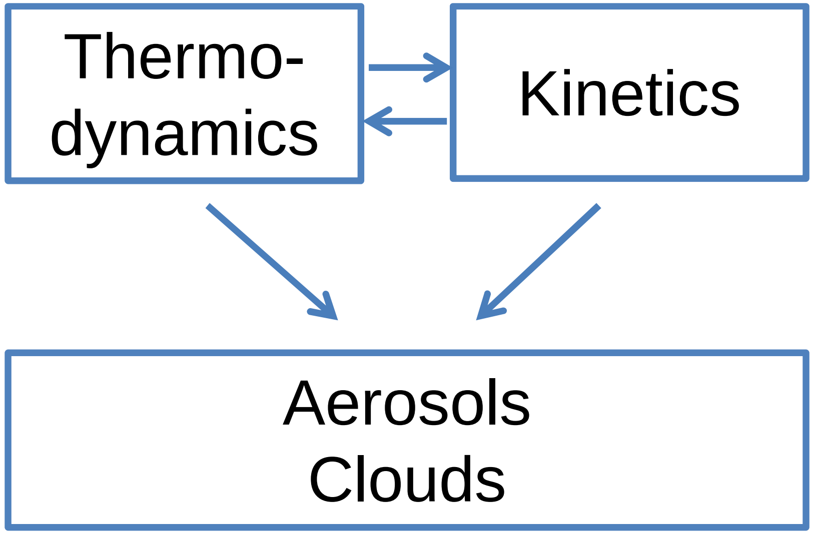


Thermo-dynamics

Kinetics

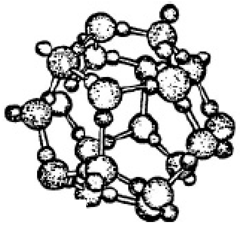
Aerosols
Clouds

Homogeneous nucleation of water droplets

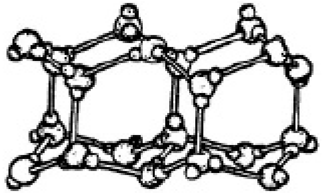
How far do we get with thermodynamics in explaining cloud formation?
When do we need a kinetic treatment?

Nucleation

Formation of a critical cluster from a sequence of bimolecular additions:



Clathrate structure



Ice –I_h structure
(Hale & Plummer, 1974)

$A + A \leftrightarrow A_2$ e.g. $A = H_2O$

$A_2 + A \leftrightarrow A_3$

…

$A_{i-1} + A \leftrightarrow A_i$ (critical cluster)

molec
dynamics
simulations

- supersaturation: necessary but not sufficient
- need to form new surface (Kelvin equation)
- need to overcome energy barrier by a critical cluster

What energy is needed to form a critical cluster?

What is the size of the critical cluster?

Excess free energy for cluster formation: $\Delta G = \Delta G_S + \Delta G_V$

$\Delta G_S > 0$ → excess free energy required to form cluster surface (expense)

$\Delta G_V < 0$ → excess free energy released from volume transformation (gain)

Nucleation: Classical Theory – a poor man's approach

$$\begin{aligned}\Delta G &= \Delta G_s + \Delta G_v \\ &= A\sigma - n\Delta\mu \\ &= 4\pi r^2\sigma - \frac{4\pi r^3}{3v_m}\Delta\mu\end{aligned}$$

μ = chemical potential

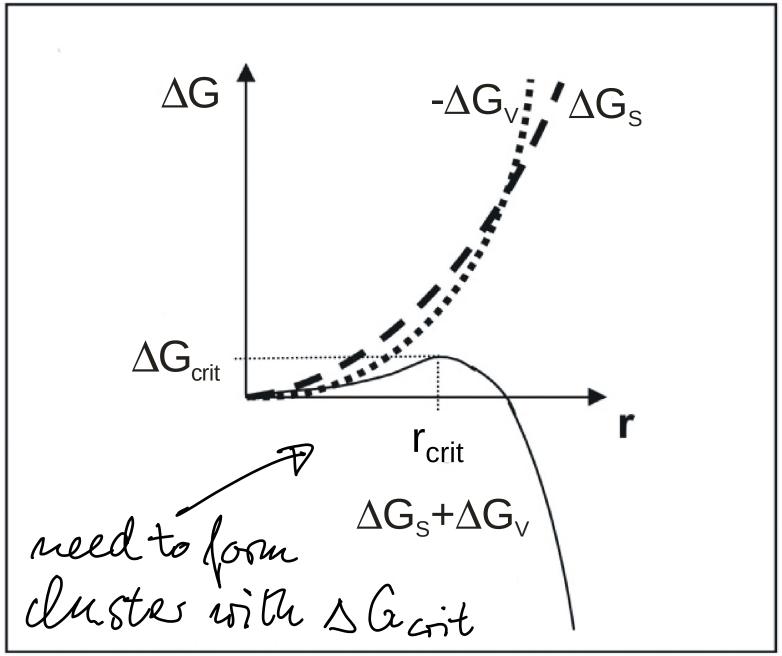
where

$$\Delta\mu = \mu_g - \mu_l = kT\ln\left(\frac{p}{p(\infty)}\right)$$

look for max (ΔG)

→ Critical radius:

$$r_c = \frac{2\sigma v_m}{\Delta\mu}$$



need to form clusters with ΔG_{crit}

→ Critical energy (barrier):

$$\begin{aligned}\Delta G_{crit} &= \frac{16\pi\sigma^3 v_m^2}{(\Delta\mu)^2} - \frac{32\pi\sigma^3 v_m^2}{3(\Delta\mu)^2} \\ &= \frac{16\pi\sigma^3 v_m^2}{3(\Delta\mu)^2} = \frac{16\pi\sigma^3 v_m^2}{3k^2T^2(\ln(p/p(\infty)))^2}\end{aligned}$$

Assumptions?

σ = surface tension
v_m = molar volume
$p(\infty)$ = flat surface vapor pressure
} from bulk

If we assume an **Arrhenius reaction velocity equation** commonly used for the rate of a thermally activated process, the rate of nucleation, J, is given as:

$$J = K \exp\left(- \frac{\Delta G_{crit}}{kT} \right) = K \exp\left(- \frac{16\pi\sigma^3 v_m{}^2}{3k^2T^2\left(\ln(p/p(\infty))\right)^2} \right)$$

Obtain prefactor *K* from kinetic collision frequency:

$$K = \left(\frac{2\sigma}{\pi m_m} \right)^{1/2} \frac{v_m N_v^2}{S}$$

m_m : molecular mass
N_v : vapor concentration

1Å = 0.1 nm

Example: critical radius, number, and nucleation rate for water droplets at 298 K

$p/p(\infty)$	r_c (Å)	$i_c = \frac{\#\text{molec}}{\text{cluster}}$	J ($cm^{-3}s^{-1}$)
1	∞	∞	$-\infty$
2	15.1	482	1.3×10^{-47}
3	9.5	121	8.9×10^{-4}
4	7.6	60	$6.4 \times 10^{+7}$
5	6.5	39	$3.8 \times 10^{+11}$

} no nucleation

} switch on nucl.

$\sigma = 0.072$ N/m ; $\nu_m = 2.99 \times 10^{-29}$ m^3 ; $m_m = 2.99 \times 10^{-26}$ kg

Experiments on homogeneous nucleation from vapors by a nucleation pulse method

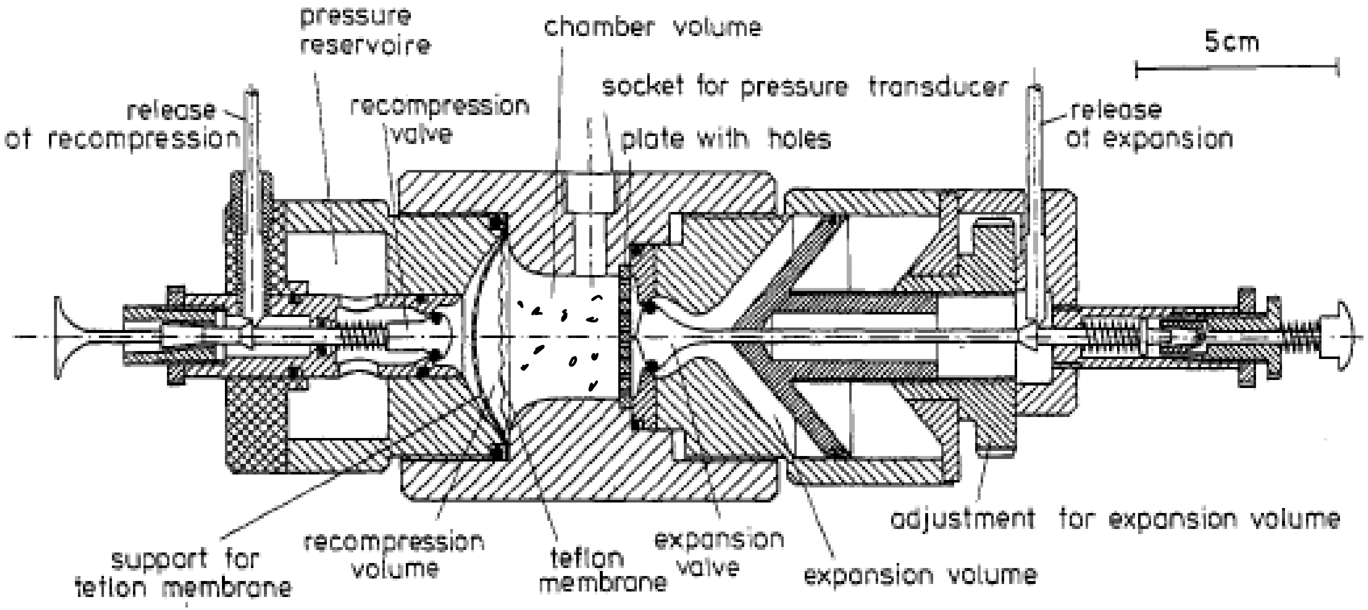
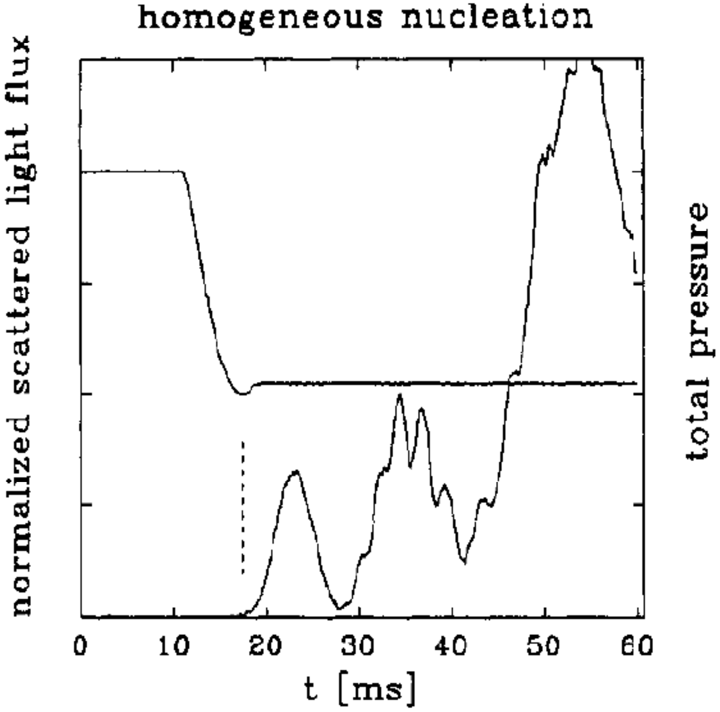


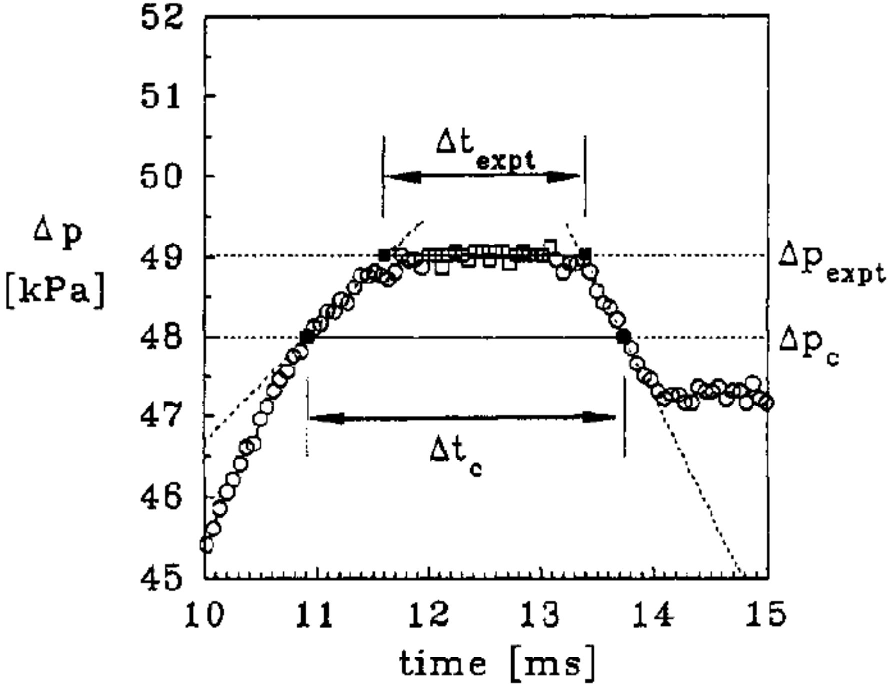
Figure 2. Cross section of the expansion chamber showing the main design features to scale. Expansion and recompression valve are released by a rotating-trigger unit in a well-defined time sequence.

tiny particles
not visible

- Premixed vapor and carrier gas (Xe, Kr, Ar, Ne or He)
- Expansion is held for t_{exp} (a few ms)
- Small recompression to quench further nucleation
  → nuclei can grow into droplets of observable size (μm)
- Number density C of the droplets obtained from scattered light
  → $J = C / t_{exp}$

Wagner & Strey, JPC 1983
Strey et al., JPC, 1994





Homogeneous nucleation exp.:

p_{tot} and scattered light flux, $\theta = 15^\circ$

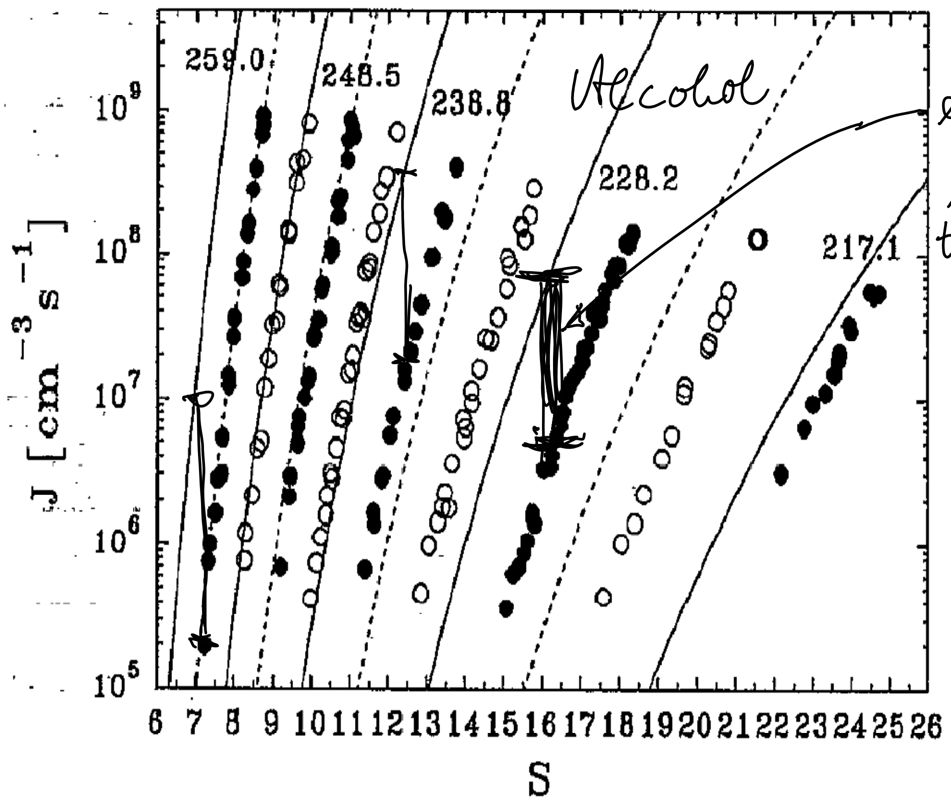
Significant light scattering occurs only ***after*** the nucleation pulse

Nucleation pulse:

Obtain experimental pressure drop Δp_{expt} and duration Δt_{expt} of the nucleation pulse

Strey et al., JPC, 1994, 98, 7748 – 7758.

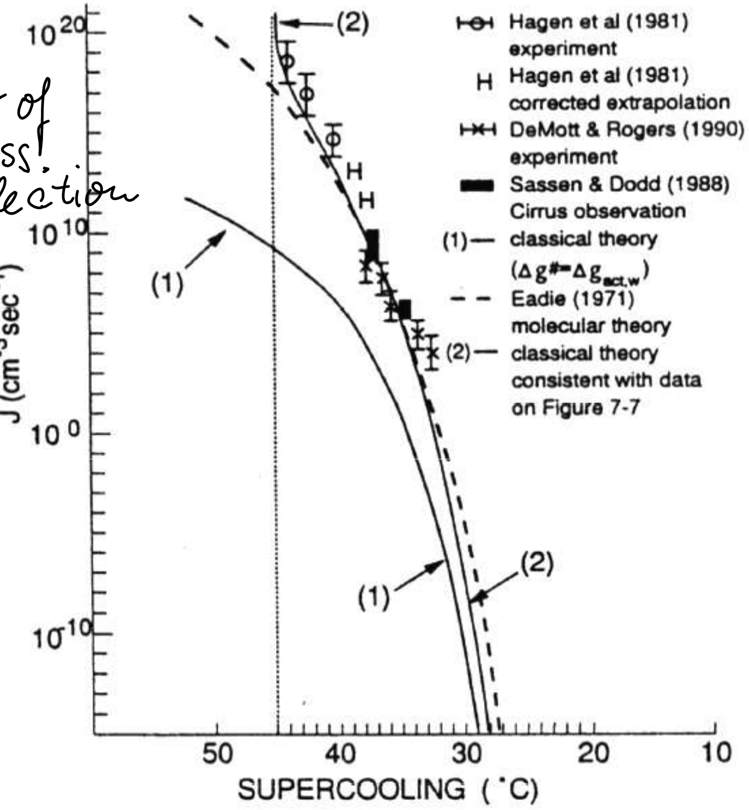
Homogeneous nucleation rates for water: gas-to-liquid and liquid-to-solid



Alcohol

error of class! nucleation thry

water → ice



Nucleation rate measurements and classical (Becker-Döring) theory (Viisanen et al., J. Chem. Phys., 1993).

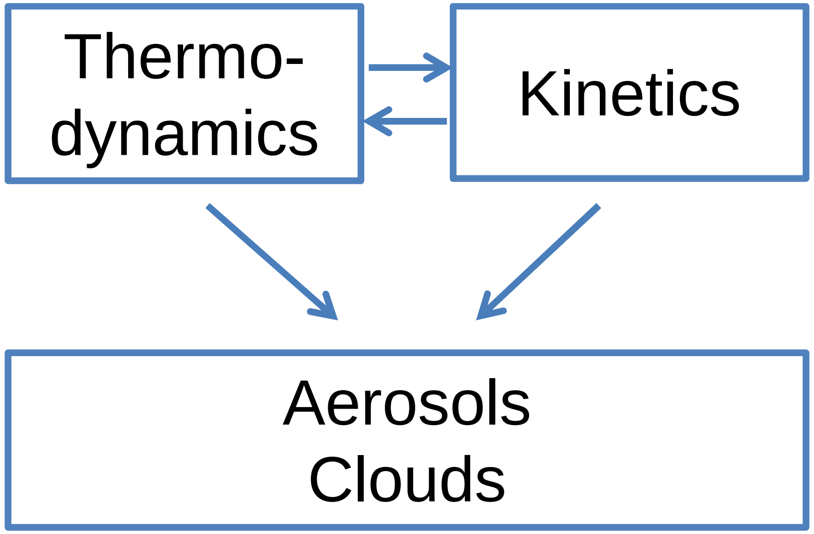
Solid lines belong to solid points.

Variation of the rate of homogeneous ice nucleation in supercooled water (from Pruppacher and Klett, Kluwer, 1997).

Formation of water clouds

Formation of Polar Stratospheric Clouds

Deliquescence of aerosols



Homogeneous nucleation of water droplets

Homogeneous nucleation of ice in aqueous solutions

How far do we get with thermodynamics in explaining cloud formation?

When do we need a kinetic treatment?

Homogeneous ice nucleation

$$p_w = p_w^0 \, a_w$$

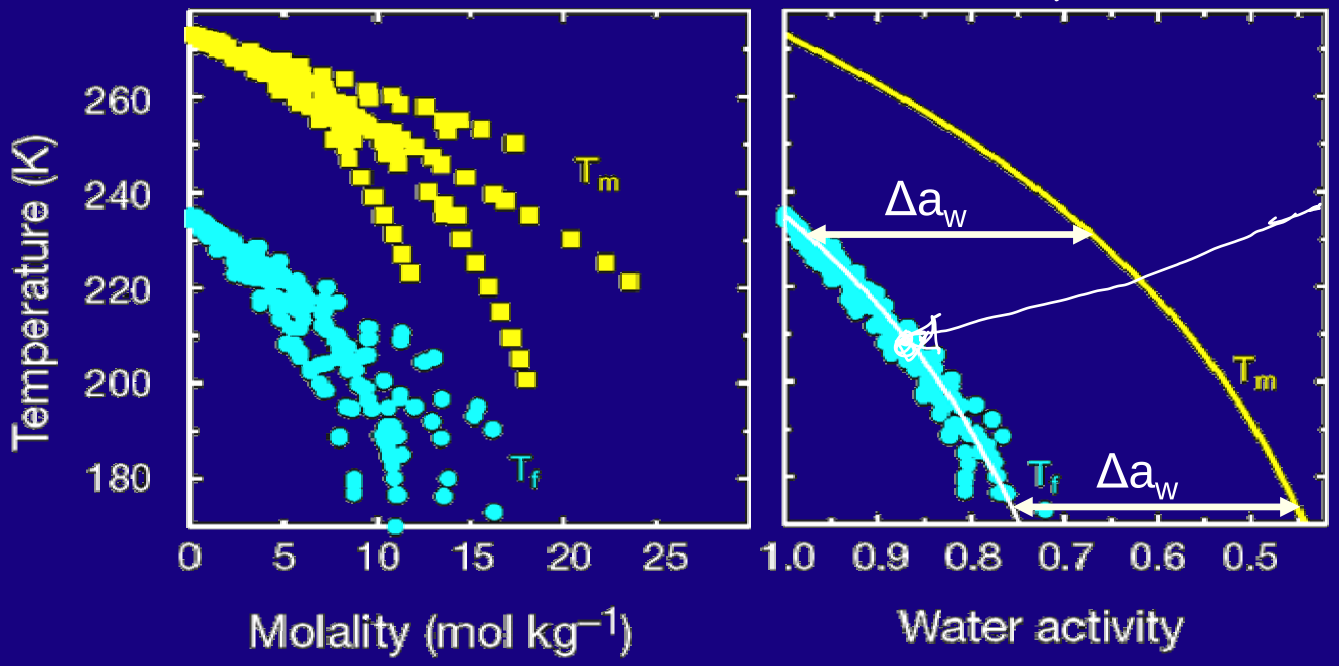
A quantitative thermodynamic ice freezing theory
Koop et al., Nature 2000

$$a_w = \frac{1}{RT} \frac{\partial G}{\partial n_w}$$

Unifies freezing nucleation temperatures and rates for 18 different aqueous solutions:

$$a_w \approx \frac{p_w^{liq}}{p_w^0} \overset{Eq}{=} RH_{liq}$$

H_2SO_4
HNO_3
HNO_3/H_2SO_4
NH_4HSO_4
$(NH_4)_2SO_4$
NH_4F
LiCl
NaCl
KCl
NH_4Cl
$CaCl_2$
$MnCl_2$
$Ca(NO_3)_2$
H_2O_2
urea
ethylene glycol
glucose



Relative humidity

Formation of water clouds

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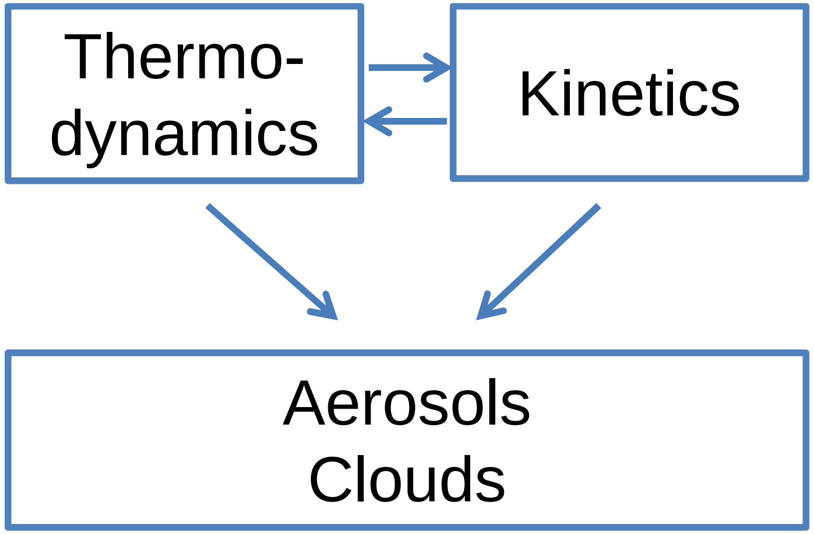

Thermo-dynamics

Kinetics

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Clouds

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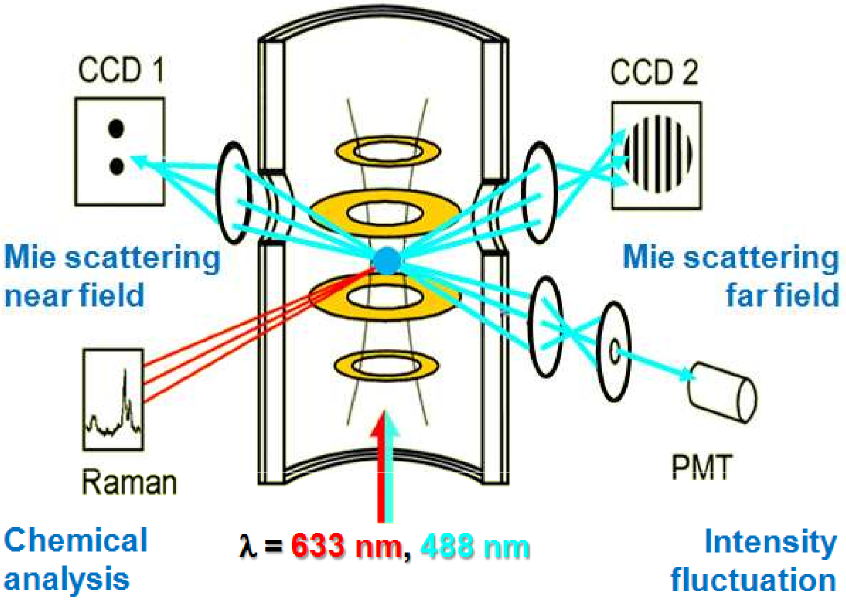
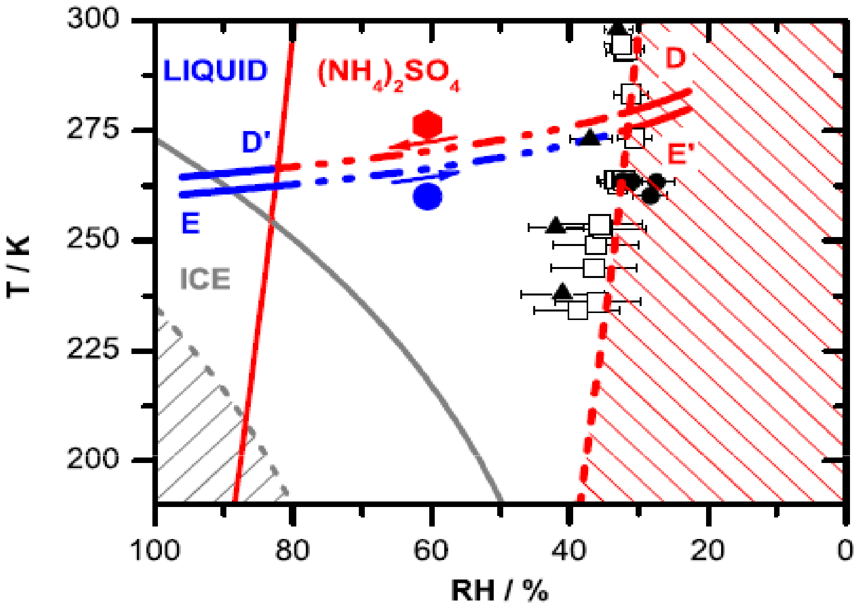
Deliquescence/efflorescence of aerosol particles





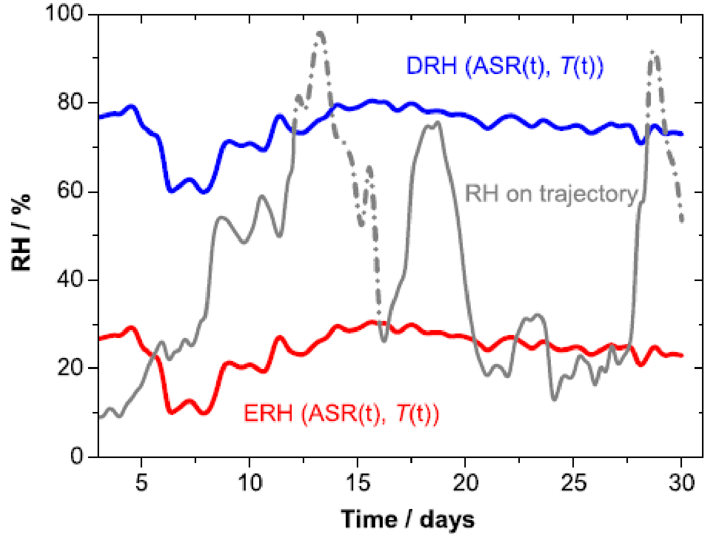
Electrodynamic particle trap

- store single micron-sized particle
- air flow with controlled RH (5-95 %)
- air flow with controlled *T* (160-310 K)
- multiple spectroscopic analysis methods

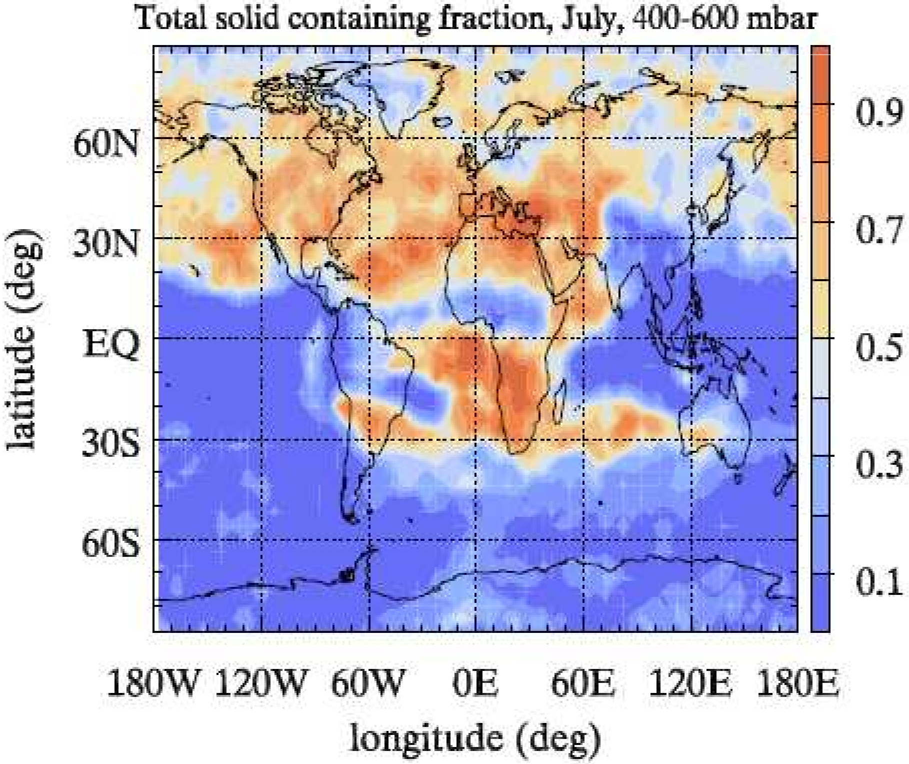
Efflorescence measurements

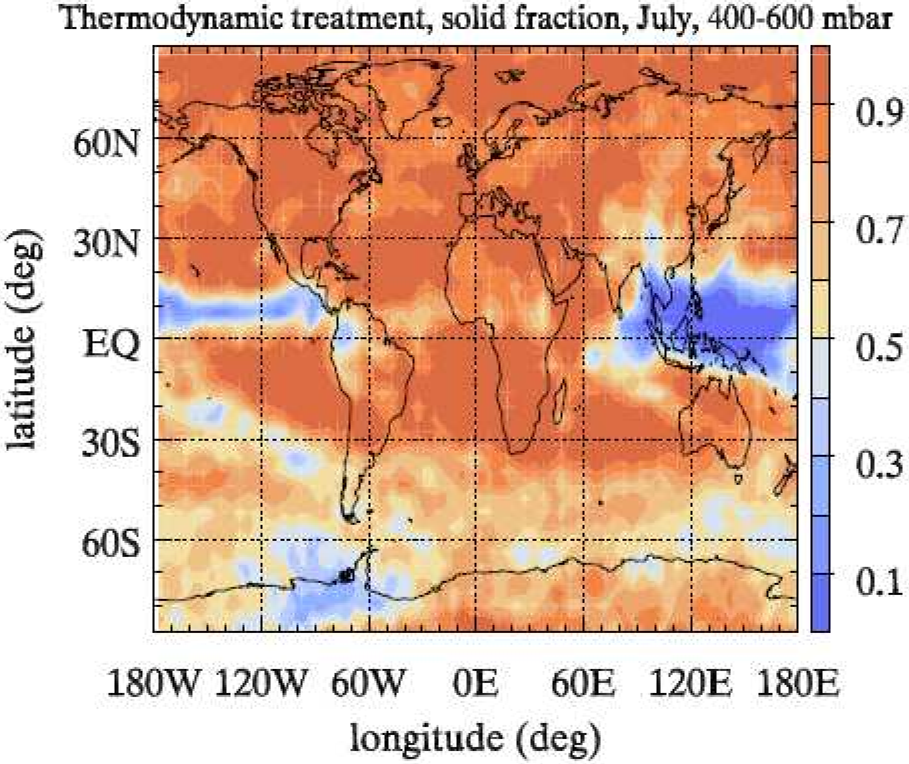
- here $(NH_4)_2SO_4$ (sulfate) particle
- also NH_4HSO_4 (bisulfate)
- and $(NH_4)_3H(SO_4)_2$ (letovicite)

$NH_4^+/HSO_4^-/SO_4^{2-}/H_2O$ hysteresis (measured in trap)



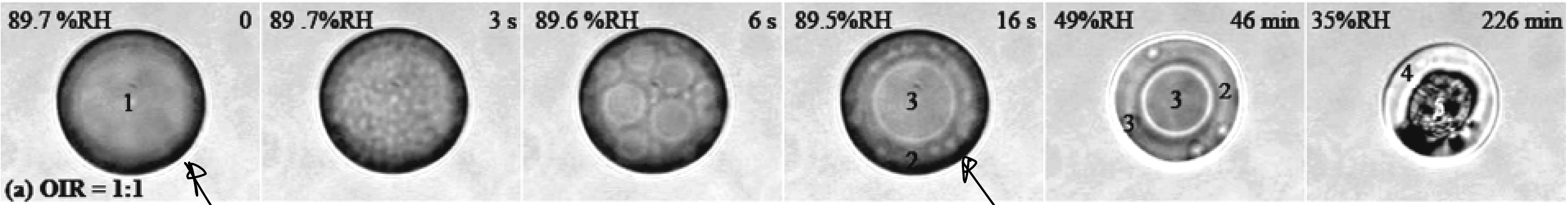
Trajectory-based global analysis (Colberg et al., 2003):
left: full account for hysteresis
right: allow efflorescence w/o supersaturation


Total solid containing fraction, July, 400-600 mbar


Thermodynamic treatment, solid fraction, July, 400-600 mbar

Thermodynamic properties of aerosols

- evidence for prevalence of liquid organic aerosols
- evidence for liquid-liquid phase separations



$N_2O_5 + H_2O \rightarrow 2HNO_3$

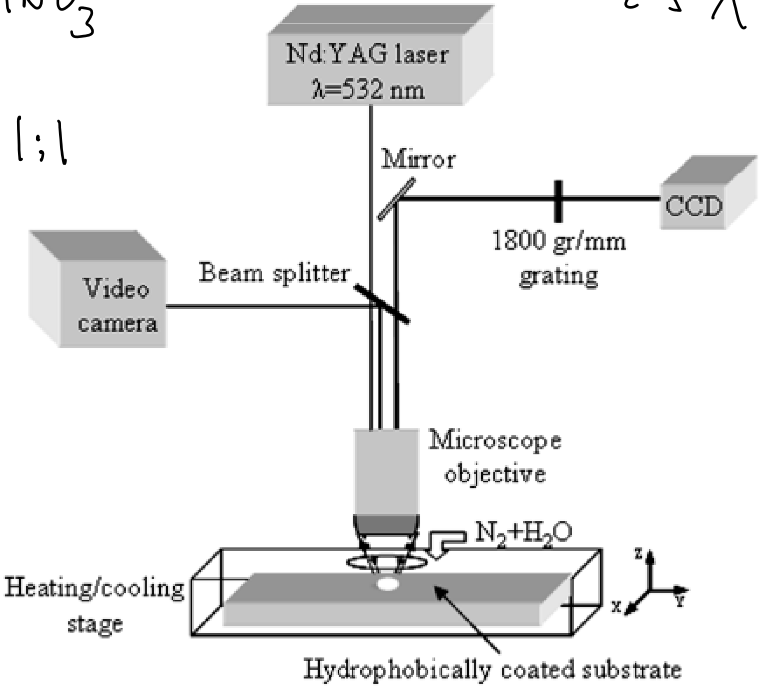
$N_2O_5 \not\rightarrow$

$(NH_4)_2SO_4$

PEG-400
proxy for organics

O:A = 1:1

Raman microscope:

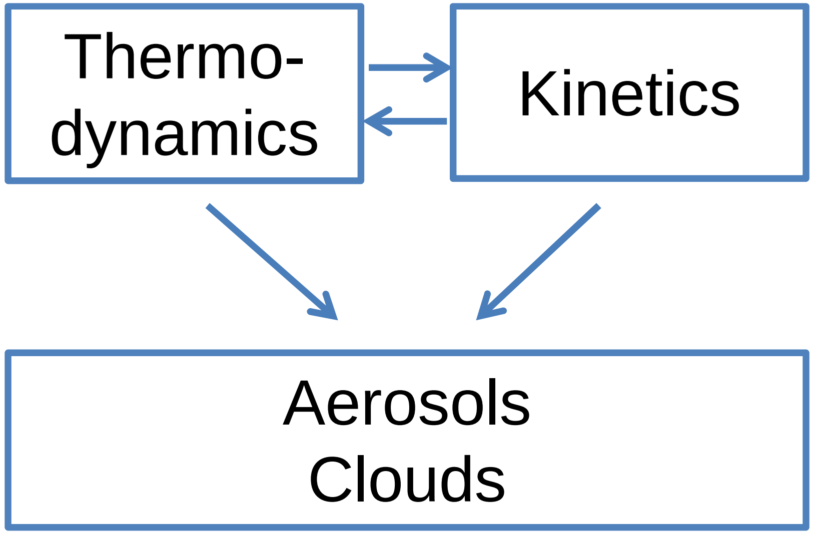


Ciobanu
et al.
JPC 2009

Formation of water clouds

Formation of Polar Stratospheric Clouds

Deliquescence of aerosols



Thermo-dynamics

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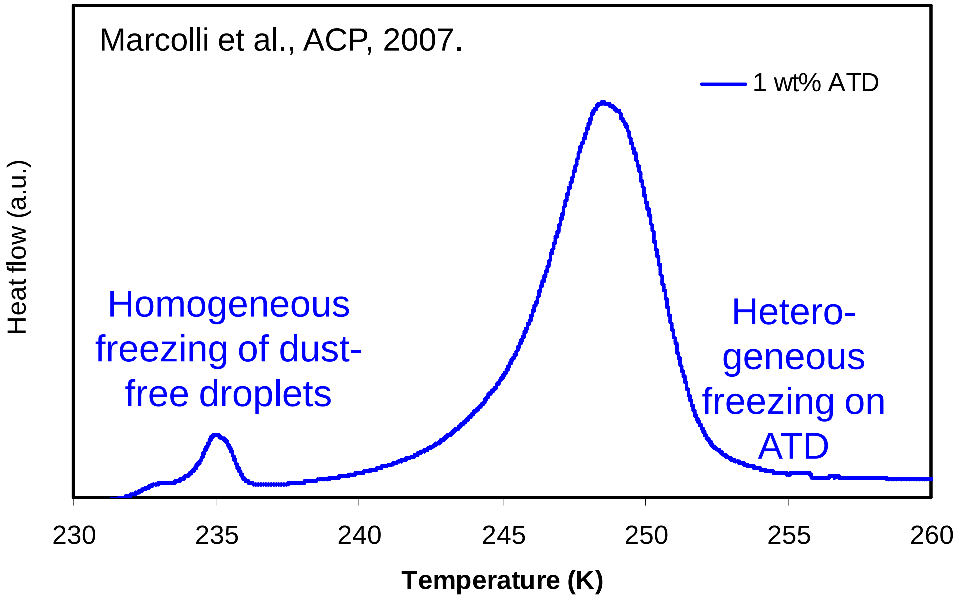
Heterogeneous nucleation on Arizona test dust (ATD):

A first active-site-attribution approach

Differential scanning spectroscopy

DSC expt on emulsified aqueous suspension of ATD (1 wt%)



Marcolli et al., ACP, 2007.

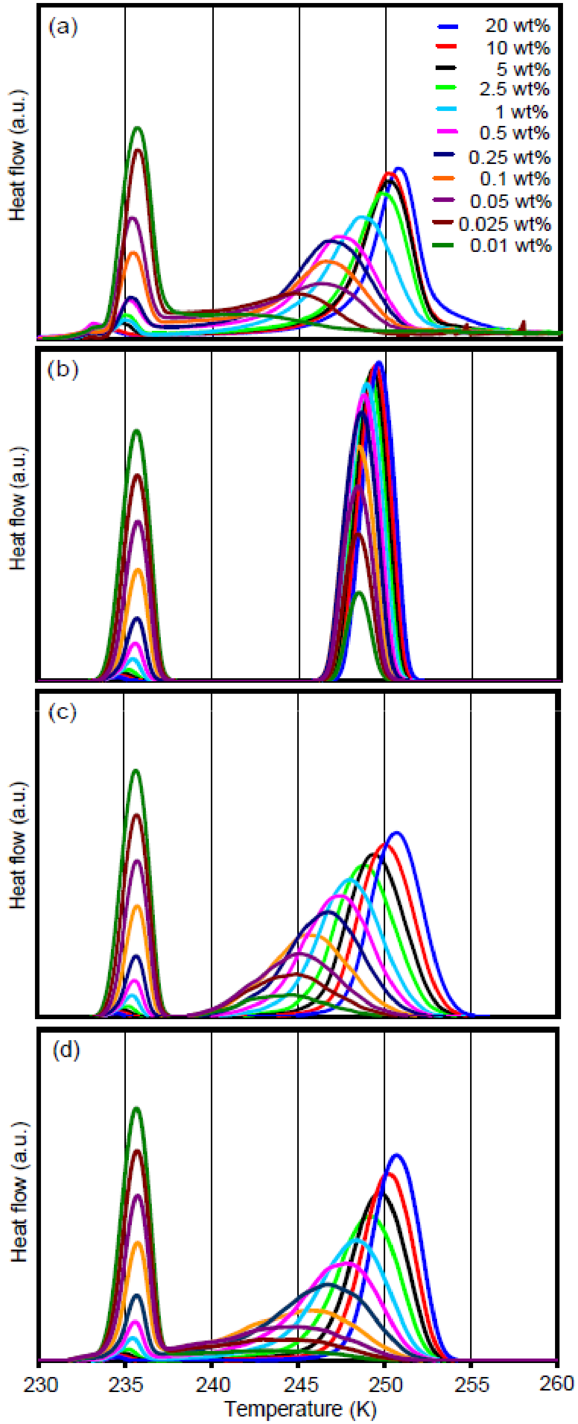
(a) DSC experiments on an emulsified ATD suspension →

(b) Assuming all ATD particles to have the same active site

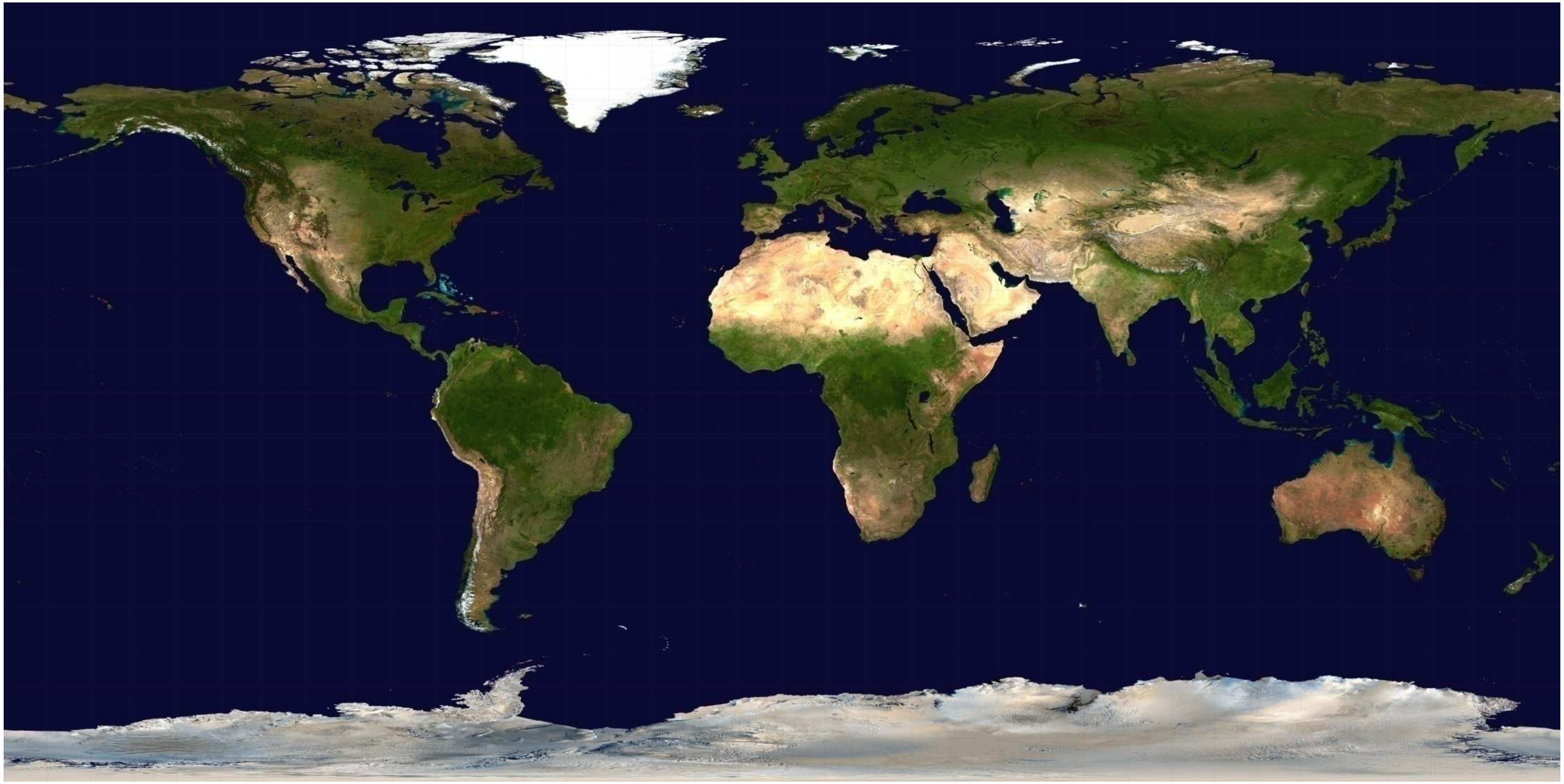
(c) Attributing stochastically a single active site per ATD ptcl

(d) Active site distribution on each ATD particle

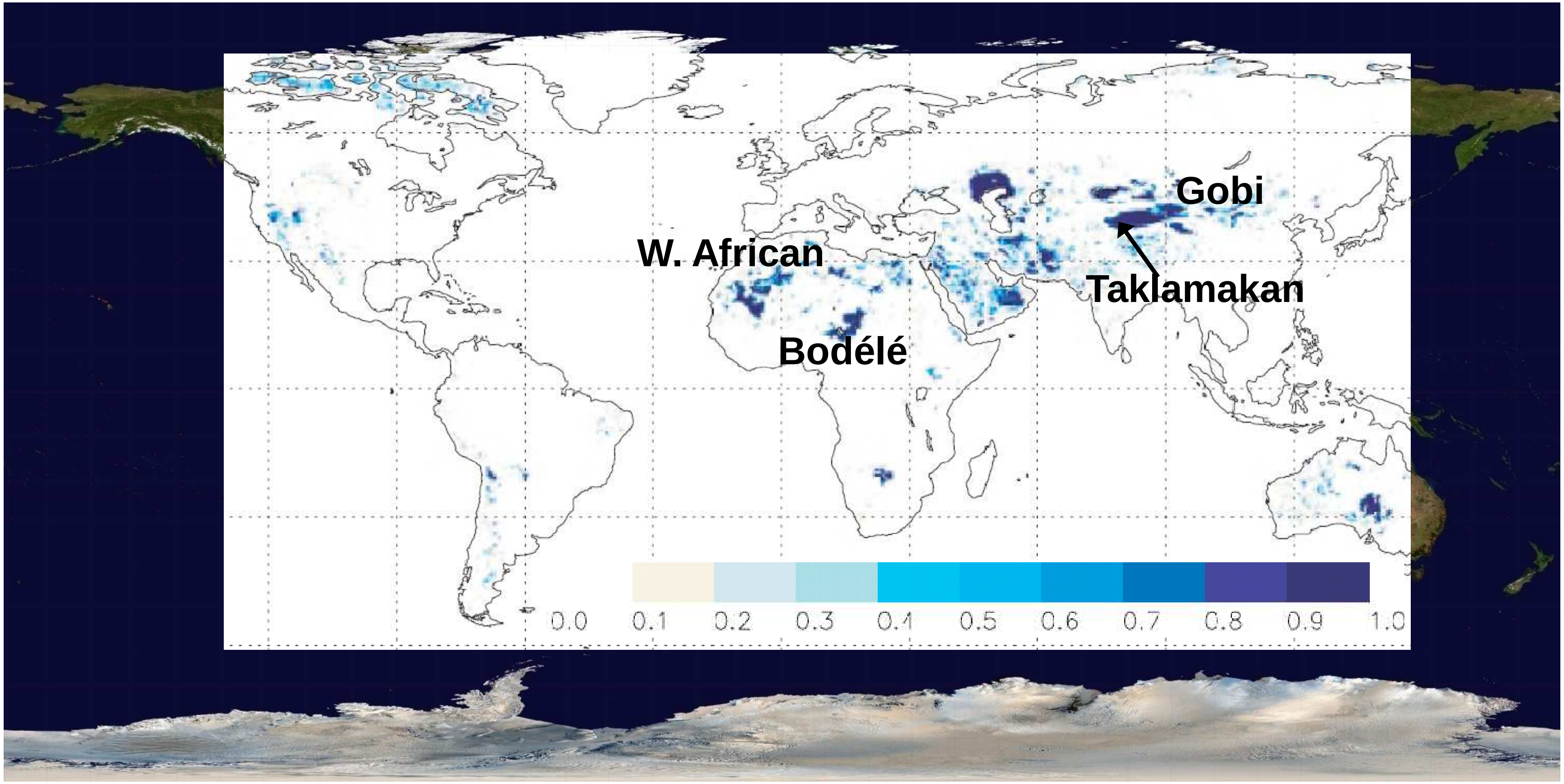
More realistic dusts than ATD: Pinti et al.



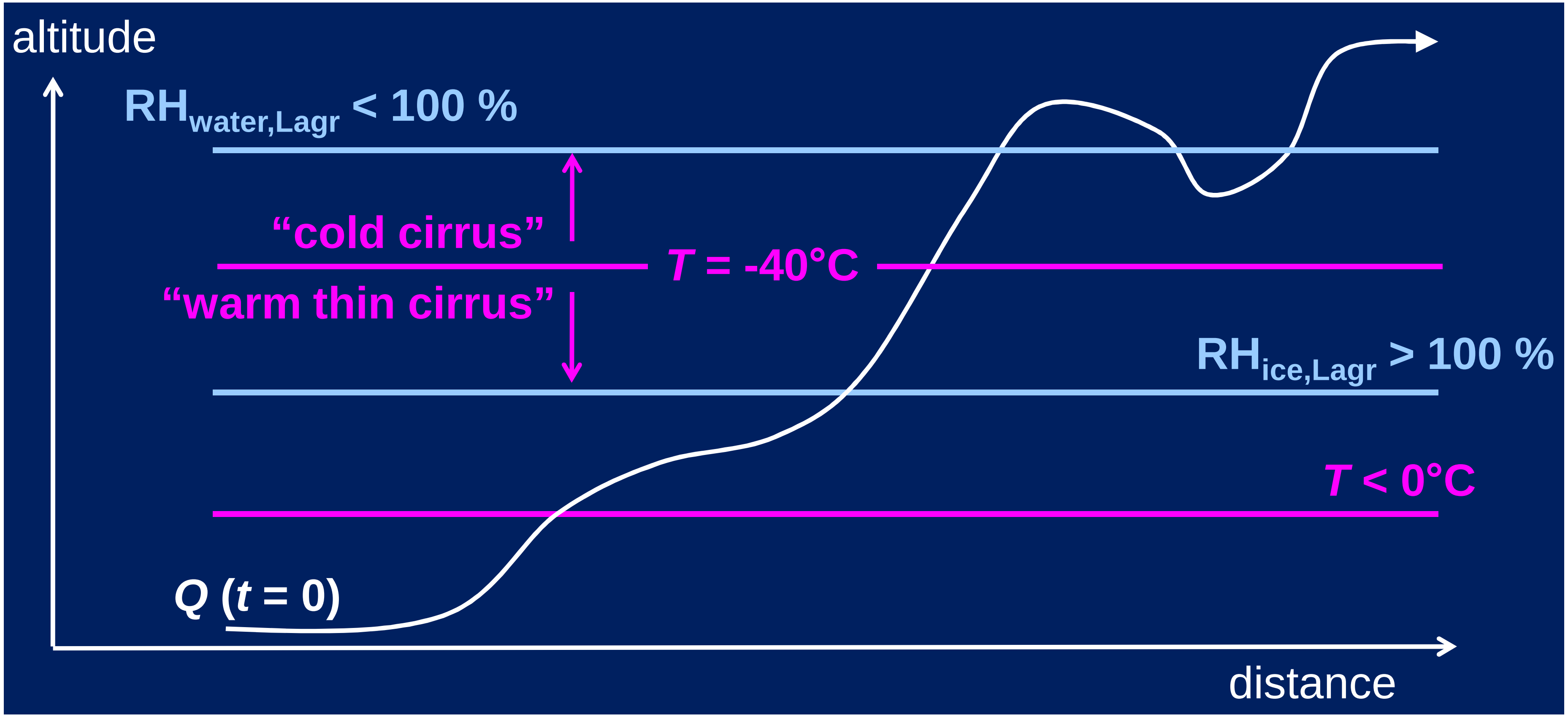
Where does mineral dust come from?



Location of preferential dust sources



Lagrangian tracing of RH_{ice}

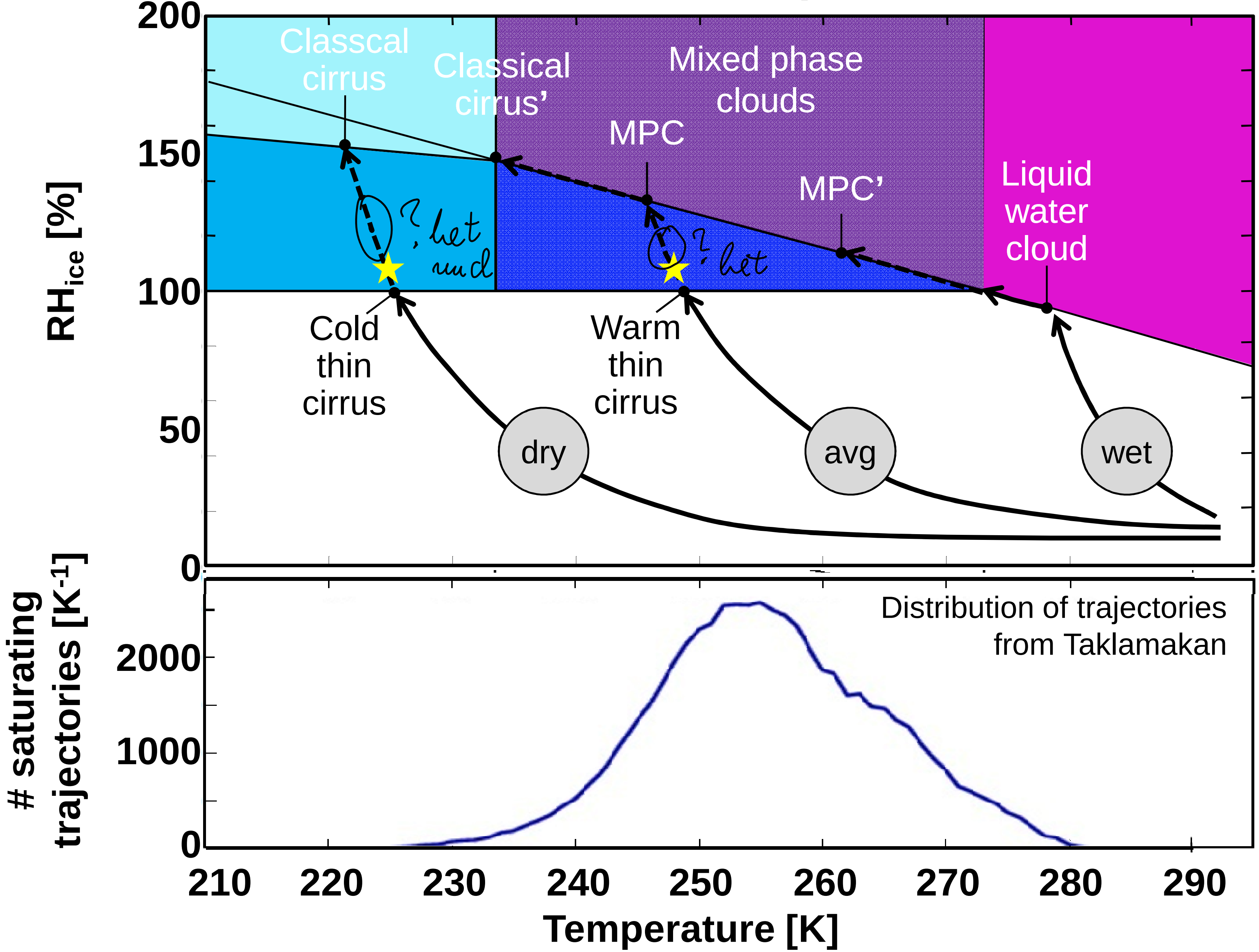


Transported specific humidity (Q) at beginning of each trajectory (t = 0)

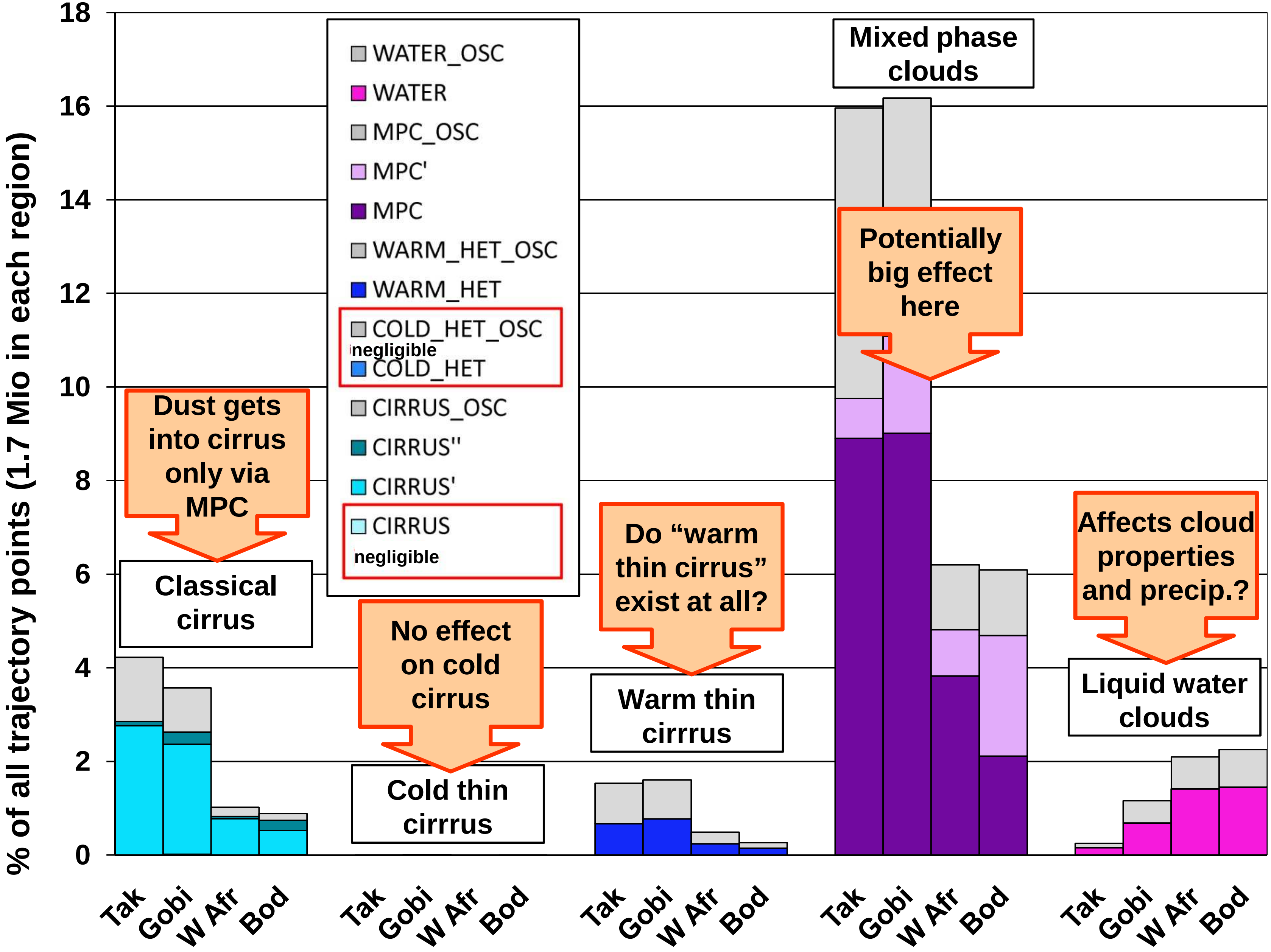
No condensation and mixing → trace Q only up to $RH_w \leq 100\%$

Checked ECMWF's $T(t = 0)$ and $Q(t = 0)$ are realistic

Cloud formation processes



Results by Cloud Type



Dust gets into cirrus only via MPC

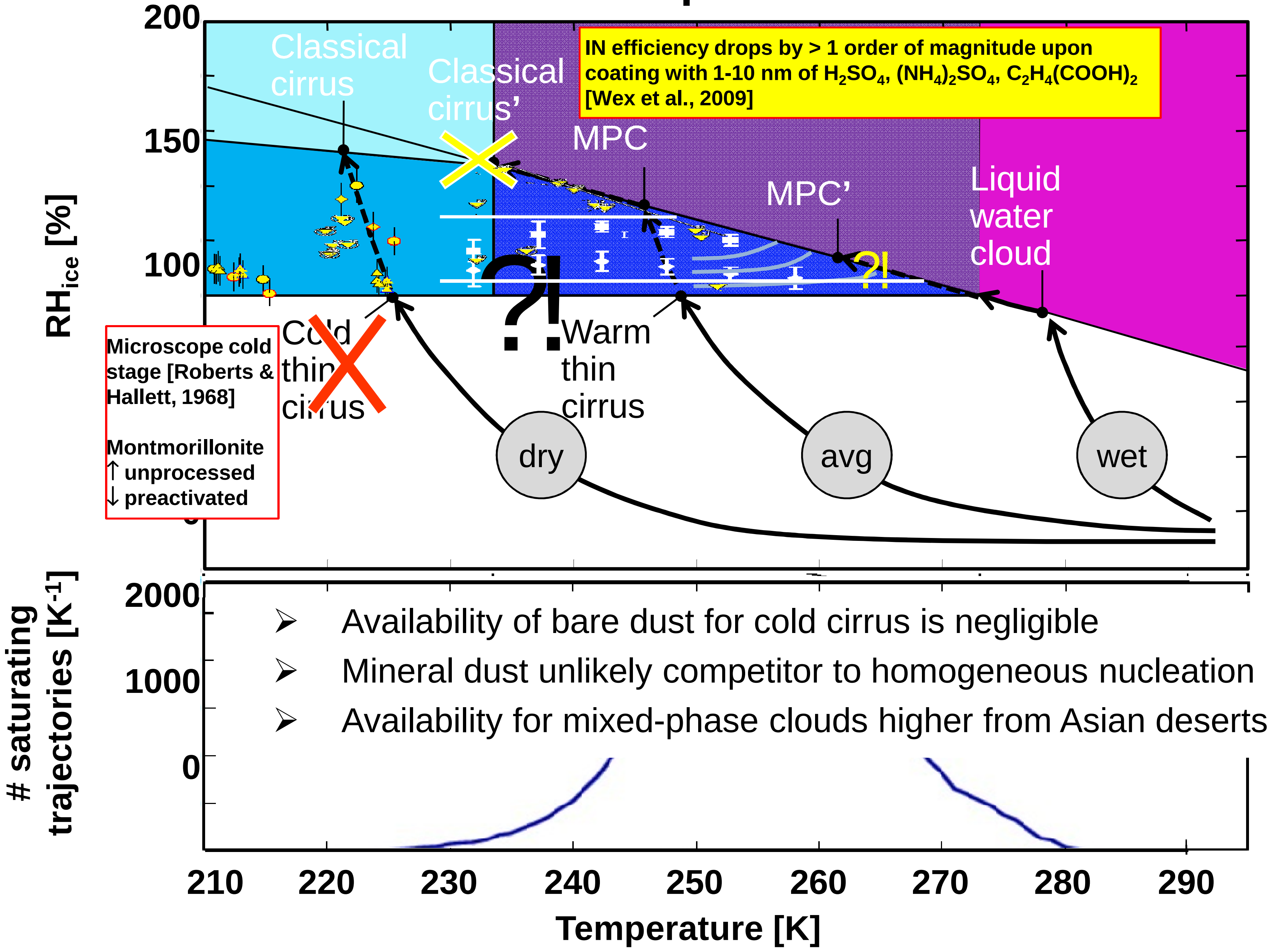
No effect on cold cirrus

Do “warm thin cirrus” exist at all?

Potentially big effect here

Affects cloud properties and precip.?

Cloud formation processes



IN efficiency drops by > 1 order of magnitude upon coating with 1-10 nm of H_2SO_4, $(NH_4)_2SO_4$, $C_2H_4(COOH)_2$ [Wex et al., 2009]

Microscope cold stage [Roberts & Hallett, 1968]

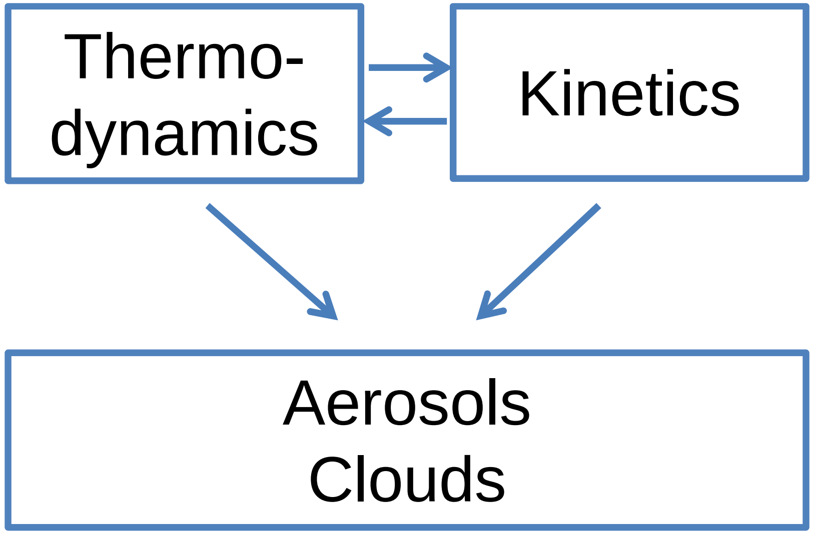
Montmorillonite
↑ unprocessed
↓ preactivated

- Availability of bare dust for cold cirrus is negligible
- Mineral dust unlikely competitor to homogeneous nucleation
- Availability for mixed-phase clouds higher from Asian deserts

Formation of water clouds

Formation of Polar Stratospheric Clouds

Deliquescence of aerosols



Thermo-dynamics

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Diffusion growth of droplet or ice particle

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Diffusion Growth of Flat Surface or Water Droplet

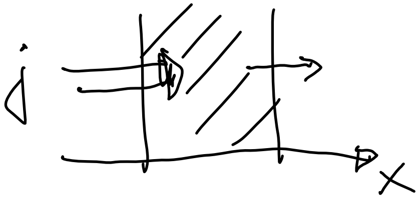
1-D

3-D

(1) Continuity equation

n = H_2O molecule number density (in the gas phase)

j = molecules per area per time = molecular flux



1-D:

$$\frac{\partial n(x,t)}{\partial t} = -\frac{\partial j(x,t)}{\partial x}$$

3-D:

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

$$\frac{\partial n}{\partial t} = -\nabla \cdot \vec{j}$$

(2) Fick's Law

Diffusive flux of molecules is a result of number density gradients:

(diffusion coefficient $[D]$ = $\mathrm{cm^2\ s^{-1}}$)

1-D:

$$j = -D\frac{\partial n}{\partial x}$$

3-D:

$$\vec{j} = -D\nabla n$$

(3) Diffusion Equation

Combine (1) and (2) :

1-D:

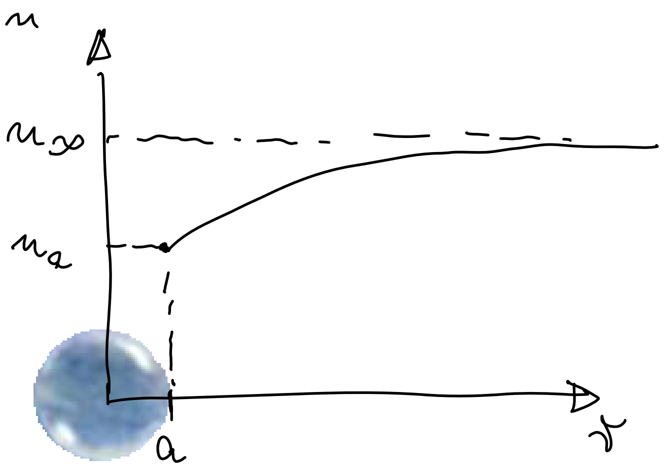
$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}$$

3-D:

$$\frac{\partial n}{\partial t} = D\nabla^2 n$$

The droplet growth problem:

r = radial coordinate
a = droplet radius
n = number density of H_2O molecules
n_∞ = number density far from droplet
n_a = number density just above droplet surface



Transform from Cartesian coordinates to spherical coordinates:

$$\nabla^2\psi = \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \underbrace{\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}}_{=0 \text{ for spherical symmetry}}$$

(e.g. formulae in Jackson's book on electrodynamics)

The droplet growth problem is in good approximation spherically symmetric. Therefore, the diffusion of H_2O molecules towards a small water droplet of radius ***a*** can be described by the radial diffusion equation:

$$\boxed{\frac{\partial n}{\partial t} = D_g \nabla^2 n = D_g \frac{1}{r} \times \frac{\partial^2}{\partial r^2}(r\,n)}$$

where D_g is the diffusion constant of H_2O molecules in air.

$$\boxed{\frac{\partial n}{\partial t} = D_g \nabla^2 n = D_g \frac{1}{r} \times \frac{\partial^2}{\partial r^2}(r\,n)}$$

Task: For stationary conditions $\underbrace{(\partial/\partial t = 0)}$, derive n from this equation.

Need two boundary conditions:

$$\left\|\begin{array}{ll} n(r \to \infty) = n_\infty = \text{const} & \text{far away} \\ n(r \to a) = n_a = \text{const} & \text{above droplet surface.} \end{array}\right.$$

$$0 = \frac{d^2}{dr^2}(r n)$$

$$r n = A + B r$$

Boundary conditions : $n_\infty = B$, $n_a = \frac{A}{a} + B$

$$\boxed{n(r) = (n_a - n_\infty)\frac{a}{r} + n_\infty \qquad \text{and} \qquad j(r) = -D_g \frac{\partial n}{\partial r} = D_g (n_a - n_\infty)\frac{a}{r^2}}$$

Interpretation:

- $p_\infty = n_\infty kT$ is the H_2O partial pressure.
- $p_a = n_a kT$ is the H_2O vapor pressure.
- $(n_a - n_\infty) < 0$ → water uptake
- $(n_a - n_\infty) > 0$ → water loss
- $(n_a - n_\infty) = 0$ → equilibrium

Droplet growth:

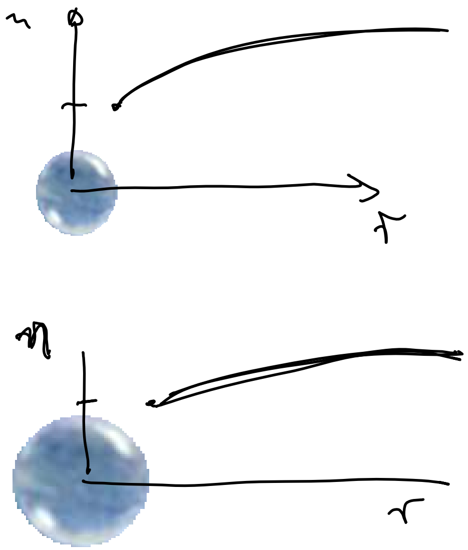
$$\oint \vec{j}\cdot d\vec{S} = \oint \vec{j}\cdot\vec{e}_r\, dS = -\frac{dN}{dt} = -\frac{1}{V_m}\frac{d\overset{\frac{4\pi}{3}a^3}{V}}{dt} = -\frac{1}{V_m}4\pi a^2\frac{da}{dt}$$

S = droplet surface area
N = # H_2O molecules in droplet
V = droplet volume
V_m = H_2O molecular volume

$$\oint \vec{j}\cdot d\vec{S} = \int j\, dS = 4\pi a^2 j(a) = 4\pi a^2\left[-D_g\frac{\partial n}{\partial r}\right]_a = 4\pi a D_g (n_a - n_\infty)$$

Growth/evaporation law for a droplet

$$\Rightarrow \quad \boxed{\frac{da}{dt} = -V_m \frac{D_g}{a}(n_a - n_\infty)}$$



$p_a = n_a kT$ is the H_2O vapor pressure

But there is a serious problem with our solution:

$\Rightarrow$ **Violation of flux limitation**

This result diverges for $a \to$. But this is physical non-sense!

The flux cannot become arbitrarily large but is limited by molecular bombardment.

Continuum Theory
diffusion equation

$\longleftrightarrow$

Molecular Theory
statistical thermodynamics

Boltzmann

In mathematical terms, we need to change our boundary condition:

Need a flux boundary condition, not a concentration boundary condition!

Molecular bombardment on surface: $\boxed{j = \frac{1}{4}\bar{v}\,n}$ ($\bar{v}$ = mean molecular thermal velocity)

$$\Rightarrow \quad \boxed{j(a) = D_g(n_a - n_\infty)\frac{1}{a} \overset{!}{=} \frac{\alpha}{4}\bar{v}(n_{vap} - n_a)}$$

Hertz-Knudsen Equation

$\bar{v}$ = mean molecular thermal velocity
α = mass accommodation coefficient
→ 1 - α is the fraction of colliding molecules that is reflected by surface

From this equation determine n_a:

$$n_a\left(\frac{D_g}{a} + \frac{\alpha\bar{v}}{4}\right) = \frac{\alpha}{4}\bar{v}\,n_{vap} - \frac{D_g}{a}n_\infty \Rightarrow n_a = \frac{n_{vap} + \frac{4D_g n_\infty}{\alpha\bar{v}a}}{1 + \frac{4D_g}{\alpha\bar{v}a}}$$

$$\boxed{\frac{da}{dt} = -V_m \frac{D_g}{a} \times \frac{n_{vap} - n_\infty}{1 + (4D_g / \alpha a \bar{v})}}$$

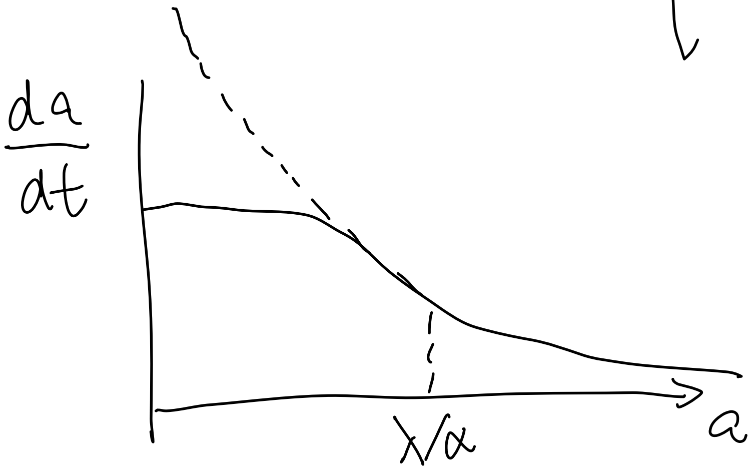
No divergence!
Finite growth and
evaporation rates!

$D_g = \frac{\bar{v}\lambda}{4}$, λ = mean free collisional path

$$\boxed{\frac{da}{dt} = -V_m \frac{D_g}{a} \times \frac{n_{vap} - n_\infty}{1 + \lambda / \alpha a}} = \begin{cases} -\frac{V_m D_g}{a}(n_{vap} - n_\infty), & a \gg \lambda/\alpha \\ -V_m \frac{\alpha \bar{v}}{4}(n_{vap} - n_\infty), & a \ll \lambda/\alpha \end{cases}$$

Continuum regime

Knudsen regime



$$\alpha = ?$$

$\alpha \approx 1$

$\alpha \ll 1$

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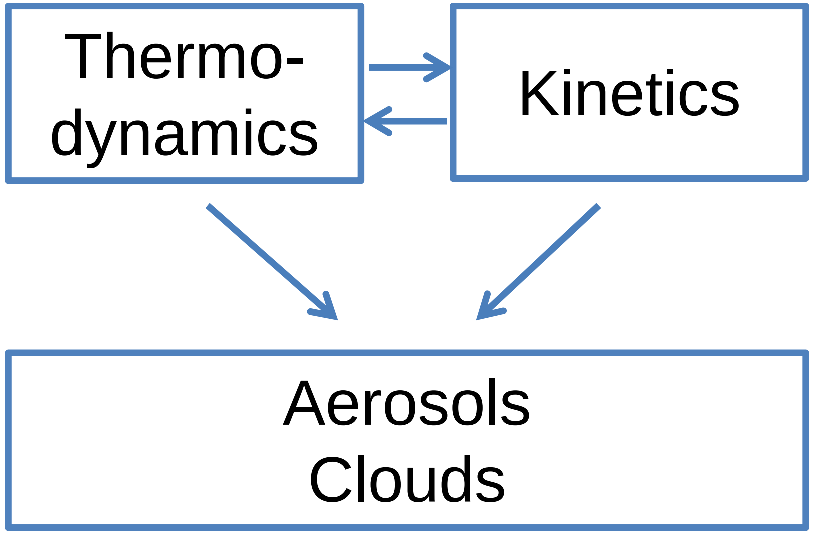

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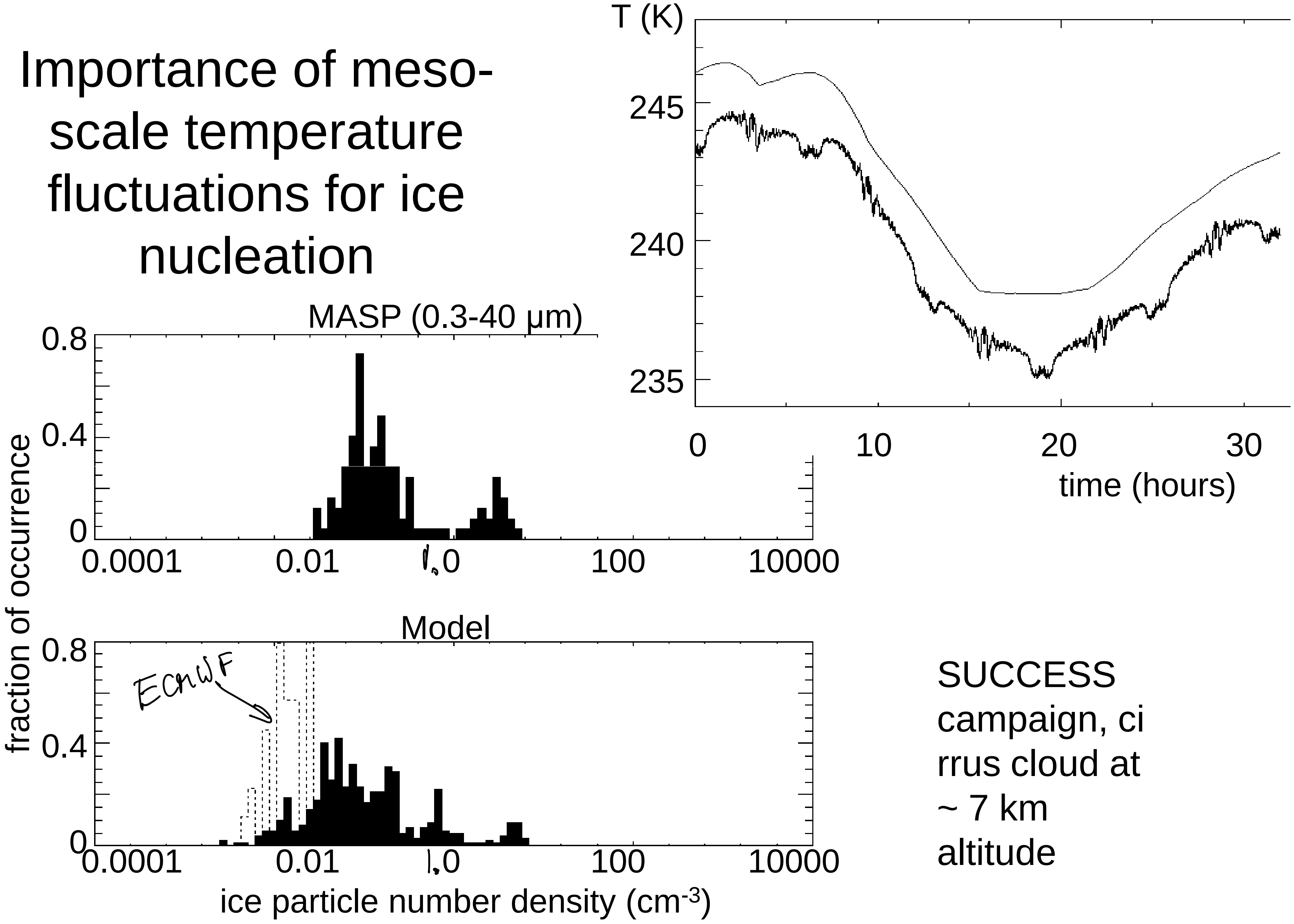
Microphysics and micrometeorological interplay

How far do we get with thermodynamics in explaining cloud formation?

When do we need a kinetic treatment?

Importance of meso-scale temperature fluctuations for ice nucleation



SUCCESS campaign, cirrus cloud at ~ 7 km altitude

Hoyle et al. (JAS, 2005)

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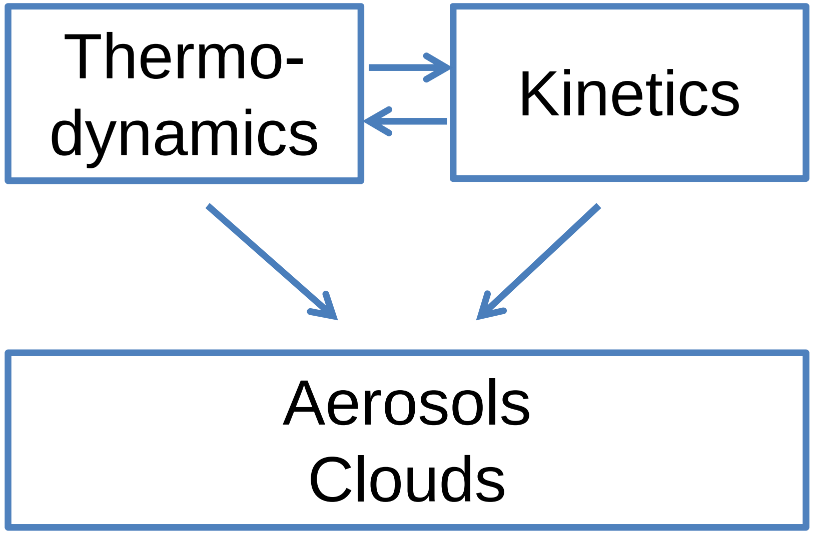
Formation of Polar Stratospheric Clouds

Deliquescence of aerosols



Thermo-dynamics

Kinetics

Aerosols
Clouds

Homogeneous nucleation of water droplets

Homogeneous nucleation of ice in aqueous solutions

Hom. efflorescence and liquid-liquid separation

Heterogeneous nucleation of ice on mineral dust

Diffusion growth of droplet or ice particle

Microphysics and micrometeorological interplay

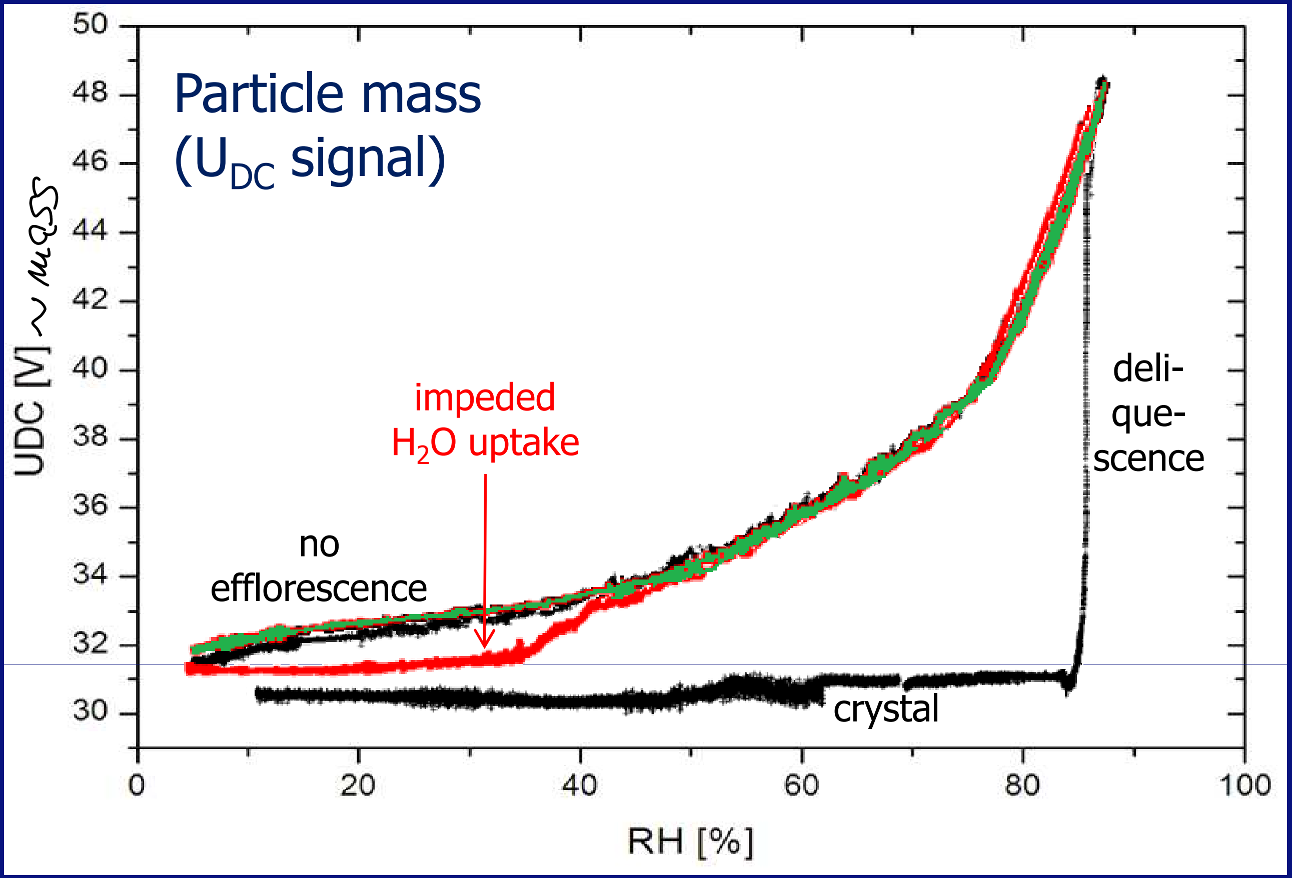
Glass formation

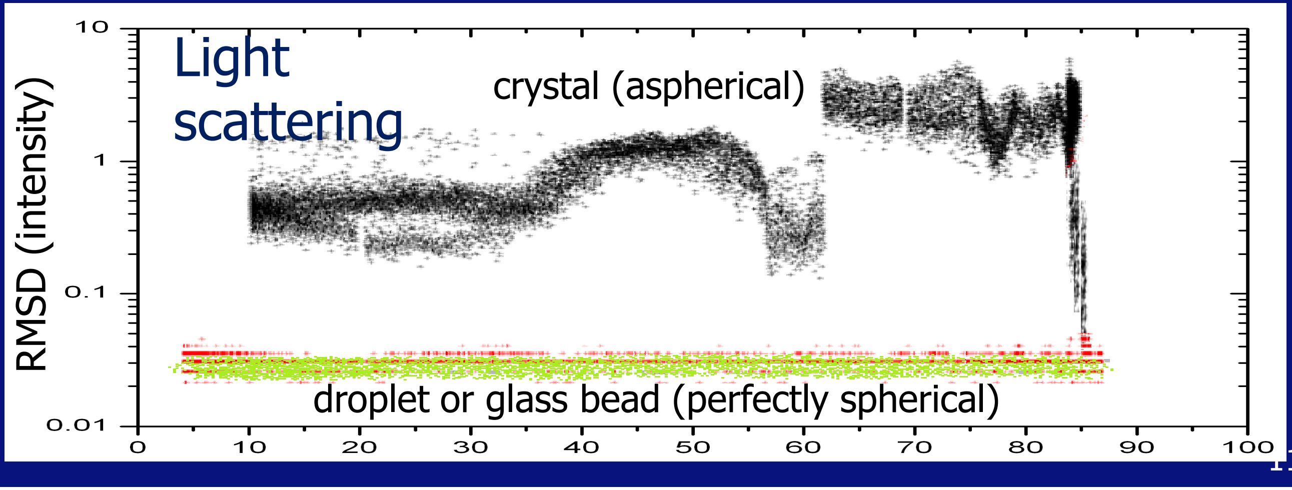
How far do we get with thermodynamics in explaining cloud formation?
When do we need a kinetic treatment?

Example:

H_2O uptake impedance of glassy aerosols: sucrose particle at 291 K

(5-day experiment, each leg ~ 1 day)

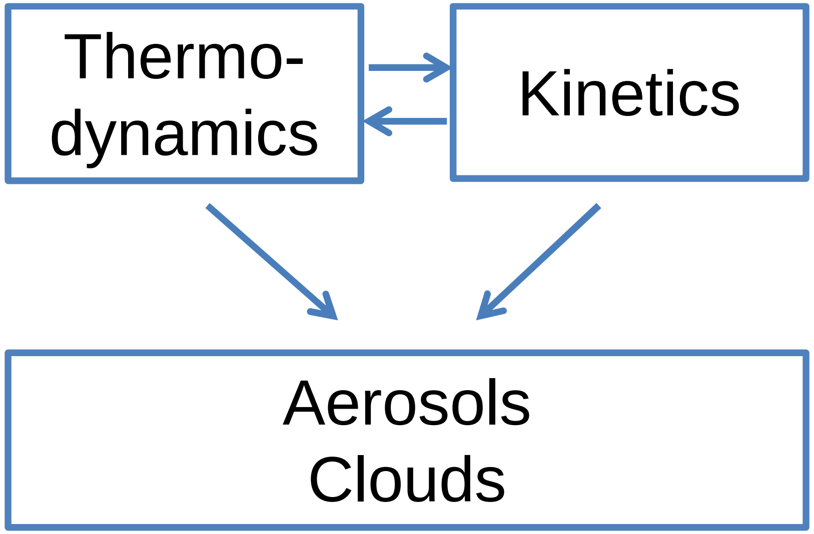




Formation of water clouds

Formation of Polar Stratospheric Clouds

Deliquescence of aerosols



Combined frost point / backscatter measurements

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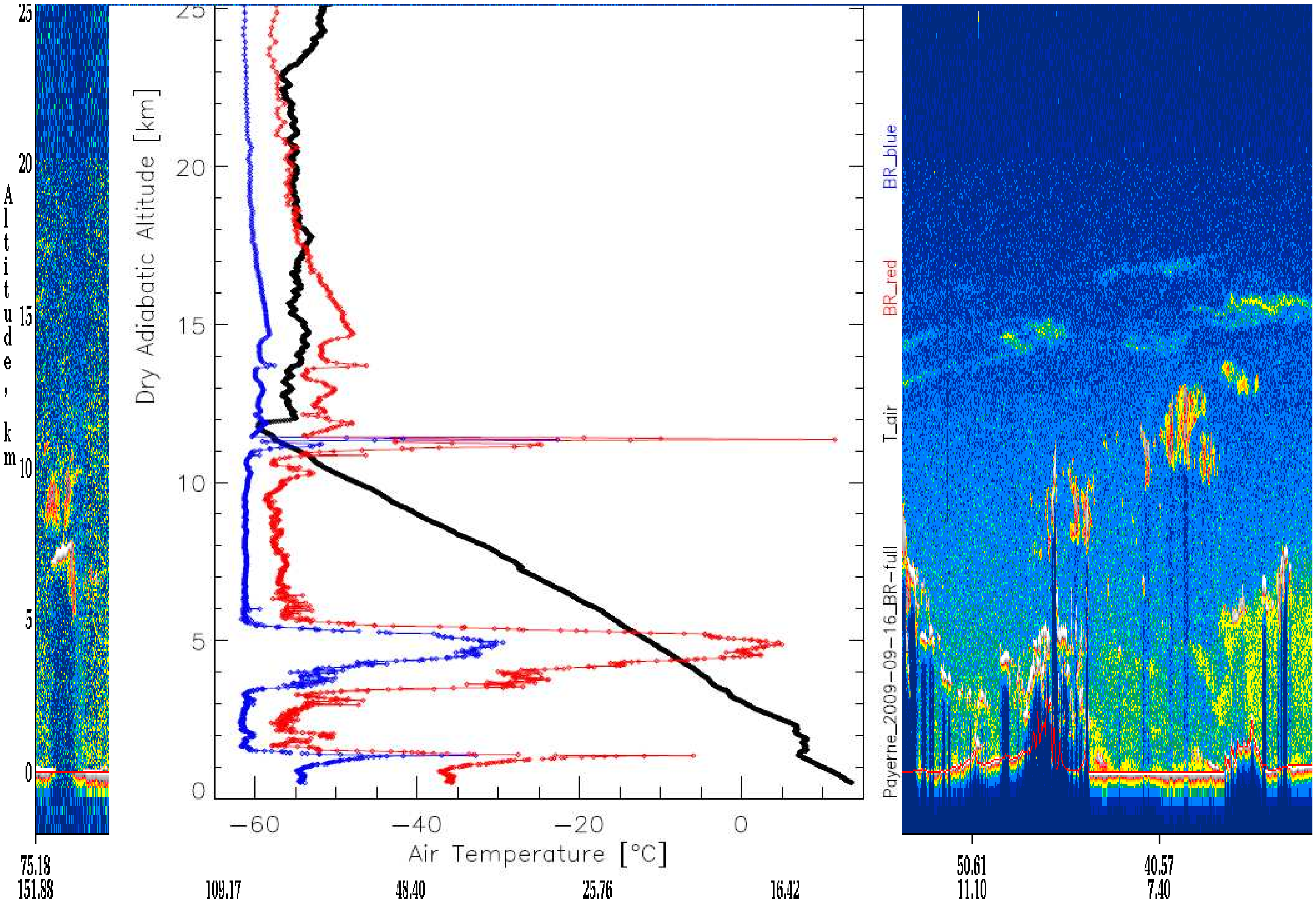
Low clouds, cirrus and stratospheric aerosol above Zurich, 16 September 2009

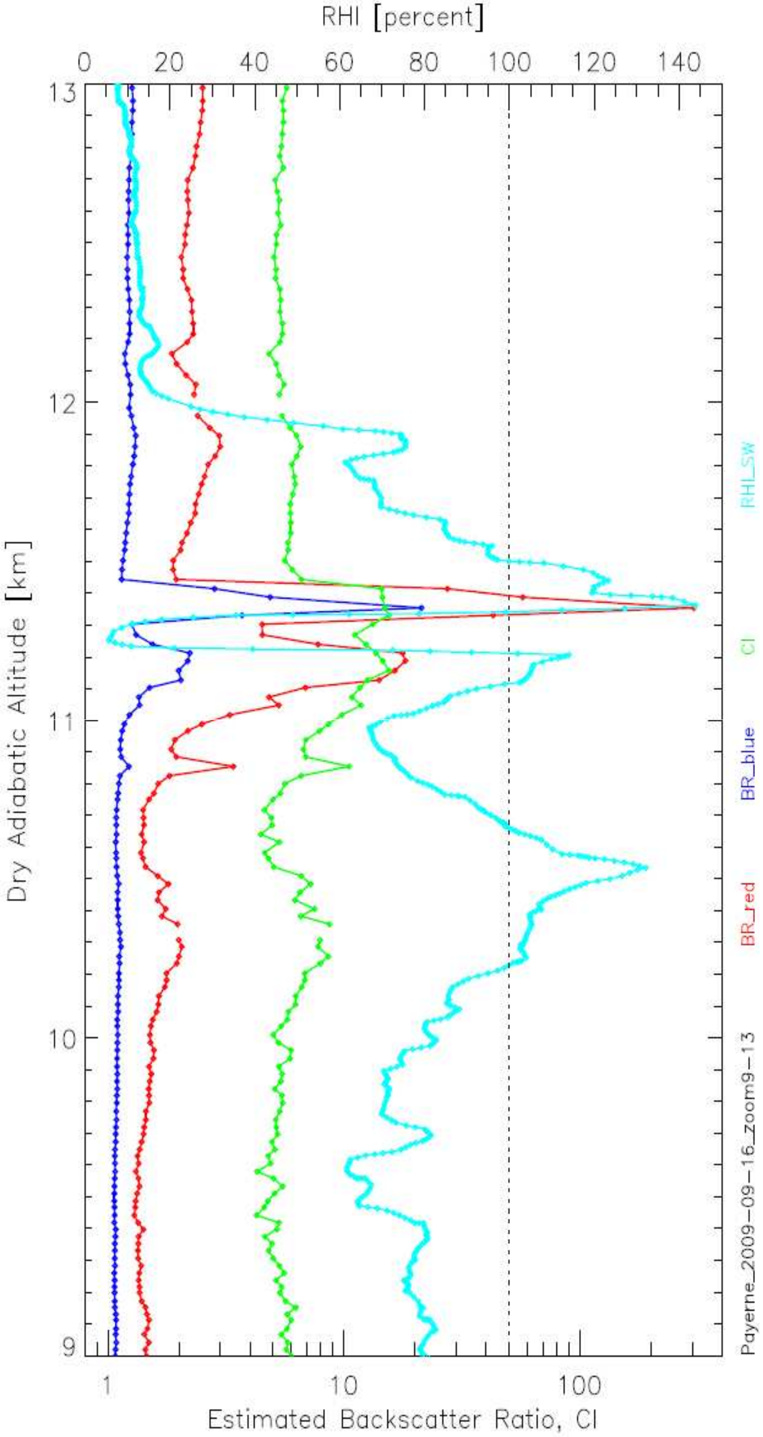


Highlight:
New Instrument development

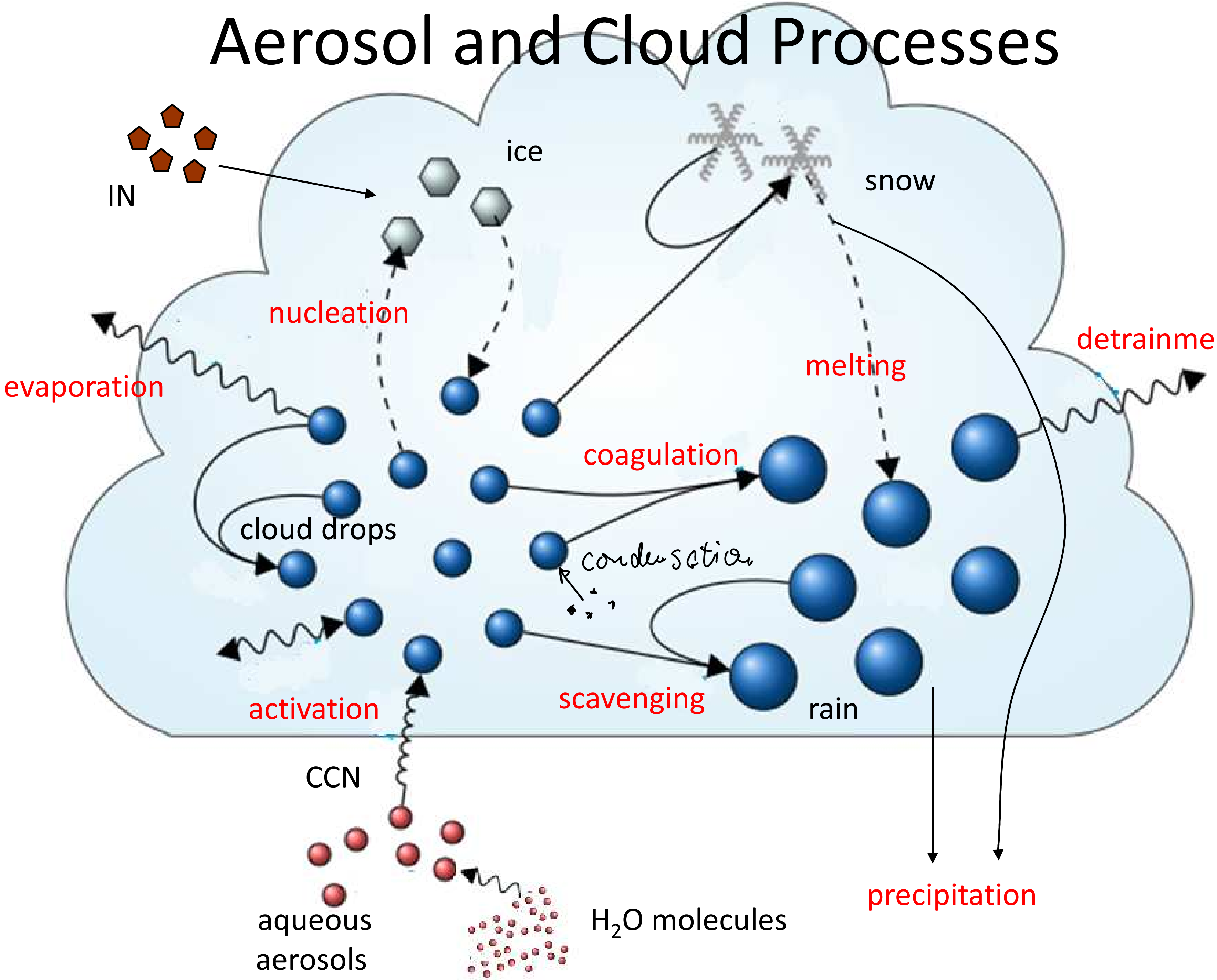
COBALD Lightweight Backscatter Sonde

Feature	Specification	Remark
wavelengths	455 nm & 870 nm	color index 1-15
Backscatter dynamic range	10^4	from unperturbed stratosph. aerosol to thick anvil outflow
time resolution	1 s	0.05-3 s selectable
dimensions	17 × 14 × 12 cm^3	incl. 3 cm insulation
total weight	540 g	suited for piggyback
power supply	8 × LR61 (1.5V AA) 2 × 6LR61 (9V)	for > 3 h of operation
data interface	19.2 kbit/s, logic level RS232	settings for SRS-C34, adaptable to telemetry
altitude range	ground to > 30 km	cp. weather sondes

More on this: Cirisan et al., future work



Aerosol and Cloud Processes



Thanks!

Last slide:

The differential particle size distribution

$$\frac{dn}{d\log r}(\vec{x},r,t) \equiv r\, n_r(\vec{x},r,t)$$

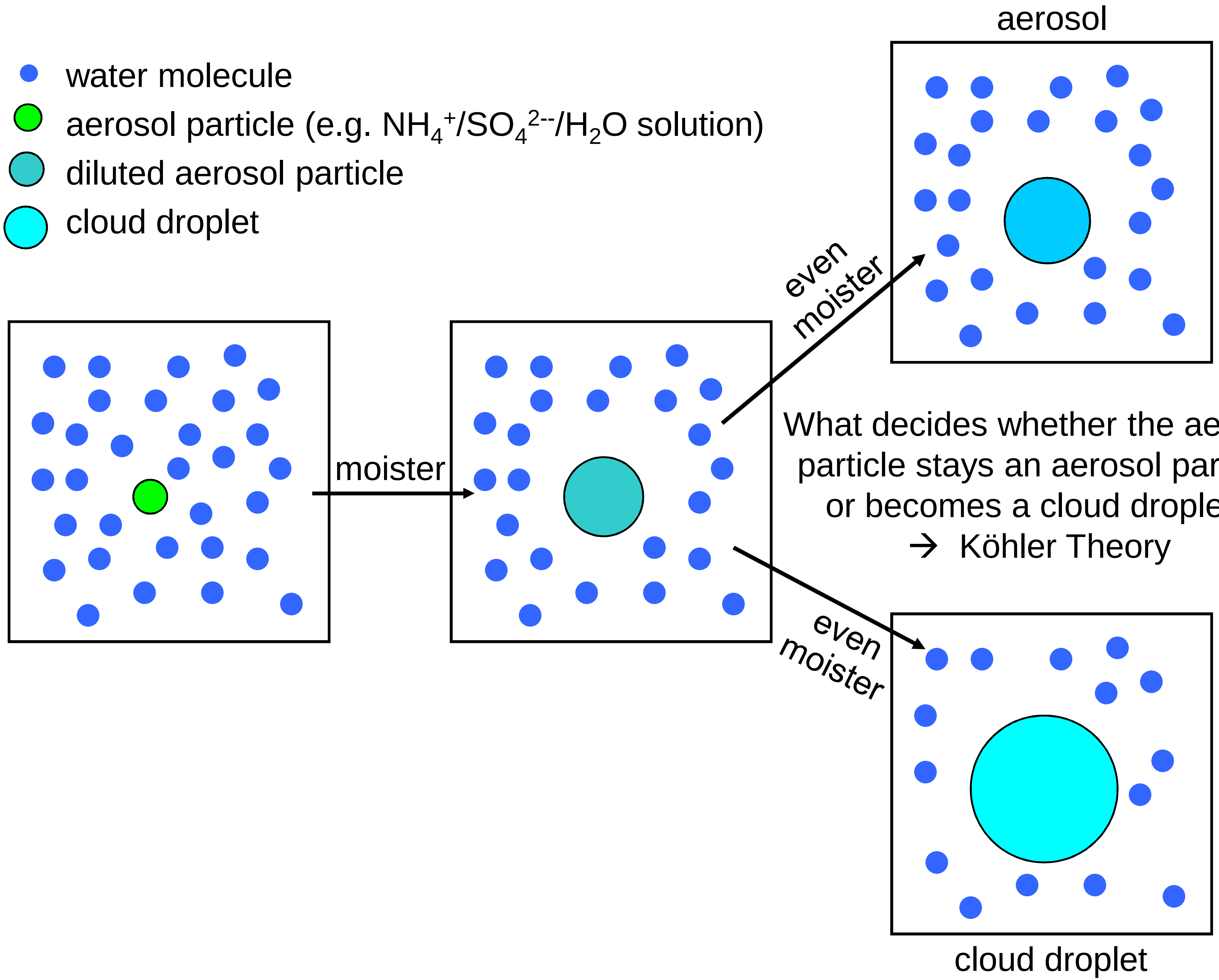
and its corresponding transport equation:

$$\frac{\partial n_r}{\partial t}(\vec{x},r,t) + \vec{v}\cdot\nabla n_r(\vec{x},r,t) + v_s\frac{\partial n_r}{\partial z}(\vec{x},r,t) + \frac{\partial v_r n_r}{\partial r}(\vec{x},r,t) + D_r\nabla^2 n_r(\vec{x},r,t)$$

$$= J_{nuc}(\vec{x},r,t)$$

$$-\int_0^\infty dr' K(r,r')n_r(\vec{x},r,t)n_r(\vec{x},r',t)$$

$$+\int_0^r dr' K(r',(r^3-r'^3)^{1/3})n_r(\vec{x},r',t)n_r(\vec{x},(r^3-r'^3)^{1/3},t)$$



● water molecule

● aerosol particle (e.g. $NH_4^+/SO_4^{2-}/H_2O$ solution)

● diluted aerosol particle

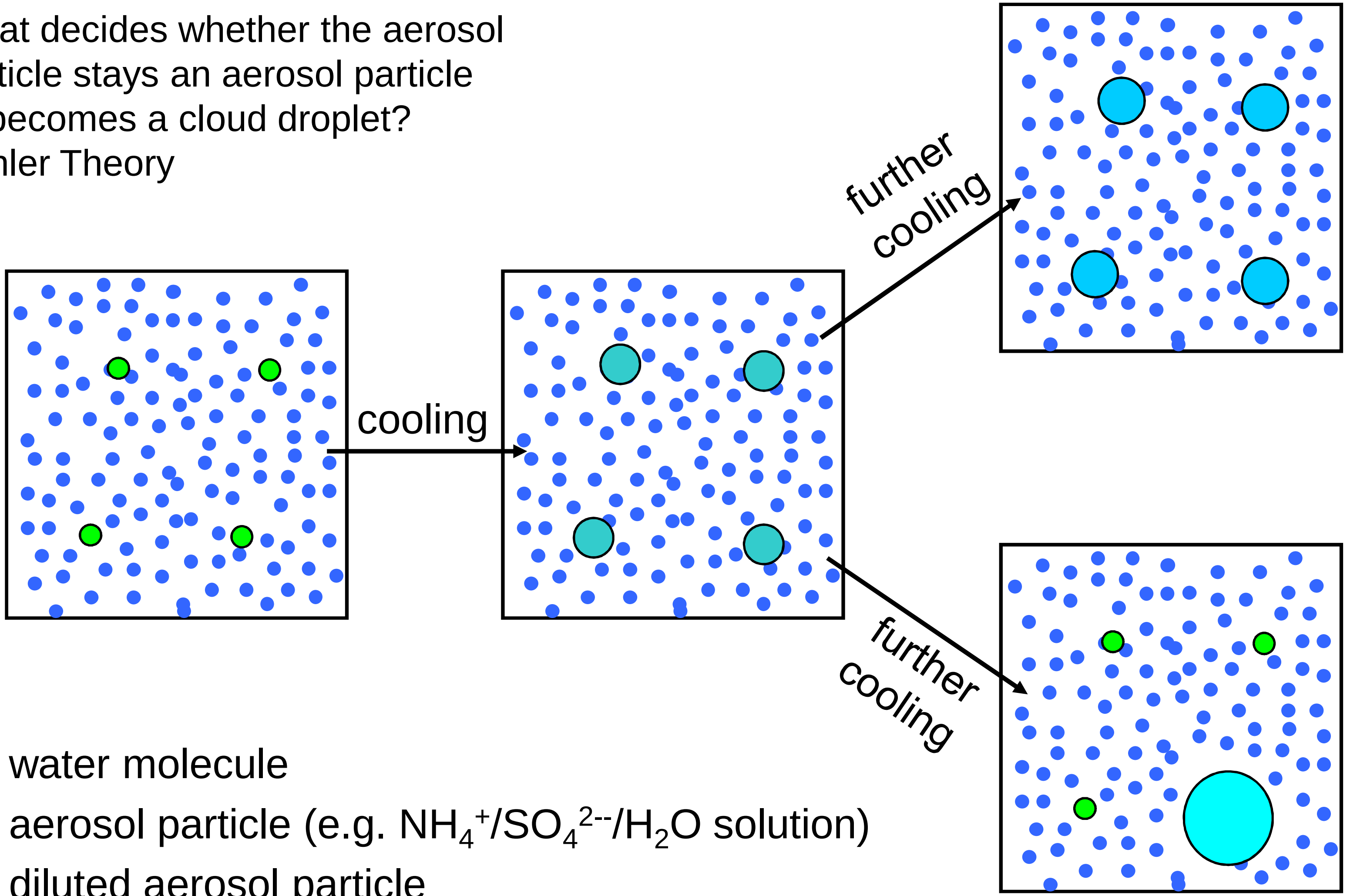
● cloud droplet

What decides whether the aerosol particle stays an aerosol particle or becomes a cloud droplet?
→ Köhler Theory

Cloud droplet formation

A fierce competition without which precipitation would be massively impeded!

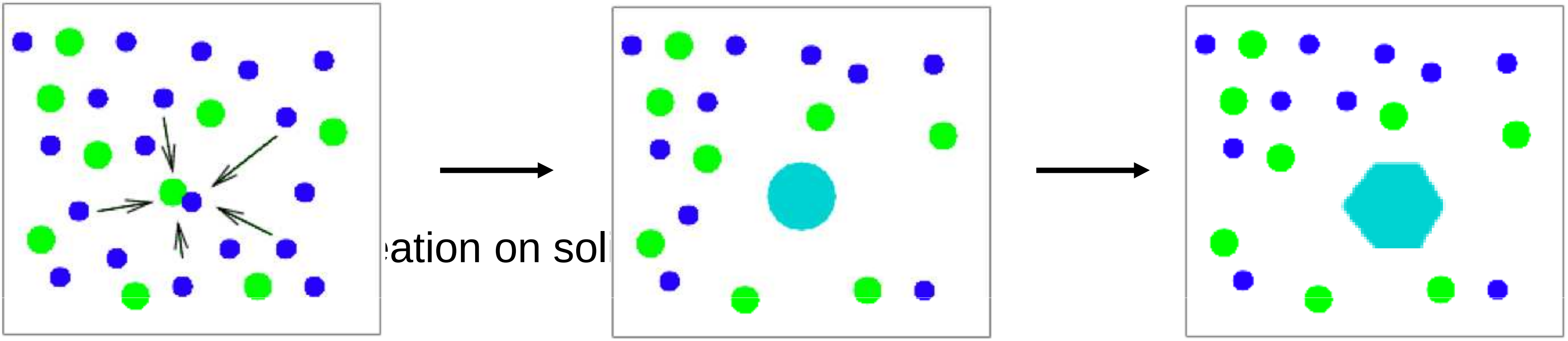
What decides whether the aerosol particle stays an aerosol particle or becomes a cloud droplet?
Köhler Theory



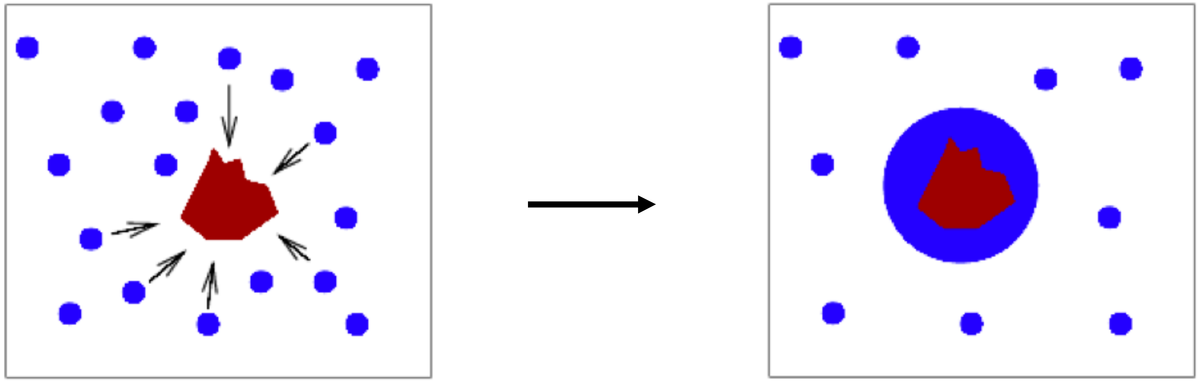
- ● water molecule
- ● aerosol particle (e.g. $NH_4^+/SO_4^{2-}/H_2O$ solution)
- ● diluted aerosol particle
- ● cloud droplet

Different pathways for ice nucleation, e.g.:

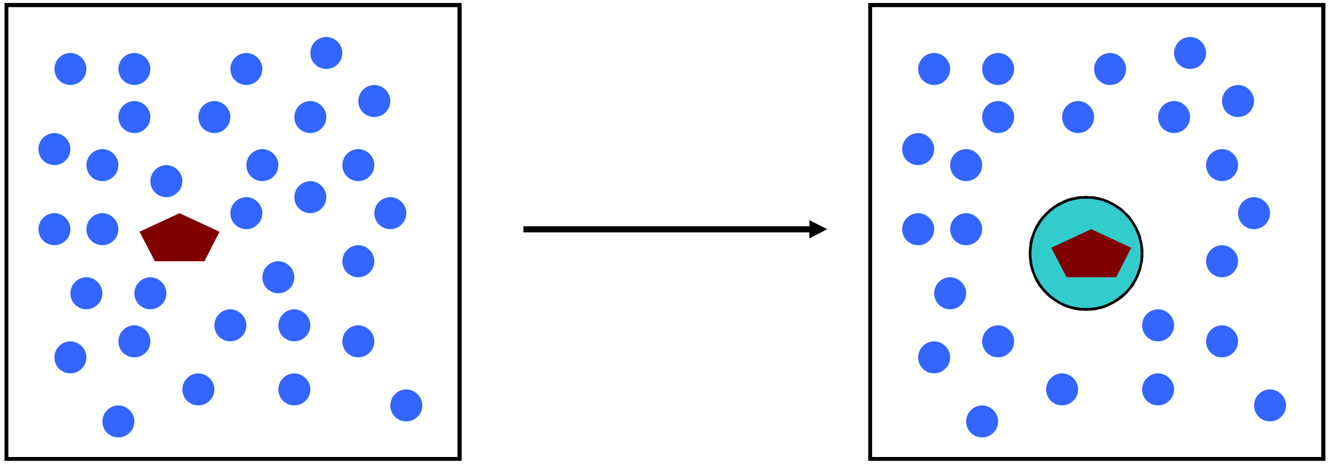
Homogeneous nucleation of solution droplets



H ation on sol



Cloud condensation nuclei
insoluble aerosol



Depending on surface, composition,
temperature, relative humidity ...

Hier Colberg

Hoyle paper

Do we need a kinetic treatment for H2o transport in strat?

Raoult lived when?

Snowwhite / Cobald