

Thermodynamics of Earth systems

Lecture 10: Surface tension, curvature, Kohler equation

Material covered in Lecture

Part 2: Framework

Phase Equilibria

- Gibbs phase rule: thermodynamic degrees of freedom, phases and components
- Energy in phase changes and chemical reactions

Part 3: Applications

Physical chemistry of water solutions – solution thermodynamics

- Colligative properties (freezing point depression, boiling point elevation)
- Phase diagram (for single and multiple component system); Clausius-Clapeyron equation;

Nucleation and Diffusional Growth

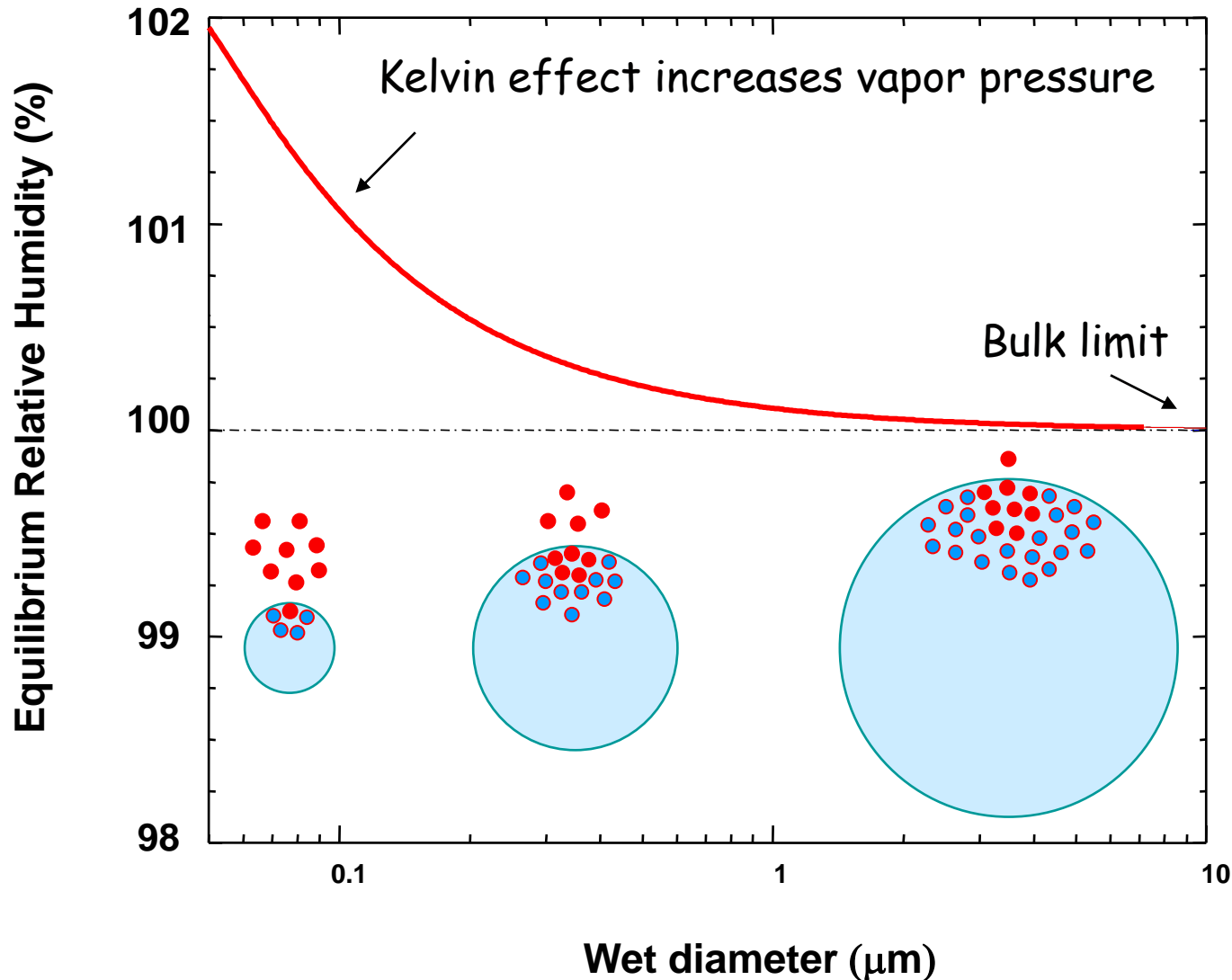
- Surface energy, surface tension - Kelvin effect
- Nucleation of the liquid and ice phase
- Adsorption effects of water

Thermodynamics of droplets: Introduction

- Everything discussed up until now considers “bulk” systems, where there is an infinite amount of each phase for interaction.
- “Bulk” thermodynamics thus assume that interfaces are “flat”.
- Sometimes this is not a good approximation.
- Curvature effects may need to be included in the thermodynamic expressions.
- Main parameters expression curvature effects:
 - Interfacial tension (“surface tension”)
 - Radius of curvature (most often, aerosol/drop radius)

Including curvature: Thermodynamics of droplets

Look at the vapor pressure of a pure H_2O drop



As the droplet size decreases, its equilibrium vapor pressure increases ("Kelvin effect")

Less molecules around in small drops to "keep" H_2O in the droplet phase

Thermodynamics of droplets: Kelvin equation

Take pure substance, with g GFE per mol in each phase (l, g):

$\mu_l^* = \mu_g$ at equilibrium, with flat interface (denoted by *)

Introducing a surface requires work, affecting g_l by $dg_l = \sigma dA$

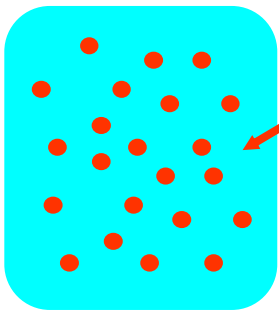
or $\int_{\mu^*}^{\mu} d\mu = \int_0^A \sigma dA \Rightarrow \boxed{\mu = \mu^* + \sigma A}$

Surface tension
Interfacial area

Curved surface g

Kelvin equation: provides vapor pressure over a droplet.

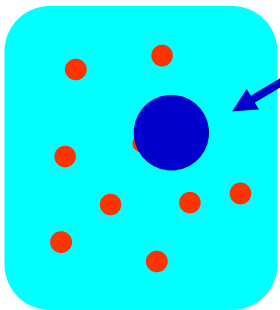
$G_b = n\mu_g$



Water vapor

Before drop formation

$G_a = n_g\mu_g + n_l\mu_l + 4\pi R_p^2\sigma$



droplet

After drop formation

Droplet radius

Thermodynamics of droplets: Kelvin equation

GFE of system before and after droplet formation:

$$\Delta G = G_a - G_b = n_g \mu_g + n_l \mu_l + 4\pi R_p^2 \sigma - n \mu_g \quad \text{but } n = n_g + n_l$$

$$\Delta G = -n_l (\mu_g - \mu_l) + 4\pi R_p^2 \sigma \quad \text{work of droplet formation}$$

$\mu_g - \mu_l \neq 0$ because of curvature, but can be expressed as a pressure ratio.

Associate μ_l with droplet (curved surface with vapor pressure P) and μ_g with "flat interface" with vapor pressure P^* . Then:

$$d\mu = -\cancel{s}dT + v dP = \frac{RTdP}{P} \Rightarrow \int_{\mu_l}^{\mu_g} d\mu = RT \int_P^{P^*} \frac{dP}{P} \Rightarrow \mu_g - \mu_l = RT \ln \frac{P}{P^*}$$

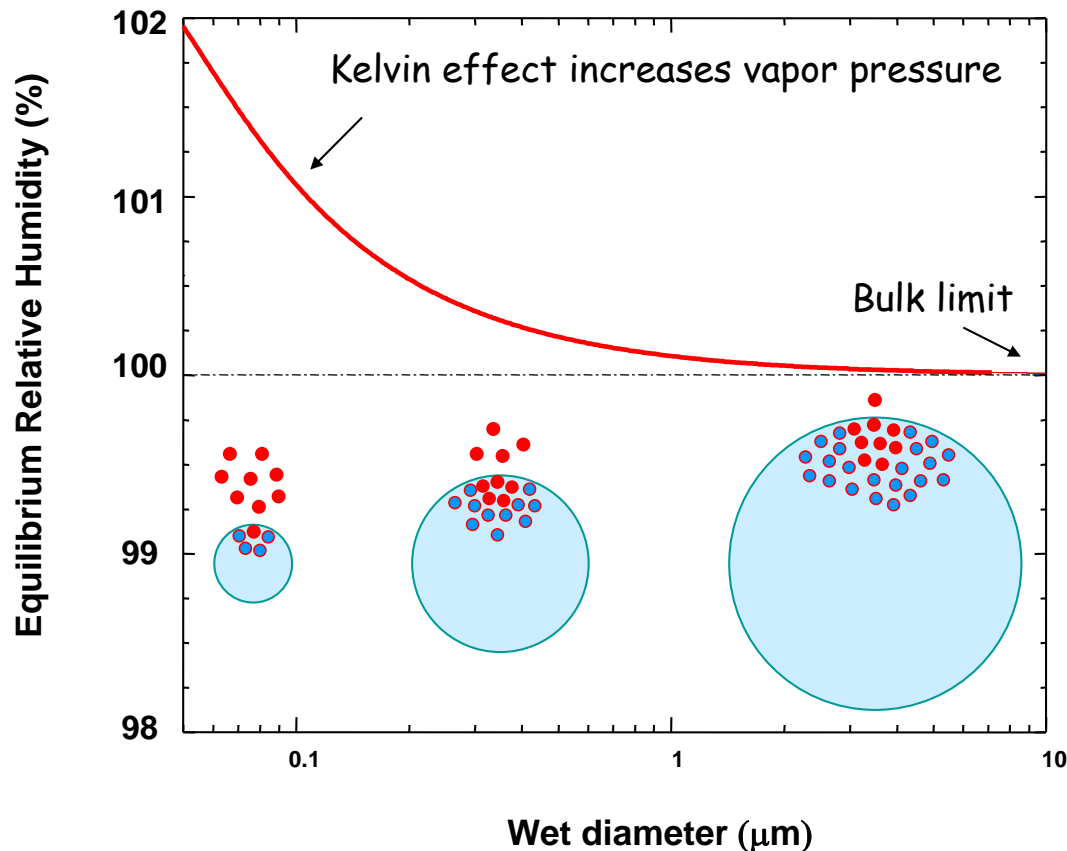
const.

$$\text{Also } n_l = \frac{4\pi R_p^3}{3 v_l} \quad \text{Liquid molar volume}$$

$$\text{So: } \Delta G = -\frac{4\pi R_p^3}{3 v_l} RT \ln \frac{P}{P^*} + 4\pi R_p^2 \sigma$$

Thermodynamics of droplets: Kelvin equation

At equilibrium $\frac{\partial}{\partial R_p} \Delta G = 0$, so: $P = P^* \exp\left(\frac{2\sigma v_l}{RTR_p}\right)$ Kelvin Equation



In general, Kelvin effect:

- negligible for $D_p > 1\mu\text{m}$
- small for $0.1\mu\text{m} < D_p < 1\mu\text{m}$
- strong for $D_p < 0.1\mu\text{m}$

Not generally considered in regional/global aerosol models.

Very important for cloud droplet formation and new particle formation theories.

Thermodynamics of droplets: Köhler equation

Apply Kelvin equation to a pure water droplet (i.e., σ_w and $v_l = \frac{M_w}{\rho_w}$)

$$P = P^* \exp\left(\frac{4M_w\sigma}{RT\rho_w D_p}\right)$$

Dissolved substances in the drop depress water vapor pressure.
Assume $\sigma_w, v_l \sim \text{const.}$ then only P^* changes (given by Raoult's law)

$$\frac{P}{P^{sat}} = x_w \gamma_w \exp\left(\frac{4M_w\sigma}{RT\rho_w D_p}\right) \quad \text{Köhler Equation}$$

The above is the full form of the equation, without simplifications

Thermodynamics of droplets: Köhler equation

One can invoke simplifying assumptions:

$$x_w = \frac{n_w}{n_w + in_s} = 1 - \frac{in_s}{n_w + in_s} \approx 1 - \frac{in_s}{n_w} = 1 - \frac{in_s}{\frac{\pi}{6} D_p^3 \frac{\rho_w}{M_w}} = 1 - \frac{6 M_w in_s}{\pi \rho_w D_p^3}$$

$$= 1 - \frac{B}{D_p^3} \quad \text{where} \quad B = \frac{6 M_w}{\pi \rho_w} in_s$$

Moles of solute in droplet
van't Hoff factor of solute in droplet

$$\gamma_w \approx 1 \quad \text{and} \quad \exp\left(\frac{4M_w\sigma}{RT\rho_w D_p}\right) \approx 1 + \frac{A}{D_p} \quad \text{where} \quad A = \frac{4M_w\sigma}{RT\rho_w}$$

Substitution into full Köhler equation, and considering leading terms:

$$S = \frac{P}{P^{sat}} = 1 + \frac{A}{D_p} - \frac{B}{D_p^3}$$

Simplified Köhler equation

↑

Saturation ratio

↑

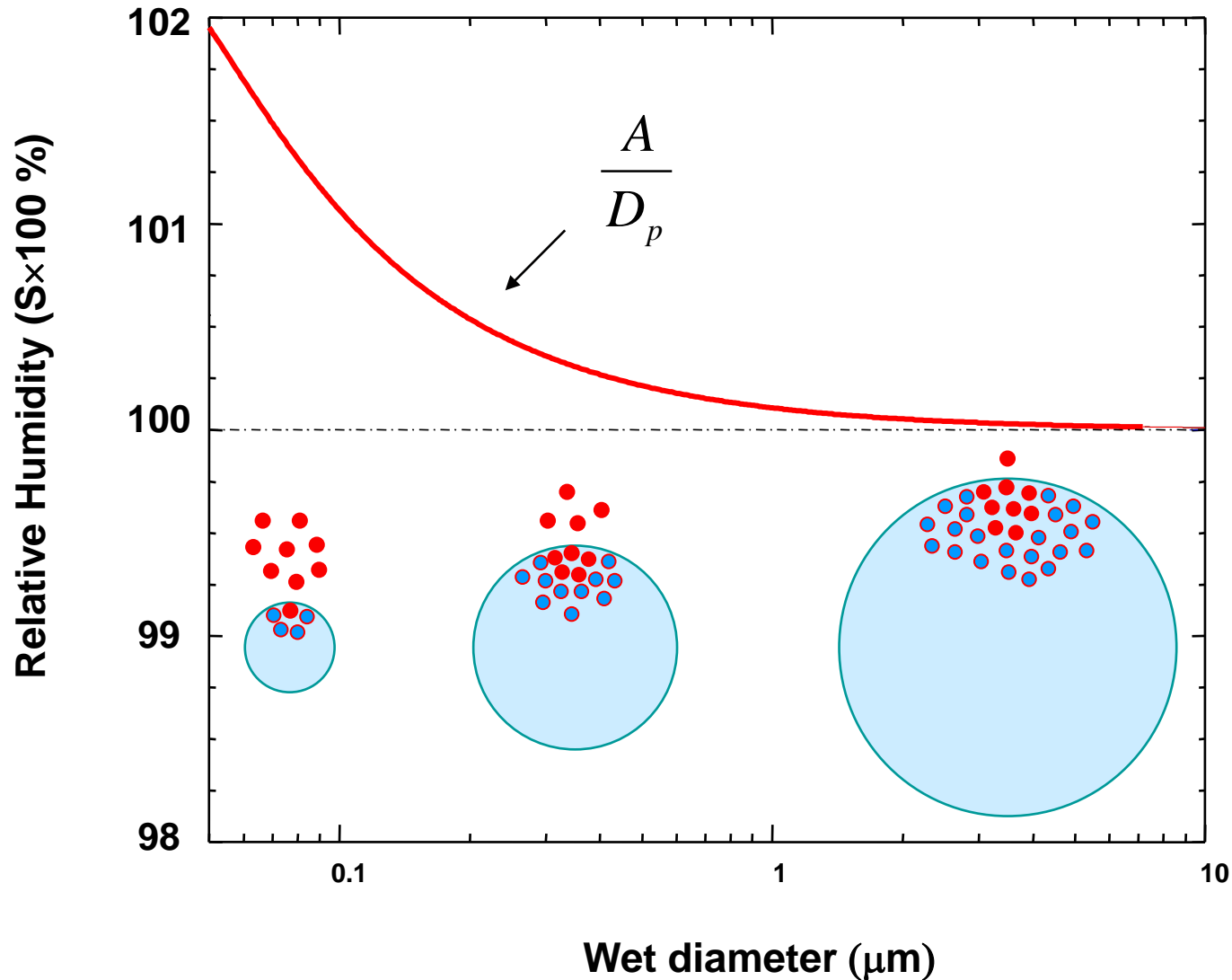
"Kelvin" term

↑

"Raoult" term

Thermodynamics of droplets: Köhler equation

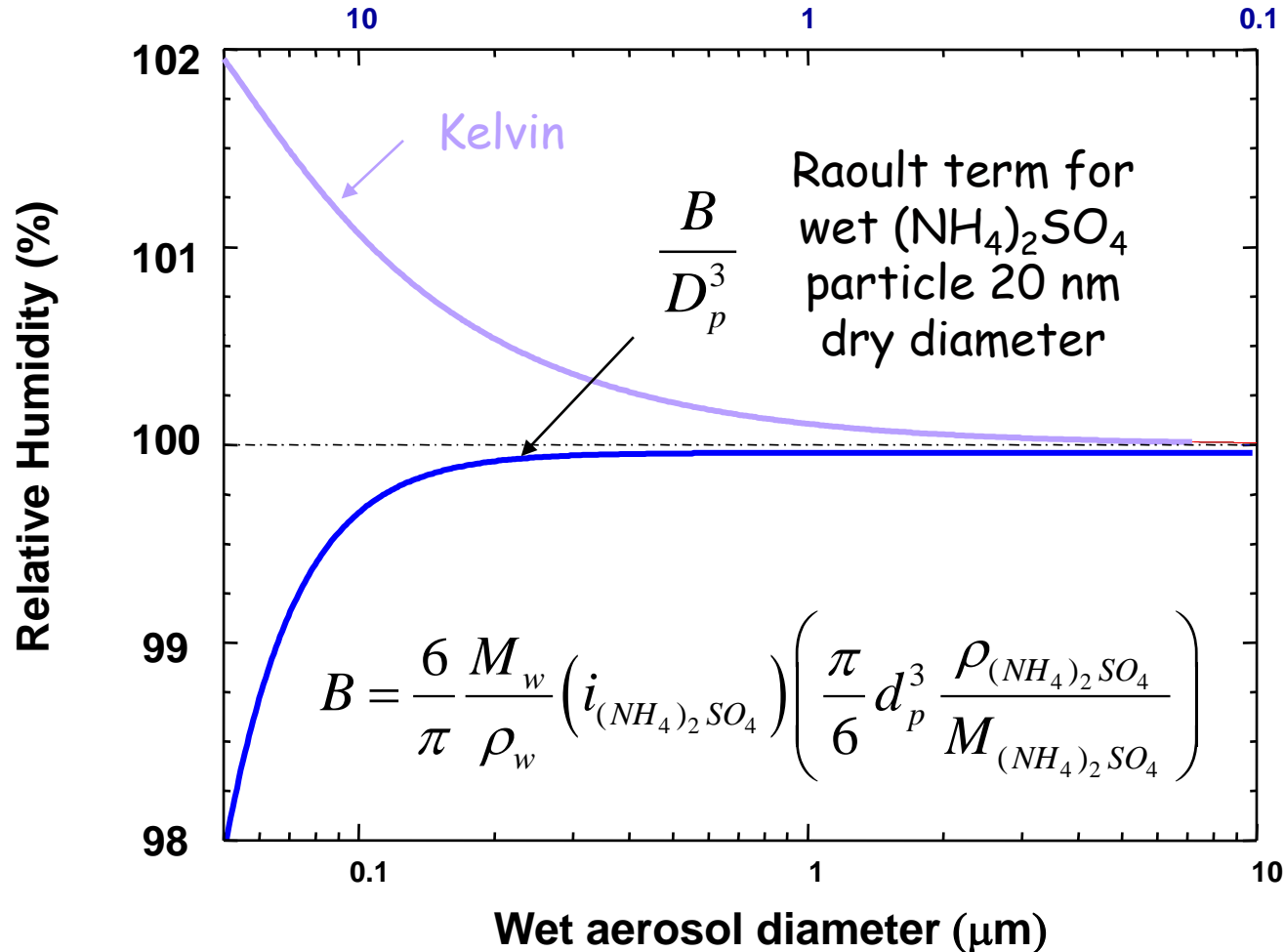
First plot the Kelvin term



Thermodynamics of droplets: Köhler equation

Take same drop and add some solute

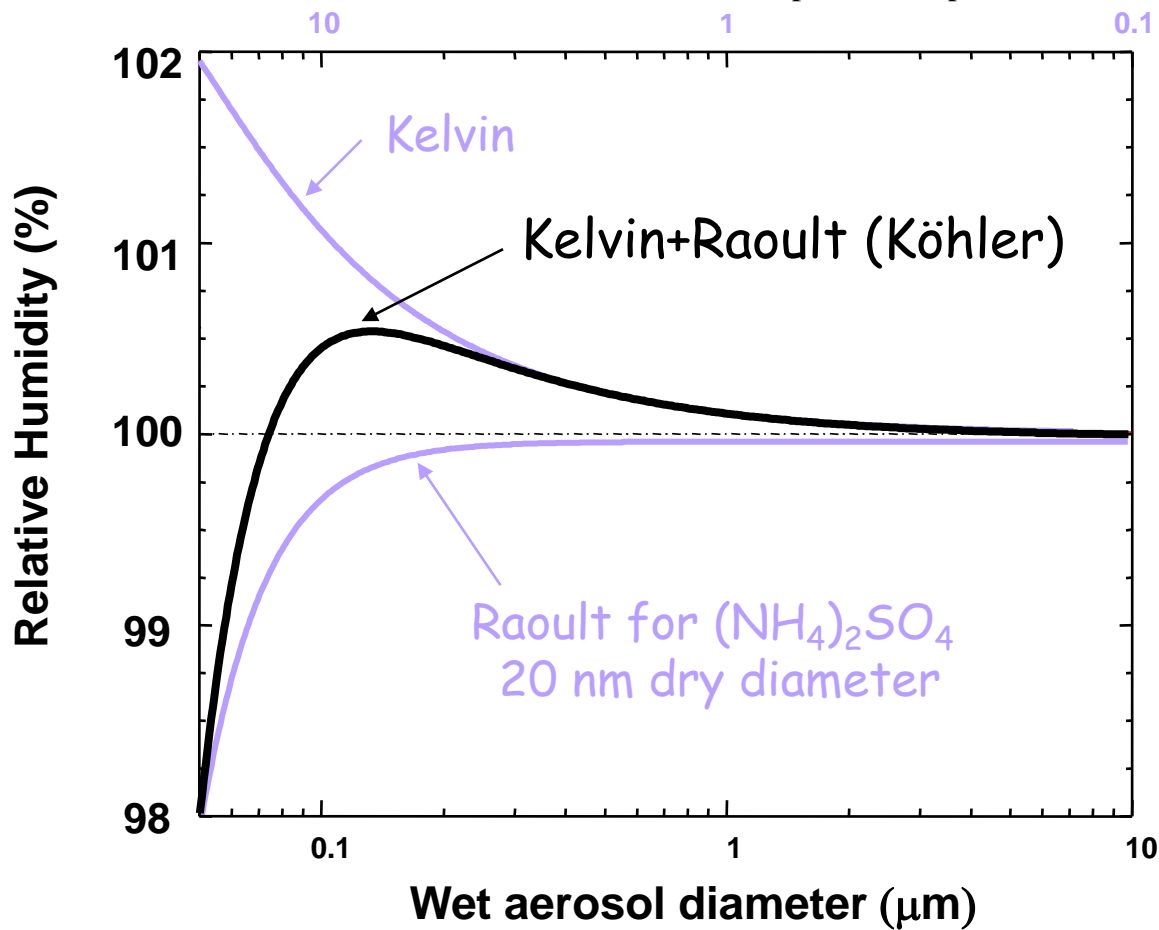
Solute Concentration (M)



Thermodynamics of droplets: Köhler equation

Both effects together: equilibrium vapor pressure of a wet aerosol.

$$S = \frac{P}{P^{sat}} = 1 + \frac{A}{D_p} - \frac{B}{D_p^3}$$



The combined Kelvin and Raoult effects is the simplified **Köhler equation**.

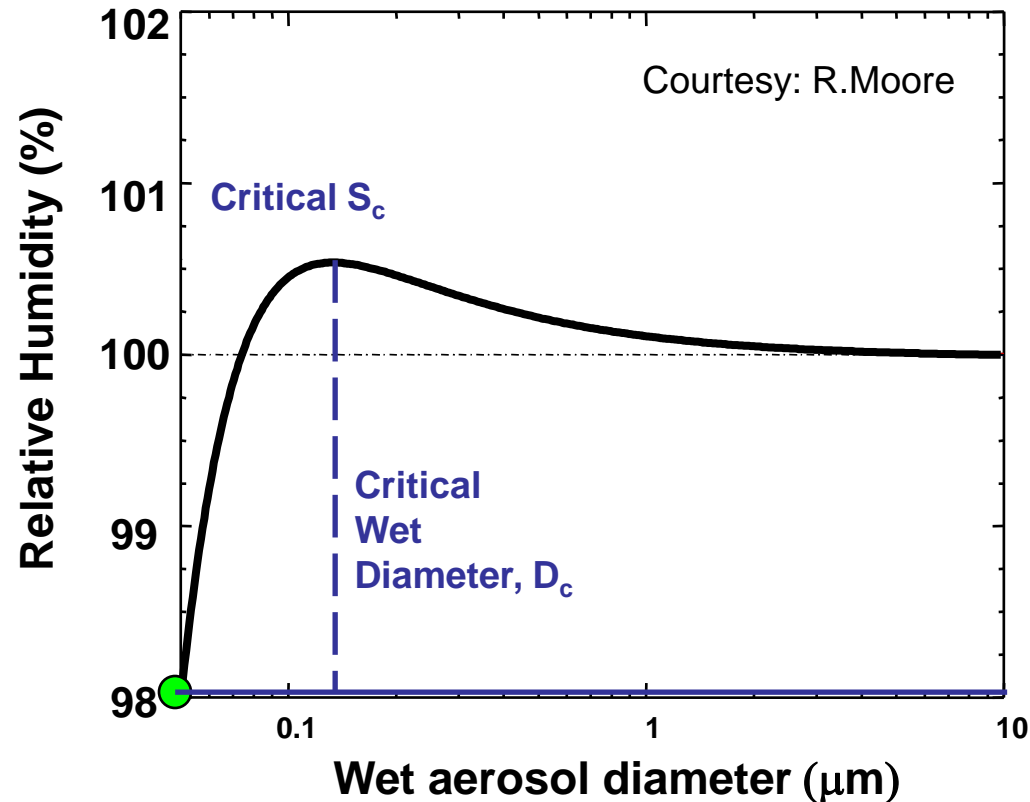
You can be in equilibrium **even if** you are above saturation.

Regions of stability/instability of ambient droplets

Dynamical behavior of an aerosol particle in a variable RH environment.

Wet Aerosol
(Haze)

Cloud Droplet

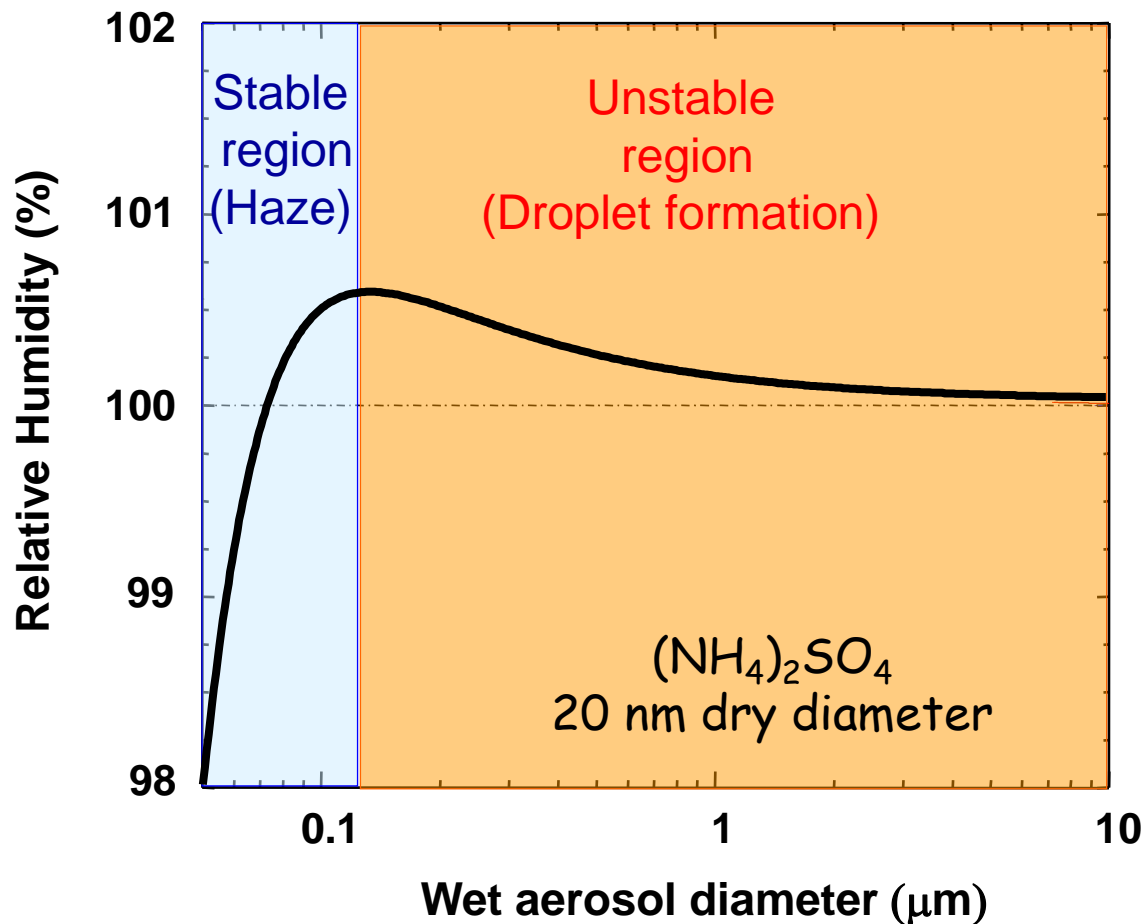


**If ambient S exceeds the maximum, particles grow uncontrollably.
They are said to act as Cloud Condensation Nuclei (CCN)**

Thermodynamics of droplets: Köhler equation

When the ambient saturation ratio $S > S_c$ AND the wet size is larger than D_c , it acts as a CCN. ($S > S_c$ sufficient).

This is the direct microphysical link between aerosols and clouds



Köhler theory:

$$s_c = \left(\frac{4A^3}{27B} \right)^{1/2}$$

$$s_c \sim d_{\text{dry}}^{-3/2}, \epsilon_{\text{soluble}}^{-1/2}$$

Size is more important than composition

Understanding & parameterizing CCN activity...

Petters and Kreidenweis (2007) expressed the solute parameter in terms of a "hygroscopicity parameter", κ

$$s_c = \left(\frac{4A^3}{27B} \right)^{1/2} \longrightarrow s_c = \left(\frac{4A^3}{27\kappa} \right)^{1/2} d^{-3/2}$$

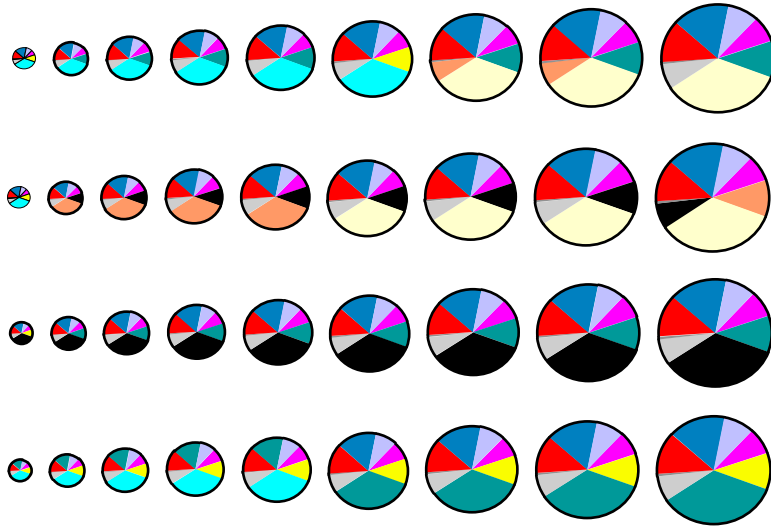
$\kappa \sim 1$ for NaCl, ~ 0.6 for $(\text{NH}_4)_2\text{SO}_4$, $\sim 0-0.3$ for organics

κ rarely exceeds 1 in atmospheric aerosol

Simple way to think of κ : the "equivalent" volume fraction of NaCl in the aerosol (the rest being insoluble).

$\kappa \sim 0.6 \Rightarrow$ particle behaves like 60% NaCl, 40% insoluble

Aerosol Problem: Complexity



An integrated “soup” of

- Inorganics, organics (1000's)
- Particles can have uniform composition with size...
- ... or not
- Can vary vastly with space and time (esp. near sources)

Organic species are a headache

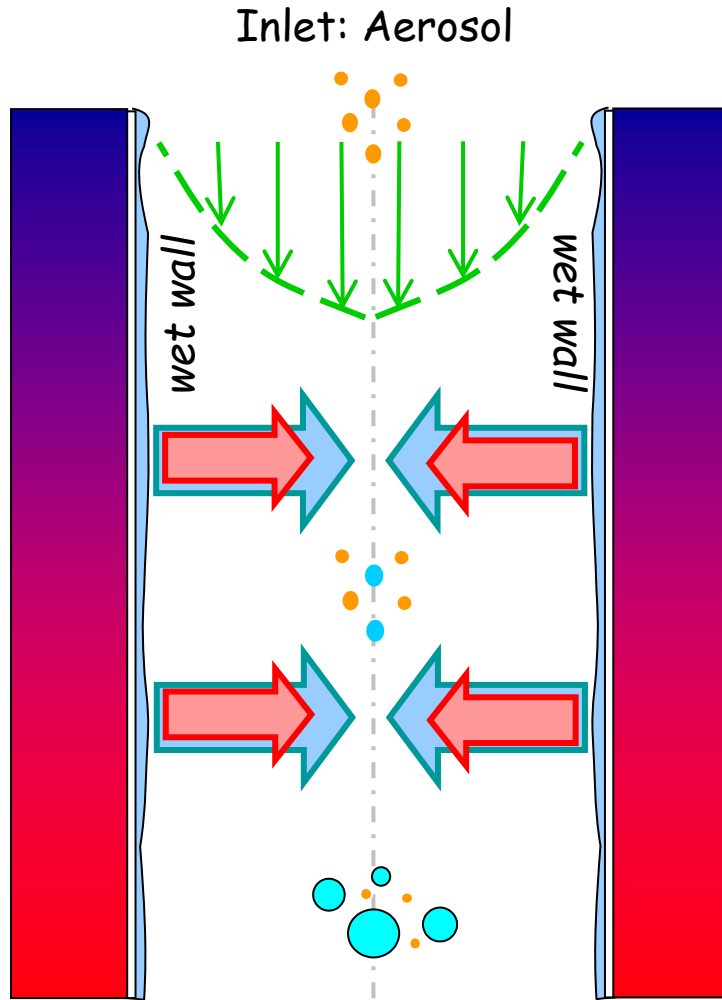
- They can facilitate cloud formation by acting as surfactants and adding solute (hygroscopicity)
- Oily films can form and delay cloud growth kinetics

In-situ data to study the aerosol-CCN link

Usage of CCN activity measurements to “constrain” the above “chemical effects” on cloud droplet formation.

Measuring CCN activity of ambient particles:

Continuous-Flow Streamwise Thermal Diffusion Chamber



Outlet: [Droplets] = [CCN]

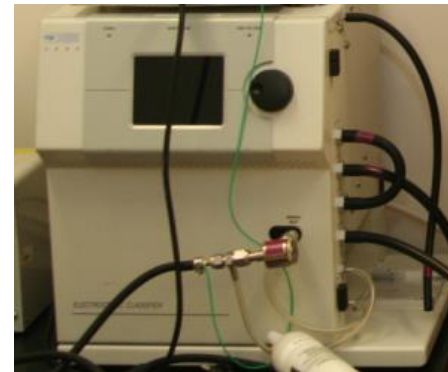
Metallic cylinder with walls wet.
Apply T gradient, and flow air.

- Wall saturated with H_2O .
- H_2O diffuses faster than heat and arrives at centerline first.
- The air is supersaturated with water vapor at the centerline.
- Flowing aerosol at center would activate some into droplets.

Count the **concentration** and **size** of droplets that form with a 1 s resolution.

Measuring hygroscopicity, κ

size-resolved CCN measurements



Size Selection

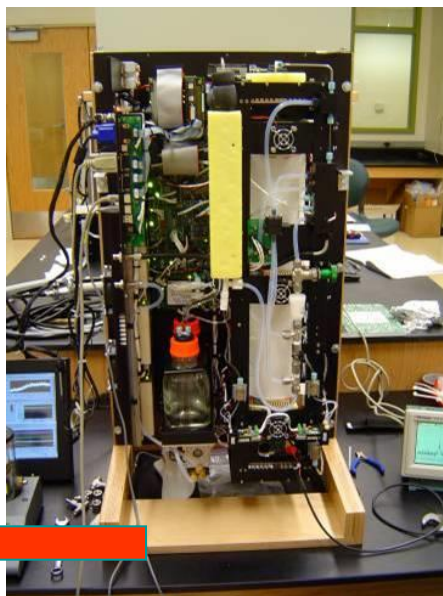


Particle Detection



Count CN

Count
CCN

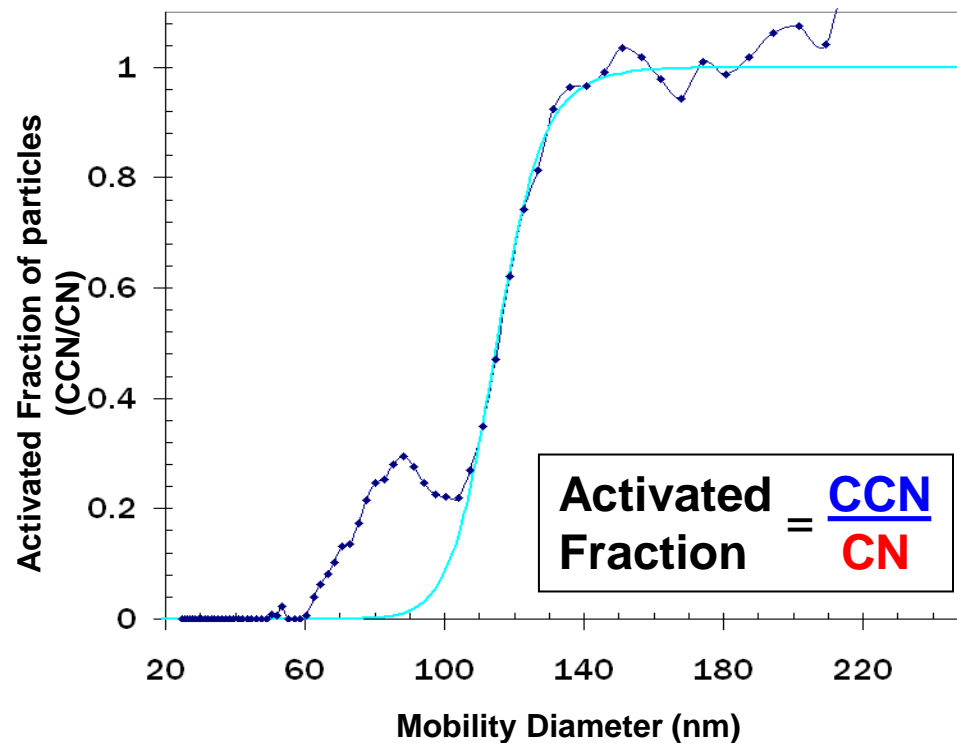


Measuring hygroscopicity, κ

size-res



Results: "activation curves"
CCN/CN as a function of d



Selection

Count
CCN



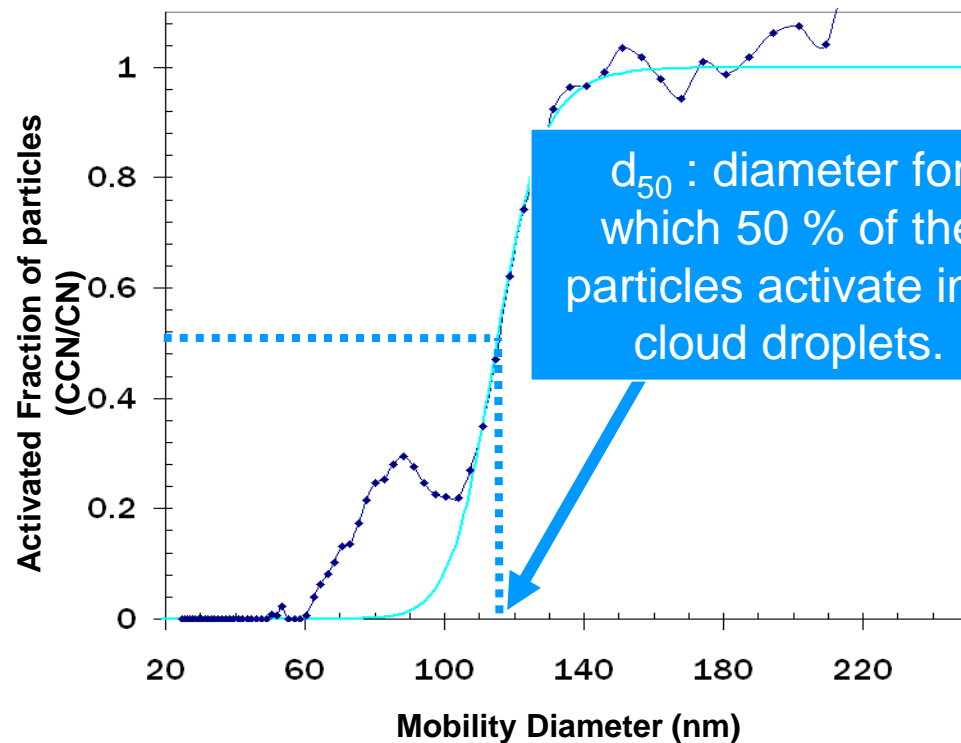
Count CN

Measuring hygroscopicity, κ

size-res



Results: "activation curves"
CCN/CN as a function of d



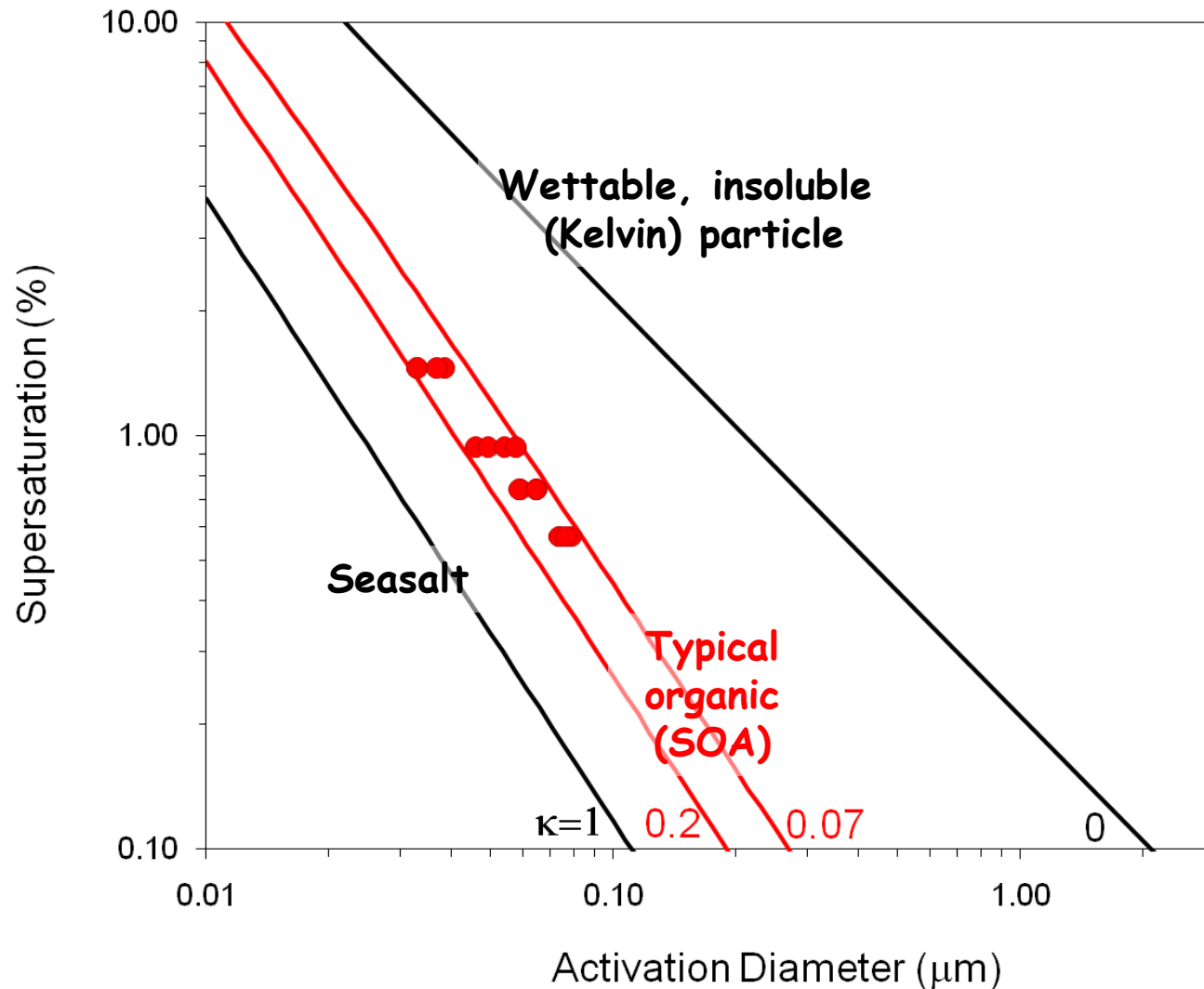
Count
CCN



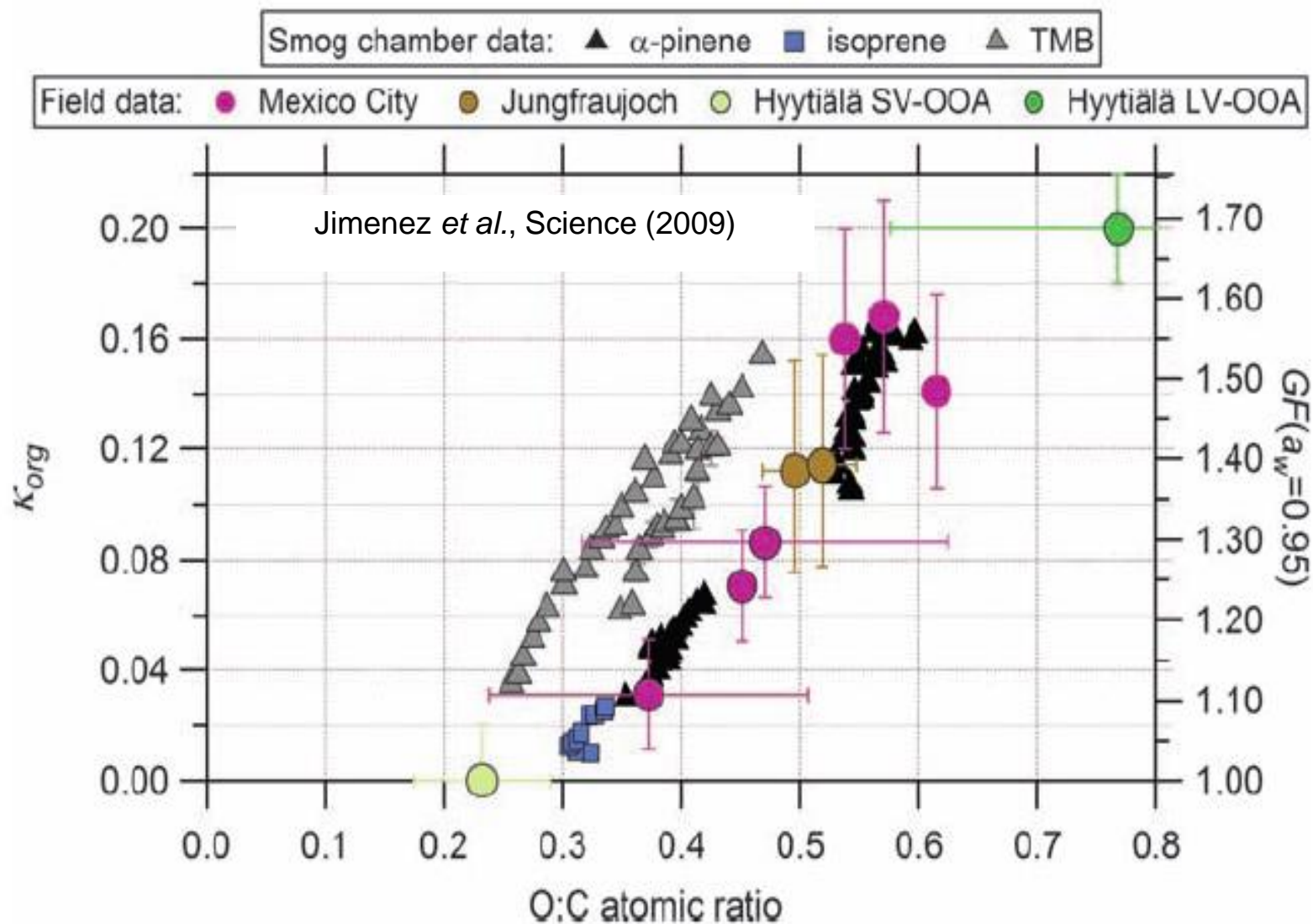
Count CN

Selection

Hygroscopicity parameter for organics

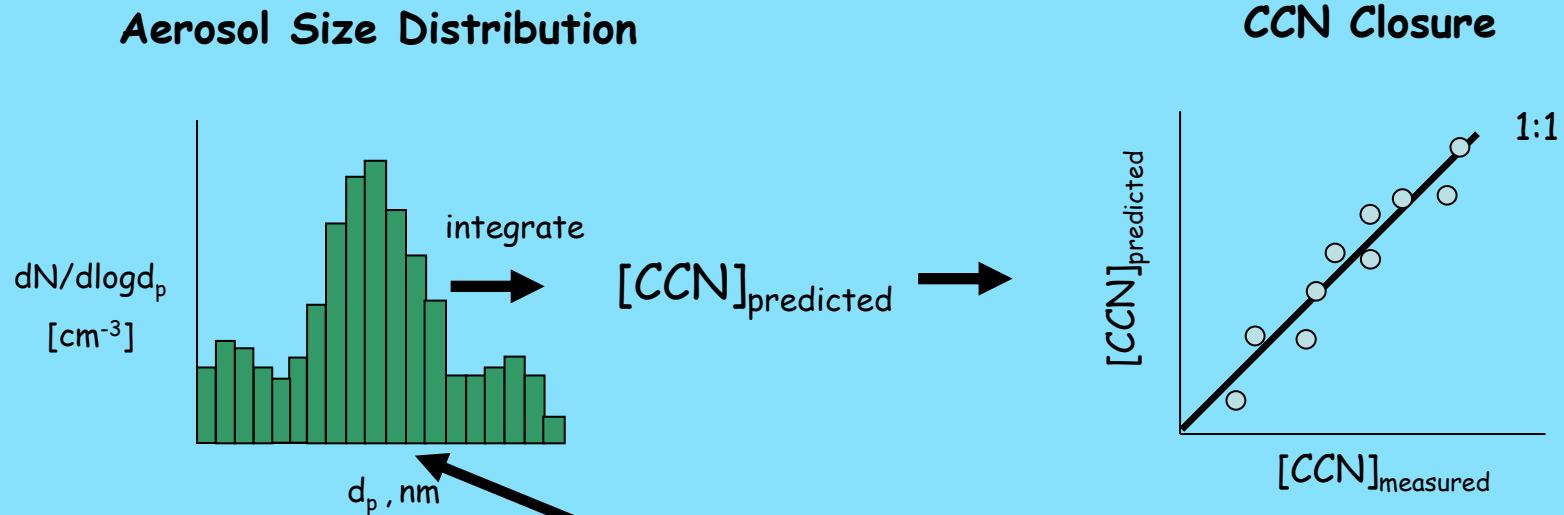


κ_{org} depends on oxidation state and precursor



CCN "Closure": test of Köhler theory

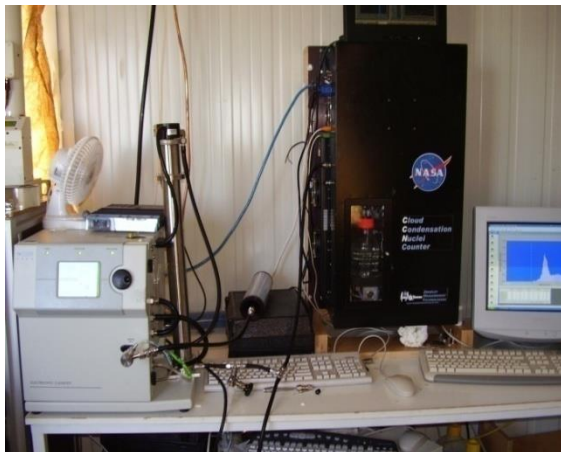
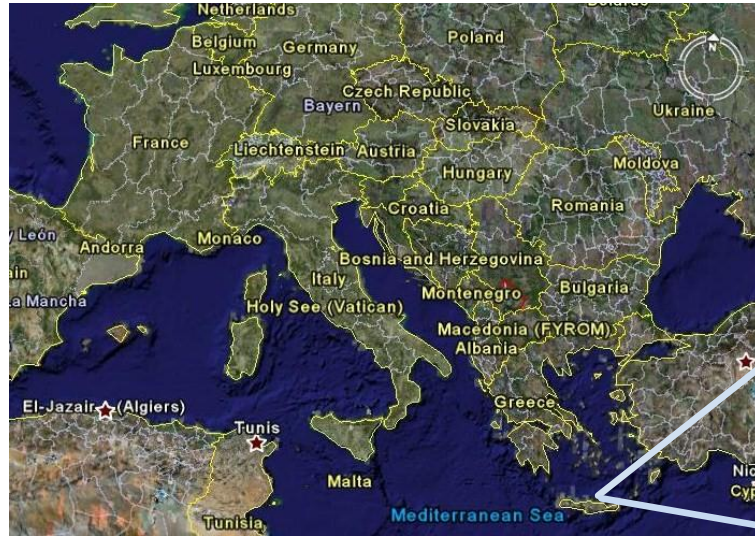
Compare measurements of CCN to predictions using Köhler activation theory and κ description



Use theory to predict the particles that can act as CCN based on measured chemical composition and CCN instrument supersaturation.

Finokalia Aerosol Measurement Campaign

(FAME-07) - Summer 2007



DMT CCN counter
Supersaturation
range: 0.2-1.0%

TSI 3080 SMPS
Size range: 20-460
nm

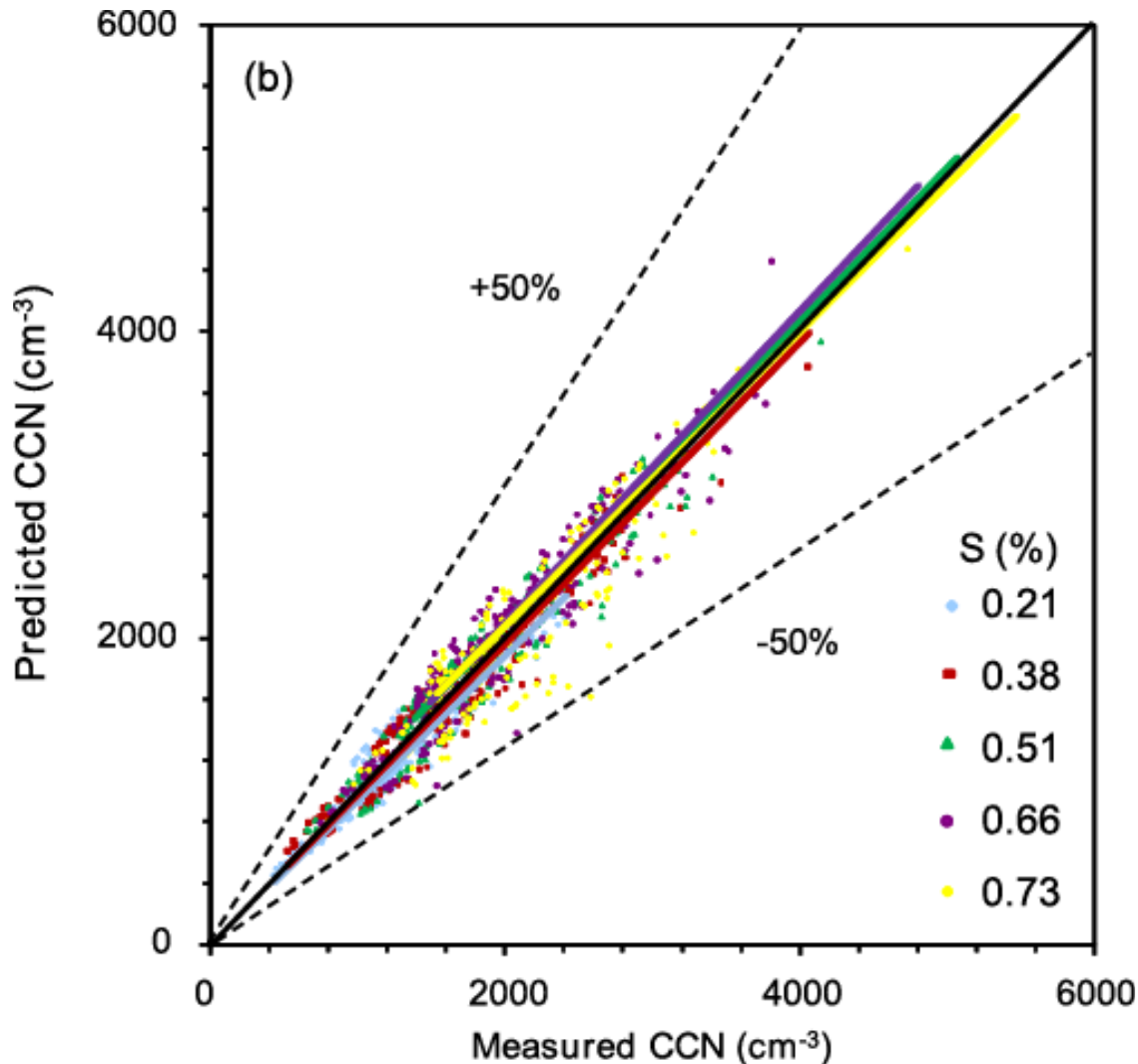
Low-vol impactor
Ionic composition
measured via IC

WSOC/EC/OC also
measured



(Bougiatioti et al., ACP, 2009)

FAME-07 CCN closure study



2% overprediction
(on average).

Introducing
comprehensive
composition into
CCN calculation
gives excellent CCN
closure.

Köhler (CCN
activation) theory
really works.

(Bougiatioti et al., ACP, 2009)

Some "take-home" messages

- Physically based formulations for description of CCN activity and the cloud droplet formation in atmospheric models rely heavily on thermodynamics.
- Single-parameter ("kappa") Köhler theory is adequate for describing the CCN of aerosol.
- Size-resolved measurements of CCN activity are very useful for constraining the extent and sources of aerosol hygroscopicity on cloud droplet formation.
- The water-soluble fraction of oxidized organics is very hygroscopic, and is surprisingly constant.
- The cumulative effect of organics on CCN activity can likely be described by simple relationships of the form:

$$\kappa_{\text{org}} = (0.25 \pm 0.05) \varepsilon_{\text{sol}} \quad \text{or} \quad \kappa_{\text{org}} \sim 0.1$$

Dust and Cloud droplets: model vs. reality

Current CCN theory makes very important assumptions about insoluble particles (dust).

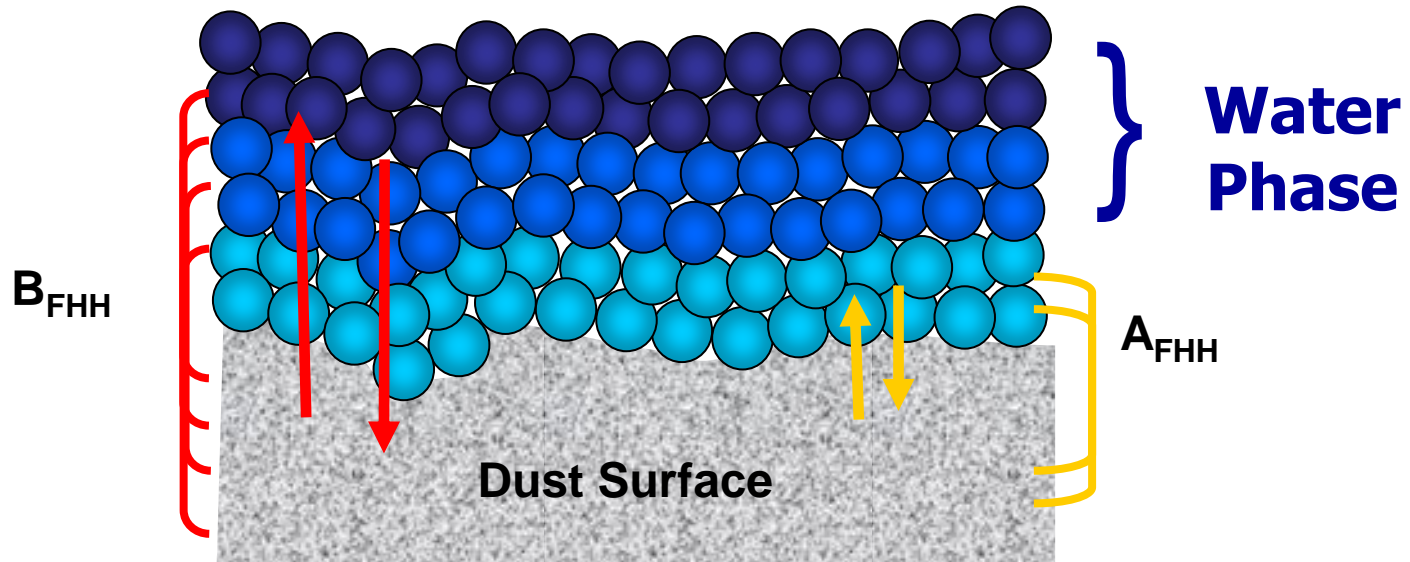
- They are not good CCN... because
- The CCN activity of solubles depends *solely* on soluble "coatings" from atmospheric processing.
- Theory works well when there is a fair amount of soluble solute in the particles ($\sim >10\%$ by mass).

Does this mean fresh dust (no solute) are not CCN?

- Dust particles are wettable, and can swell. This means they do interact with water, but only on their surface.
- Look at the process of *adsorption* of water on dust, and its potential impact on droplet formation.

Describing water adsorption on Dust

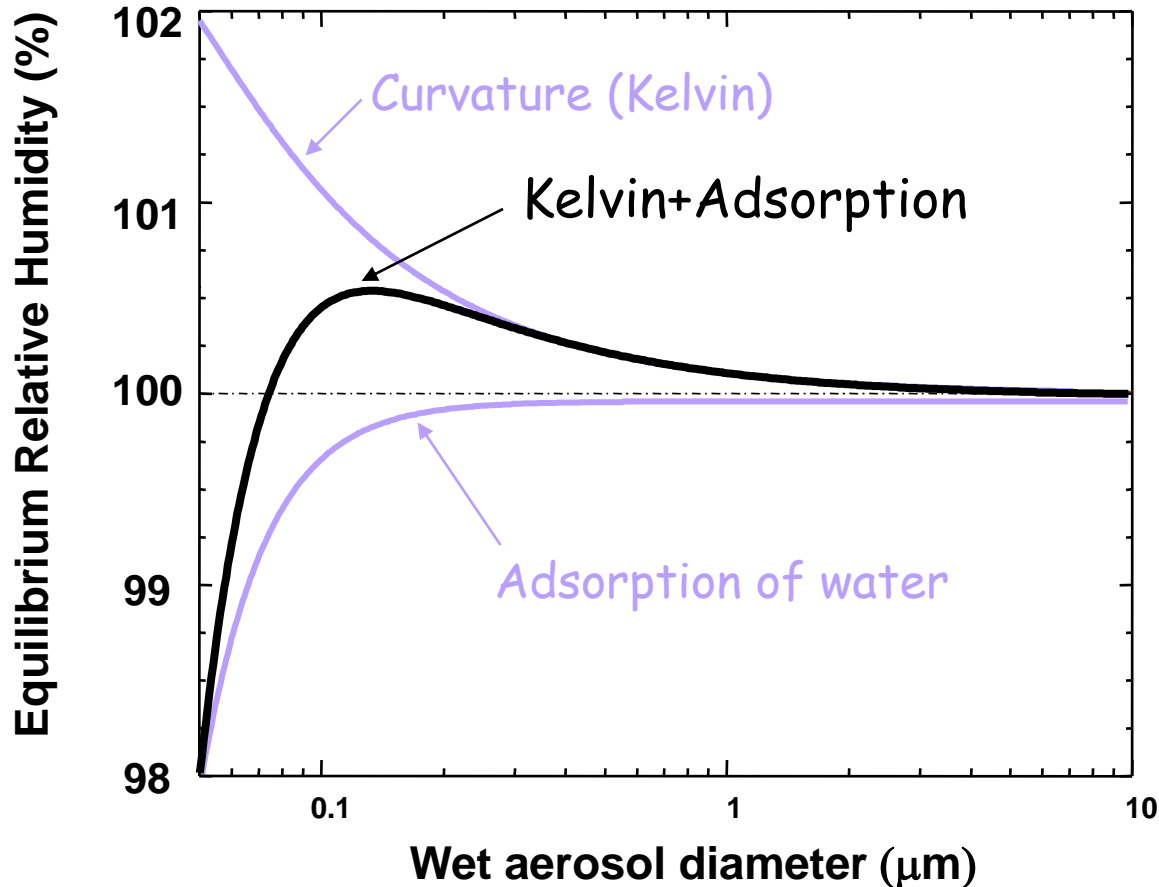
Use the **Frenkel-Halsey-Hill** (FHH) multilayer physisorption isotherm to describe the interaction of water vapor with the dust surface.



- Long-range Van-der-Waals interactions between surface and upper layers are considered by A_{FHH} & B_{FHH} .
- A_{FHH} accounts for interactions between the first monolayer and substrate.
- B_{FHH} quantitatively accounts for the adsorption strength of each additional H₂O monolayer.

Adsorption Activation: new CCN theory

Consider curvature and adsorption effects on water activity



The combined curvature and effects determines the wet diameter at equilibrium.

Looks like a "classical" CCN!

Köhler: $S_c \sim d_{\text{dry}}^{-1.5}$

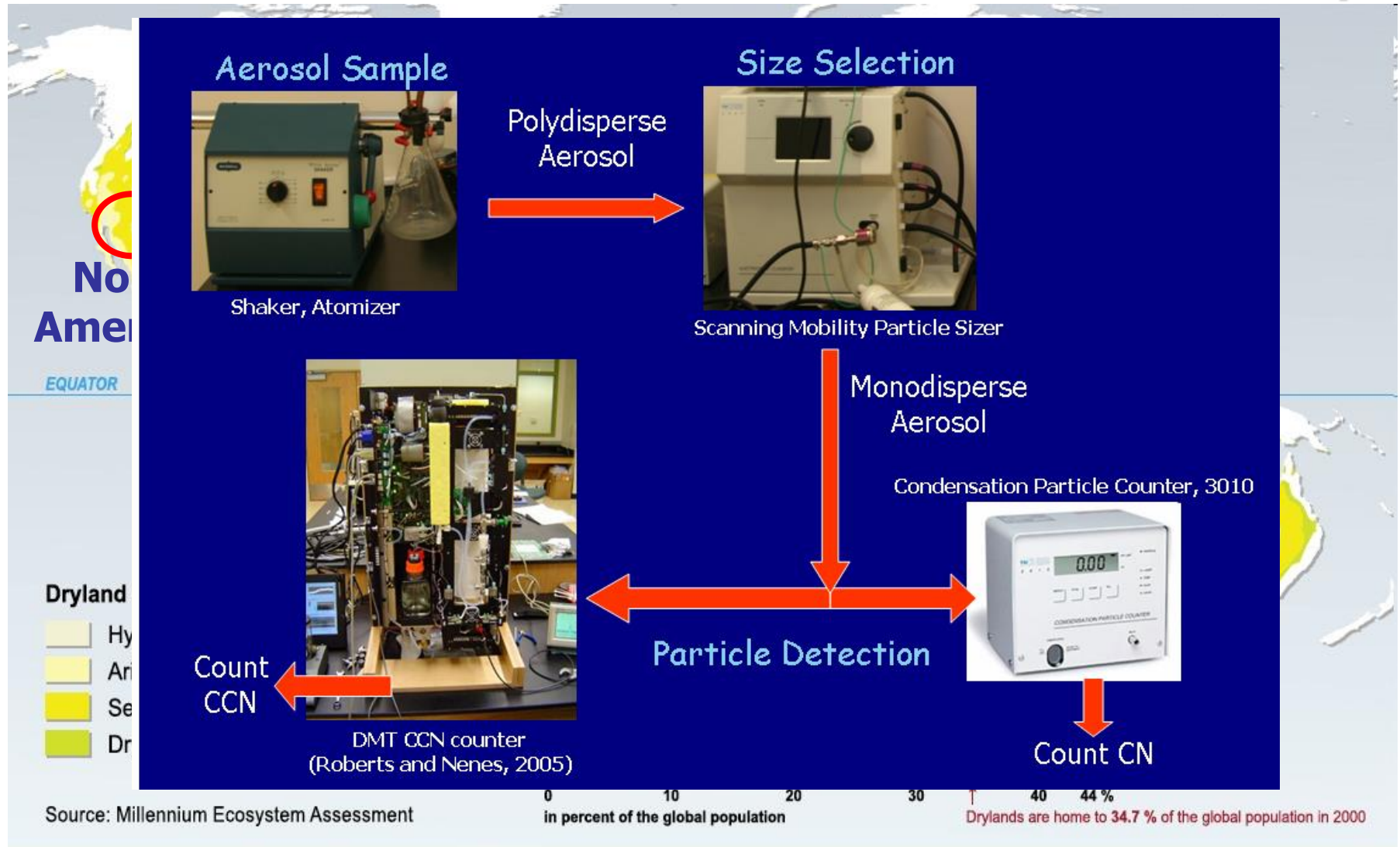
Adsorption $S_c \sim d_{\text{dry}}^x$
with $x < -1.5$

x can be used to infer the type of physics! (adsorption, Köhler)

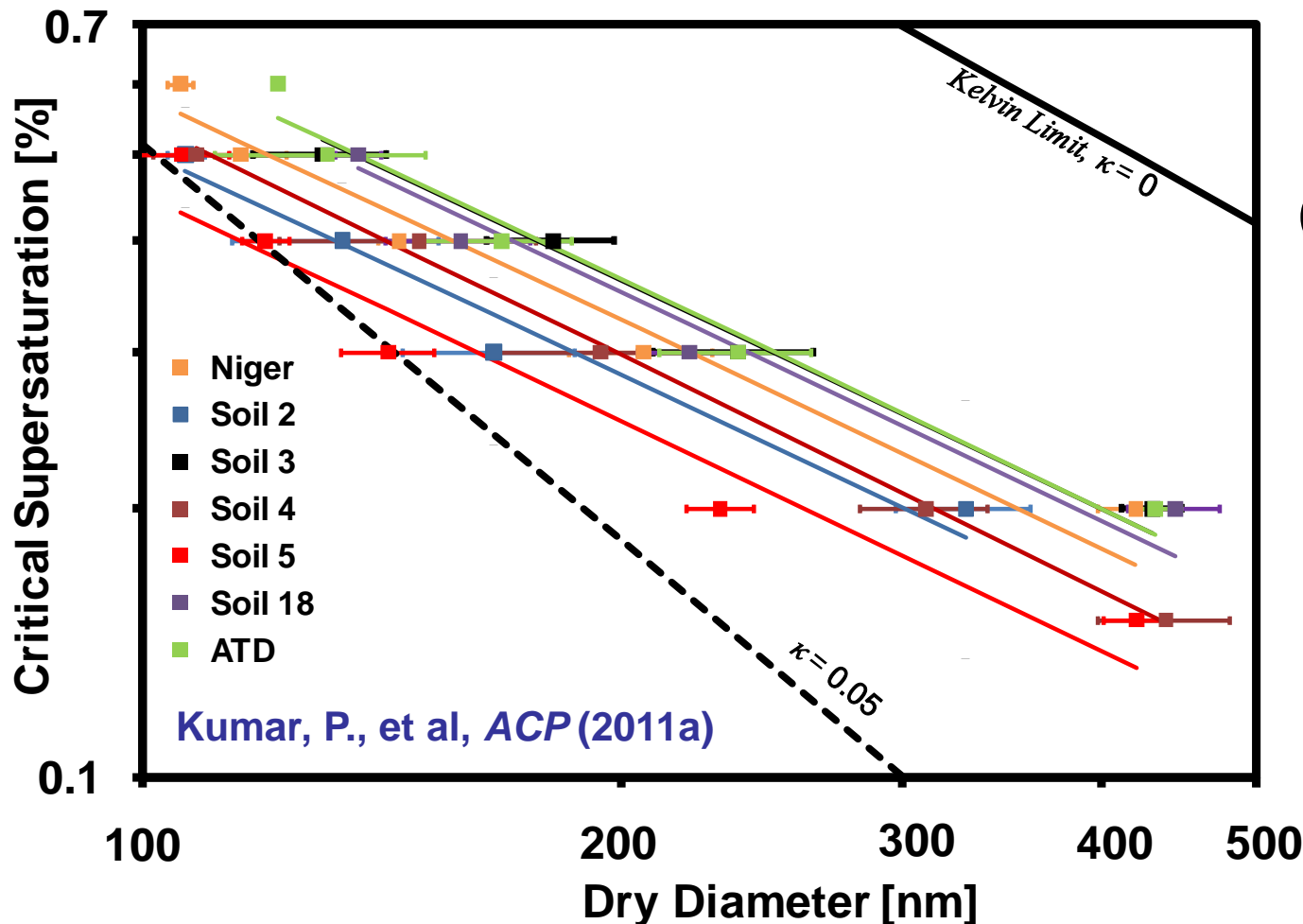
CCN activity of dry-generated dust

Collected soils from dust source regions

Generate dust & analyze



CCN activity of dry-generated dust



CCN activity is
region dependent
(Asian > Niger > ATD)

... but not terribly
variable

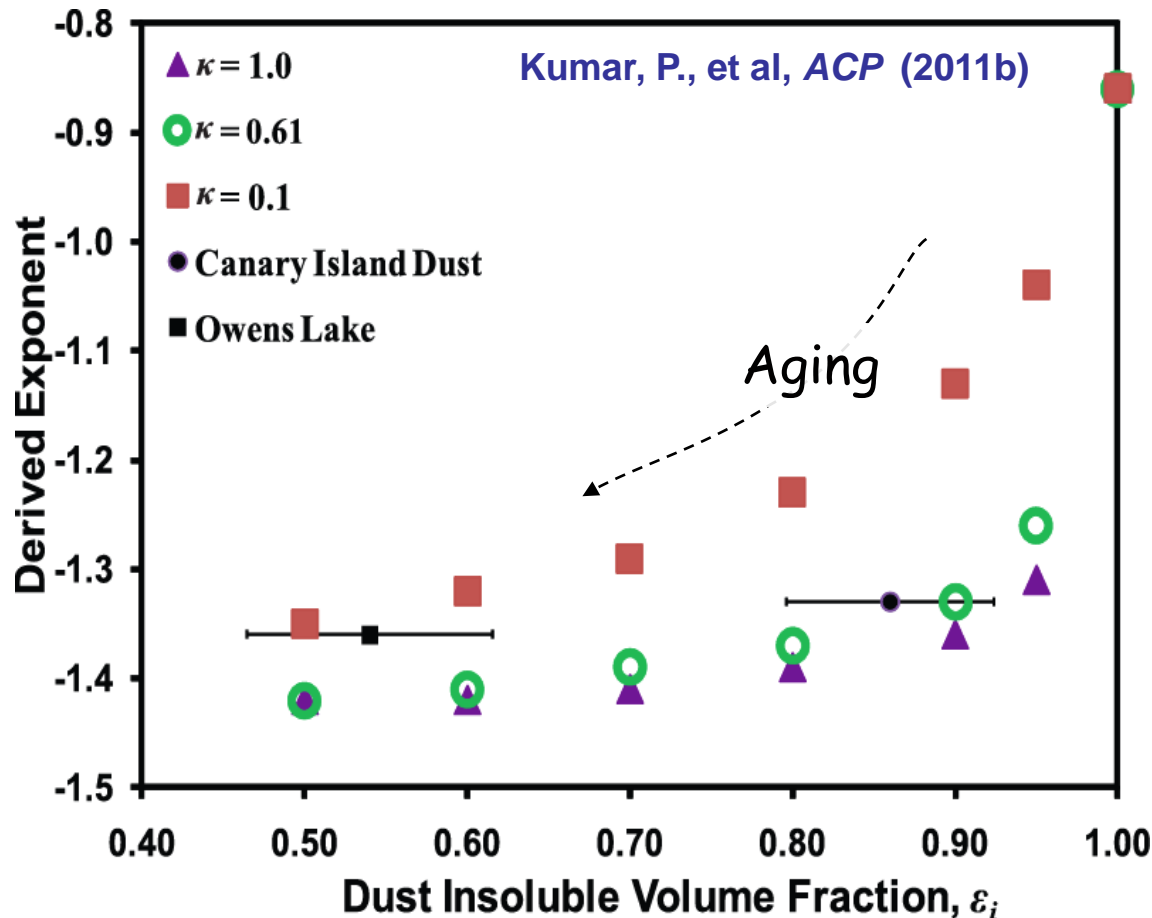
D_{dry} exponent $x < -1$

Adsorption
dominates CCN
activity!

- Fine mode dust is CCN active – equivalent to having up to 10% vol. fraction of ammonium sulfate (@ 100 nm). Without ANY solute present.
- "Average" dust: $A_{FHH} \sim 2.50 \pm 0.50$ $B_{FHH} \sim 1.20 \pm 0.10$

Including ageing effects on dust

- Aged dust contains soluble material as well. One can combine both KT and FHH-AT to provide a **unified framework for dust activation**, from which you can compute the x for $S_c \sim d_{\text{dry}}^x$.



This means: the CCN framework developed for adsorption activation can be used to describe aged dust as well!

Simple, comprehensive treatment of dust-water cloud interactions

Some References: Bulk Thermodynamics

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Some References: Bulk Thermodynamics

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Some References: Droplet Thermodynamics

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- Kumar, P., Sokolik, I.N., and Nenes, A. (2011) Measurements of Cloud Condensation Nuclei Activity and Droplet Activation Kinetics of Fresh Unprocessed Regional Dust Samples and Minerals, *Atmos.Chem.Phys.*, **11**, 3527-3541
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- <http://nenes.eas.gatech.edu> (CCN measurements & techniques)

An aerial photograph of a rugged mountain range, likely the Himalayas, showing deep valleys and snow-capped peaks. A semi-transparent rectangular box is centered over the middle of the image, containing the text 'THANK YOU !!' in a bold, red, sans-serif font with a black outline.

THANK YOU !!