

# 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

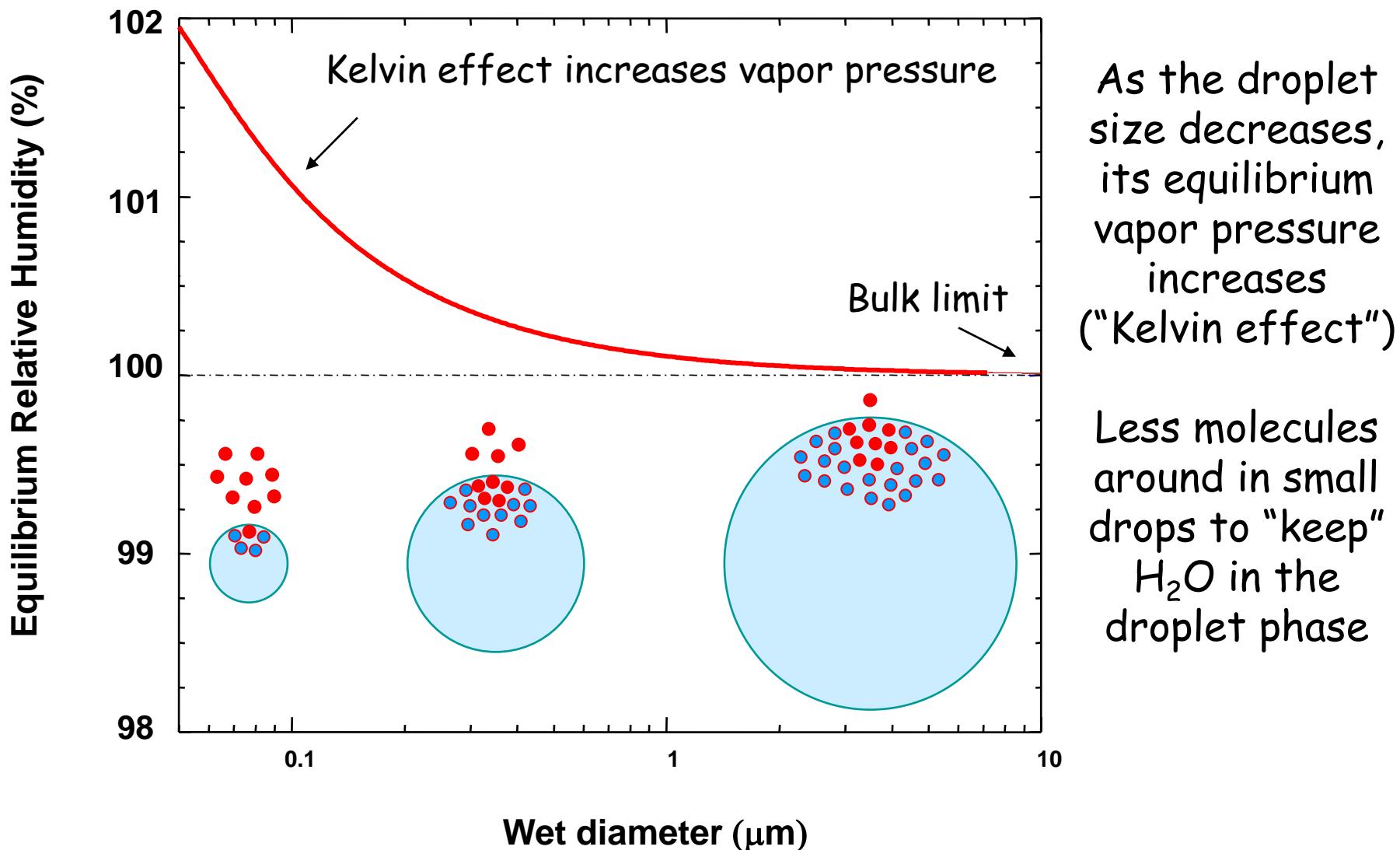
# Thermodynamics of droplets: Introduction

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- 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<sub>2</sub>O drop



# Thermodynamics of droplets: Kelvin equation

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

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

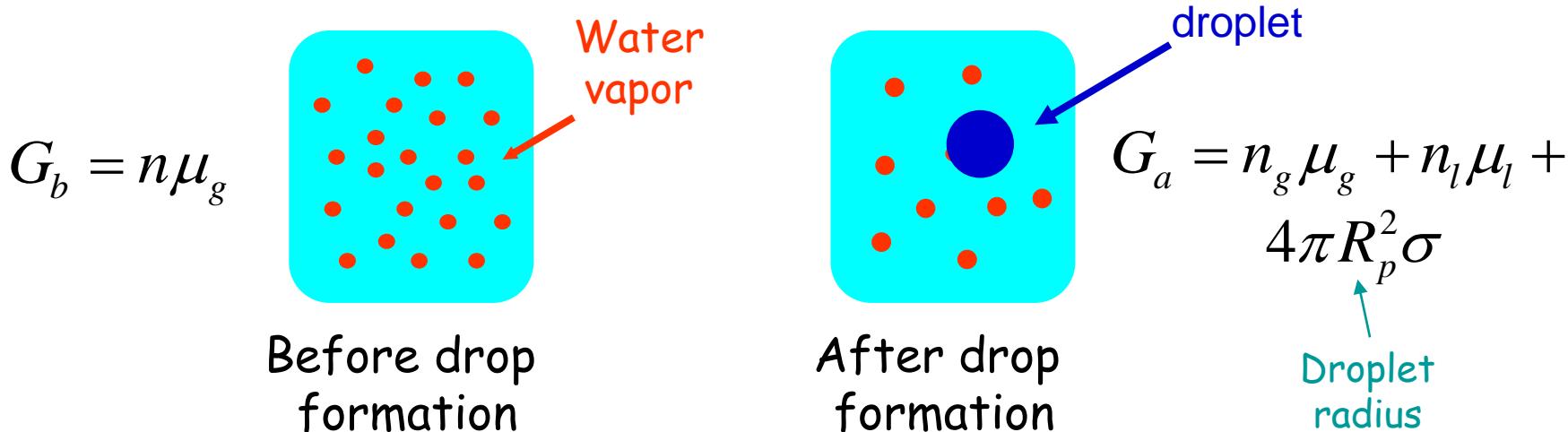
Introducing a surface requires work, affecting  $g_l$  by  $dg_l = \sigma dA$

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

Curved surface  $g$

Surface tension      Interfacial area

**Kelvin equation:** provides vapor pressure over a droplet.



# Thermodynamics of droplets: Kelvin equation

GFE of system before and after droplet formation:

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

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

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

Associate  $\mu_l$  with droplet (curved surface with vapor pressure  $P$ ) and  $\mu_g$  with "flat interface" with vapor pressure  $P^*$ . Then:

$$d\mu = -sdT + vdP = \frac{RTdP}{P} \Rightarrow \int_{\mu_l}^{\mu_g} d\mu = RT \int_P^{P^*} \frac{dP}{P} \Rightarrow \mu_g - \mu_l = RT \ln \frac{P}{P^*}$$

const.

Also  $n_l = \frac{4}{3} \frac{\pi R_p^3}{v_l}$

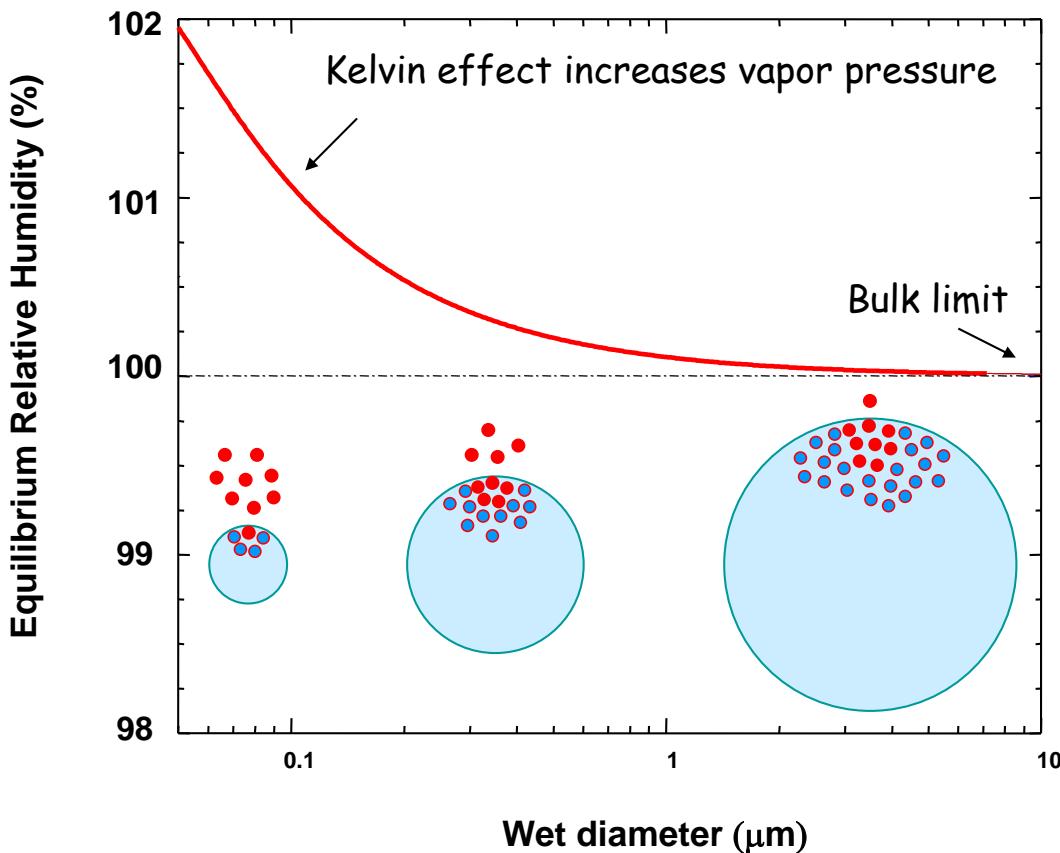
Liquid molar volume

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

# Thermodynamics of droplets: Kelvin equation

At equilibrium  $\frac{\partial}{\partial R_p} \Delta G = 0$ , so:

$$P = P^* \exp\left(\frac{2\sigma v_l}{R T R_p}\right) \quad \text{Kelvin Equation}$$



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.,  $\sigma_w$  and  $\nu_l = \frac{M_w}{\rho_w}$  )

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

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

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

Köhler  
Equation

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

# Thermodynamics of droplets: Köhler equation

One can invoke simplifying assumptions:

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

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

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

Substitution into full Köhler equation, and considering leading terms:

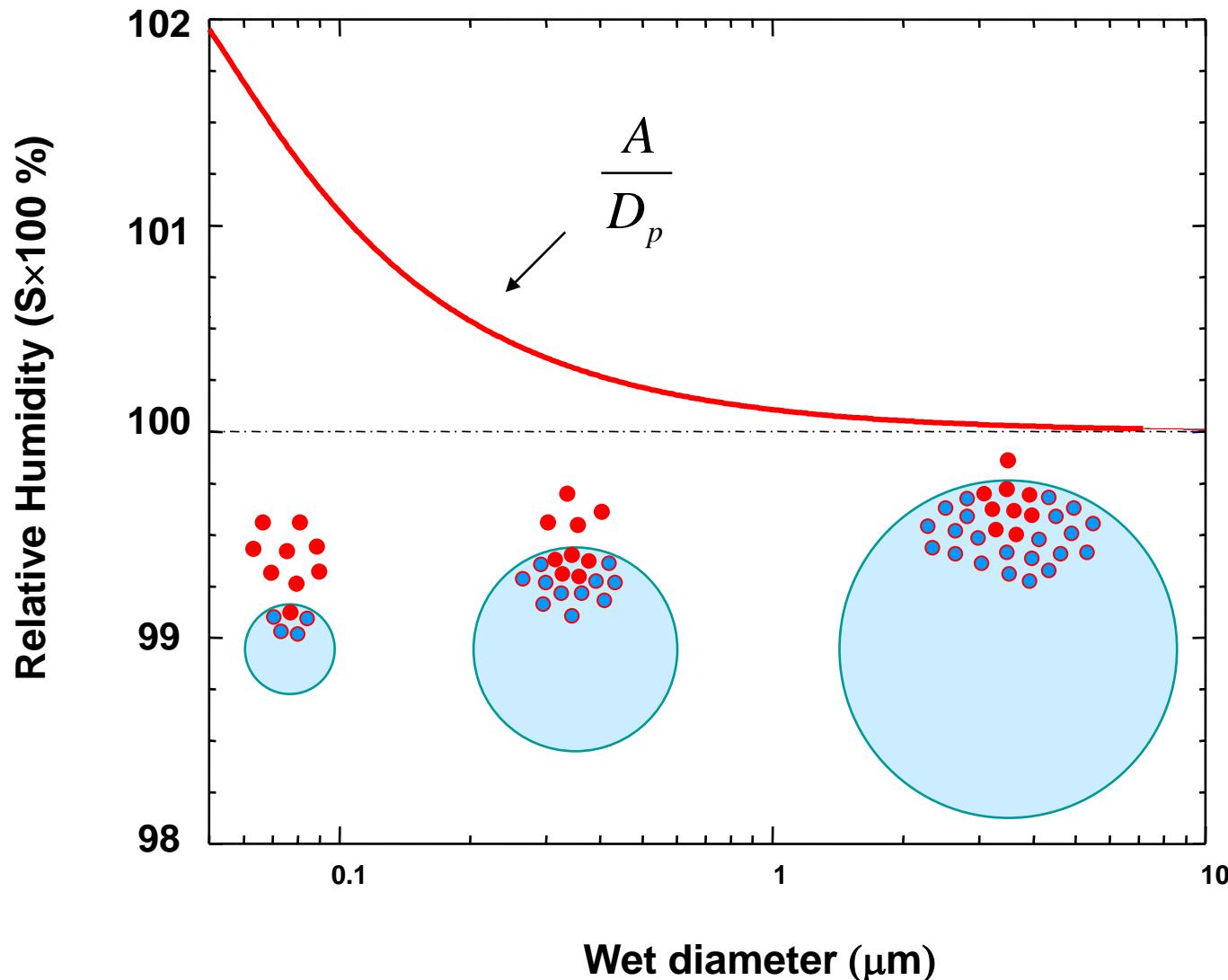
$$S = \frac{P}{P^{sat}} = 1 + \frac{A}{D_p} - \frac{B}{D_p^3}$$

Simplified Köhler equation

Saturation ratio      "Kelvin" term      "Raoult" term

# Thermodynamics of droplets: Köhler equation

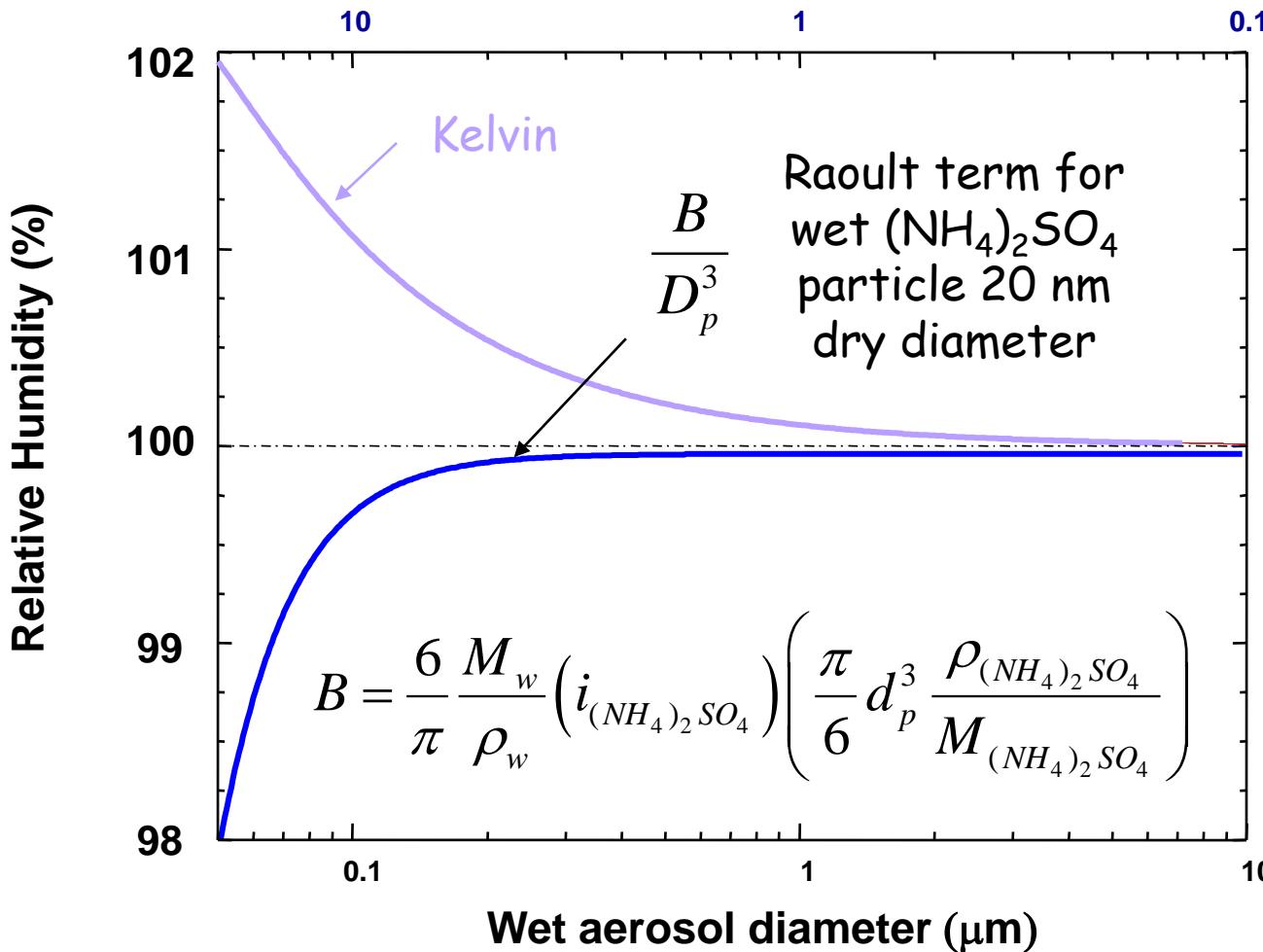
First plot the Kelvin term



# Thermodynamics of droplets: Köhler equation

Take same drop and add some solute

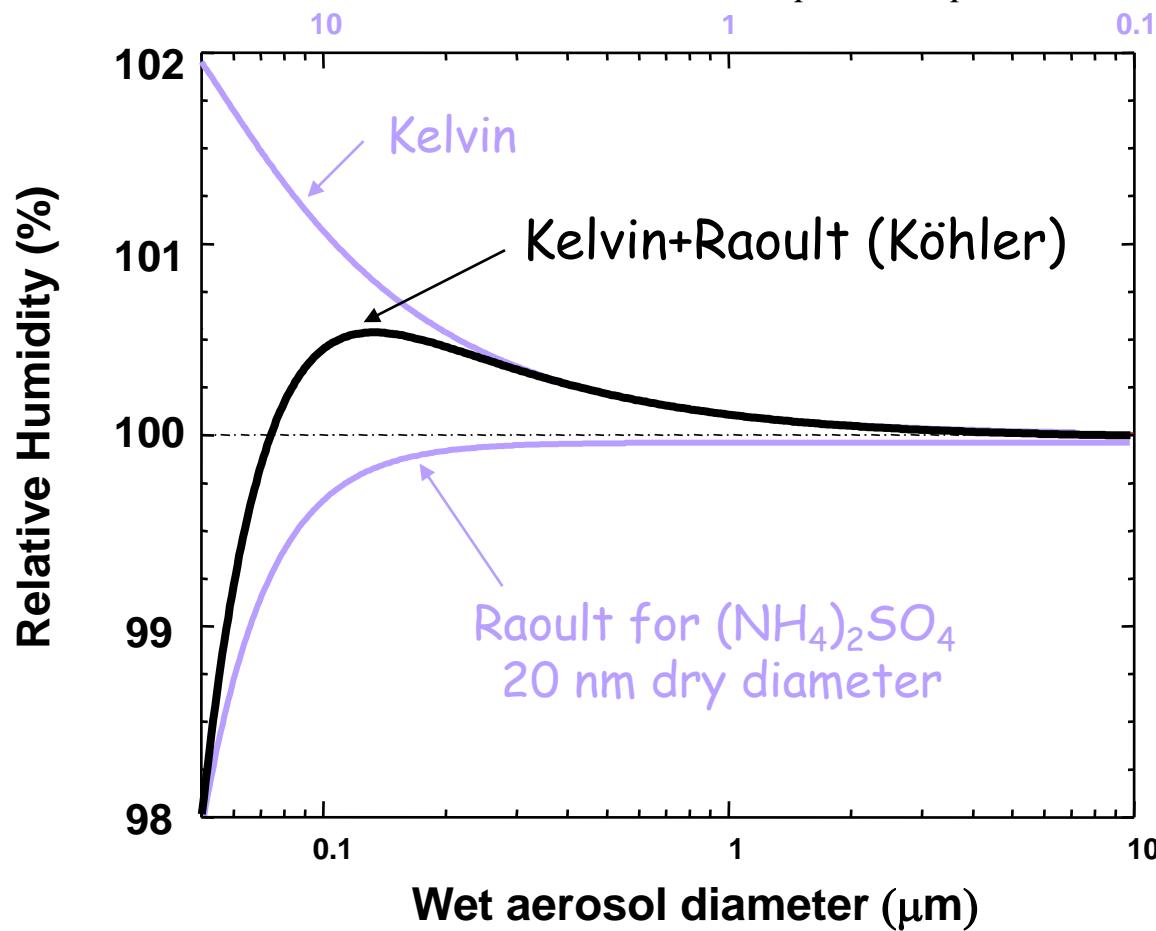
Solute Concentration (M)



# Thermodynamics of droplets: Köhler equation

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

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

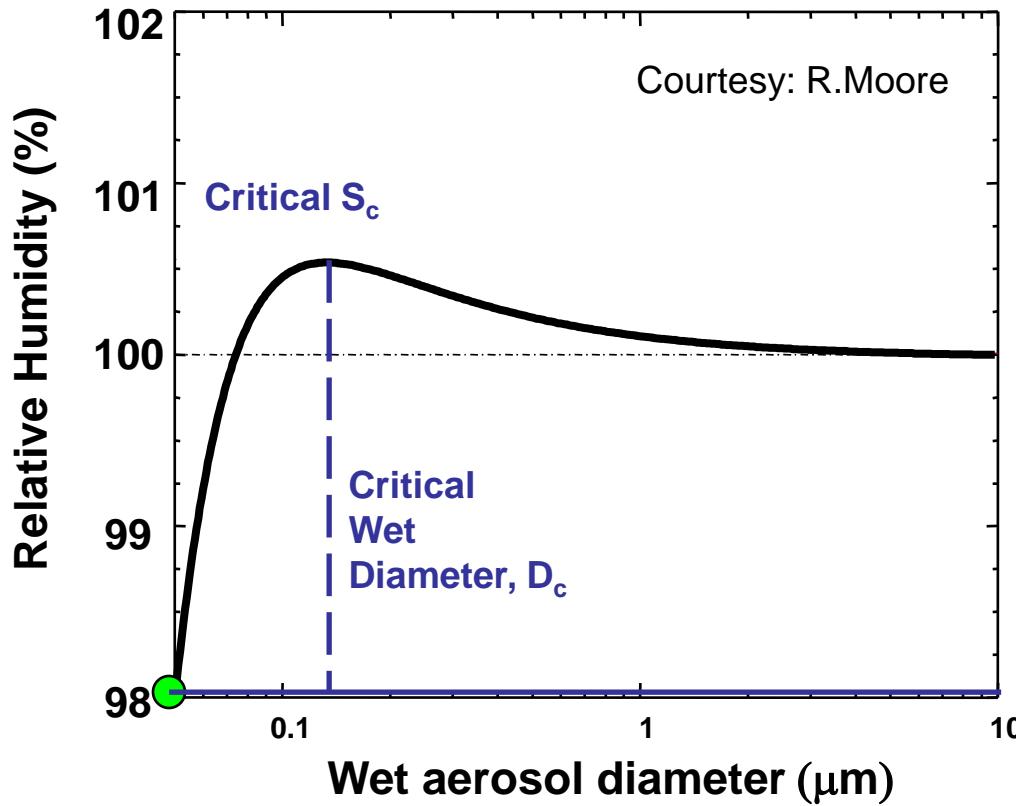
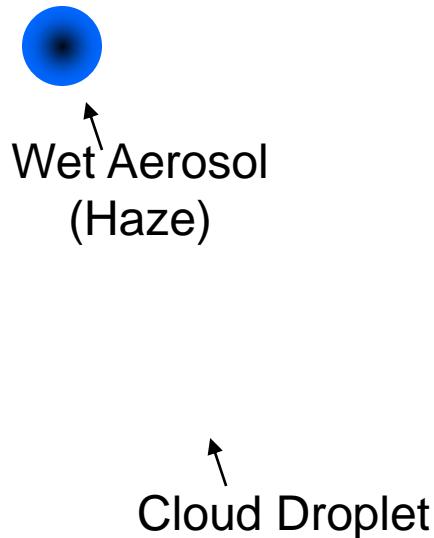


The combined Kelvin and Raoult effects is the simplified Köhler equation.

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.

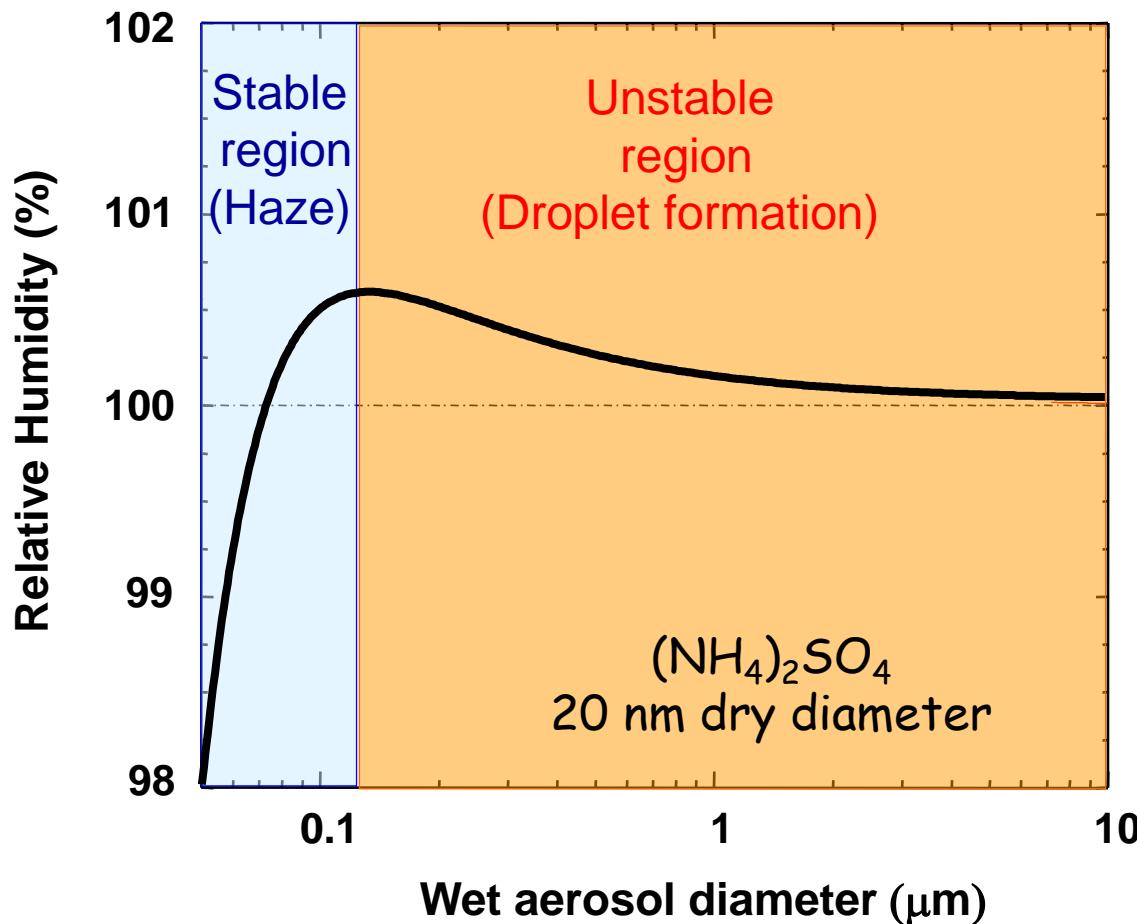


If ambient  $S$  exceeds the maximum, particles grow uncontrollably.  
They are said to act as Cloud Condensation Nuclei (CCN)

# 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:

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

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

Size is more important than composition

# Understanding & parameterizing CCN activity...

Petters and Kreidenweis (2007) expressed the solute parameter in terms of a “hygroscopicity parameter”,  $\kappa$

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



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

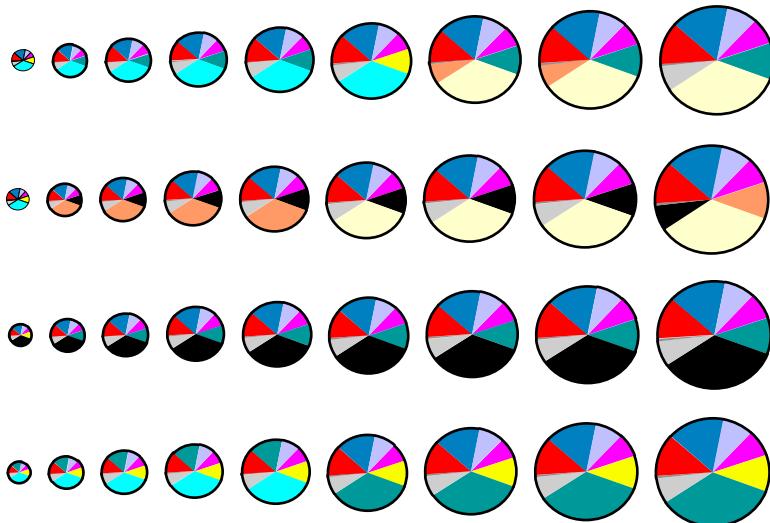
$\kappa \sim 1$  for NaCl,  $\sim 0.6$  for  $(\text{NH}_4)_2\text{SO}_4$ ,  $\sim 0-0.3$  for organics

$\kappa$  rarely exceeds 1 in atmospheric aerosol

Simple way to think of  $\kappa$ : 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

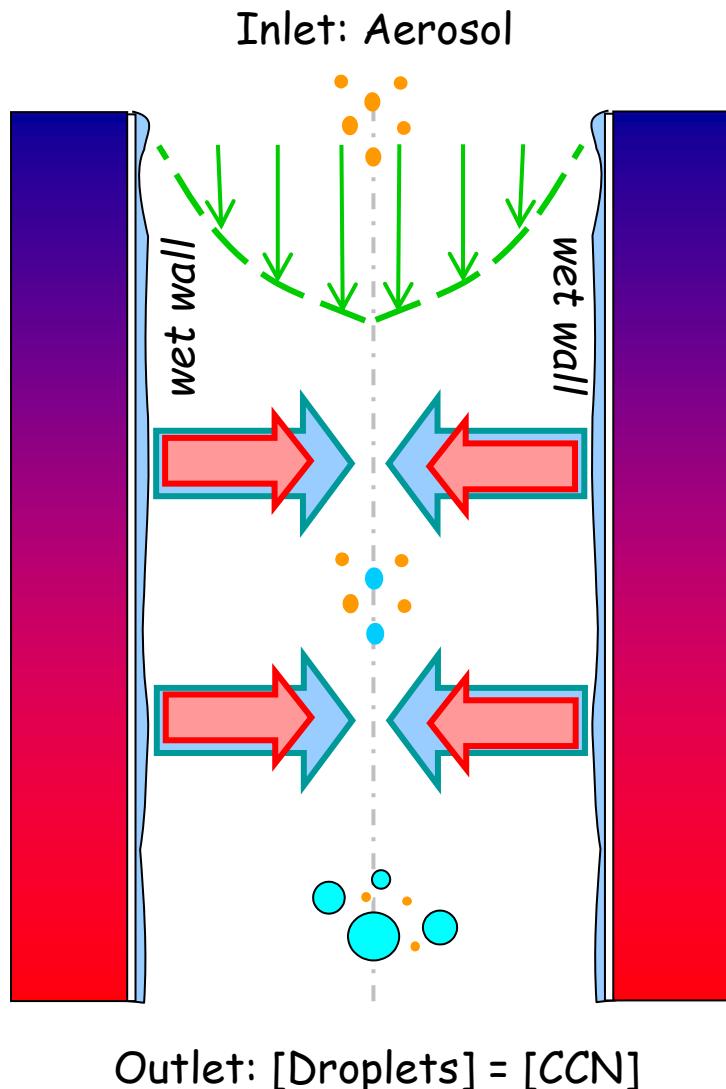
- They can facilitate cloud formation by acting as surfactants and adding solute (hygroscopicity)
- Oily films can form and delay cloud growth kinetics

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



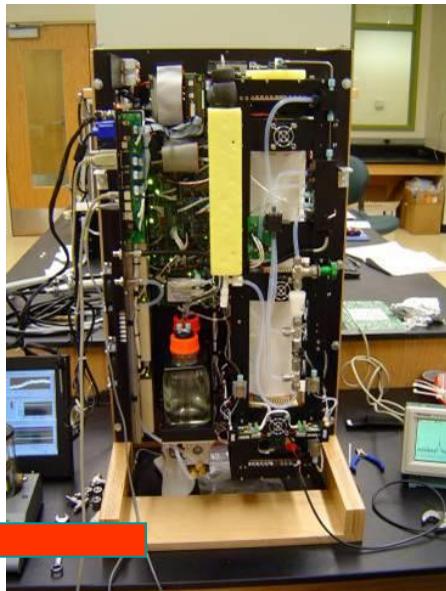
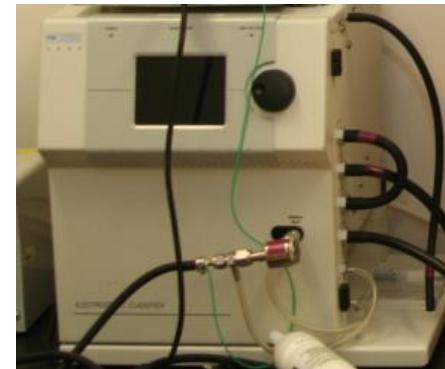
Metallic cylinder with walls wet. Apply T gradient, and flow air.

- Wall saturated with  $\text{H}_2\text{O}$ .
- $\text{H}_2\text{O}$  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, $\kappa$

## size-resolved CCN measurements



Particle Detection

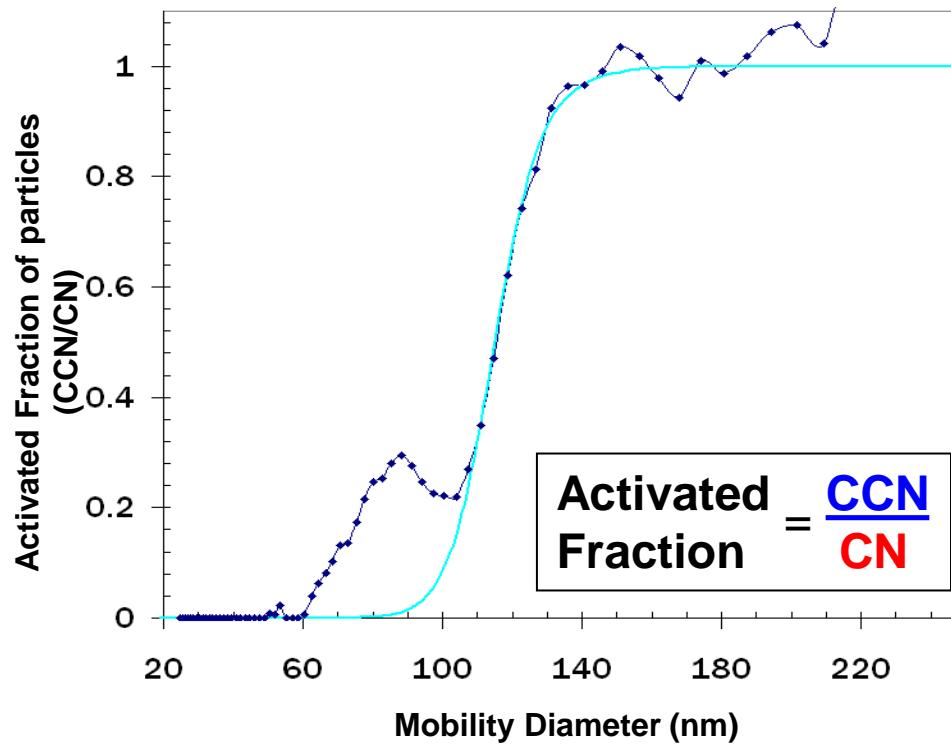


# Measuring hygroscopicity, $\kappa$

size-res



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



Count  
CCN



size Selection



Count CN

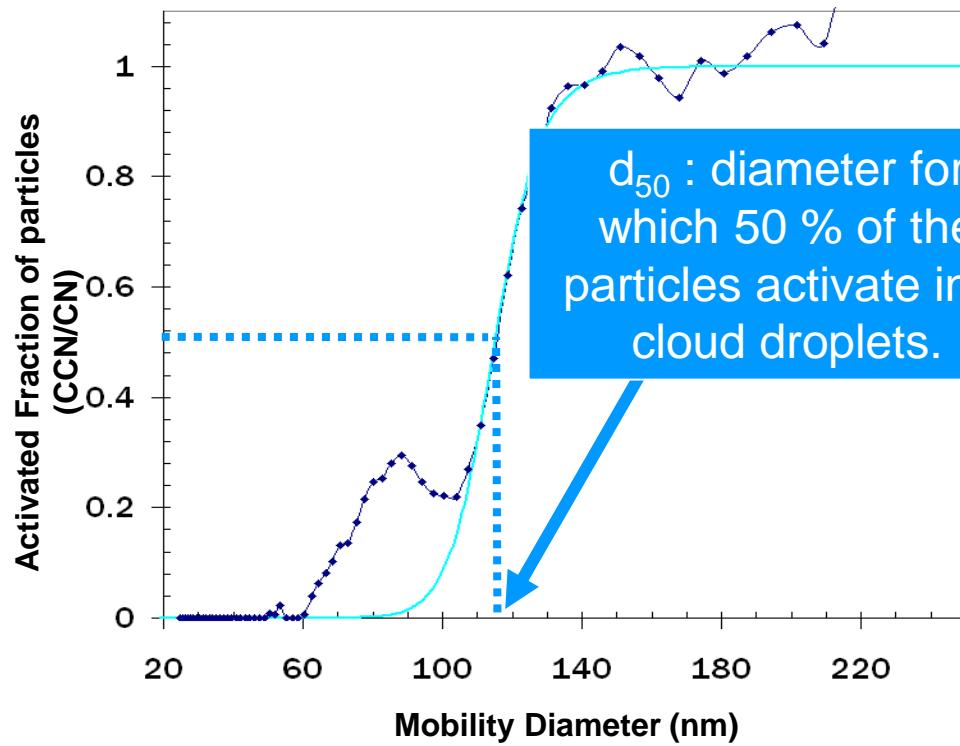


# Measuring hygroscopicity, $\kappa$

size-res



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



Count  
CCN



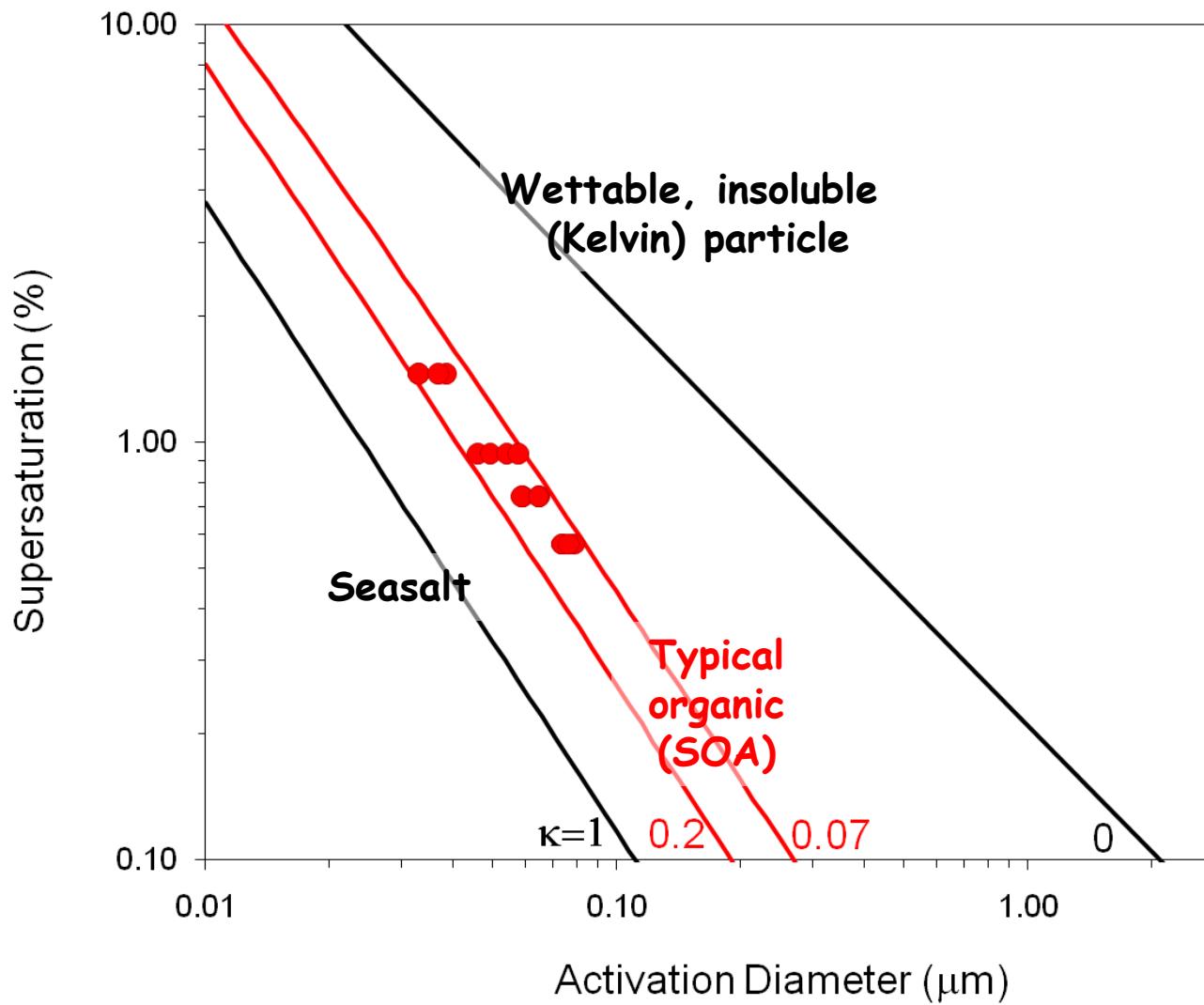
size Selection



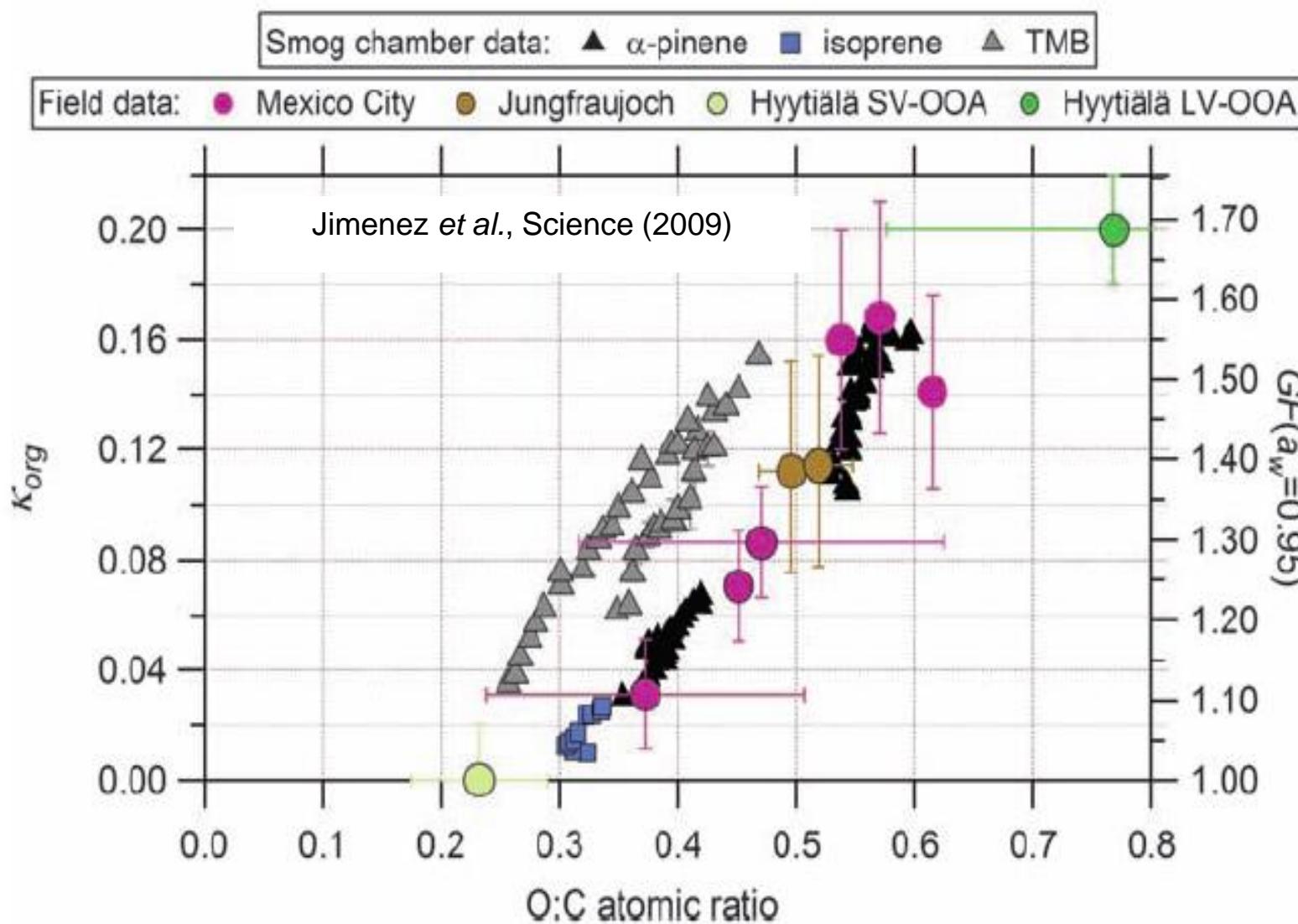
Count CN



# Hygroscopicity parameter for organics

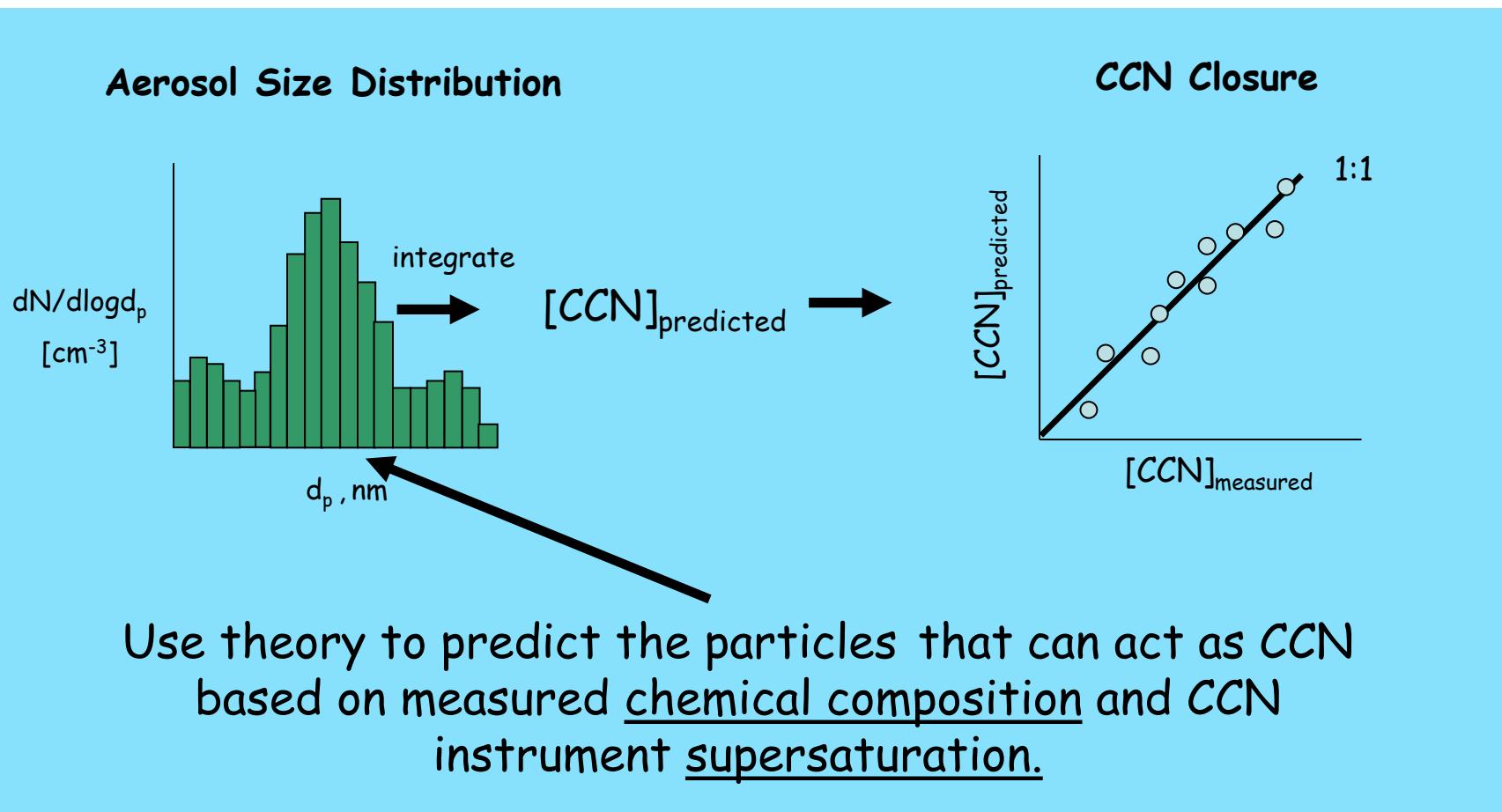


# $\kappa_{\text{org}}$ depends on oxidation state and precursor



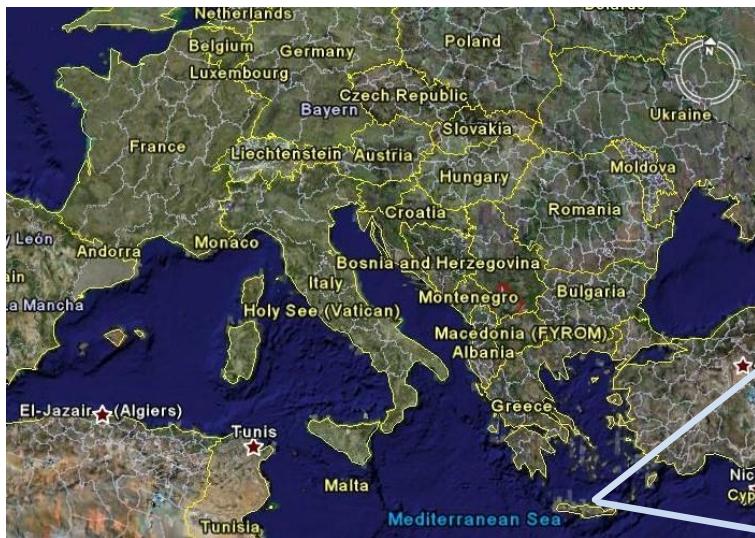
# CCN "Closure": test of Köhler theory

Compare measurements of CCN to predictions using Köhler activation theory and  $\kappa$  description



# 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*

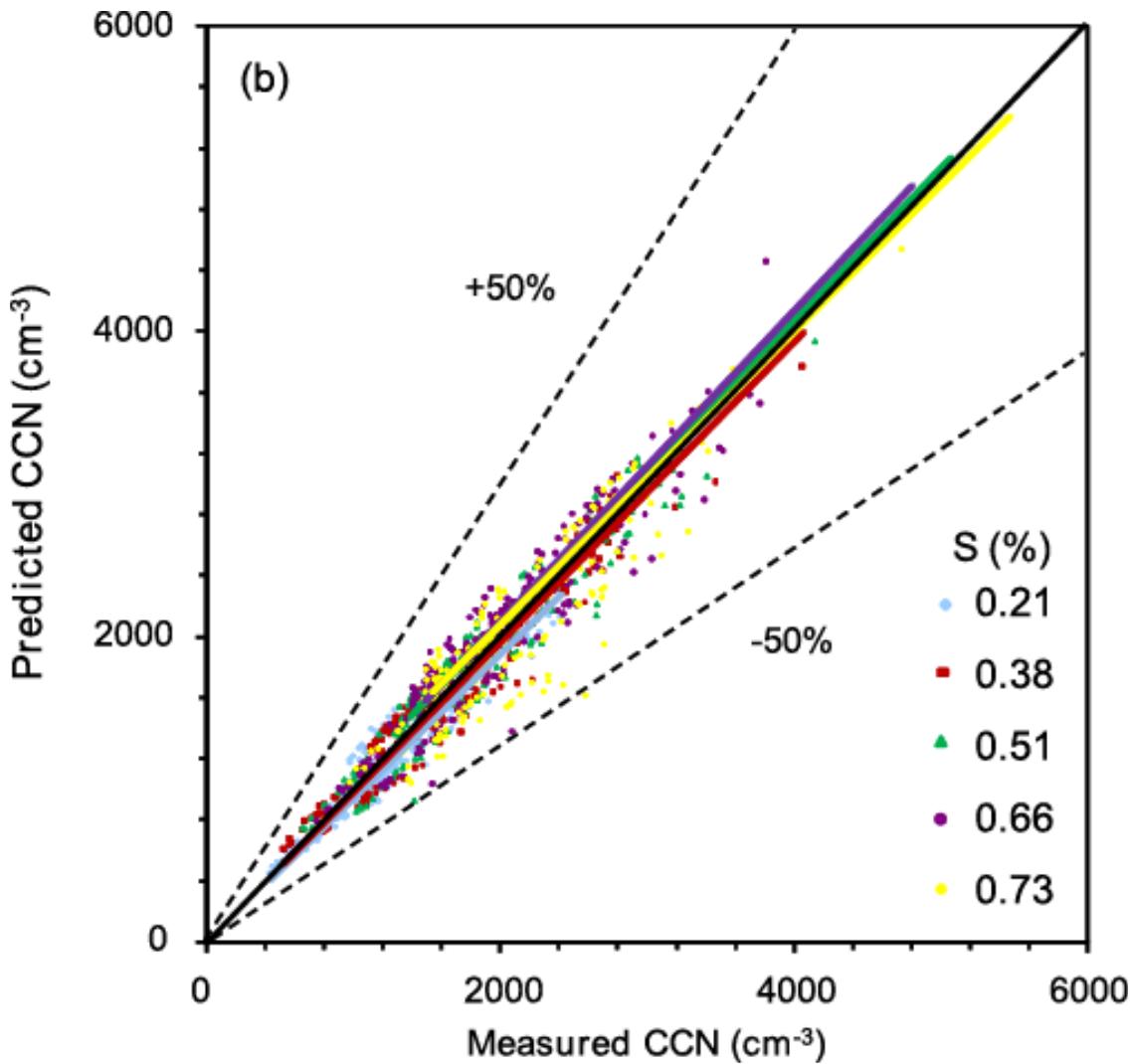
**Low-vol impactor**  
*Ionic composition measured via IC*

*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

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- 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

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

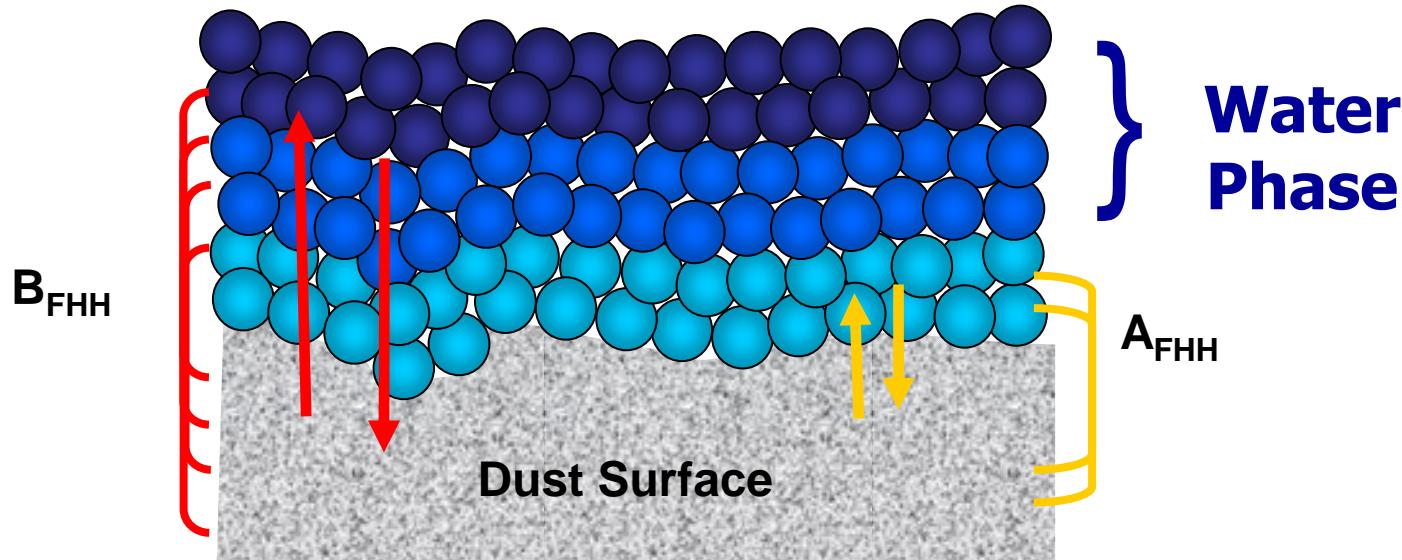
- They are not good CCN... because
- The CCN activity of solubles depends *solely* on soluble "coatings" from atmospheric processing.
- Theory works well when there is a fair amount of soluble solute in the particles ( $\sim >10\%$  by mass).

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

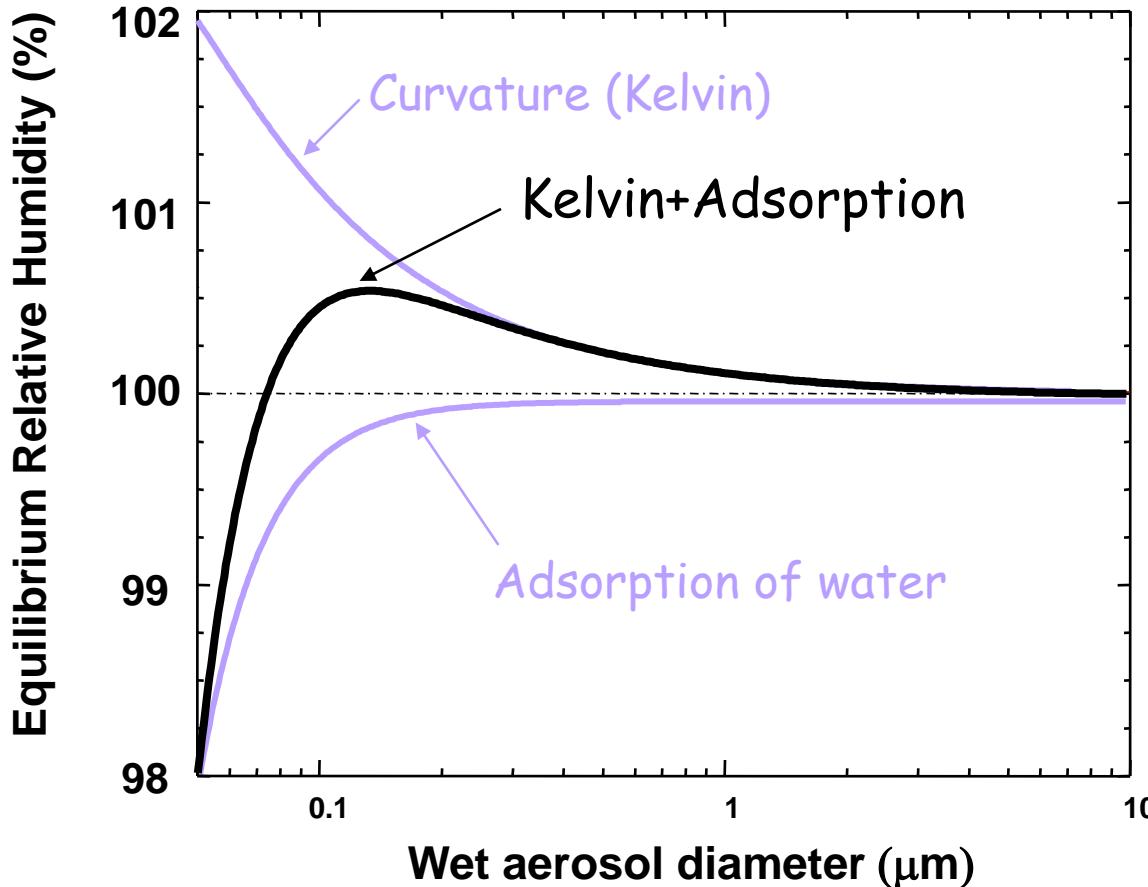
Use the **Frenkel-Halsey-Hill** (FHH) multilayer physisorption isotherm to describe the interaction of water vapor with the dust surface.



- Long-range Van-der-Walls 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  $H_2O$  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:  $S_c \sim d_{\text{dry}}^{-1.5}$

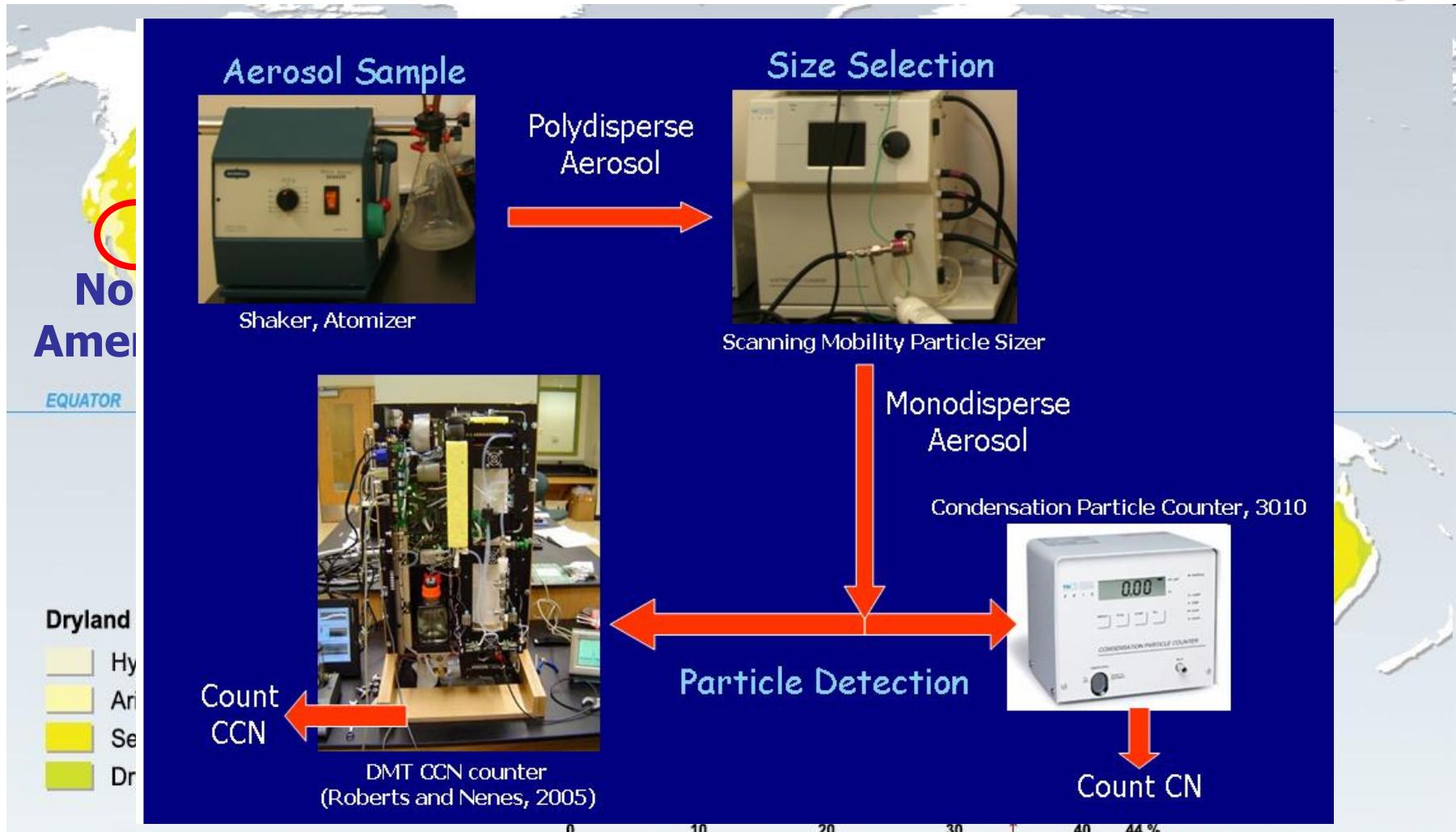
Adsorption  $S_c \sim d_{\text{dry}}^x$  with  $x < -1.5$

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

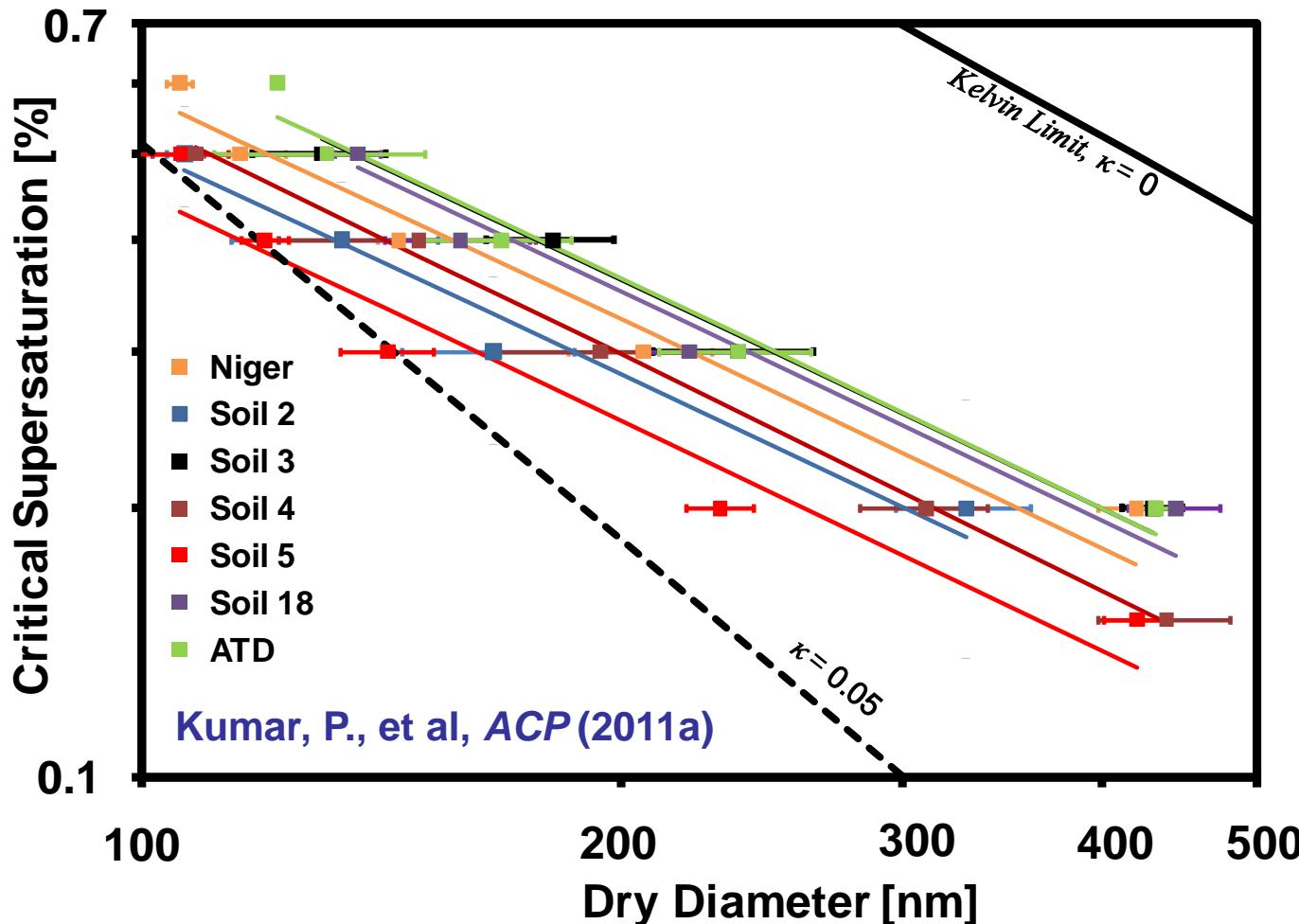
# CCN activity of dry-generated dust

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

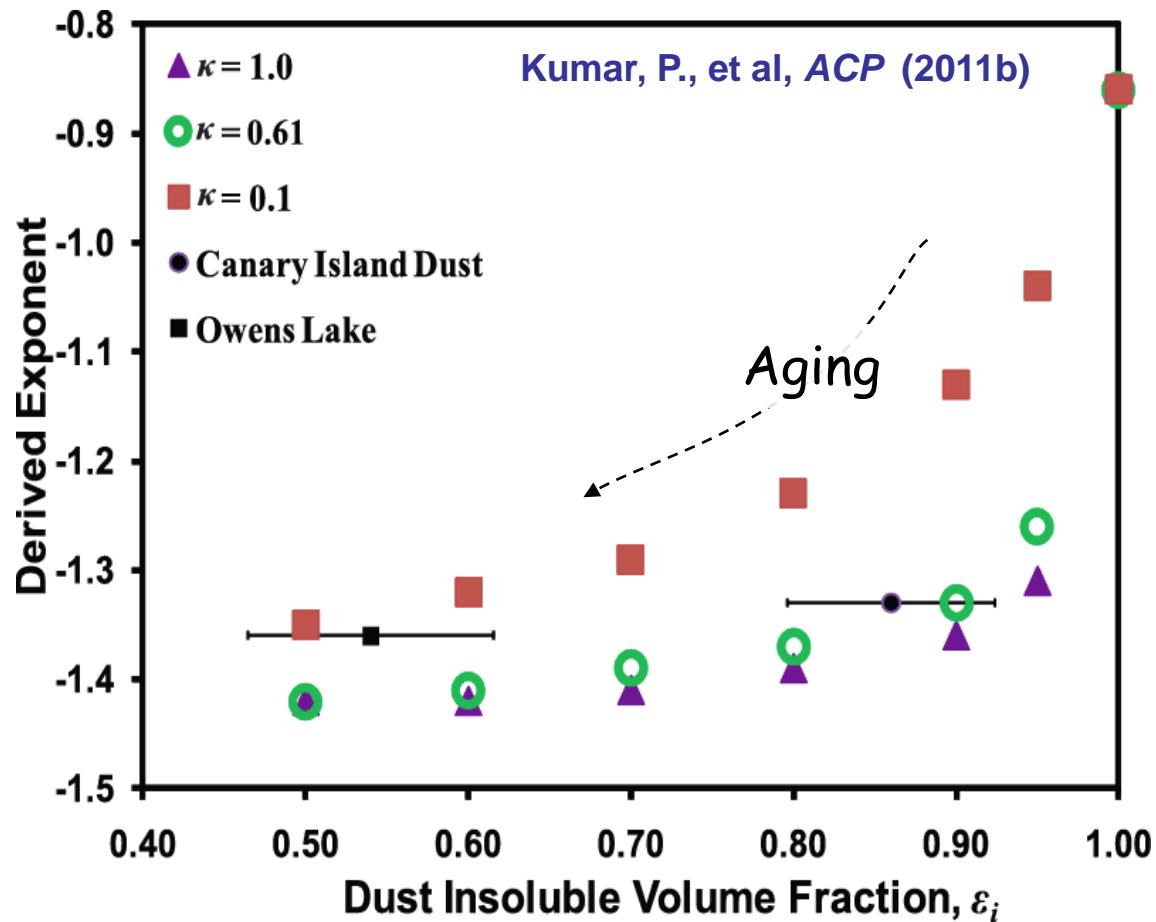
$D_{dry}$  exponent  $x < -1$

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  $\times$  for  $S_c \sim d_{dry}^{\times}$ .



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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- Zaveri, R.A., Easter, R.C., and L.K., Peters, A computationally efficient multicomponent equilibrium solver for aerosols (MESA), *J. Geophys. Res.*, 110, D24203, doi:10.1029/2004JD005618, 2005a.
- Wexler, A.S., and S.L., Clegg, Atmospheric aerosol models for systems including the ions  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{H}_2\text{O}$ , *J. Geophys. Res.*, 107, 4207, doi:10.1029/2001JD000451, 2002.
- Seinfeld, J.H., and S.N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, Inc., 2006.
- Fountoukis, C. and Nenes, A., ISORROPIA II: A Computationally Efficient Aerosol Thermodynamic Equilibrium Model for  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$  Aerosols, *Atmos. Chem. Phys.*, 7, 4639, 2007
- Kim, Y.P., Seinfeld, J.H., and P., Saxena, Atmospheric gas - aerosol equilibrium I. Thermodynamic model, *Aerosol Sci. Technol.*, 19, 157, 1993a.
- Jacobson, M.Z., Studying the effect of calcium and magnesium on size-distributed nitrate and ammonium with EQUISOLV II, *Atmospheric Environment*, 33, 3635, 1999b.

# Some References: Bulk Thermodynamics

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- Amundson N.R., Caboussat A., He J.W., Martynenko A.V., Savarin V.B., Seinfeld J.H., and K.Y., Yoo, A new inorganic atmospheric aerosol phase equilibrium model (UHAERO), *Atmos. Chem. Phys.*, 6, 975, 2006.
- Ansari A.S., and S.N., Pandis, Prediction of multicomponent inorganic atmospheric aerosol behavior, *Atmospheric Environment*, 33, 745, 1999a.
- Clegg, S., Seinfeld, J.H., Brimblecombe, P. Thermodynamic modelling of aqueous aerosols containing electrolytes and dissolved organic compounds, *J. Aerosol Science*, 32, 713, 2001
- Clegg, S., Seinfeld, J.H., Improvement of the Zdanovskii-Stokes-Robinson Model for Mixtures Containing Solutes of Different Charge Types, *J. Phys. Chem. A*, 108, 1008, 2004
- <http://nenes.eas.gatech.edu/ISORROPIA>
- <http://www.aim.env.uea.ac.uk/aim/aim.htm>
- <http://aero.math.uh.edu>

# Some References: Droplet Thermodynamics

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- Bougiatioti, A., Fountoukis, C., Kalivitis, N., Pandis, S.N., Nenes, A. and Mihalopoulos, N., Cloud Condensation Nuclei Measurements in the Marine Boundary Layer of the Eastern Mediterranean: CCN closure and droplet growth kinetics, *Atmos. Chem. Phys.*, 9, 7053-7066, 2009
- Facchini, M., M. Mircea, S. Fuzzi, and R. Charlson, Cloud albedo enhancement by surface-active organic solutes in growing droplets, *Nature*, 401, 257– 259, 1999
- Seinfeld, J.H., and S.N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, Inc., 2006.
- Petters, M. D., and S. M. Kreidenweis (2007), A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, *Atmos. Chem. Phys.*, 7, 1961– 1971.
- Kumar, P., Sokolik, I. N., and Nenes, A. (2011) Measurements of Cloud Condensation Nuclei Activity and Droplet Activation Kinetics of Wet Processed Regional Dust Samples and Minerals, *Atmos. Chem. Phys.*, 11, 8661-8676
- 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
- Engelhart, G. J., Moore, R. H., Nenes, A. and Pandis, S.N. (2011) CCN Activity of Isoprene Secondary Organic Aerosol, *J. Geoph. Res.*, 116, D02207, doi:10.1029/2010JD014706
- Jimenez, J. L., Canagratna, M. R., Donahue, et al. (2009) Evolution of organic aerosols in the atmosphere, *Science*, 326, 1525–1529, doi:10.1126/science.1180353
- <http://nenes.eas.gatech.edu> (CCN measurements & techniques)

A high-angle aerial photograph of a desert landscape. The terrain is characterized by light brown and tan colors, with darker, more arid areas in the foreground and more vegetated, greenish-brown areas in the background. A prominent, winding white line, likely a riverbed or a path, cuts through the center of the image. In the distance, a range of mountains with some snow-capped peaks is visible under a clear blue sky.

**THANK YOU !!**