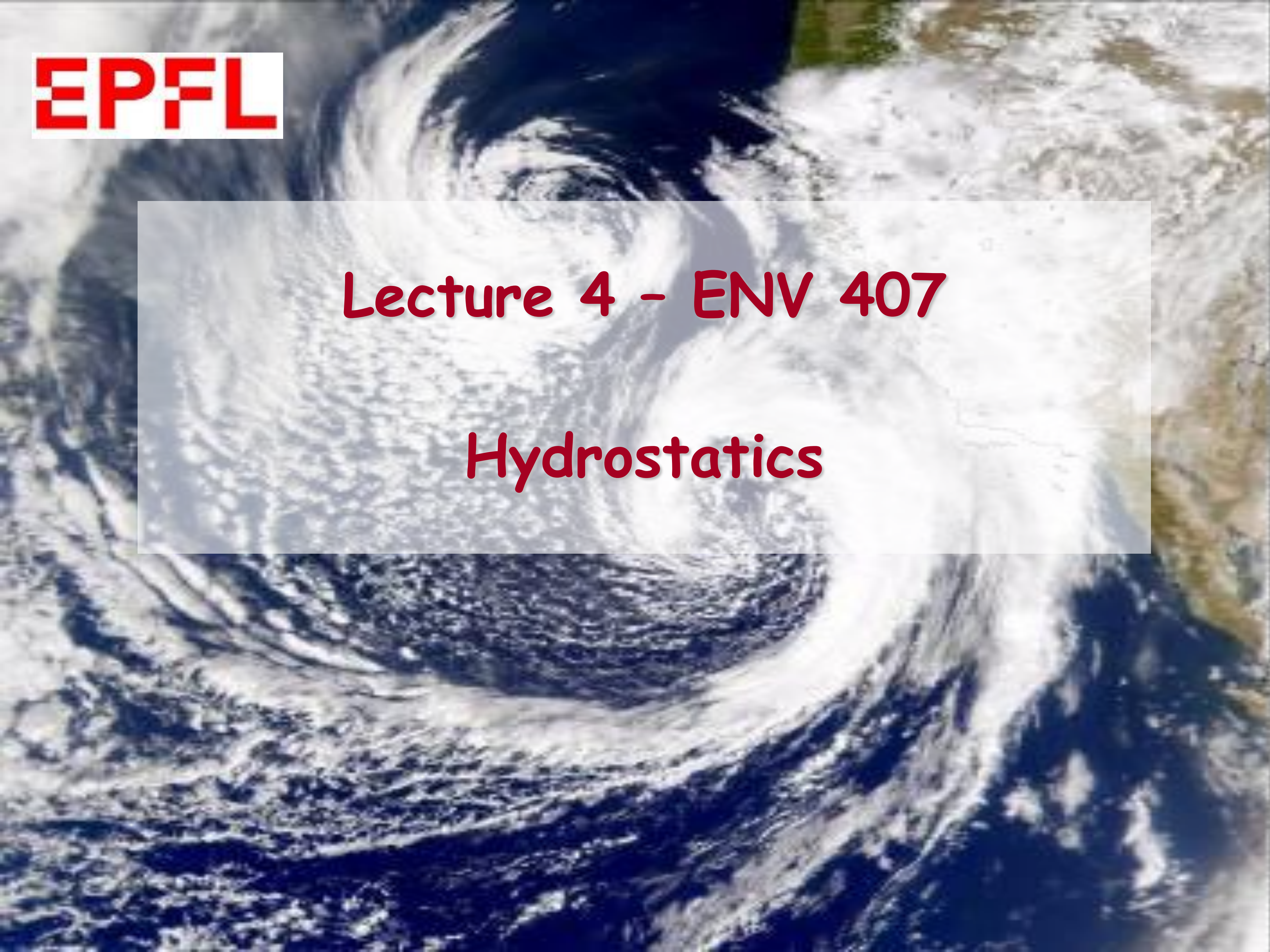


Lecture 4 – ENV 407

Hydrostatics

Hydrostatic Balance

Although the horizontal atmosphere is in a constant state of motion, vertical velocities are fairly small (especially averaged over the large scale). Consequently, to understand the vertical structure of the atmosphere, we can approximate it to be largely steady.

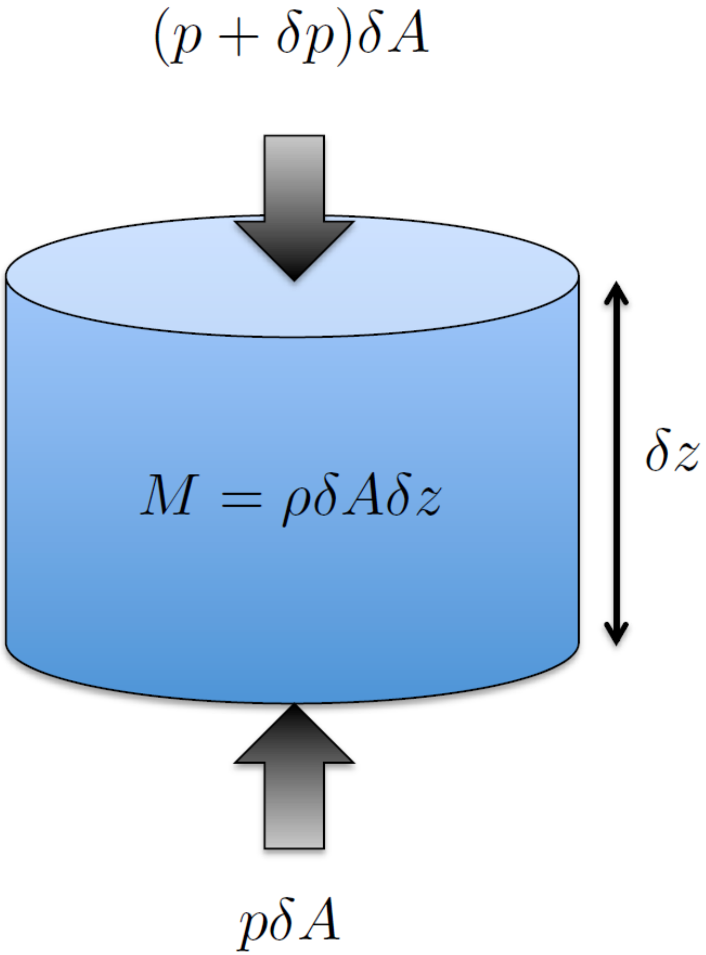


Figure: A vertical column of air of density ρ, horizontal cross-section δA, height δz and mass $M = \varrho\ \delta A\ \delta z$. The pressure at the lower surface is p, the pressure at the upper surface is $p + \delta p$.

Slides courtesy of Paul Ullrich (UC Davis)

Hydrostatic Balance

If the cylinder of air is not accelerating, it must be subject to zero net force. The vertical forces are:

Pressure acting on bottom face

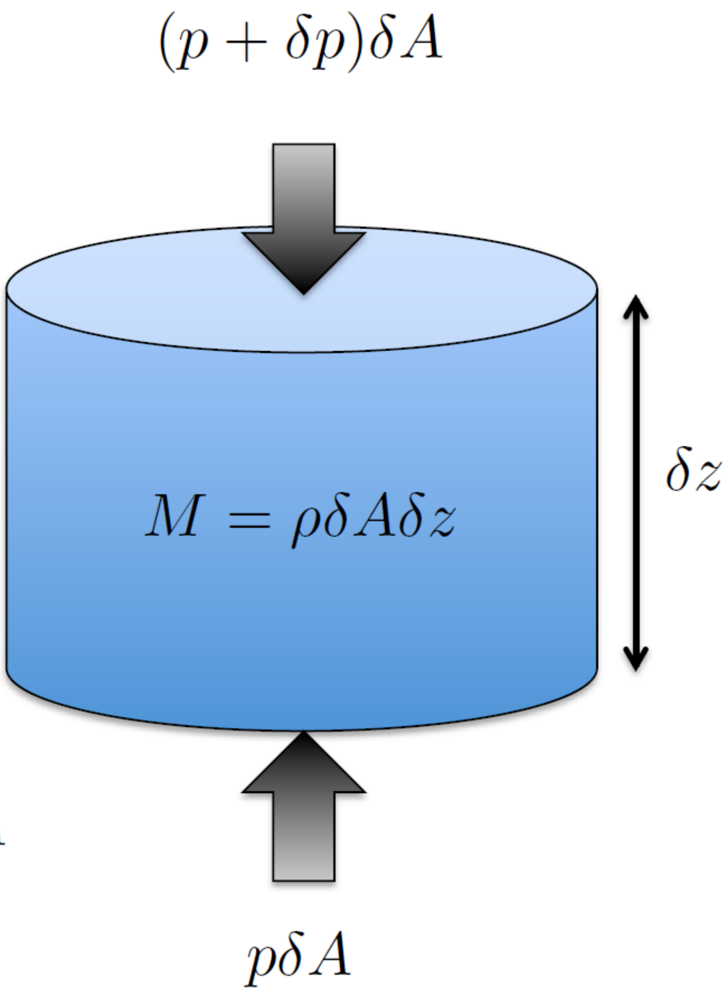
$$F_B = p\delta A$$

Gravity

$$F_g = -gM$$
$$= -g\rho\delta A\delta z$$

Pressure acting on top face

$$F_T = -(p + \delta p)\delta A$$



Slides courtesy of Paul Ullrich (UC Davis)

Hydrostatic Balance

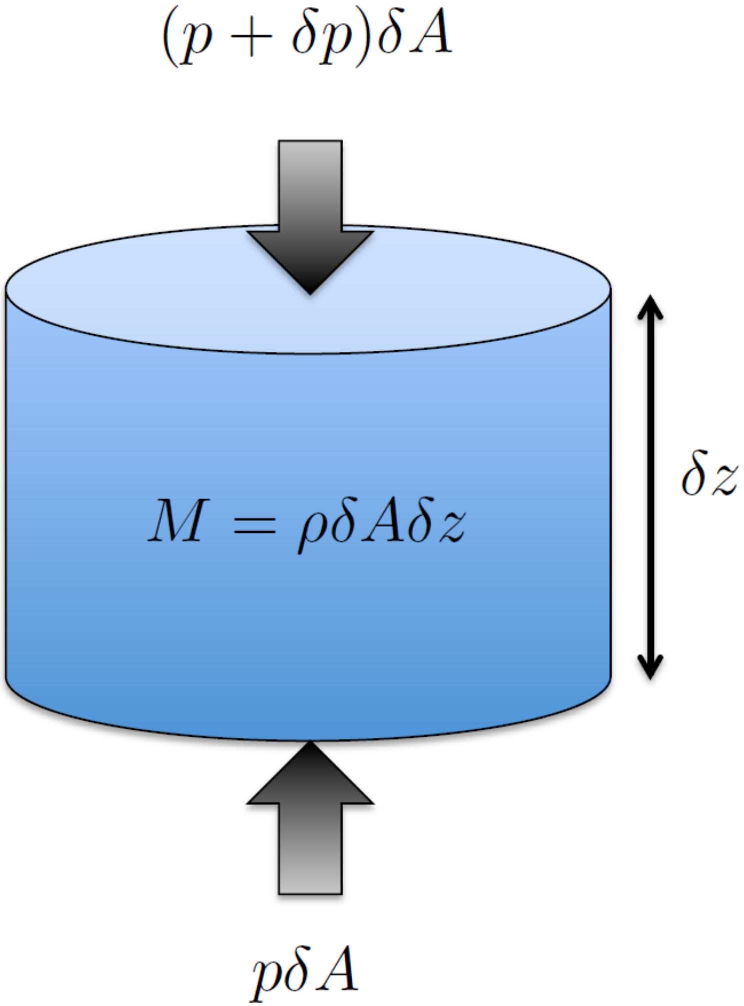
$$F_g + F_T + F_B = 0$$

$$\delta p + g\rho\delta z = 0$$

Taylor Series $\delta p \approx \frac{\partial p}{\partial z}\delta z$

Hydrostatic Balance

$$\frac{1}{\rho}\frac{\partial p}{\partial z} = -g$$



Slides courtesy of Paul Ullrich (UC Davis)

Aside: Consider the special case of an isothermal (constant temperature) atmosphere:

$$\frac{1}{\rho}\frac{\partial p}{\partial z} = -g$$

Hydrostatic Balance

This equation does not give pressure explicitly in terms of height, since the density of air is not known.

Ideal gas law

$$\rho = \frac{p}{R_d T}$$

$$\Rightarrow \quad \frac{\partial p}{\partial z} + \frac{pg}{RT} = 0$$

For an isothermal atmosphere $(T = T_0)$ this equation can be exactly solved:

$$\Rightarrow \quad p(z) = p_s \exp\left(-\frac{zg}{R_d T}\right)$$

Exponential decay

Slides courtesy of Paul Ullrich (UC Davis)

Aside: Consider the special case of an isothermal (constant temperature) atmosphere:

➡ $$p(z) = p_s \exp\left(-\frac{gz}{R_d T_0}\right)$$

Definition: The **scale height** of an isothermal atmosphere is given by: $$H = \frac{R_d T_0}{g}$$

➡ $$p(z) = p_s \exp\left(-\frac{z}{H}\right)$$

The **scale height** is an example of a quantity which imparts a notion of a "natural measuring stick" for an idealized atmosphere. This notion will generalize to more realistic atmospheric flows as well.

Slides courtesy of Paul Ullrich (UC Davis)

Aside: Consider the special case of an isothermal (constant temperature) atmosphere:

For an isothermal atmosphere $T = T_0$

$$p(z) = p_s \exp\left(-\frac{z}{H}\right)$$

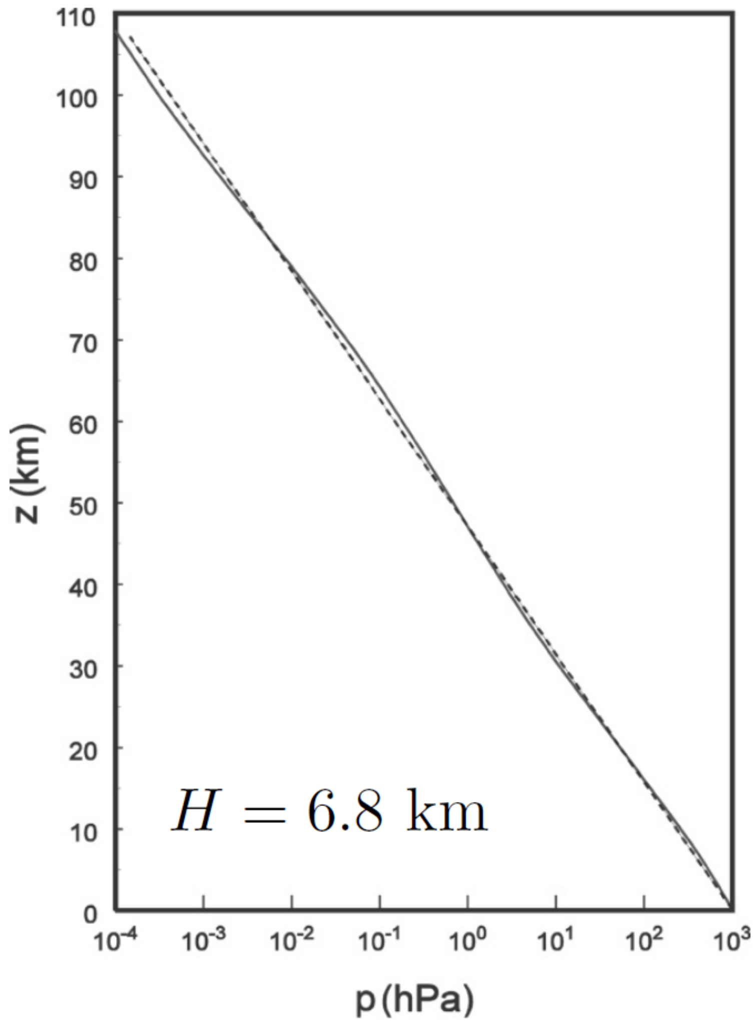


Figure: Observed profile of pressure (solid) plotted against isothermal profile. Observed temperature variations only lead to small variations in the pressure from an exponential profile.

Slides courtesy of Paul Ullrich (UC Davis)

Geopotential

$$\boxed{\nabla\Phi = g\mathbf{k}}$$

In height coordinates, geopotential is purely a function of z

→ $$\frac{d\Phi}{dz} = g$$

Integrate → $$\Phi(z) - \Phi(0) = \int_0^z g dz$$

Define $\Phi(0) = 0$ → $$\Phi(z) = \int_0^z g dz = gz$$

Slides courtesy of Paul Ullrich (UC Davis)

The use of **geopotential on constant pressure surfaces** is analogous to the use of **pressure on constant height surfaces**.

Question: How are geopotential and pressure connected?

From $\frac{d\Phi}{dz} = g$ $\Rightarrow$ $g dz = d\Phi$

From $\frac{dp}{dz} = -\rho g$ $\Rightarrow$ $g dz = -\frac{dp}{\rho}$

Hydrostatic balance

Ideal gas law $\rho = \frac{p}{R_d T}$

$$d\Phi = -\frac{R_d T dp}{p}$$

Slides courtesy of Paul Ullrich (UC Davis)

The use of **geopotential on constant pressure surfaces** is analogous to the use of **pressure on constant height surfaces**.

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Hydrostatic balance

Ideal gas law $\rho = \frac{p}{R_d T}$

$$\Downarrow$$

$$d\Phi = -\frac{R_d T dp}{p}$$

Slides courtesy of Paul Ullrich (UC Davis)

$$d\Phi = -\frac{R_d T\, dp}{p}$$

Recall: From elementary calculus, $\frac{dp}{p} = d\ln p$

$$d\Phi = -R_d T\, d\ln p$$

Integrate over a layer

$$\Phi(z_2) - \Phi(z_1) = -R_d \int_{p_1}^{p_2} T\, d\ln p$$

Use geopotential height

$$Z_2 - Z_1 = -\frac{R_d}{g} \int_{p_1}^{p_2} T\, d\ln p$$

$Z_2 - Z_1$ is the thickness of the layer bounded above by p_2 and below by p_1
This thickness is proportional to the temperature of the layer.

Slides courtesy of Paul Ullrich (UC Davis)

Hypsometric Equation

From hydrostatic balance and the ideal gas law we have

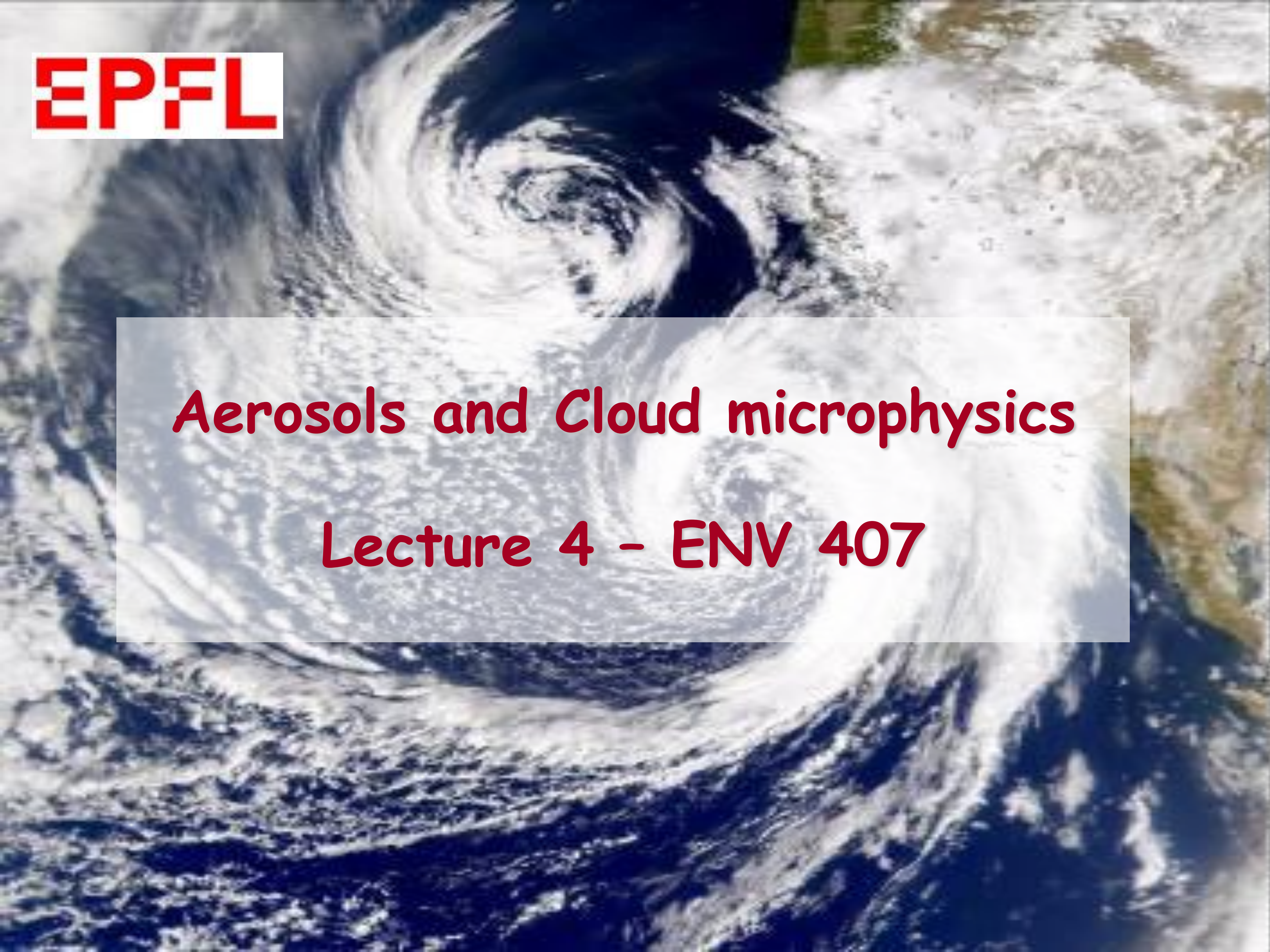
$$Z_2 - Z_1 = -\frac{R_d}{g}\int_{p_1}^{p_2} T\,d\ln p$$

If the temperature in a layer is constant then

$$\boxed{h = Z_2 - Z_1 = \frac{R_d T}{g}\ln\left(\frac{p_1}{p_2}\right)}$$

Hypsometric Equation

This is the relationship between layer thickness and temperature.



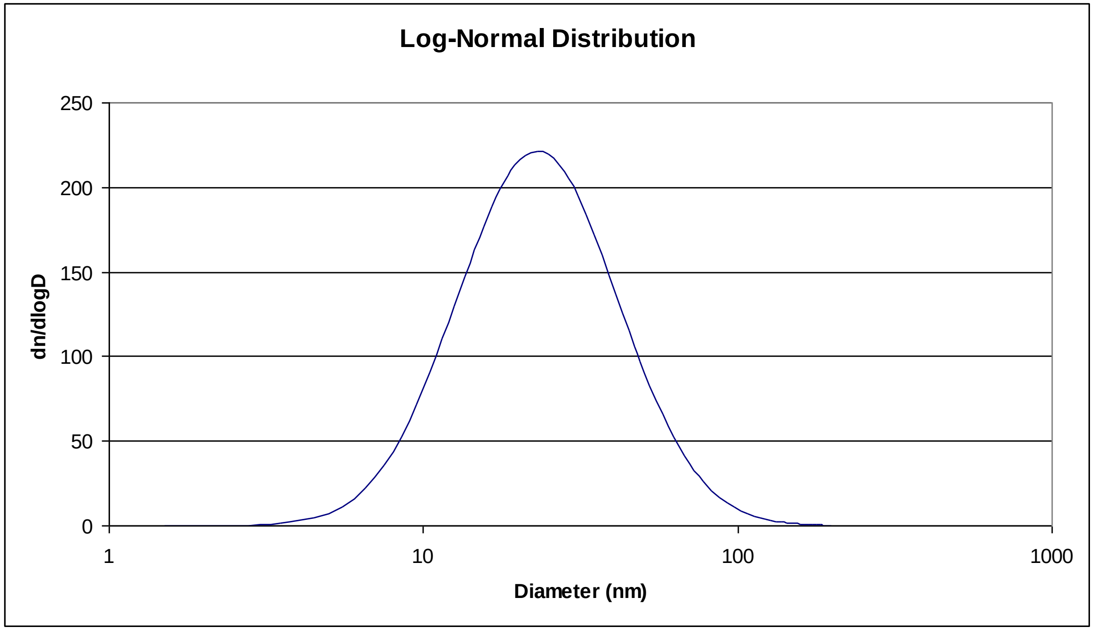
Aerosols and Cloud microphysics

Lecture 4 – ENV 407

Aerosol lognormal distributions

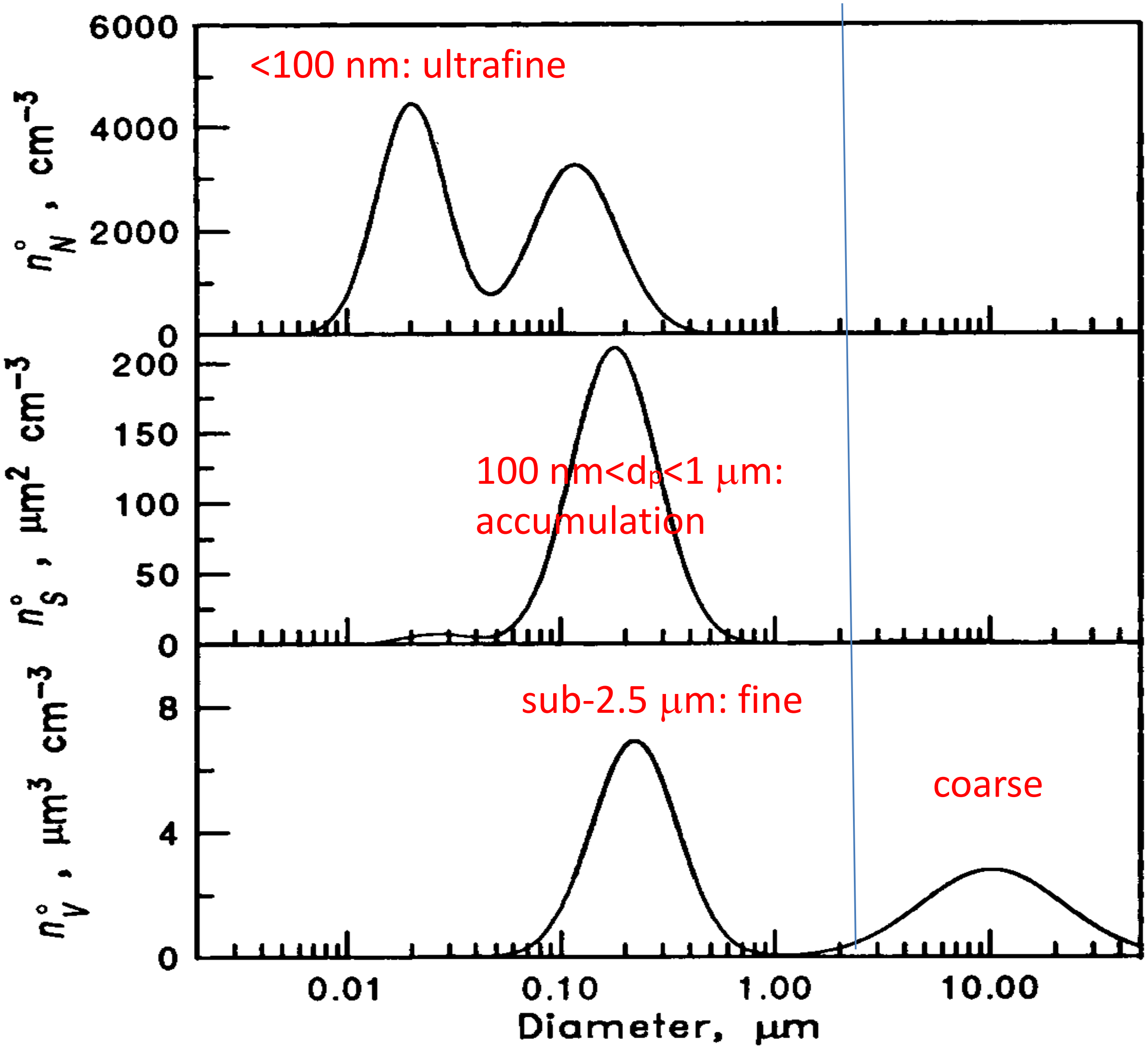
- Appears as a normal distribution when x-axis is plotted on log scale

$$n(D) = \frac{N}{(2\pi)^{1/2}\ln\sigma_D}\exp\left[-\frac{(\ln D - \ln D_g)^2}{2\ln^2\sigma_D}\right]$$



Geometric Mean Diameter = 23 nm; Geometric Standard Deviation (σ) = 1.8

Size Distribution: Remote continental air



<100 nm: ultrafine

100 nm<d_p<1 µm: accumulation

sub-2.5 µm: fine

coarse

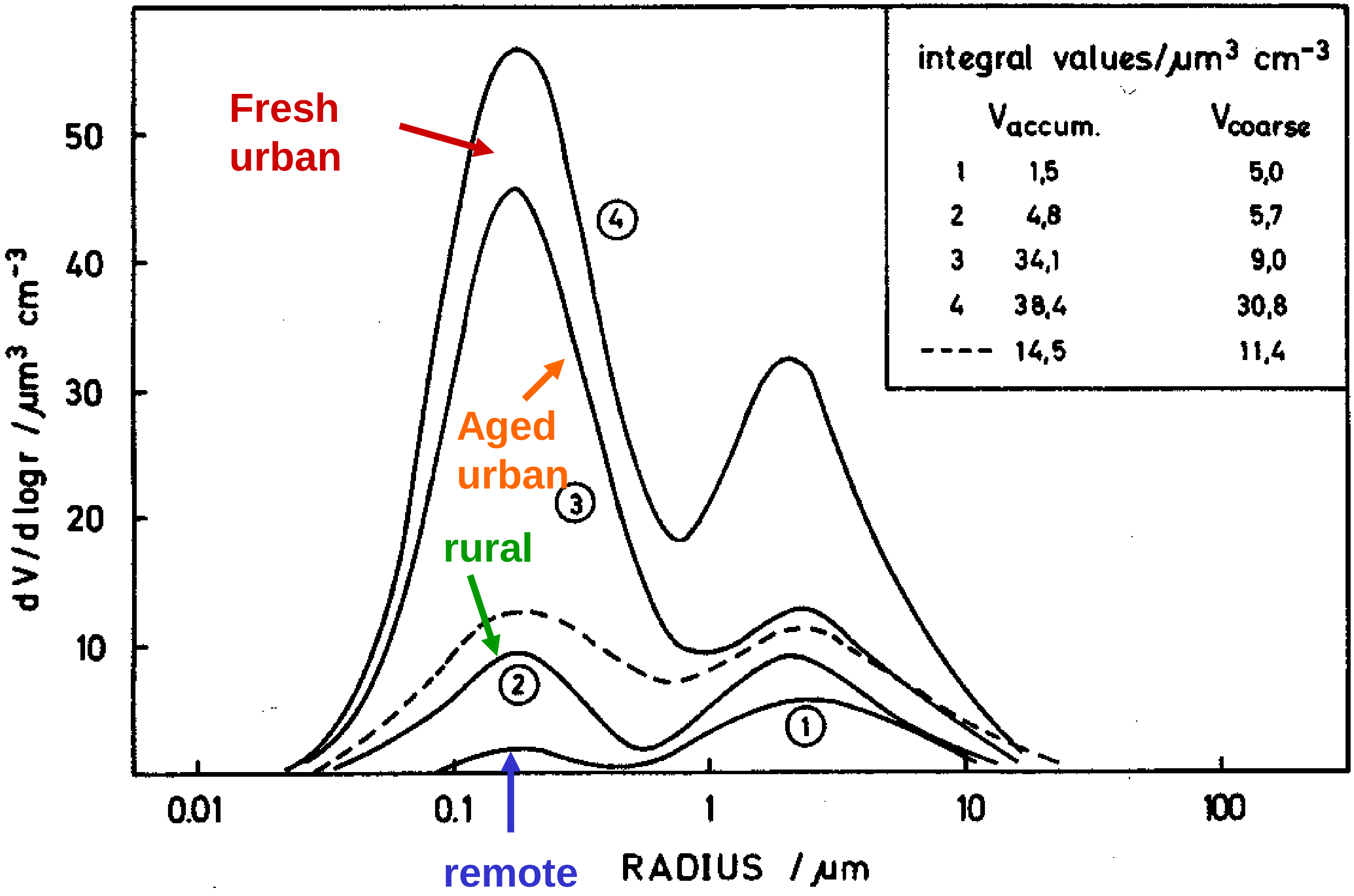
Number

Surface

Volume

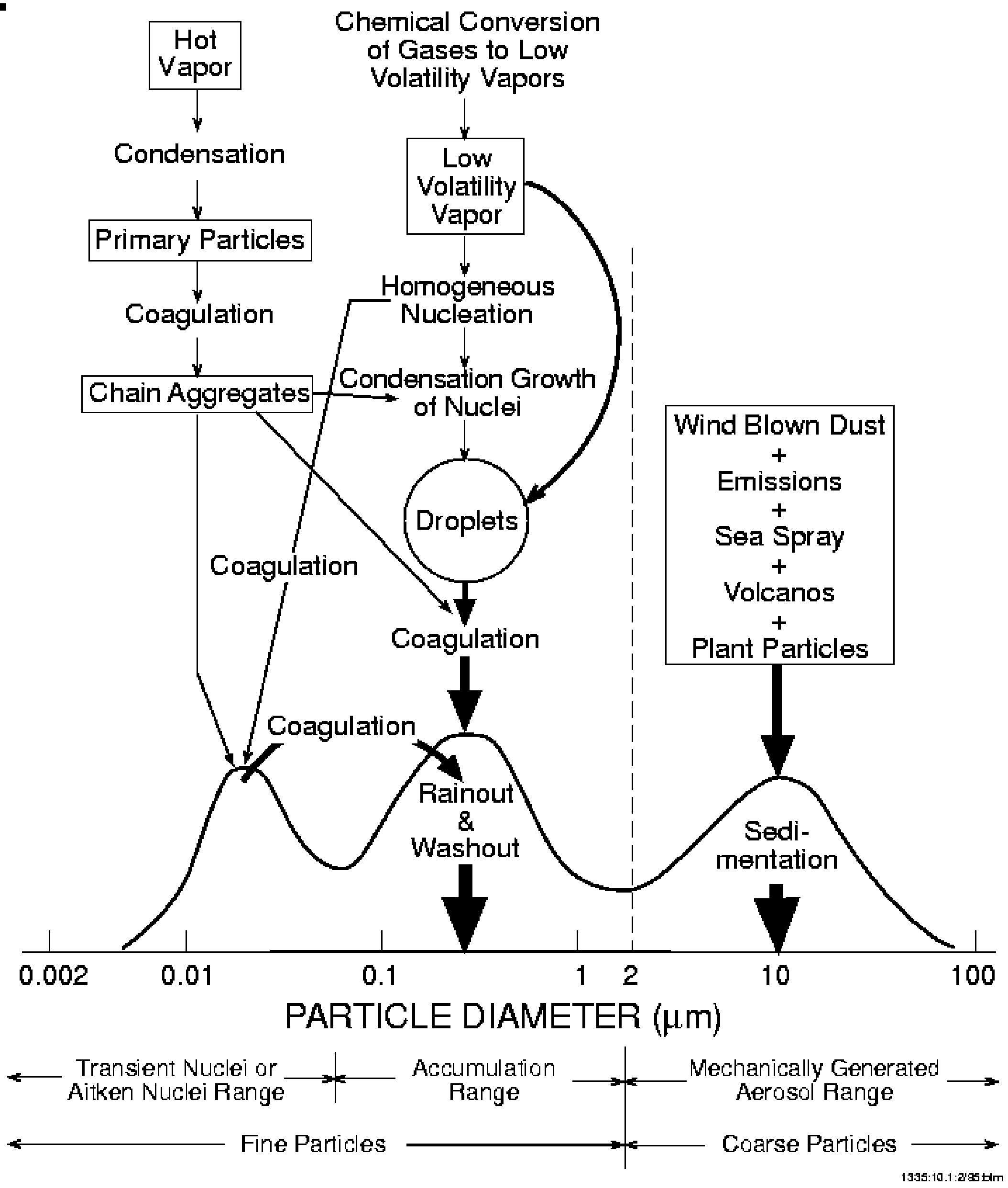
Seinfeld and Pandis

Size distributions vary a lot



Warneck [1999]

Size distribution is shaped by the processes present



Seinfeld and Pandis

LIQUID cloud microphysics

- **Ice (cold) clouds**: Made of ice crystals at $T < 235$ K.
- **Mixed Phase clouds**: Mixture of liquid droplets and ice for T between 235 and 273K
- **Liquid (warm) clouds**: Made of liquid droplets at $T > 273$ K

Cloud particles are not created directly from the vapor phase but from **suspended aerosol particles**

http://www.ucar.edu/news

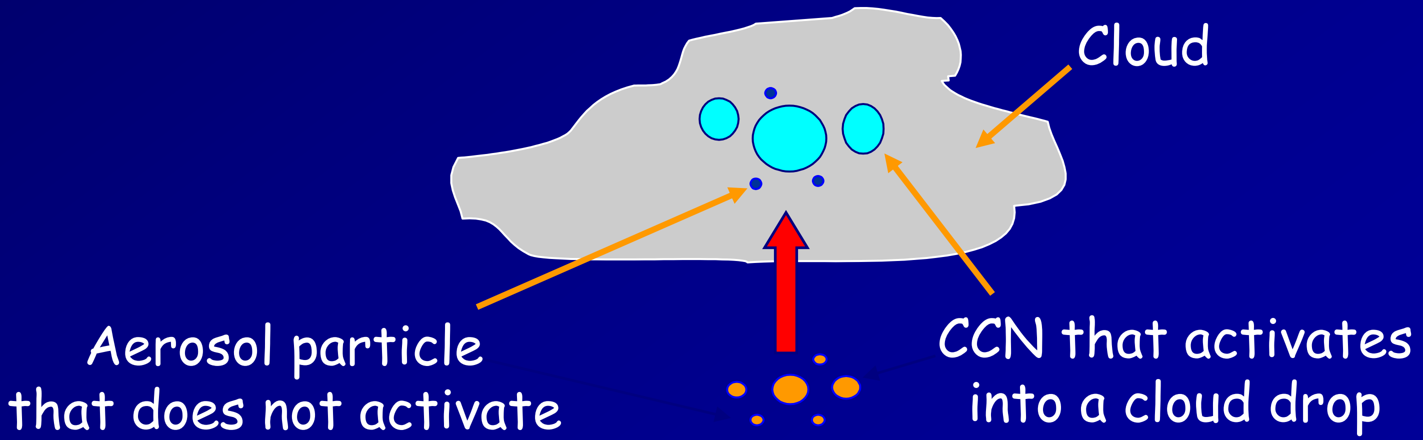
How do (liquid water) clouds form?

Clouds form in regions of the atmosphere where there is too much water vapor (it is “supersaturated”).

This happens when air is cooled (primarily through expansion in updraft regions and radiative cooling).

Cloud droplets nucleate on pre-existing particles found in the atmosphere (aerosols) with ~ 0.1μm diameter.

Aerosols that can become droplets are called cloud condensation nuclei (CCN).



Cloud

Aerosol particle
that does not activate

CCN that activates
into a cloud drop

Increases in aerosol affects warm clouds

You make clouds that are "whiter", precipitate less (persist longer) and potentially cover larger areas of the globe. This is thought to yield a net cooling on climate and is termed as the "**indirect climatic effect of aerosols**".

Clean Environment
(few CCN)

Polluted Environment
(more CCN)

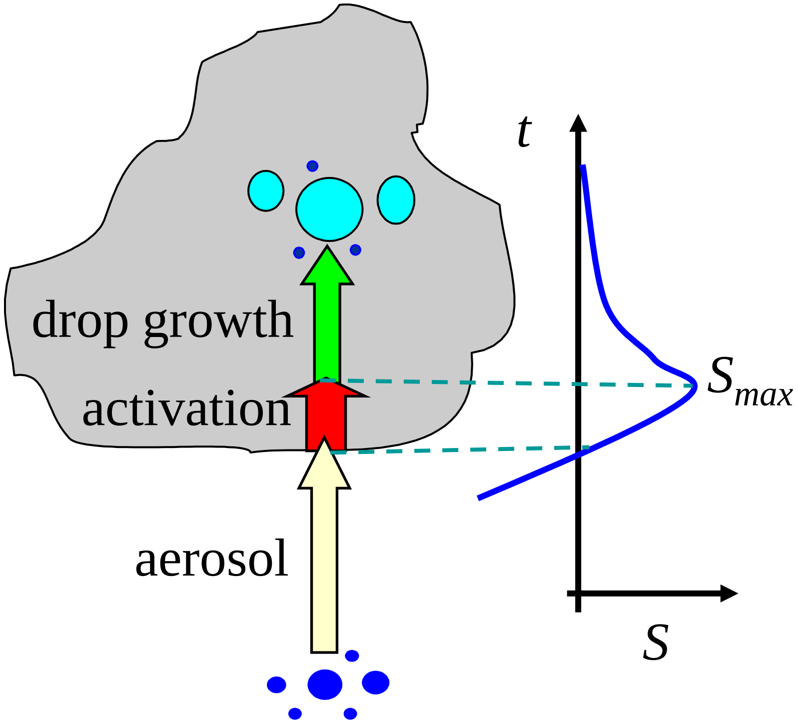
Increasing particles tends to cool climate (potentially alot).

Quantitative assessments done with climate models.

Droplet formation: The essence

Goal: Link cloud droplet concentration with precursor aerosol

Approach: Use the "simple story of cloud formation".

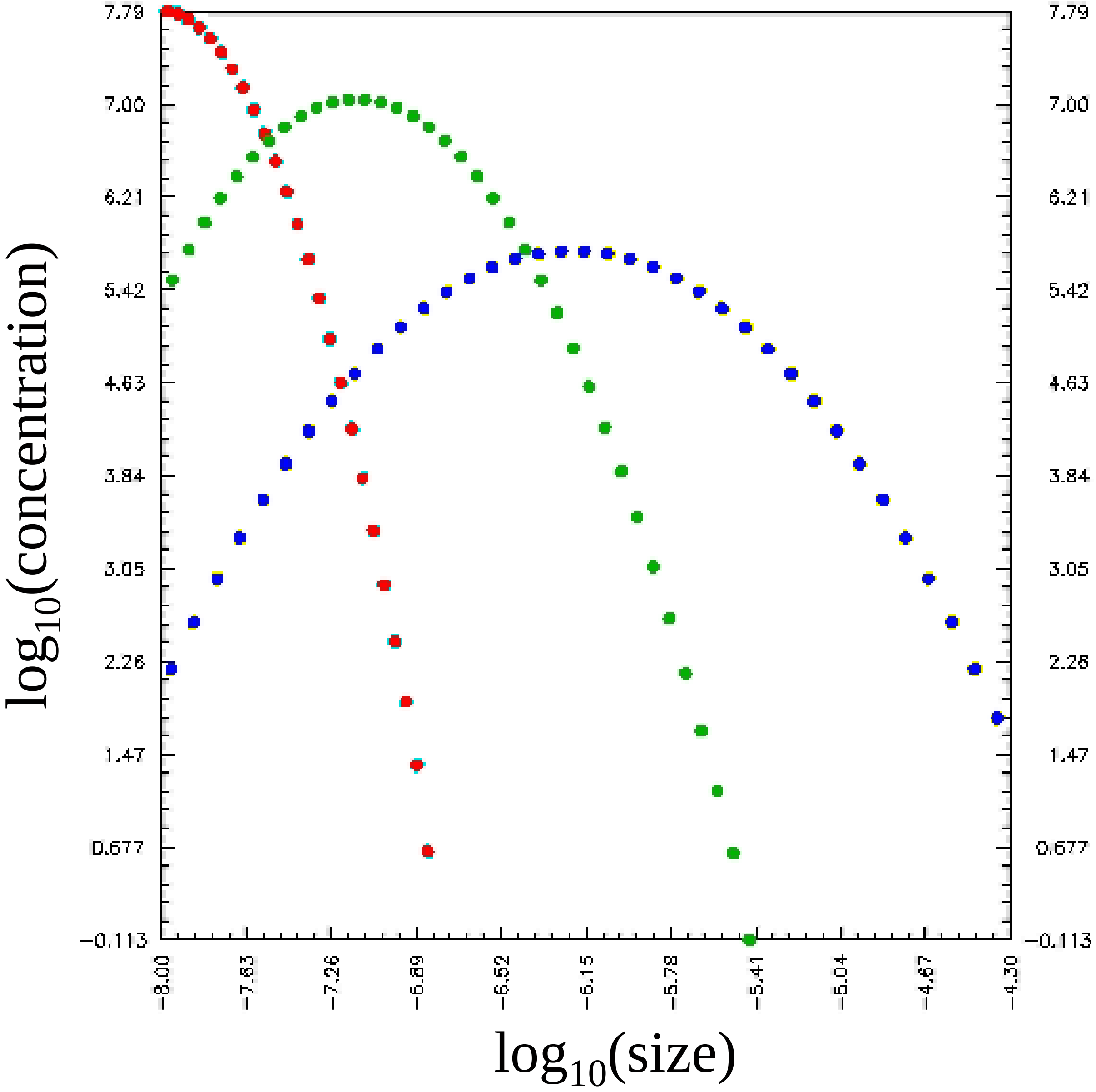


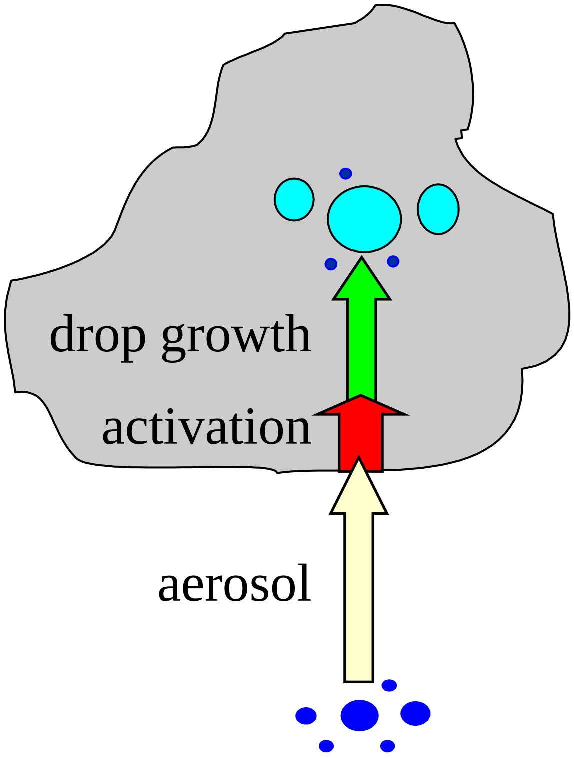
Conceptual steps are:

- Air parcel cools, exceeds dew point
- Water vapor is **supersaturated**
- Droplets start forming on existing CCN.
- Condensation of water on droplets becomes intense.
- Humidity reaches a **maximum**
- No more additional drops form

A "classical" nucleation/growth problem

Simulation of cloud droplet formation



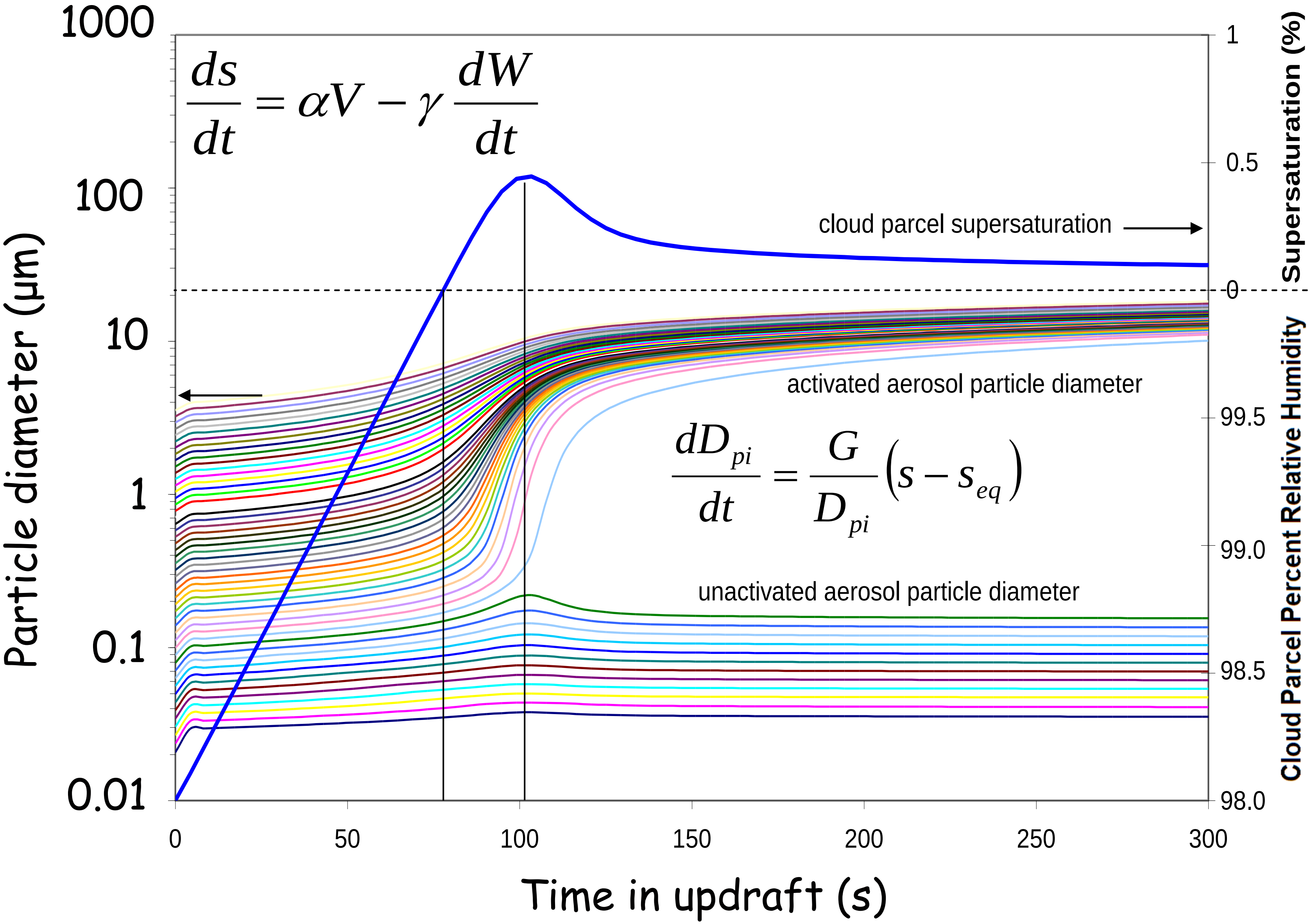


drop growth

activation

aerosol

Simulation of cloud droplet formation



$$\frac{ds}{dt} = \alpha V - \gamma \frac{dW}{dt}$$

$$\frac{dD_{pi}}{dt} = \frac{G}{D_{pi}}\left(s - s_{eq}\right)$$

Drop formation: coupled nonlinear system

Supersaturation (and s_{max}) depends strongly on the expansion rate (updraft velocity V) and the condensation rate of water:

$$\frac{ds}{dt} = \alpha V - \gamma \left(\frac{dW}{dt} \right)$$

Water condensation rate on droplets

Water condensation rate on droplets determined from the contribution of each aerosol "size class" i

Mass transfer coefficient of water from the gas phase

$$\frac{dD_{p,i}}{dt} = \frac{G_i}{D_{p,i}} \left(s - s_{eq,i} \right)$$

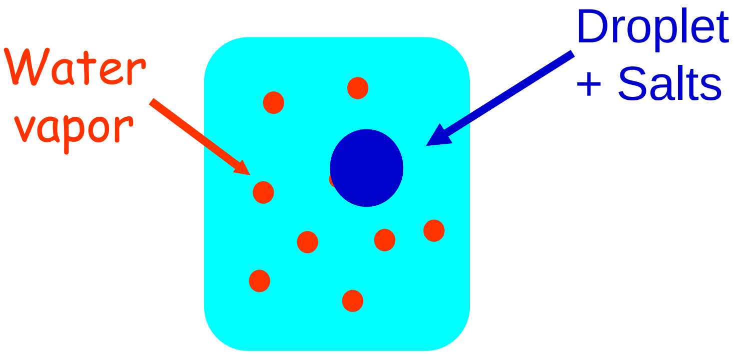
Equilibrium saturation (relative humidity) of droplet

We need to know:

1. $S_{eq,i}$ for aerosol and droplets (thermodynamics)
2. G_i depends on the water vapor diffusivity (P,T) and the *water vapor mass transfer coefficient* (kinetics).

Thermodynamics 101: essentials

- Equilibrium vapor pressure of water over pure water



$$P_{H_2O_{(g)}} = P_{sat}(T)$$

- Effects of dissolved solutes

Dissolved salts decrease the energy of your system (why?).

This reduces the equilibrium $P_{H_2O_{(g)}} < P_{sat}(T)$

Mol fraction of water in solution $\dfrac{n_w}{n_w + n_{salts}}$

$$P_{H_2O_{(g)}} = P_{sat}(T)x_{H_2O_{(l)}}$$

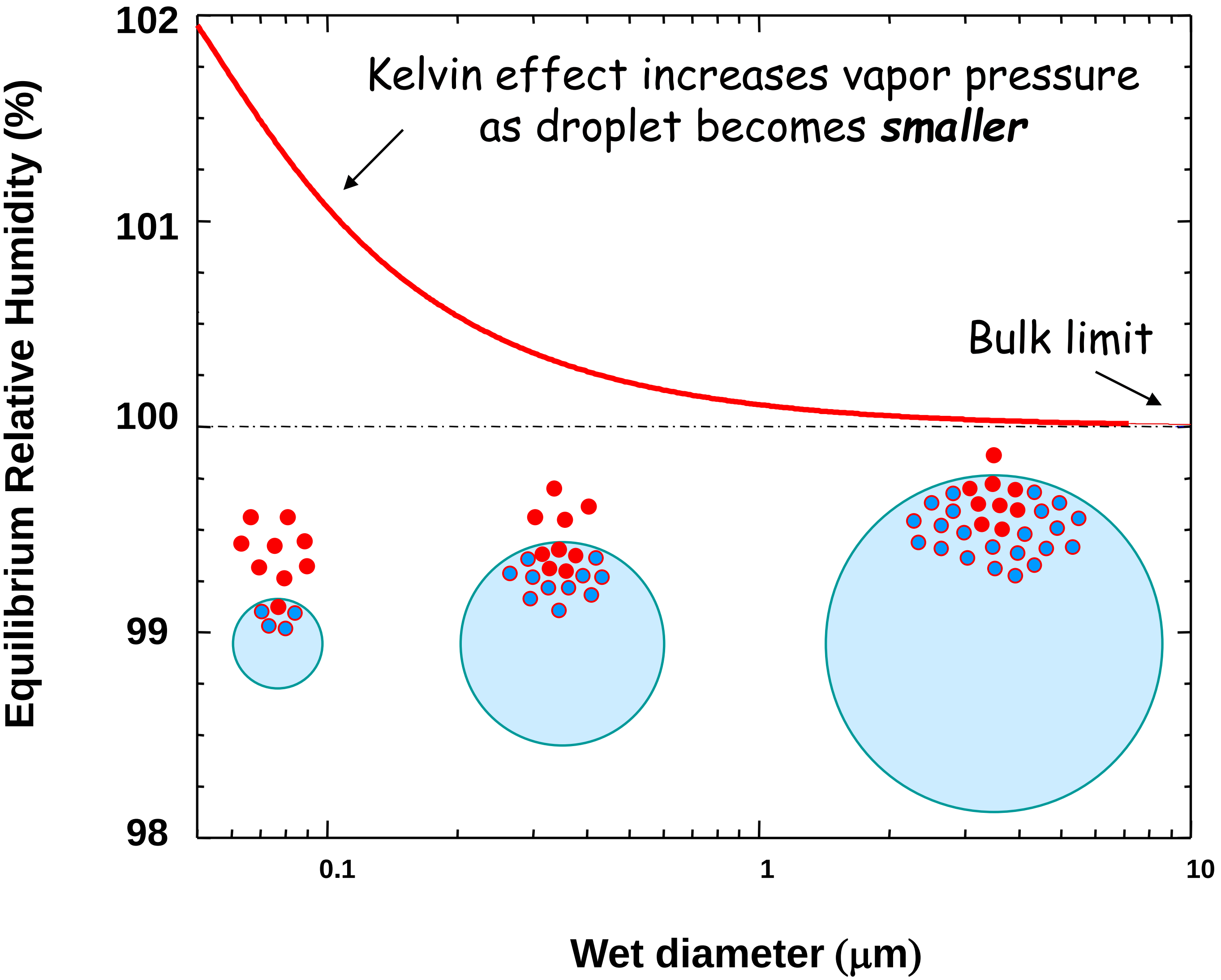
Raoult's Law (for ideal solutions)

Droplet thermo: special considerations

- Aerosol thermo mentioned before considered aerosol as a "bulk" system, 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

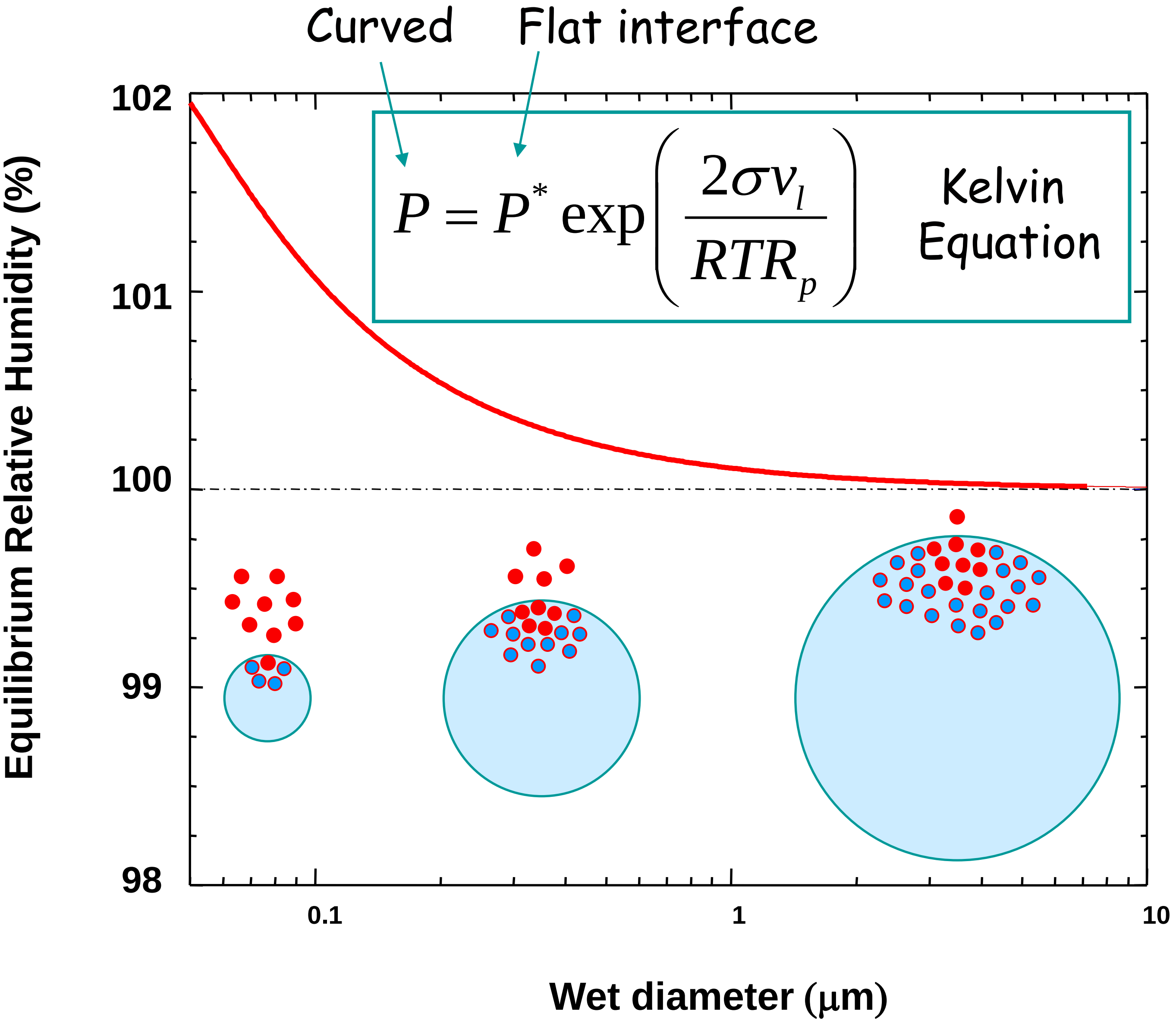
Impact of curvature: "the physical explanation"



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

Including curvature: Thermodynamics of droplets



Curved

Flat interface

$$P = P^{*} \exp\left(\frac{2\sigma v_l}{RTR_p}\right)$$

Kelvin Equation

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

Hugely important equation.

Needed for any nucleation process

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. If $\sigma_w, v_l \sim$ **const**. then only P^* changes (given by Raoult's law: $P^* = P^{sat}\gamma_w x_w$)

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

Köhler Equation

Equilibrium relative humidity of a particle when it has absorbed water and acquired a wet diameter, D_p

Thermodynamics of droplets: Köhler equation

One can then invoke simplifying assumptions:

$$x_w = \frac{n_w}{n_w + i n_s} = 1 - \frac{i n_s}{n_w + i n_s} \sim 1 - \frac{i n_s}{n_w} = 1 - \frac{i n_s}{\frac{\pi}{6} D_p^3 \frac{\rho_w}{M_w}} = 1 - \frac{\frac{6}{\pi}\frac{M_w}{\rho_w} i n_s}{D_p^3}$$

$$= 1 - \frac{B}{D_p^3}$$ where $$B = \frac{6}{\pi}\frac{M_w}{\rho_w} i n_s$$

Moles of solute in droplet

van't Hoff factor of solute in droplet

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

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

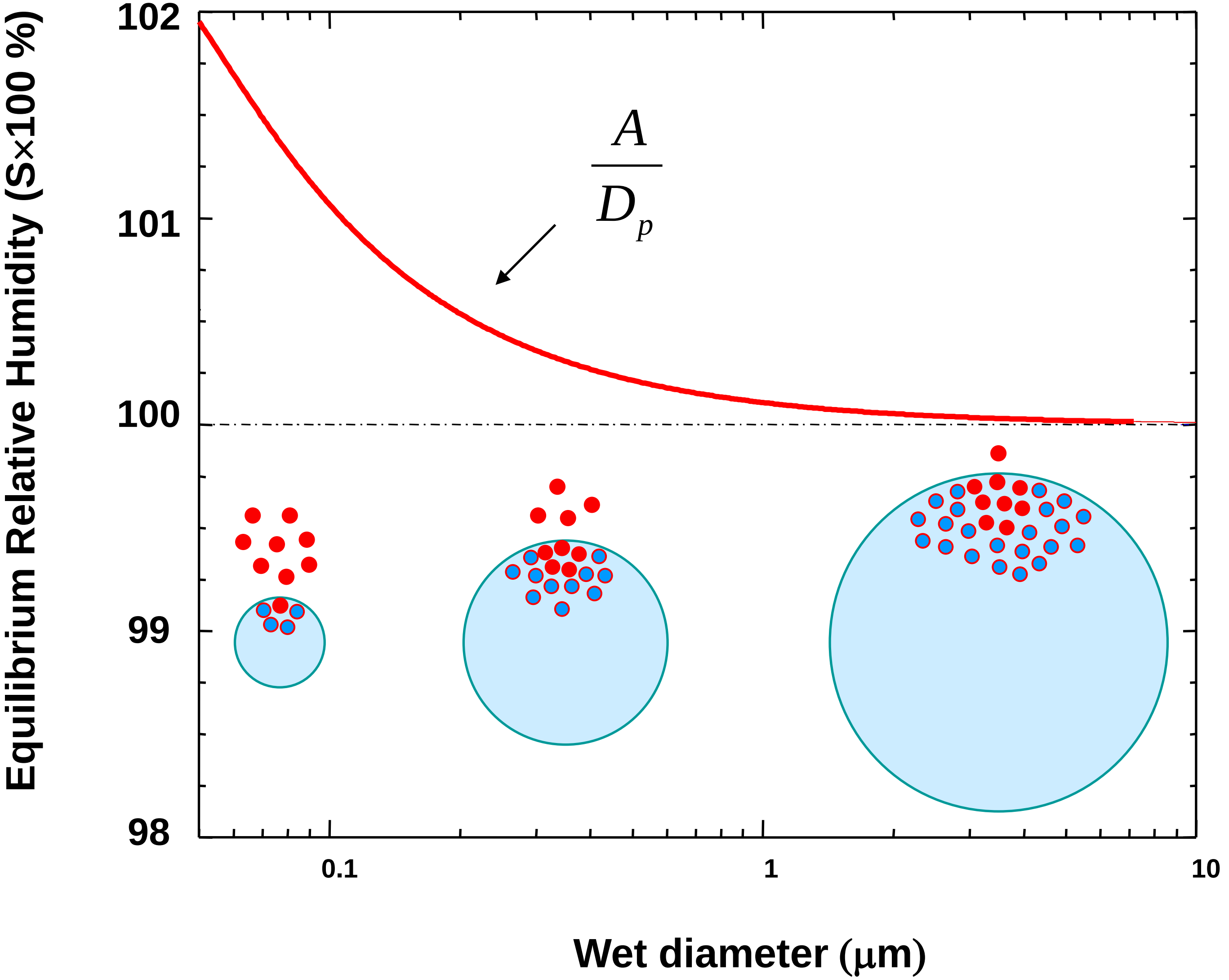
Saturation ratio

"Kelvin" term

"Raoult" term

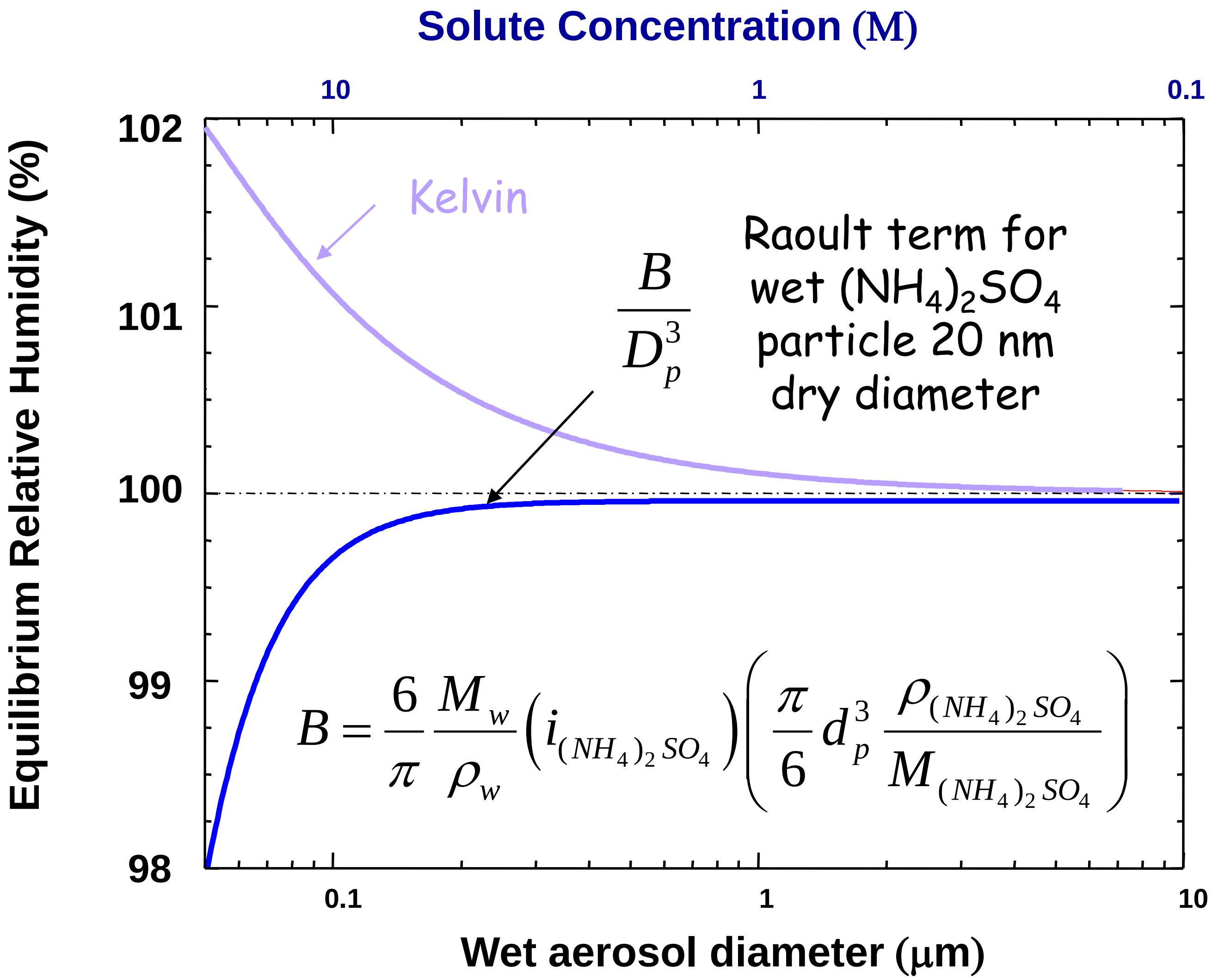
Thermodynamics of droplets: Köhler equation

First plot the Kelvin term



Thermodynamics of droplets: Köhler equation

…then plot the Raoult term



$$\frac{B}{D_p^3}$$

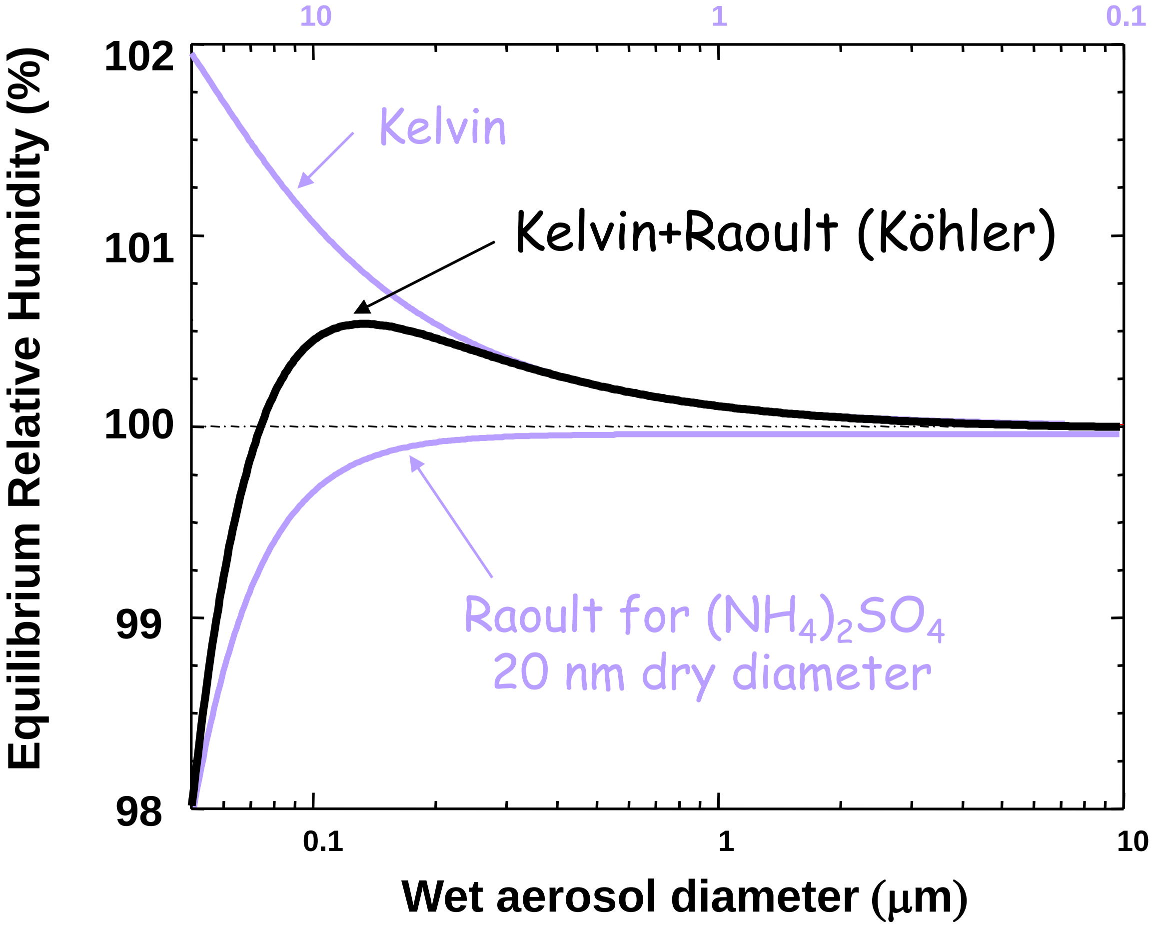
Raoult term for wet $(NH_4)_2SO_4$ particle 20 nm dry diameter

$$B = \frac{6}{\pi}\frac{M_w}{\rho_w}\left(i_{(NH_4)_2SO_4}\right)\left(\frac{\pi}{6}d_p^3\frac{\rho_{(NH_4)_2SO_4}}{M_{(NH_4)_2SO_4}}\right)$$

Thermodynamics of droplets: Köhler equation

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

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

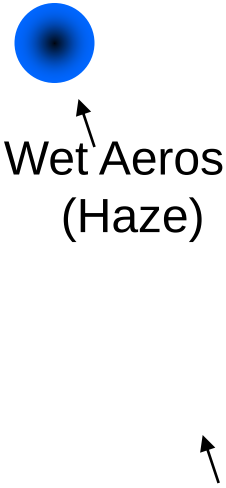


The combined Kelvin and Raoult effects is the simplified **Köhler equation**.

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

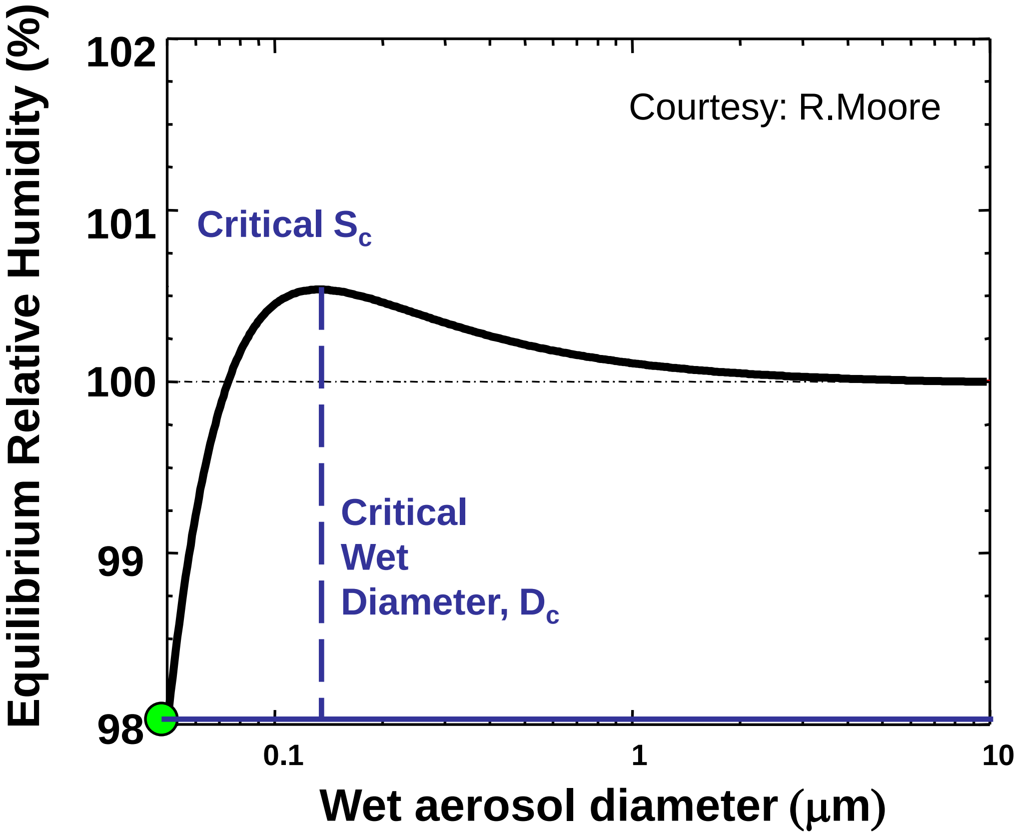
Regions of stability/instability of ambient droplets

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



Wet Aerosol
(Haze)

Cloud Droplet

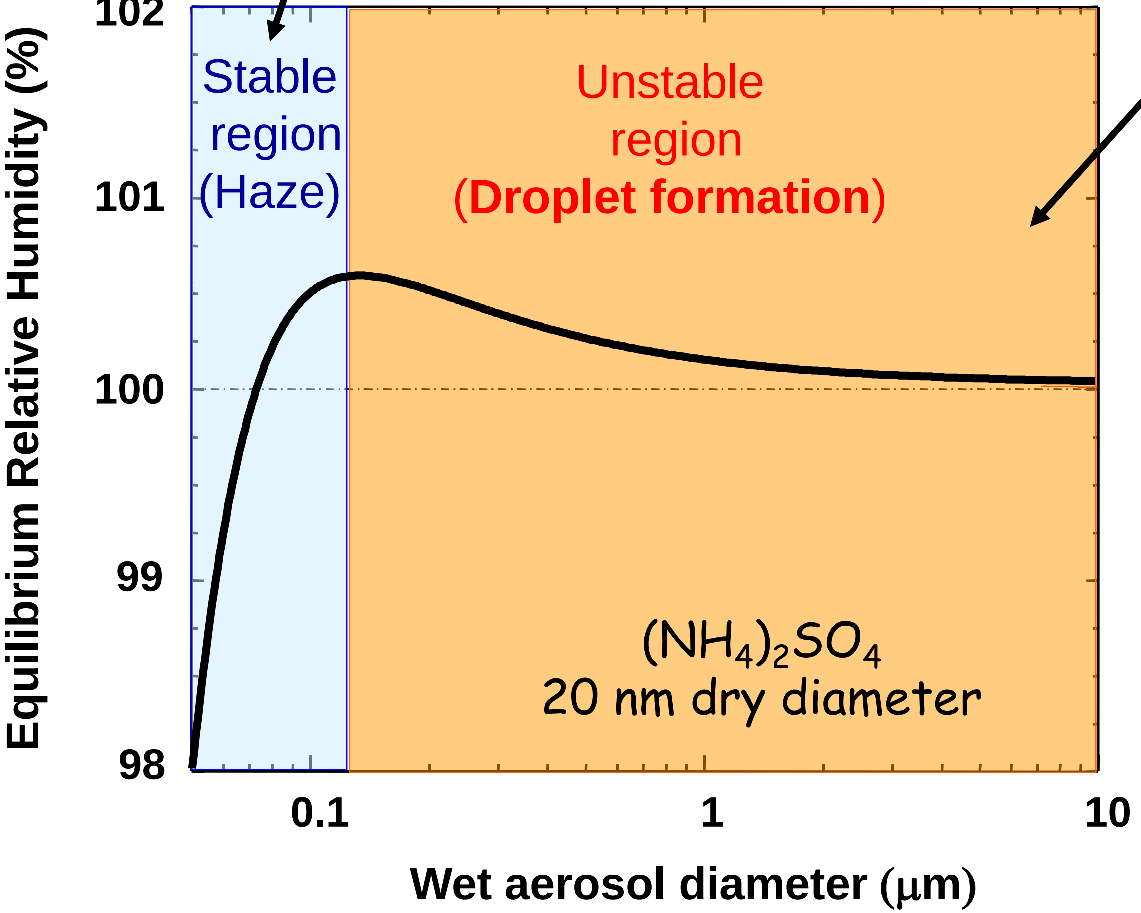


If ambient S exceeds the maximum, particles grow uncontrollably. They are said then to act as Cloud Condensation Nuclei (CCN)

When does an aerosol particle act as a CCN ?

Ambient RH **less** than S_c ->
stable equilibrium.

Ambient RH **above** S_c ->
unstable equilibrium.
Particles act as CCN
and make droplets



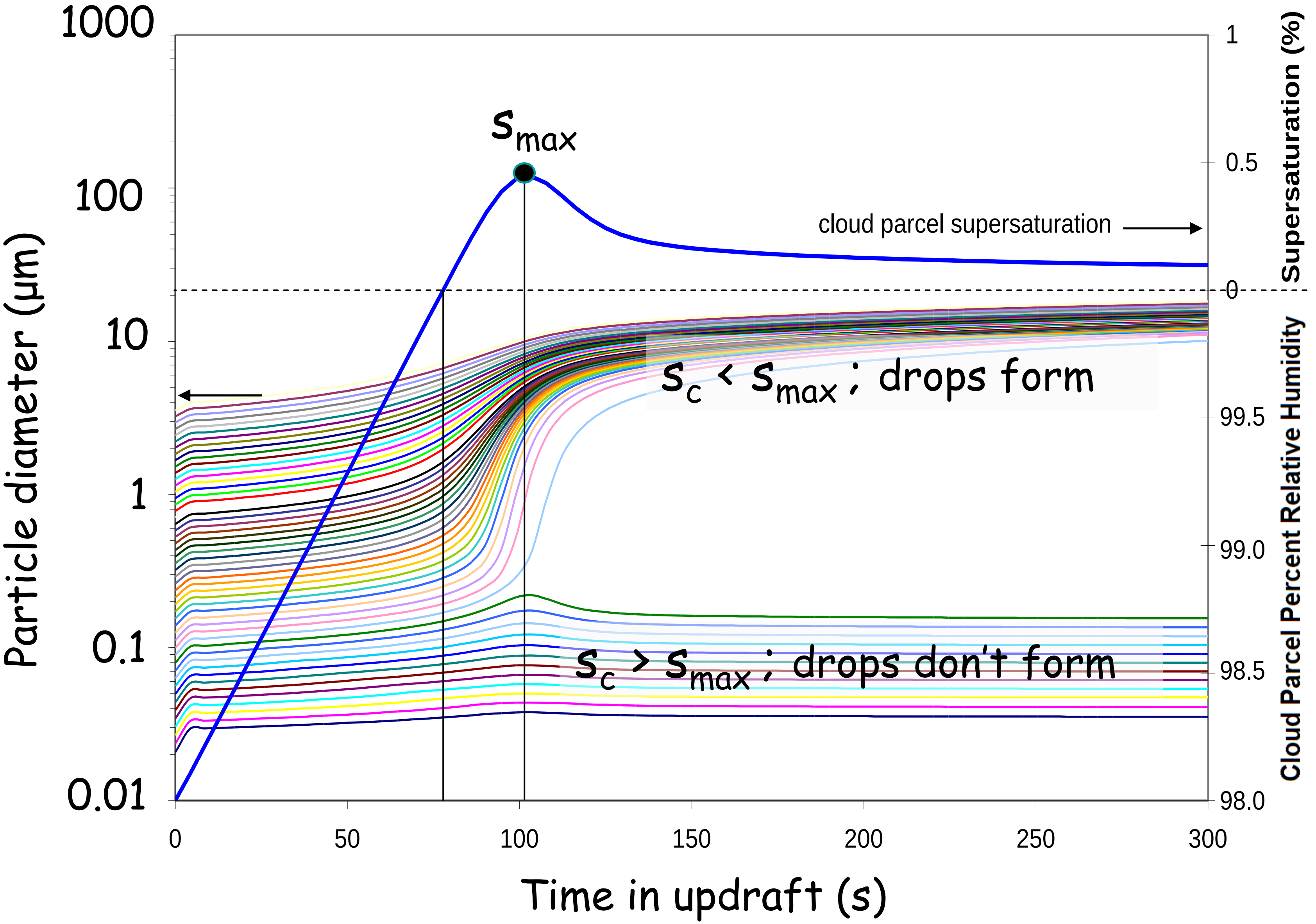
Köhler theory:

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

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

Size is more
important than
composition

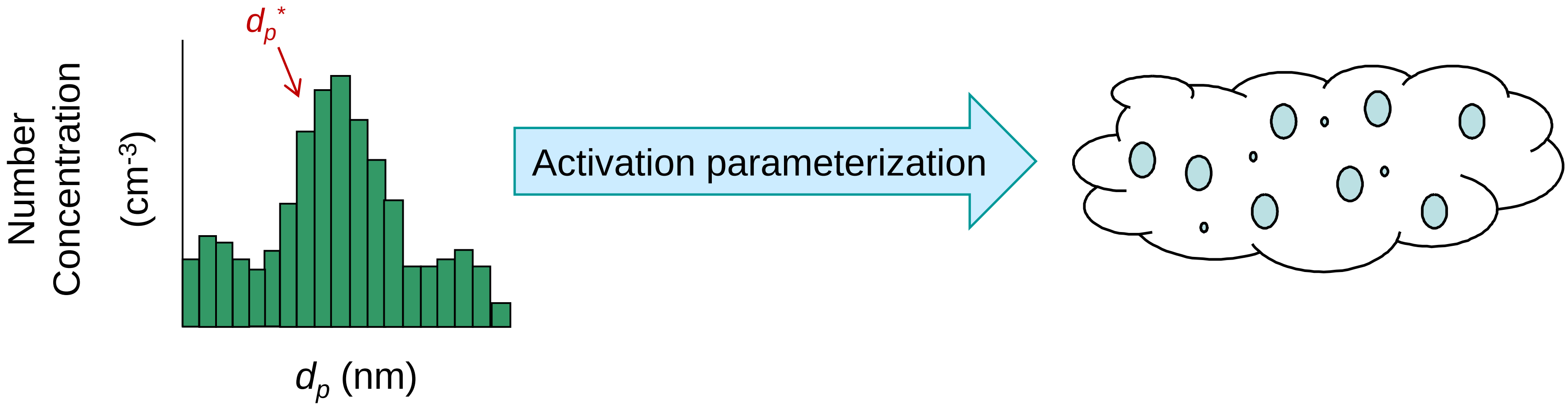
Now we understand droplet formation



Describing droplet formation in models…

Droplet calculation in models then is:

Calculated size distribution + κ + vertical velocity

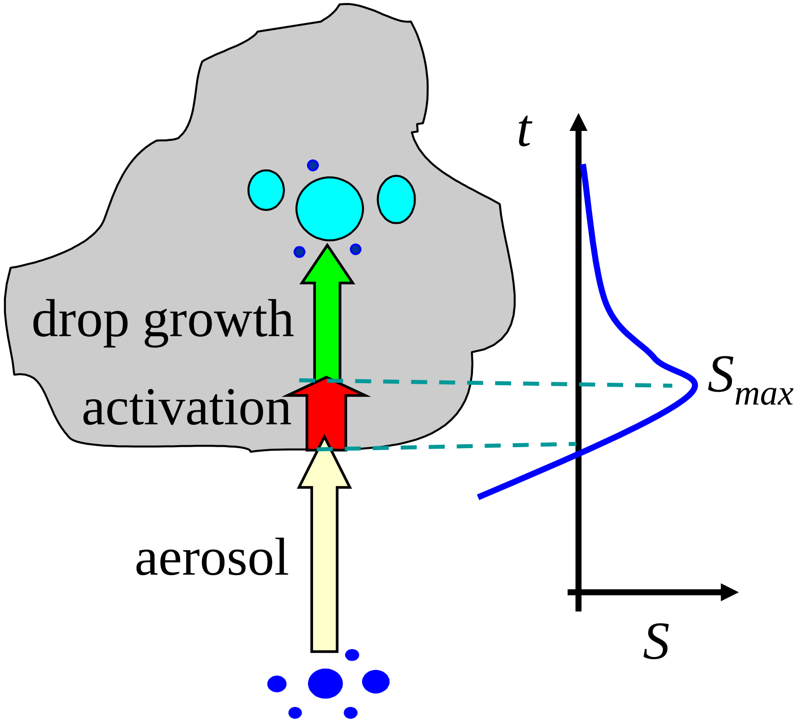


Activation parameterization is either a correlation or a solution to the parcel model equations that describe the activation process in clouds.

Droplet number needs CCN and max.cloud RH…

Algorithm for calculating N_d (Mechanistic parameterization):

1. Calculate s_{max} (approach-dependent)
2. N_d is equal to the CCN with $s_c \leq s_{max}$



Mechanistic Parameterizations: Twomey (1959); Abdul-Razzak et al., (1998); Nenes and Seinfeld, (2003); Fountoukis and Nenes, (2005); Kumar et al. (2009), Morales and Nenes (2014), and others.

Input: P,T, vertical wind, particle size distribution,composition.

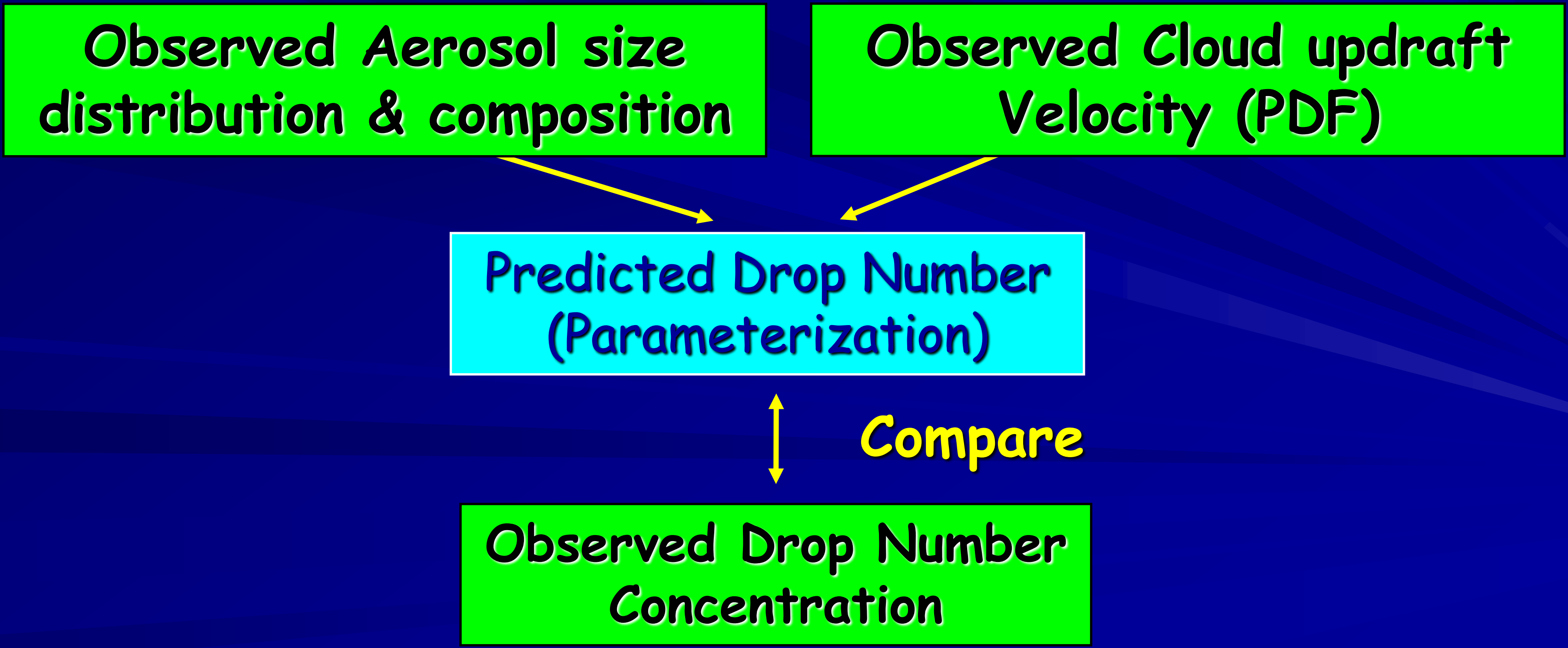
Output: Cloud properties (droplet number, size distribution).

Comprehensive review & intercomparison:
Ghan, et al., *JAMES* (2011); Morales and Nenes (2014)

Is this description of droplet formation real

Evaluate with in-situ data from airborne platforms

CIRPAS Twin Otter



Observed Aerosol size distribution & composition

Observed Cloud updraft Velocity (PDF)

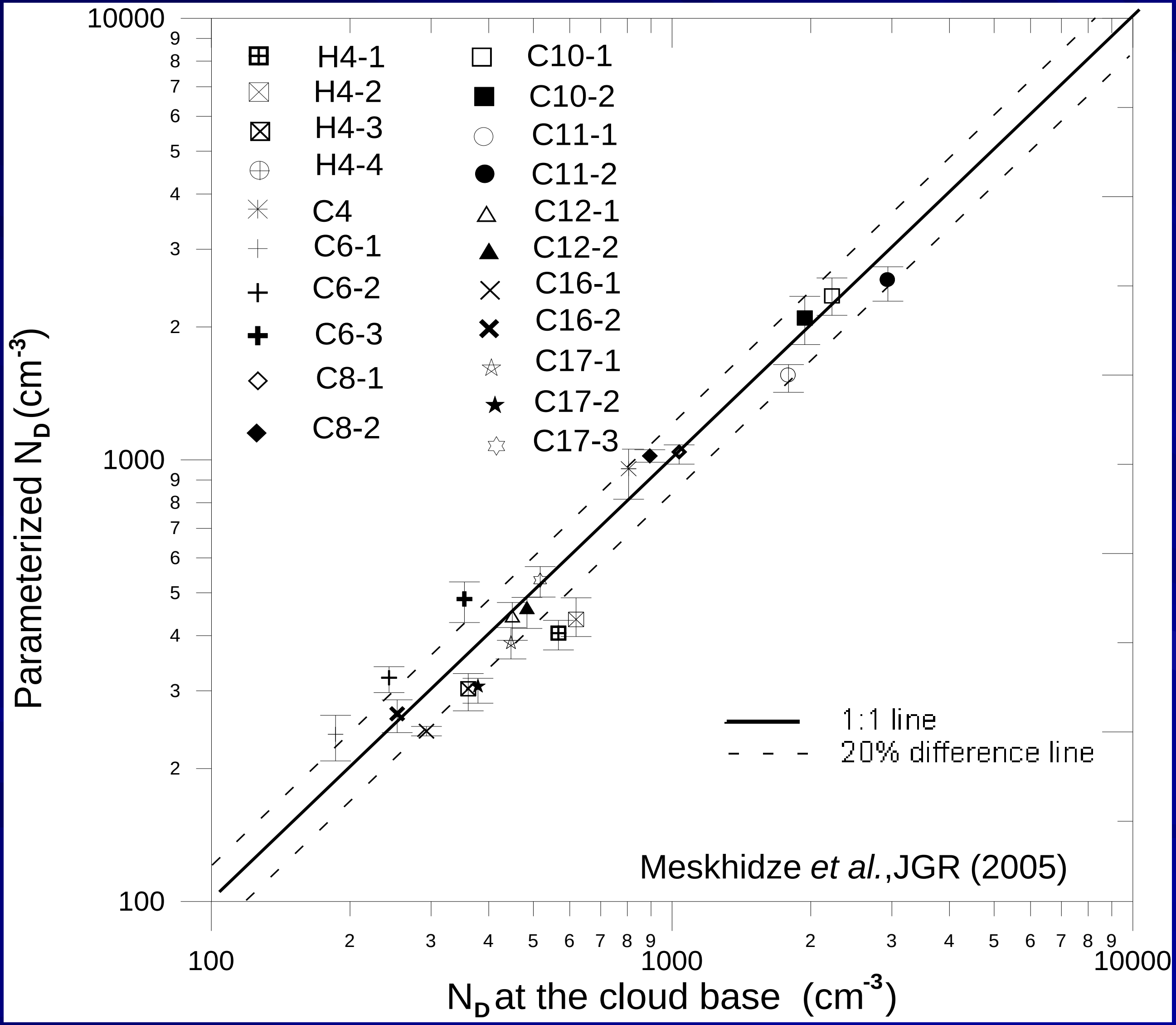
Predicted Drop Number (Parameterization)

Compare

Observed Drop Number Concentration

CRYSTAL-FACE (2002)
Cumulus clouds

CIRPAS Twin Otter



Meskhidze *et al.*,JGR (2005)

Paramet'n agrees with observed cloud droplet number

Agreement to within a few % (on average)!

…when you know everything about aerosol composition and size

Issue: aerosols are complex

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Primary emissions

Automobiles, industry, domestic, vegetation, forest fires, seasalt, ...

Secondary transformations

Oxidation of precursors (by O_3, H_2O_2, OH, NO_3, etc.) generates organic compounds.

Reaction of volatile bases (NH_3) with acids, dust and seasalt form salts like $(NH_4)_2SO_4$.

Parameterizing "characteristic" CCN activity…

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

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

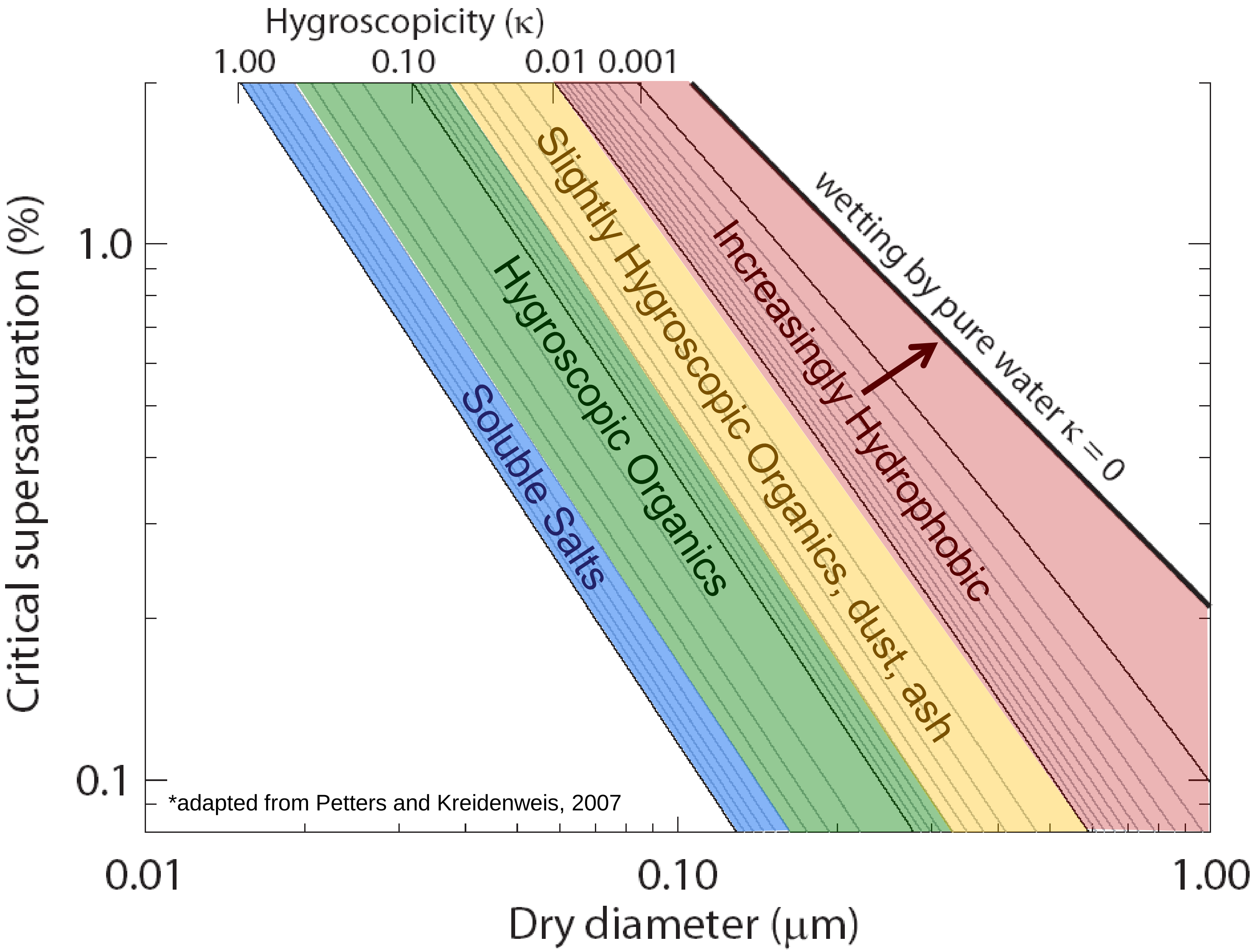
$\kappa \sim 1$ for seasalt, ~ 0.6 for $(NH_4)_2SO_4$, ~ 0-0.3 for organics

κ rarely exceeds 1 in atmospheric aerosol

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

$\kappa \sim 0.6$ ⇨ particle behaves as 60% seasalt, 40% insoluble

Hygroscopicity Space

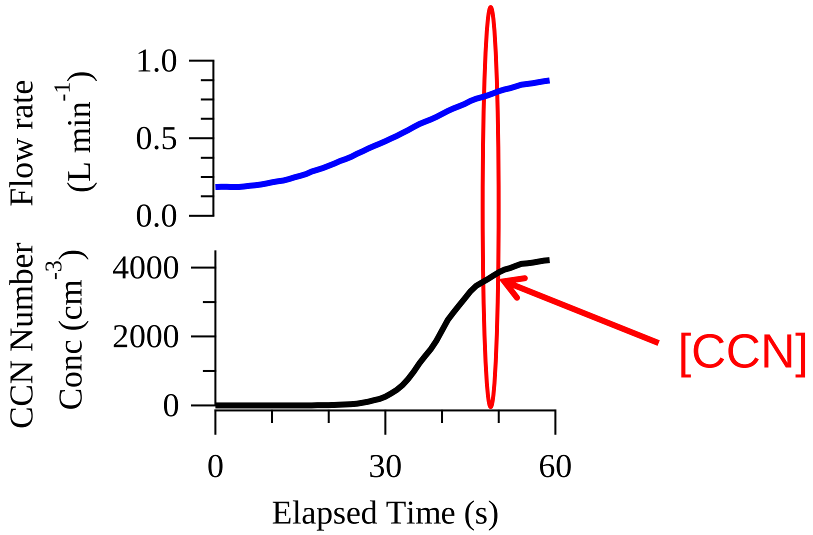


*adapted from Petters and Kreidenweis, 2007

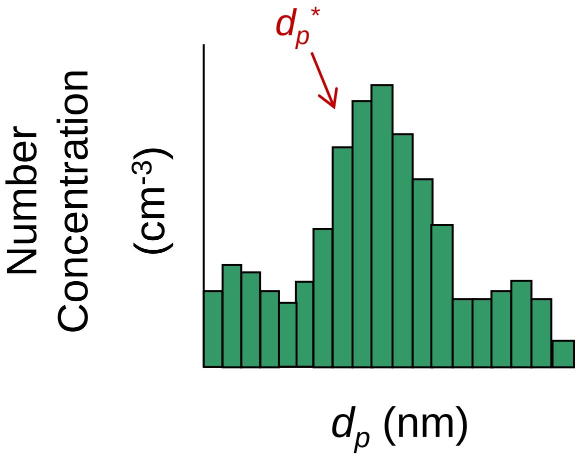
- κ is used to parameterize the activation of particles in the atmosphere

Getting κ from CCN Measurements

1. Measure CCN concentration, [CCN], at a given *s**



2. Find where backwards integrated size distribution = [CCN] to obtain the critical diameter, d_p^*



3. Calculate κ

$$\kappa \approx \frac{4A^3}{27 d_p^3 s^{*2}} = \frac{M_w \rho_s}{\rho_w M_s} \upsilon \varepsilon_s$$

**Moore and Nenes (2009)*

Measuring CCN: Basic Principles

Operation: Expose particle sample to a known water vapor supersaturation, and measure those that become droplets.

Desired range: 0.01% - 1.0% supersaturation (S)

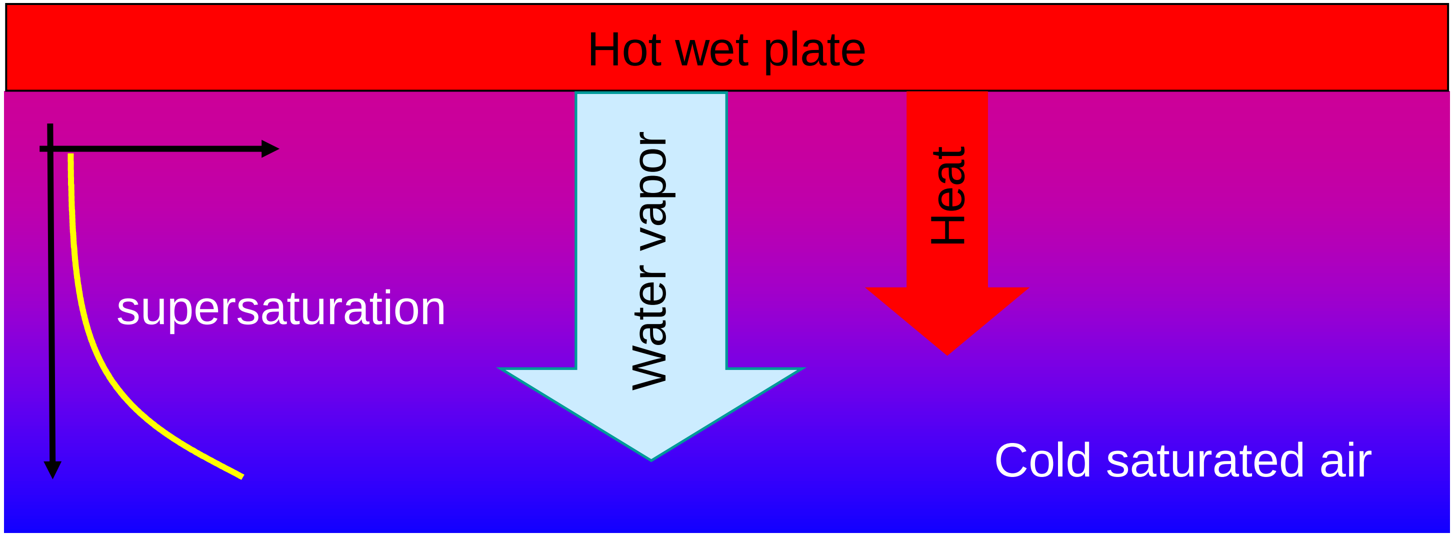
Main challenges:

Generating a highly controlled level of supersaturation
- *Fluctuations in supersaturation are always a problem*
- *This is more difficult for low supersaturations*

Droplet detection
- *Need to differentiate from particles that do not become droplets*
- *Generally more difficult for low supersaturations*

CCN Instruments: Generating Supersaturation

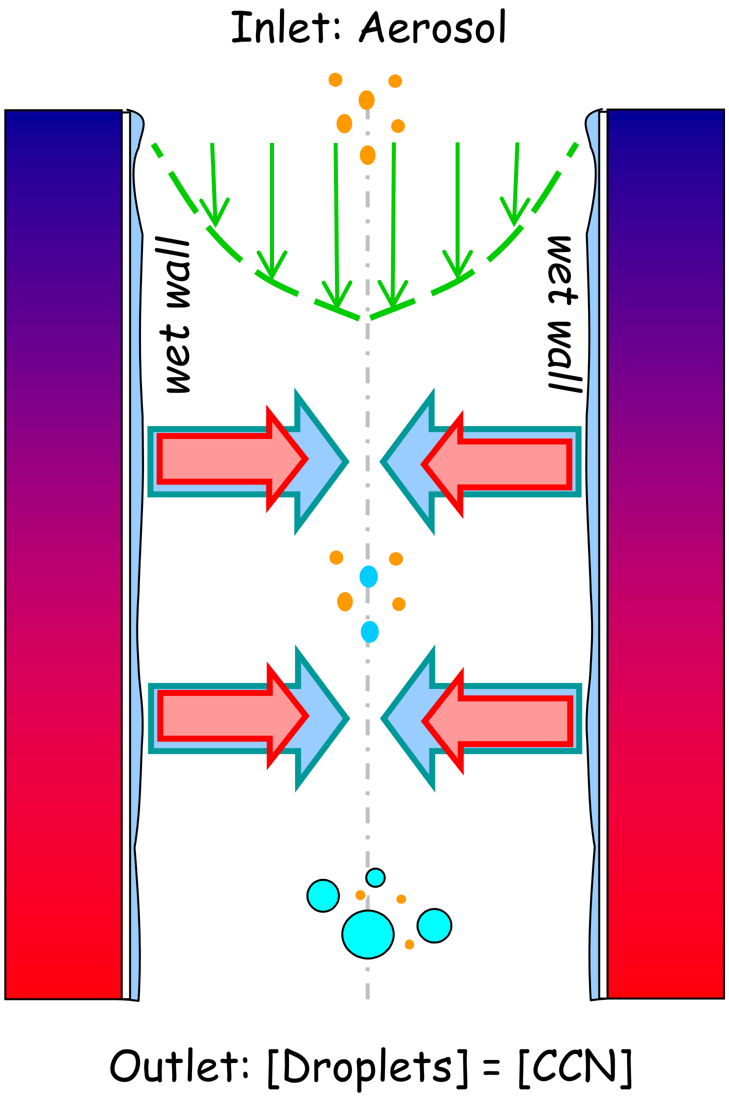
Relative Diffusion Instruments: Exploiting the difference in diffusivity between heat and water vapor.



- Generate a condition where saturated water vapor diffuses into a (saturated) colder region.

- *Supersaturation* develops in the "cold" region (why? Hint: H_2O molar mass 18, air molar mass ~ 29).

Continuous-Flow Streamwise Thermal Gradient Chamber



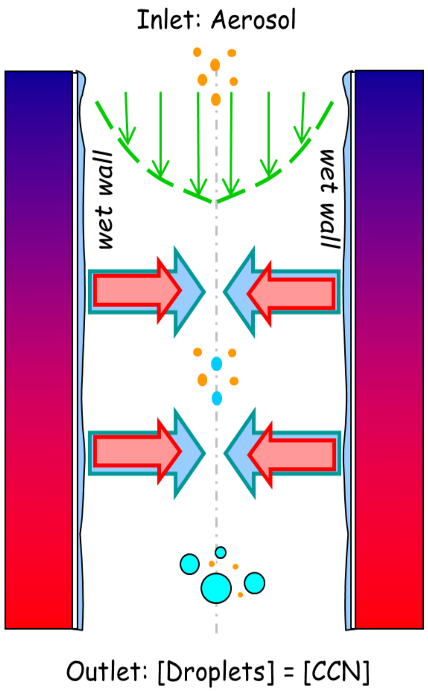
- Standard CCN measurement (>120 instruments in operation).
- Metal cylinder with wetted walls
- Streamwise Temp. Gradient
- Water diffuses faster than heat
- Supersaturation, S, generated at the centerline = *f* (Flowrate, Pressure, and Temp. Gradient)
- Operated as a *spectrometer* using Scanning Flow CCN Analysis (Moore and Nenes, 2009)

Roberts and Nenes (2005), US Patent 7,656,510

Lance et al., (2006), Lathem and Nenes (2011), Raatikainen et al. (2012, 2013)

In-situ (and remote sensing data) key for studying the aerosol-CCN (microphysical) link

The CFSTGC or "DMT CCN Counter"



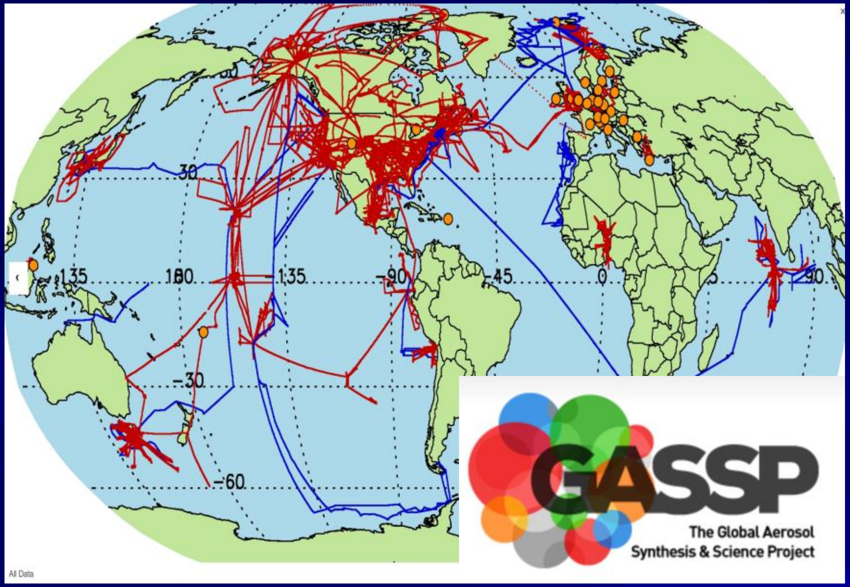
- Metal cylinder with wetted walls
- Streamwise Temp. Gradient
- Water diffuses faster than heat to centerline of flowtube
- Supersaturation, S, generated at the centerline = *f* (Flowrate, Pressure, and Temp. Gradient)

Roberts and Nenes (2005), US Patent 7,656,510

Used to test theory and develop a climatology over 15 years...

The community has obtained a CCN climatology over the 15 years

Some locations sampled …



Measured:

CCN, Aerosol concentrations and size distributions, and aerosol chemistry

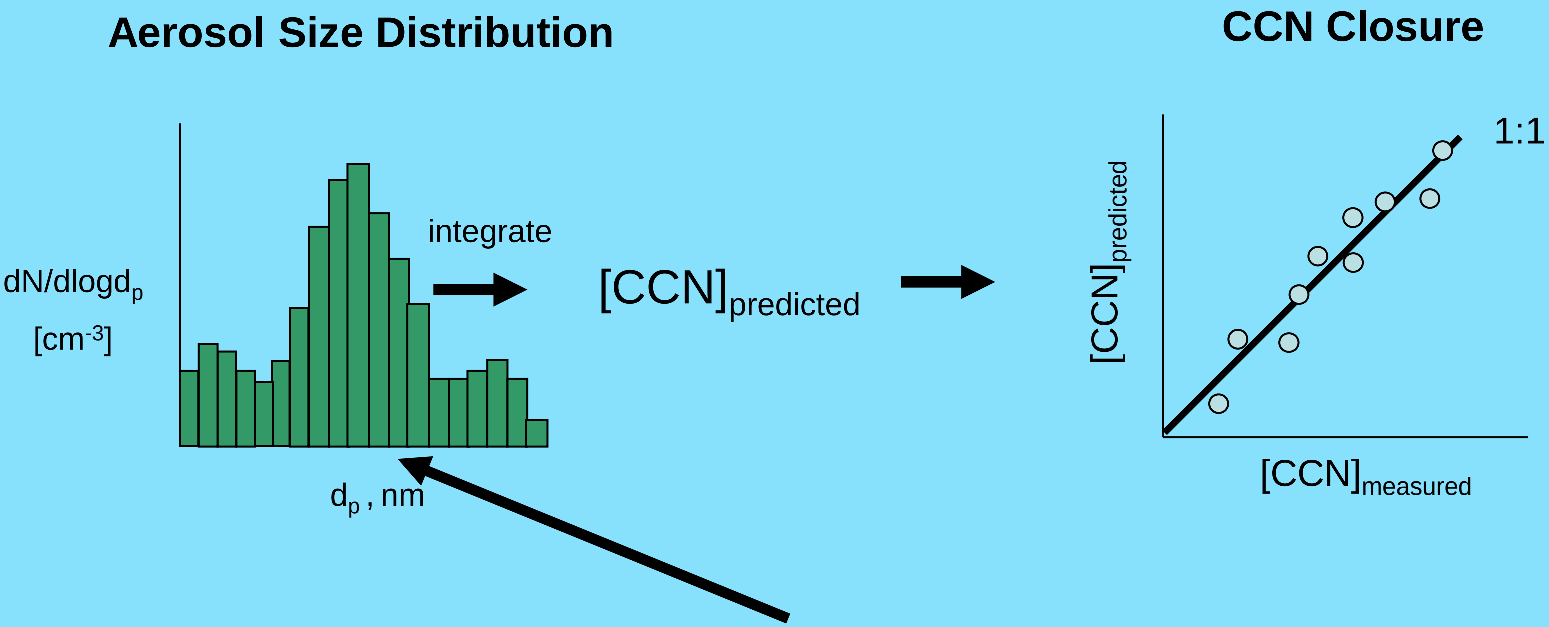
Cloud hydrometeor distributions (liquid/ice) and dynamics.

Environments:

Arctic, urban pollution, biomass burning, marine aerosol, hurricanes, oil spills, the tropics….

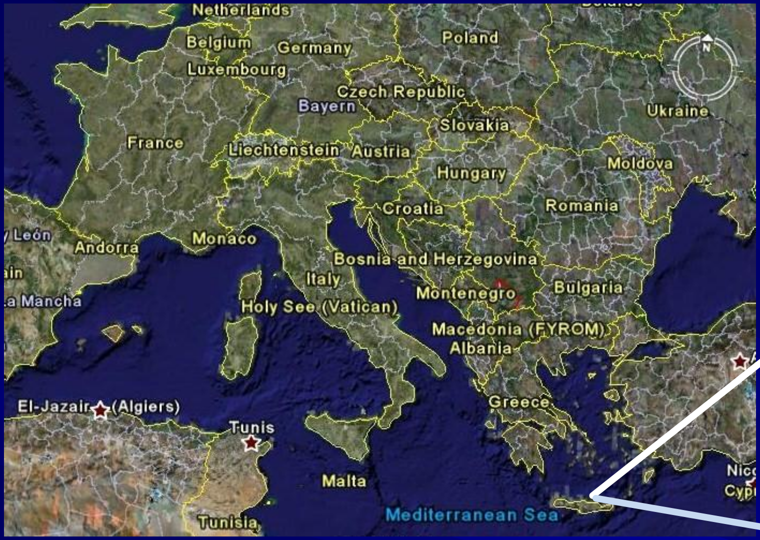
Testing CCN activation theory: CCN "Closure" studies

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.

(The first) Finokalia Aerosol Measurement Campaign (FAME-07) – Summer 2007



DMT CCN counter
Supersaturation range: 0.2-1.0%

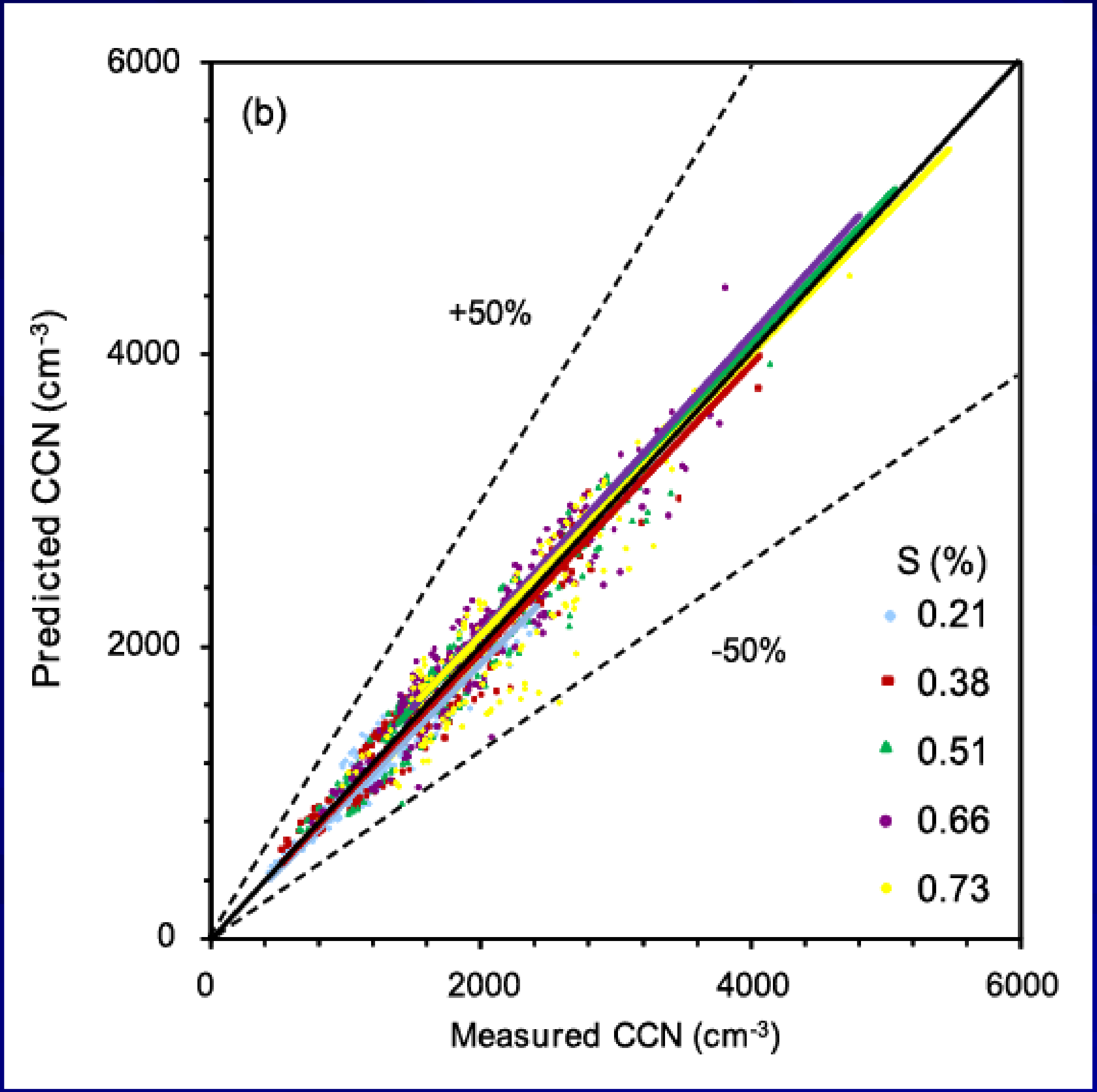
TSI 3080 SMPS
Size: 20-460 nm

Low-vol impactor
Ionic composition measured via IC

WSOC/EC/OC also measured

(Bougiatioti et al., ACP, 2009)

Finokalia Aerosol Measurement Campaign (FAME-07) – CCN closure



Organics: very oxidized (MO-OOA) κ ~ 0.15

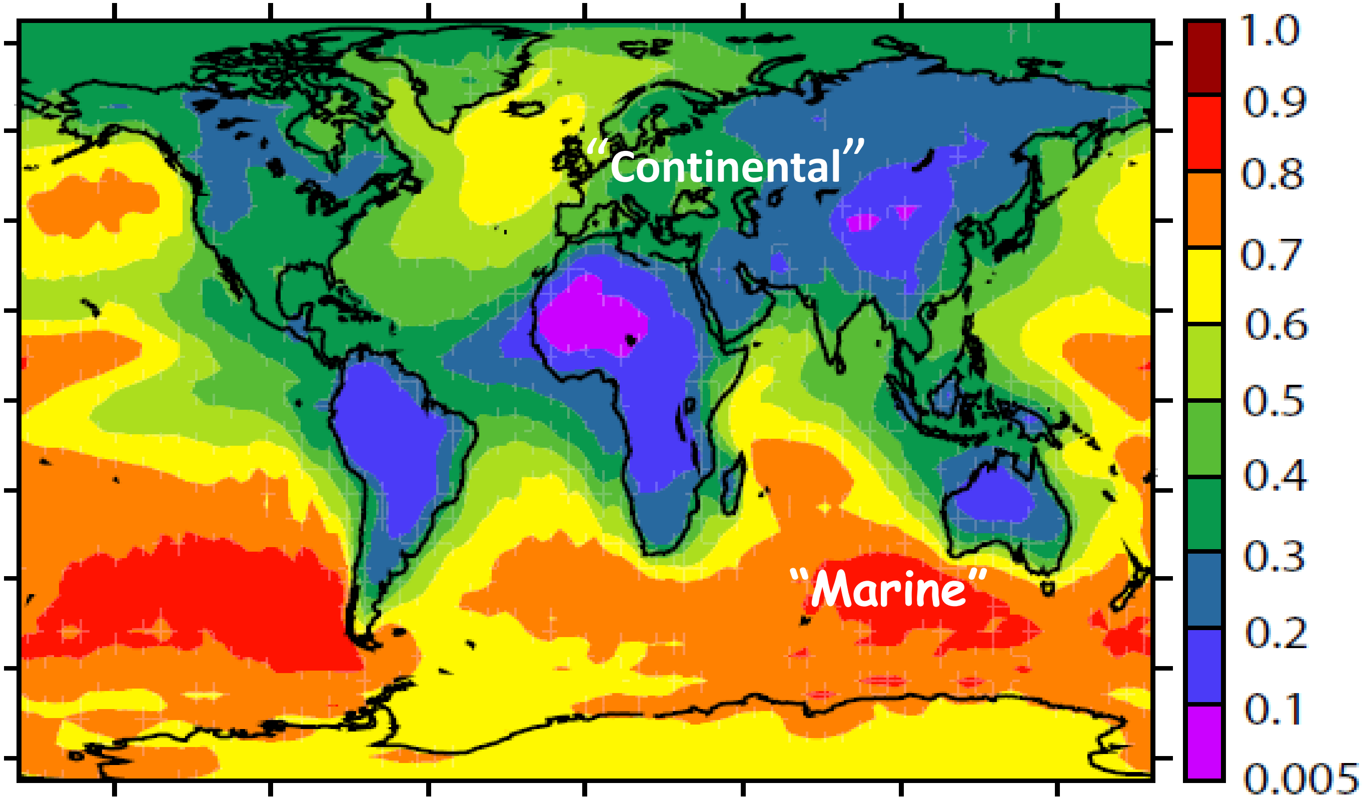
Excellent CCN closure (error ~ 2%).

Köhler (CCN) theory *really* works.

Simple treatments of hygroscopicity in general work "well enough" for CCN/CDNC predictions

(Bougiatioti et al., ACP, 2009)

Global “average” distribution for κ



Pringle et al., ACP, (2010)

Fig. 2. Annual mean distribution of κ at the altitude of the planetary boundary layer.