

Kelvin Equation

→ Applies to curved surfaces relate vapor pressure over flat w.r.t curved surfaces.

→ we define a Gibbs free energy per unit mol of substance g .

two phases → gas, liquid

$g_l = g_{gas}$ when the interface is planar

let's call that g_l^*

$g_l \neq g_l^*$, b/c of the effect of surface tension

↑ curved surface

How much? e const. T, P

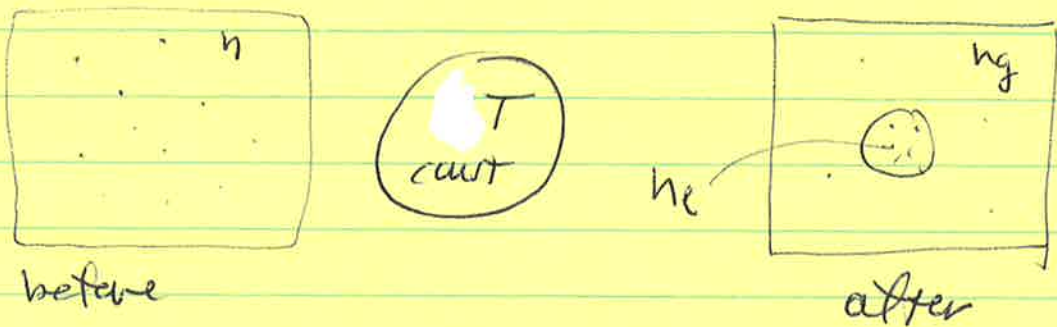
$$\int_{g_l^*}^{g_l} dg = \int_0^A \sigma dA \Rightarrow g_l = g_l^* + \sigma A$$

└
 Enhancement in chem. p.
 from s.t.

So let's see how the s.t. change affects vapor pressure

(2)

Take two states (before/after drop formation)
closed system, constant P, T



$$G_b = n g_g$$

$$G_f = n_g g_g + n_e g_e + \underbrace{4\pi R_p^2 \sigma}_A$$

$$\Delta G = G_f - G_b = n_g g_g + n_e g_e + 4\pi R_p^2 \sigma - n g_g \quad \left. \begin{array}{l} \text{but } n = n_e + n_g \\ \text{(conservation of mass)} \end{array} \right\} \Rightarrow$$

$$\begin{aligned} \Rightarrow \Delta G &= n_g g_g + n_e g_e + 4\pi R_p^2 \sigma - n_e g_g - n_g g_g = \\ &= -n_e (g_g - g_e) + 4\pi R_p^2 \sigma \quad (2) \end{aligned}$$

we said before that $g_g - g_l \neq 0$ (b/c we are talking about curved interfaces. So what we do is relate g_e to the curved surface and

g_g to a flat surface in equilibrium with it:

$$dg = -s dt + v dp = \frac{RT}{P} dp \Rightarrow \int_{g_0}^{g_g} dg = \int_{P^*}^P \frac{RT}{P} dP \Rightarrow$$

$$\Rightarrow g_g - g_l = RT \ln \frac{P}{P^*} \quad (1)$$

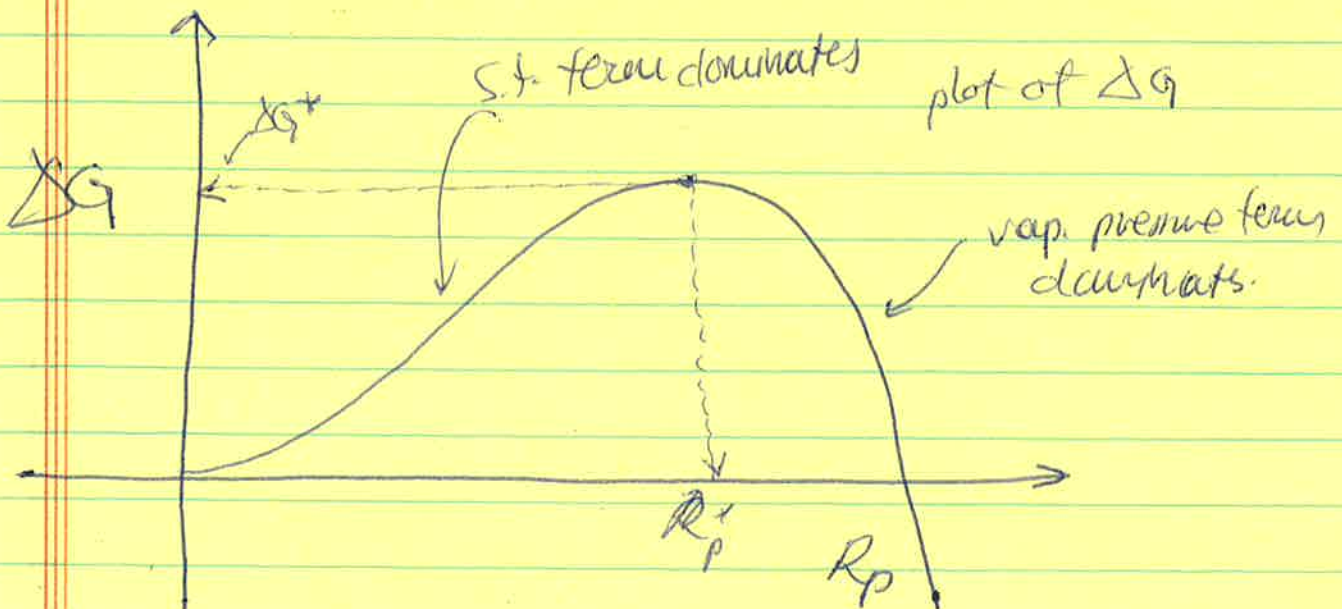
$$\begin{aligned} (1) + (2) \Rightarrow \Delta G &= -n_l RT \ln \frac{P}{P^*} + 4\pi R_p^2 \sigma \\ &= -n_l RT \ln \frac{P}{P^*} + 4\pi R_p^2 \sigma \quad (3) \end{aligned}$$

P^* equil. vap. pressure over flat surface
 P vapor pressure when $R = R_p$

$$n_l = \frac{\text{Volume of drop}}{\text{molar volume of } H_2O(l)} = \frac{\frac{4}{3}\pi R_p^3}{V_l} \quad (4)$$

(4) + (3):

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



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@ equilibrium, $\frac{\partial \Delta G}{\partial R_p} = 0$. It's where the two terms balance each other

$$\frac{\partial \Delta G}{\partial R_p} = - \frac{4\pi R^2 \gamma}{R_p^2} \ln \frac{P}{P^*} + 2 \cdot 4\pi R_p \sigma = 0 \Rightarrow$$

$$\Rightarrow \frac{R_p^* \ln \frac{P}{P^*}}{R_p} + 2\sigma = 0$$

where R_p^* is the R_p for which $\frac{\partial \Delta G}{\partial R_p} = 0$.

$$\ln \frac{P}{P^*} = \frac{2\sigma V_l}{RT R_p^*} \Rightarrow \boxed{P = P^* \exp\left(\frac{2\sigma V_l}{RT R_p^*}\right)}$$

Kelvin Equation.

$$V_l = \frac{M}{\rho}$$

so E.E becomes

$$P = P^* \exp\left(\frac{2\sigma M}{RT \rho R}\right)$$

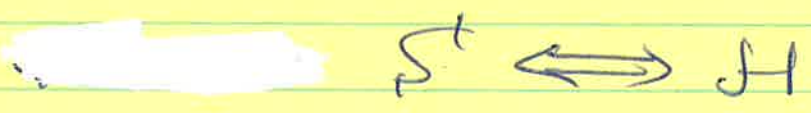
← Curvature effect.

↑
Vapor pressure over curved surface

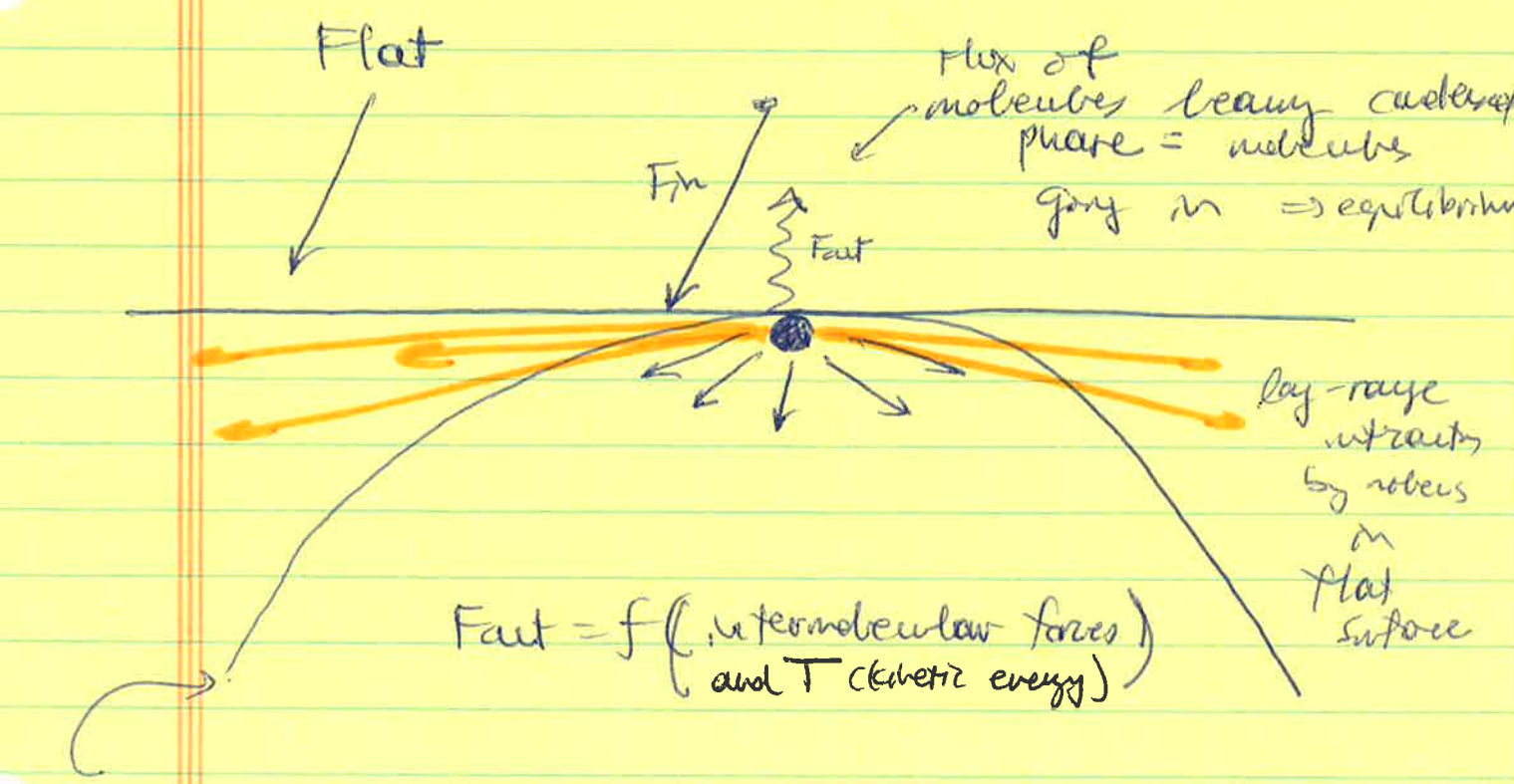
↑
vapor pressure over flat surface

$$s_0 = \frac{P}{P^*} > 1$$

↑
This is referred to as "saturation ratio", s
 $s > 1$ is often called supersaturation, s^*

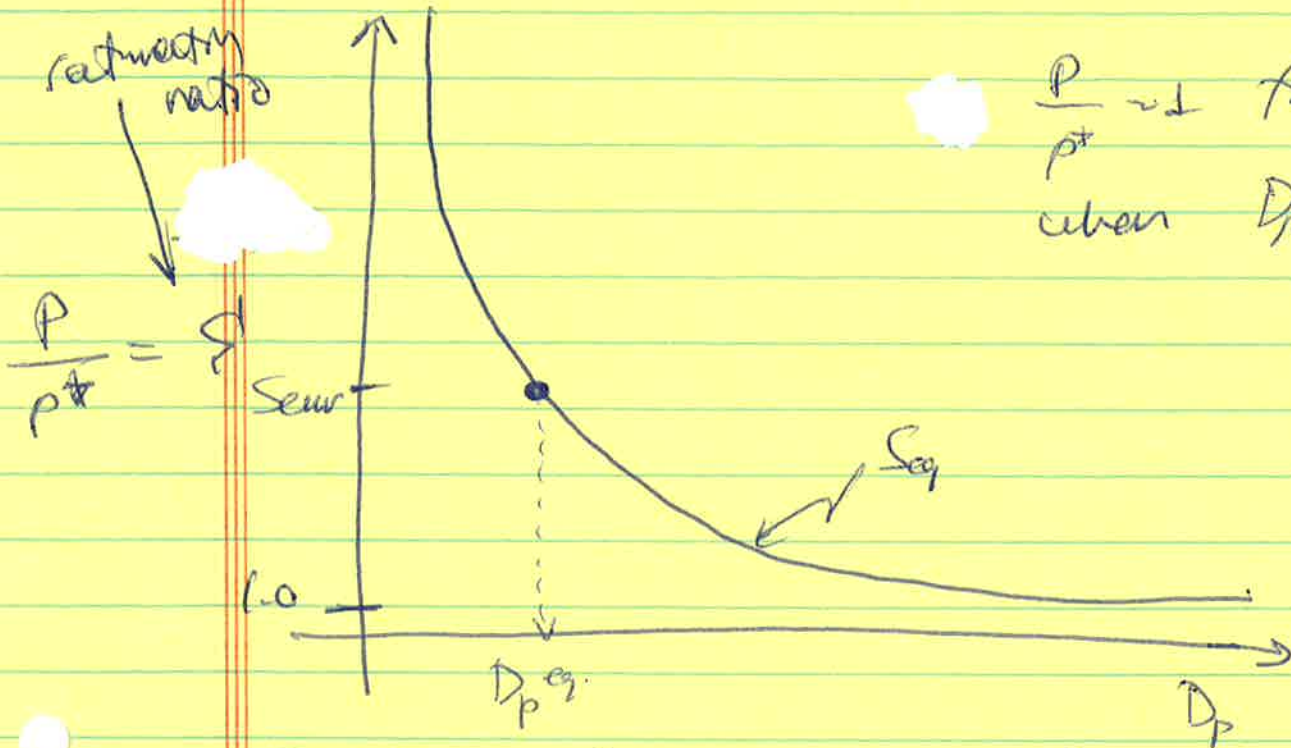


Kelvin equation says that $P \uparrow$ when $R_p \downarrow$. Why does that happen physically?



$R_p \downarrow$, lay-range interactions \downarrow , $F_{act} \uparrow$
vapor pressure \uparrow

Implication of The Kelvin Equation



$\frac{P}{P^*} \sim 1$ for water
when $D_p \sim 0.15 \mu m$

Stability of a drop with respect to its environment

→ Take drop in equilibrium with its environment.

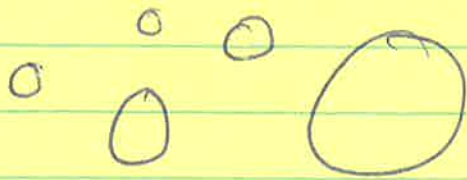
$$\frac{dm}{dt} = h_m (S_{ew} - S_{eq})$$

stability analysis.

→ Pure water droplets are always unstable!

(6)

Take a population of water droplets



generated by, say, an atomizer.

- Is this droplet population in equilibrium ever?
- what will happen?
- Is this in agreement with A & B in physical systems?
- Phenomenon called Ostwald Ripening
(known since the 1800's).

(7)

Curvature solute effects - Köhler Eqn

→ Pure water droplets don't exist in the atmosphere, unless they are very large.

→ This created a lot of controversy in the 1960's and 1970's about how droplets are generated - sea spray?

- how about hygroscopic nuclei?

→ Köhler figured it out, with the observation of Aitken that there are a lot of carbonaceous nuclei (pre-existing particles). Thus, known as Köhler Theory.

→ Assume we have a crystalline particle of known dry size, d . The particle is completely deliquescent, i.e. it changes into an aqueous solution at some characteristic size $fL < d$ (i.e. $f < 1$).

When that happens, the particle is an aqueous solution surrounded by water vapor.

So, let's first assume particle is in equilibrium, neglecting curvature effects:

← partial pressure of H₂O in gas phase (ideal gas).

$$\textcircled{1} \quad \mu_{\text{H}_2\text{O}(g)}(T, P) = \mu_{\text{H}_2\text{O}(l)}(T, P) \quad \text{equality of chem. potential between liq + gas for H}_2\text{O}$$

we know that b/c of the solute, $\mu_{\text{H}_2\text{O}(l)}$ drops, being equal to:

← standard reference chemical potential at pressure P and temperature T

$$\textcircled{2} \quad \mu_{\text{H}_2\text{O}(l)} = \mu_{\text{H}_2\text{O}(pure), l}^* + RT \ln X_{\text{H}_2\text{O}}$$

we also know that when the gas is at an equilibrium P which is different from 1 atm, $\mu_{\text{H}_2\text{O}(g)}$ is given by:

← ideal, Standard ref. chem. potential at P=1atm and T

$$\textcircled{3} \quad \mu_{\text{H}_2\text{O}(g)}(P, T) = \mu_{\text{H}_2\text{O}(pure), g}^{\Delta}(T) + RT \ln y_{\text{H}_2\text{O}} P \quad \leftarrow \text{total pressure}$$

← not frac. of H₂O in gas phase

$$= \mu_{\text{H}_2\text{O}(pure), g}^{\Delta}(T) + RT \ln P \quad \leftarrow \text{partial pressure of H}_2\text{O}$$

Combining 1, 2, 3:

$$\mu_{\text{H}_2\text{O}(pure), l}^* + RT \ln X_{\text{H}_2\text{O}} = \mu_{\text{H}_2\text{O}(pure), g}^{\Delta}(T) + RT \ln P$$

$$\text{From which} \quad \frac{P}{X_{\text{H}_2\text{O}}} = \exp \left\{ \frac{\mu_{\text{H}_2\text{O}(pure), g}^{\Delta}(T) - \mu_{\text{H}_2\text{O}(pure), l}^*}{RT} \right\} \quad \textcircled{4}$$

That means $\exp\left\{\frac{\mu^s(r) - \mu^l(r)}{RT}\right\} = P_{\text{flat}}$, so:

$P = \gamma_w \times w \times P^{\text{sat}}$ (5) Raoult's Law

i.e. Raoult's Law is a natural consequence of chemical equilibrium!

If you consider curvature effects.

P is actually affected by the diameter

$P = P_{\text{flat}} \exp\left(\frac{2\sigma_w}{RT \cdot r}\right)$
Curved

$P = \gamma_w \times w \times P^{\text{flat}} \exp\left(\frac{2\sigma_w}{RT \cdot r}\right) \Rightarrow$

$\frac{P}{P^{\text{sat}}} = \gamma_w \times w \times \exp\left(\frac{2\sigma_w}{RT \cdot r}\right)$

Most general form of Köhler equation

Simplifications to Köhler equation.

$$\frac{p}{p_{sat}} = \mathcal{F} = \gamma_w \times w \exp\left(\frac{2\sigma_w v}{RT R_p}\right) \quad (6)$$

Two is of the droplet, i.e. the molar volume of solute-water solution

simplification of K. term:

- $v \approx v_l$ ← "dilute approximation", i.e. most of the solution is H₂O
- $\sigma \approx \sigma_w$ ← surface tension of water. Very good approximation for salts, may not be as good for organics
- $R_p > 0.1 \mu\text{m} \Rightarrow$ Kelvin effect is "small", which means $\exp(-) = \mathcal{O}(1)$, i.e. of order unity
The argument in exponential is small

hence $\exp\left(\frac{2\sigma v}{RT R_p}\right) \approx 1 + \frac{2\sigma v}{RT R_p} \approx$

↑
Taylor expansion.

$$\approx 1 + \frac{2\sigma_w v_w}{RT R_p}$$

Expanding at v_w and expressing R_p as $D_p = 2R_p$

$$\exp\left(\frac{2\sigma v}{RT R_p}\right) \approx 1 + \frac{4\sigma_w M_w}{RT \rho_w D_p} \quad (7)$$

Simplifications to the Raoult (solute term)

$$f_w \times w$$

- $f_w \approx 1$ ← b/c of dilute approximation, most of solution is water, hence behaves ideally.

$$x_w = 1 - x_s \leftarrow \text{mol fraction of "salt" ions in solution} \leftarrow \text{(from } x_w + x_s = 1)$$

$$= 1 - \frac{n_s}{n_s + n_w} \leftarrow \text{number of moles of ions in particle (after dissociation)}$$

- if $n_s \ll n_w$ (dilute approximation) $\Rightarrow n_s + n_w \approx n_w$

$$x_w \approx 1 - \frac{n_s}{n_w}$$

but $n_s = \frac{\left(\frac{\pi}{6} d^3\right) \rho_s \leftarrow \text{volume of salt in particle} \leftarrow \text{van't Hoff factor}}{M_s \leftarrow \text{molar volume of salt}}$

$$= \frac{\pi}{6} \frac{d^3 \rho_s v_s}{M_s}$$

and $n_w = \frac{V_{\text{droplet}} - V_{\text{dry particle}}}{V_w} \approx \frac{\pi}{6} D_p^3 \frac{\rho_w}{M_w}$ negligible if $\leftarrow \text{dry particle is very small}$

$$\text{So } x_w \approx 1 - \frac{\rho_s}{\rho_w} \frac{M_w}{M_s} \frac{d^3 v_s}{D_p^3} \quad \textcircled{8}$$

Substituting (6), (7) into equation (6), we get

(11)

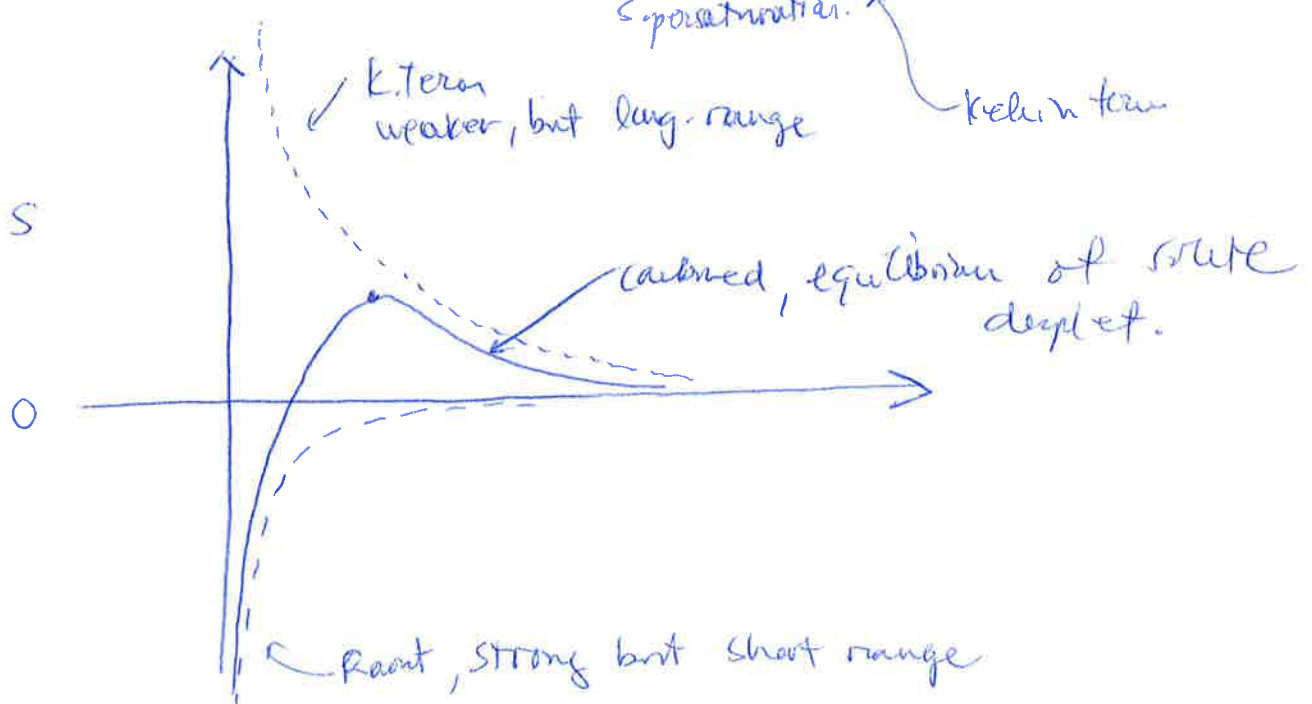
$$S^+ = \left(1 - \underbrace{\frac{\rho_s}{\rho_w} \frac{M_w}{M_s} \frac{d^3 V_s}{D_p^3}}_B \right) \left(1 + \underbrace{\frac{4\alpha_w M_w}{RT \rho_w D_p}}_A \right) =$$

$$= \left(1 - \frac{B}{D_p^3} \right) \left(1 + \frac{A}{D_p} \right) = 1 + \frac{A}{D_p} - \frac{B}{D_p^3} - \frac{AB}{D_p^4} \Rightarrow$$

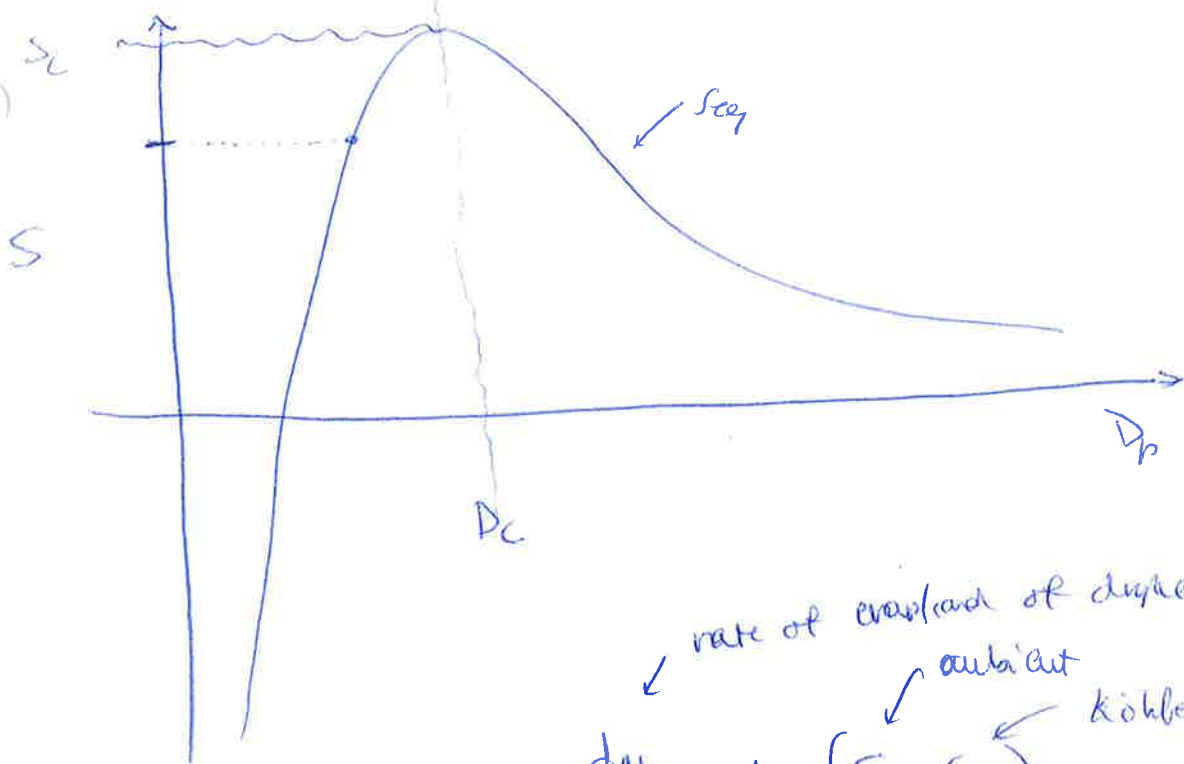
$\Rightarrow S^+ \approx 1 + \frac{A}{D_p} - \frac{B}{D_p^3}$ "classical" Köhler equation

assume very small compared to $\frac{B}{D_p^3}$

otherwise written as $S - 1 = s = \frac{A}{D_p} - \frac{B}{D_p^3}$ Raoult term



Stability analysis of droplet with solute



$$\frac{dD_p}{dt} = k_m (S - S_{eq})$$

← rate of evaporation of droplet ← rate of growth of droplet
 ← Köhler curve

• If you are to the left of D_c (i.e. $D_p < D_c$) then a slight fluctuation of S above S_{eq} will give a driving force that will eventually lead to an equilibrium (as long as you do not exceed S_c !)

• If you are to the right of D_c , you can either have unstable growth, or "shrink" to an equilibrium size with $S = S_{eq}$... There are unstable drops, or drops that are much smaller and are in eq. with their environment

So if $S > S_c \Rightarrow$ particle is unstable and forms a drop.

Hence S_c is a very important property and is called "critical supersaturation". D_c is called "critical wet diameter". (13)

Calculation of S_c : $\frac{\partial S_{eq}}{\partial D_p} = 0$

$$\frac{\partial}{\partial D_p} \left(\frac{A}{D_p} - \frac{B}{D_p^3} \right) = -\frac{A}{D_p^2} + \frac{3B}{D_p^4} = \frac{1}{D_p^2} \left[\frac{3B}{D_p^2} - A \right]$$

$$\text{So } \frac{\partial S_{eq}}{\partial D_p} = 0 \Rightarrow$$

$$\frac{3B}{D_p^2} - A = 0 \Rightarrow D_p = \left(\frac{3B}{A} \right)^{1/2} = D_c$$

↑ wet diameter at maximum, i.e. it's D_c .

$$S_c = \frac{A}{D_c} - \frac{B}{D_c^3} = \frac{A}{\left(\frac{3B}{A} \right)^{1/2}} - \frac{B}{\left(\frac{3B}{A} \right)^{3/2}} = \left(\frac{A}{3B} \right)^{1/2} \left[A - \frac{A}{3} B \right]$$

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

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

S_0 to summarize:

(14)

• if ambient $S > S_c$, particle becomes unstable and grows without stopping.

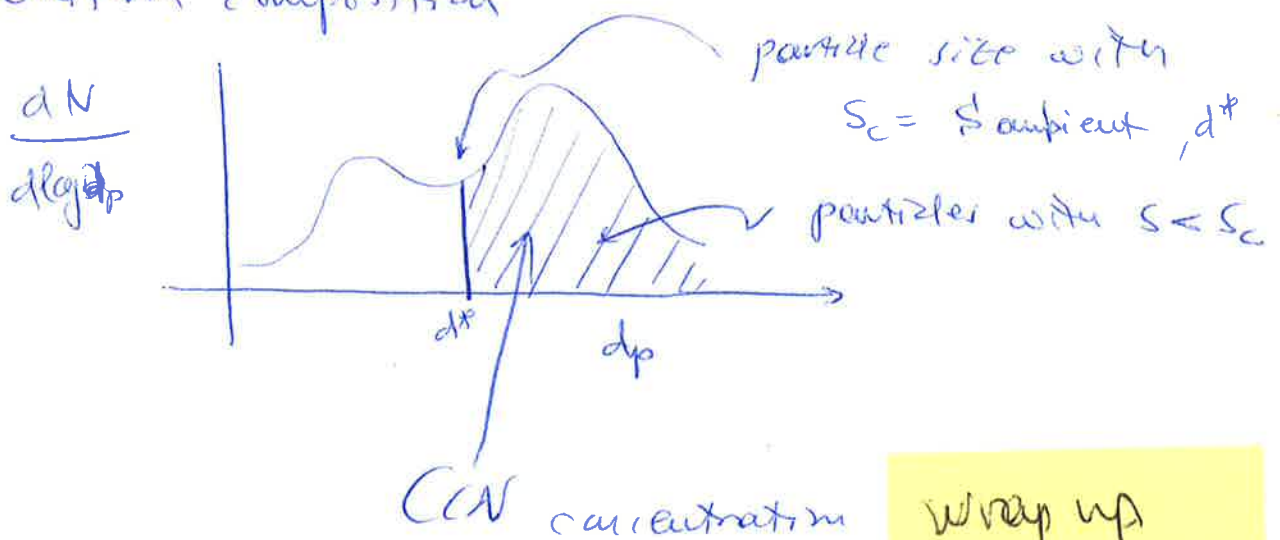
• if ambient $S < S_c$, particles shrink and attain equilibrium with $S \Rightarrow$ interstitial

\rightarrow hence, if we know S and particle composition + size distribution, we can calculate the number of droplets that would form (assuming

we allow particles enough time exposed to S .

\rightarrow This is how we calculate CCN concentration.

(a) Simplest possible case: particles are of uniform composition

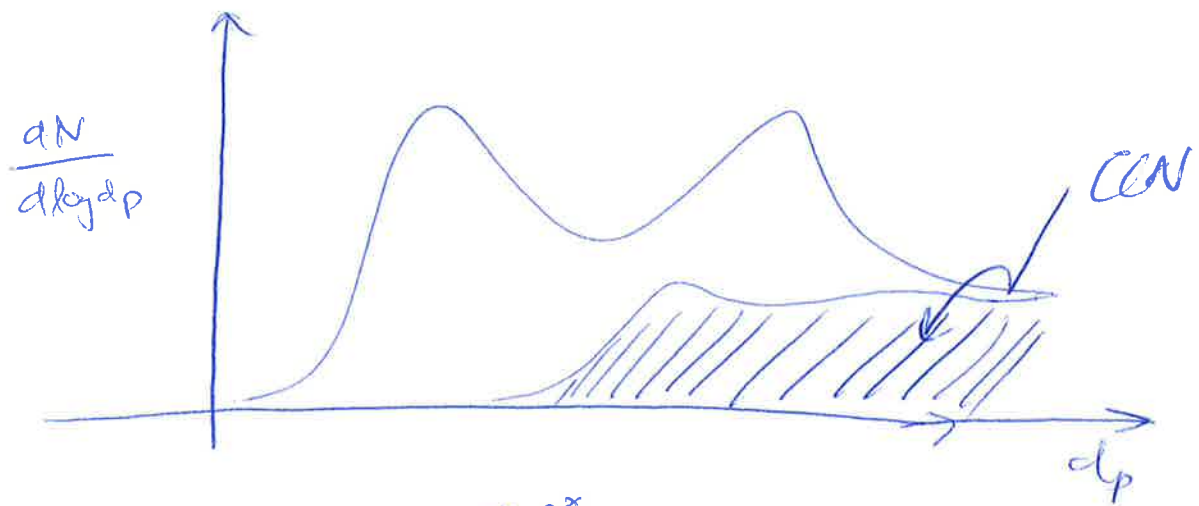


wrap up presentation

$$[CCN] = \int_{d_p^*}^{\infty} \left(\frac{dN}{d \log d_p} \right) d \log d_p$$

~ particles are not uniform composition
 or particles are "externally mixed"

(15)



$$[CCN] = \int_0^{\infty} \underbrace{f_s(d_p, S)}_{\uparrow} \left(\frac{dN}{d \log d_p} \right) d D_p$$

fraction of activation of
 particles of diameter d_p @ supersaturation S .

Characterizing CCN distributions in the atmosphere

Empirically, CCN distribution functions (also called "CCN Spectra") have been assumed to follow empirical (prescribed) functions, much like the aerosol distribution. In fact, much of the same distributions of aerosol are assumed to apply for CCN spectra.

This is because $\frac{dN}{d \log d_p}$ can be expressed, via Köhler Theory, into a differential CCN spectrum:

$$\frac{dN}{dlogD}$$

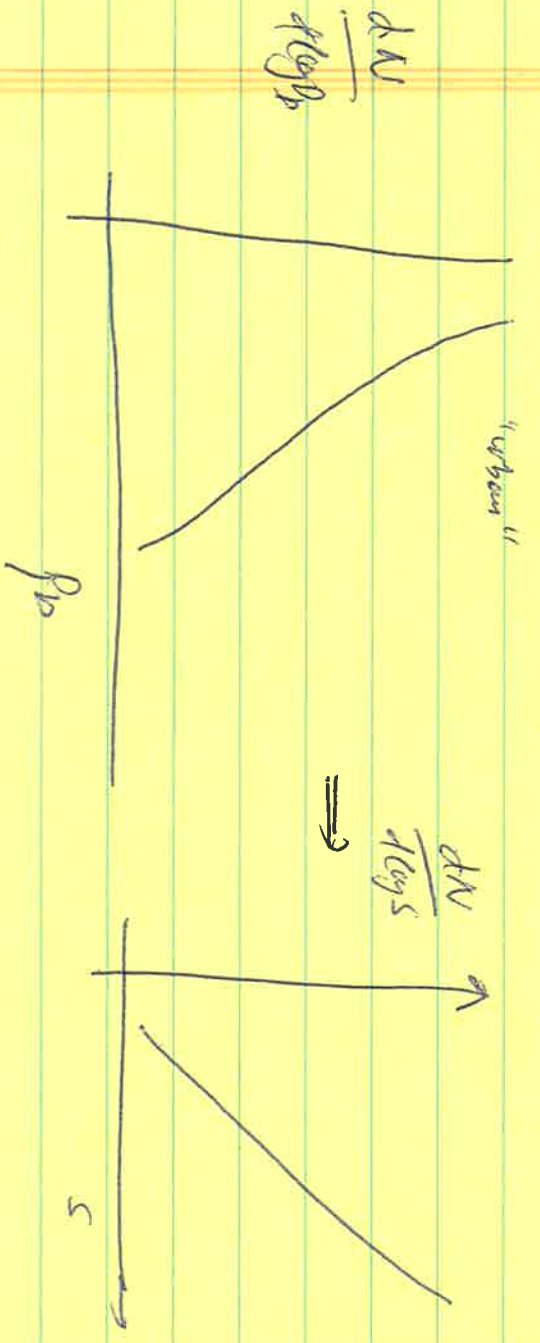
$$S = w d^{-3/2} \Rightarrow \log S = -\frac{3}{2} w \log D$$

reverse (shift) order of axes
"-1" means given

$$\left. \begin{matrix} \Rightarrow \\ \end{matrix} \right\} \frac{dN}{dlogD} = -\frac{2}{3} w \frac{dN}{dlogS}$$

depends on geometry

So for example a distribution for
ocean and can spectra might look like



Main functional forms used:

→ Power law (also known as "Turey Spectrum")
[CAN] = C S^k C, k are empirical constants.

By convention C corresponds to concentration of
can @ 1% speedurbation (Typically arrived on
upper part in clouds) and k depends on
the slope of the distribution and compression.

Some characteristic values:

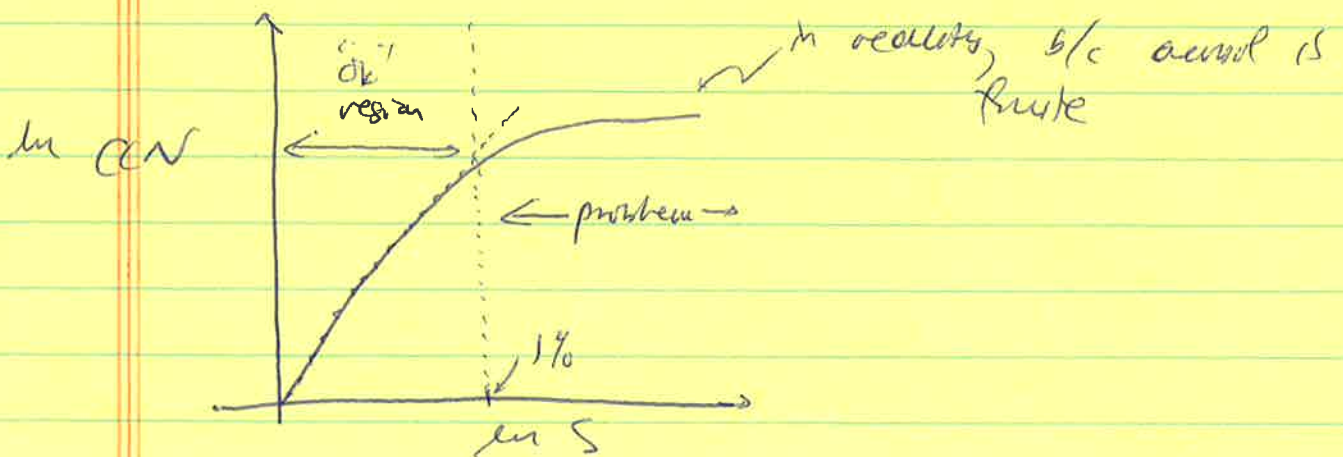
Aircraft type	c	k	"coloured name"
Maine	310	0.3	"coloured name"
	125	0.3	Australia
	100	0.5	Atlantic ocean
Continental	2000	0.4	Australia
	3500	0.9	NE US

k varies between 0.3 - 1.0 and of course
 c varies between 50 - 10000

→ Power law very simple to use, but has some disadvantages

a) unbounded; as $s \rightarrow \infty$, $cN \rightarrow 0$. We know that is not true! (why?)

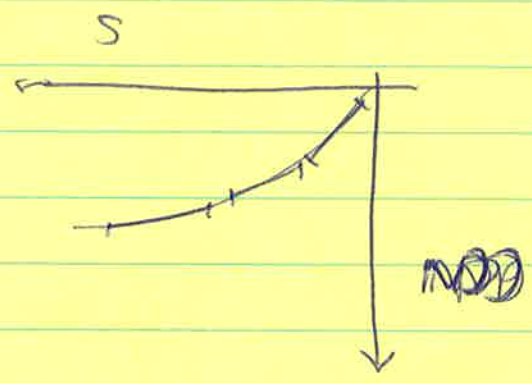
b) k is a condensation of size distribution and composition. Not always can you capture shape of spectrum with a single parameter



Q is total average concentration
 k_1, k_2 are fitting coefficients

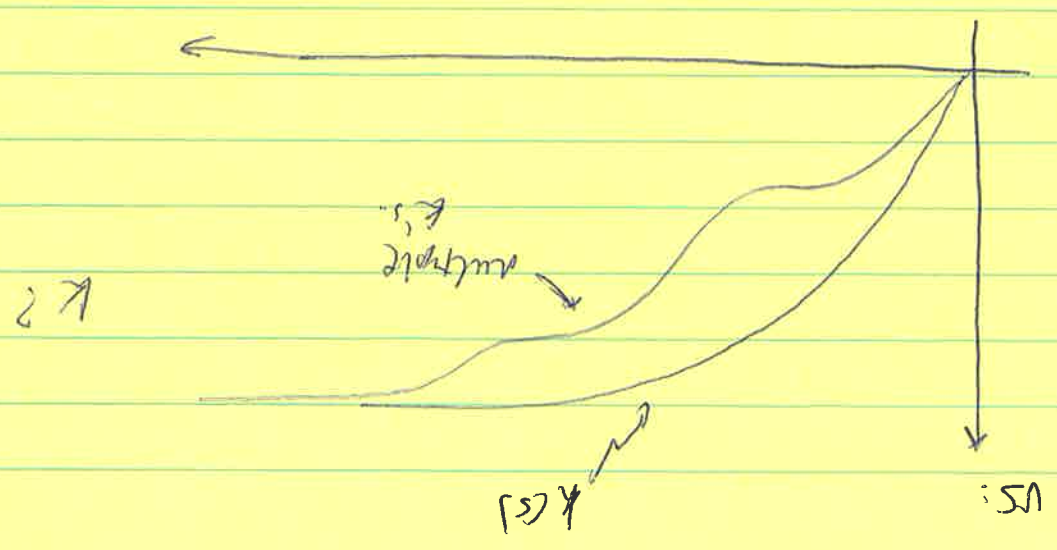
$$C(x,t) = \frac{Q k_1 S^{k_1}}{(1 + k_1 x^2)^{k_1}}$$

— modified power law
 (Ceballos et al, 1998, 2000)



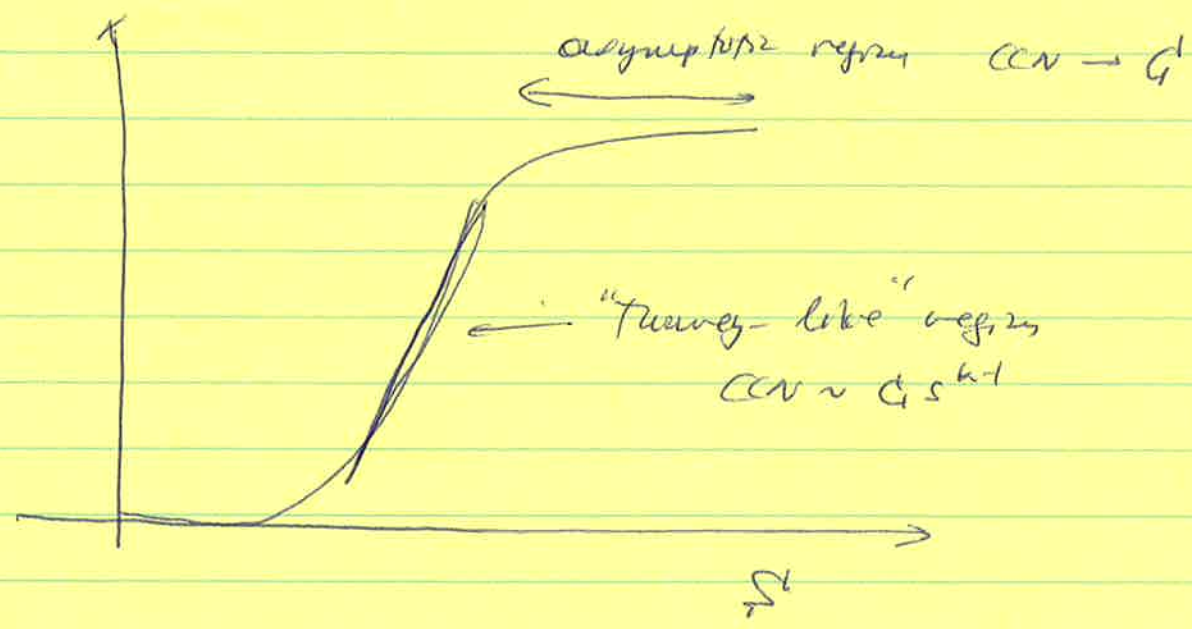
regions of k_1 and k_2

Over the years, other can graphs have been proposed
 — piecewise power law (analogy of "binned" sensor distribution). Used in some cloud models



The characteristics of this function is that:

- a) it is continuous
- b) it is realistic
- c) it is related to "older" power law forms
- d) Khvorostyanov and Ony (2008) showed that η, a, k can be related to lognormal distribution of aerosol



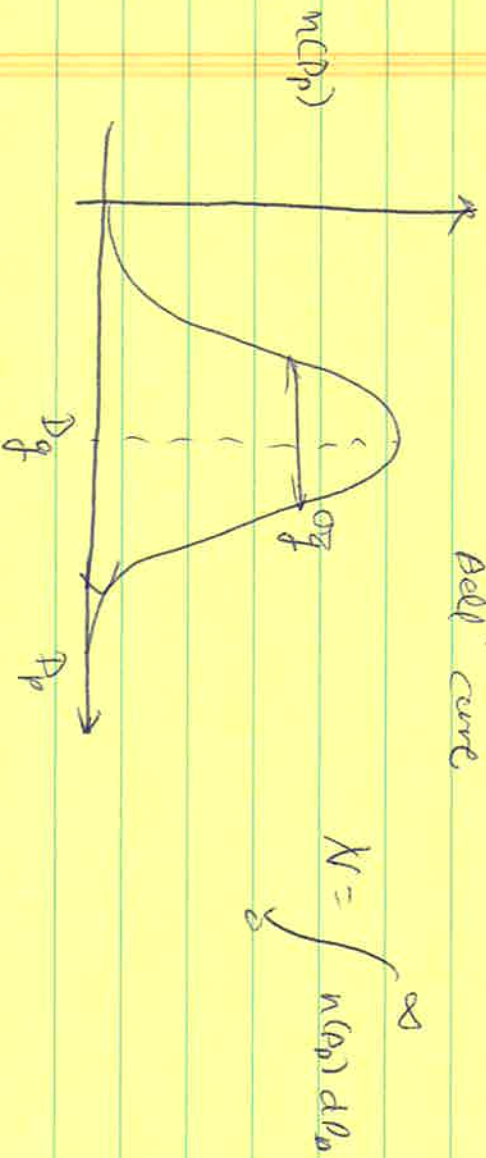
- Error function, erf()

it is complicated, but directly related to a lognormal aerosol size distribution, which is widely used in aerosol science.

Start off with lognormal aerosol distribution

$$\frac{dN}{d\log D_p} := n(D_p) = \frac{N}{\sqrt{2\pi} \ln \sigma_g} \exp \left\{ - \frac{\ln^2(D_p/D_{pg})}{2 \ln^2 \sigma_g} \right\}$$

where σ_g, D_g is the geometrical standard deviation and mean diameter of the mode and N is the total number concentration of aerosol "Bell" curve



The number of particles between a and D_p diameter is then easily calculated as:

$$N(a, D_p) = \int_a^{D_p} \frac{N}{\sqrt{2\pi} D_g \sigma_g} \exp \left\{ -\frac{\ln^2 (D_p/D_g)}{2 \ln^2 \sigma_g} \right\} dD_p =$$

$$= \frac{N}{2} \left\{ 1 + \operatorname{erf} \left(\frac{\ln(D_p/D_g)}{\sqrt{2} \ln \sigma_g} \right) \right\}$$

where erf is the 'error function', given

by:

$$\operatorname{erf} z = \frac{2}{\sqrt{\pi}} \int_0^z e^{-u^2} du$$

note: to evaluate integral, you do the 'trick'

define $\eta = \frac{\ln(D_p/D_{pg})}{\sqrt{2} \ln \sigma_g}$ so that

$$\int_0^{D_p^*} \frac{N}{\sqrt{2\pi} \ln \sigma_g} \exp\left\{-\frac{\ln^2(D_p/D_{pg})}{2 \ln^2 \sigma_g}\right\} dD_p =$$

$$= \frac{N}{\sqrt{\pi}} \int_{-\infty}^{\eta^*} e^{-\eta^2} d\eta = \frac{N}{\sqrt{\pi}} \left\{ \int_{-\infty}^0 e^{-\eta^2} d\eta + \int_0^{\eta^*} e^{-\eta^2} d\eta \right\} =$$

$$= \frac{N}{\sqrt{\pi}} \left\{ \frac{\sqrt{\pi}}{2} + \frac{\sqrt{\pi}}{2} \operatorname{erf}\{\eta^*\} \right\}$$

$$= \frac{N}{2} \left\{ 1 + \operatorname{erf}\eta^* \right\}$$

(from Sempf + Penold, 1998 edition)
chapter 7

so now, to transform the size distribution into a CCN spectrum, we use the chain rule:

$$\frac{dN}{ds} = \frac{dN}{d \ln D_p} \cdot \frac{d \ln D_p}{ds}$$

since $S = \frac{w}{c} D_p^{-3/2} \Rightarrow \frac{d \ln D_p}{ds} = -\frac{2}{3S}$

we can show that this is $= \frac{2}{\sqrt{B}} \left(\frac{A}{3}\right)^{3/2} \Rightarrow$

according to classical Köhler theory.

and $\frac{D_p}{D_g} = \left(\frac{S_g}{S}\right)^{2/3}$, where $S_g \Rightarrow$

The critical supersaturation of a particle with $D_p = D_g$

$$\Rightarrow \frac{dN}{ds} = n_s(s) = \frac{2}{3} \frac{N}{S \sqrt{2\pi} \ln \sigma} \exp \left\{ \frac{\ln^2 \left(\frac{S_g}{S} \right)^{2/3}}{2 \ln^2 \sigma_g} \right\}$$

so the CCN spectrum is also a lognormal distribution; integration of which gives:

$$CCN(s) = \int_s^{\infty} n_s(s) ds =$$

$$= \frac{N}{2} \left\{ 1 - \operatorname{erf} \left(\frac{2 \ln \left(\frac{S_g}{s} \right)}{3 \sqrt{2} \ln \sigma_g} \right) \right\}$$