

## MODULE 3: Atmospheric Aerosols

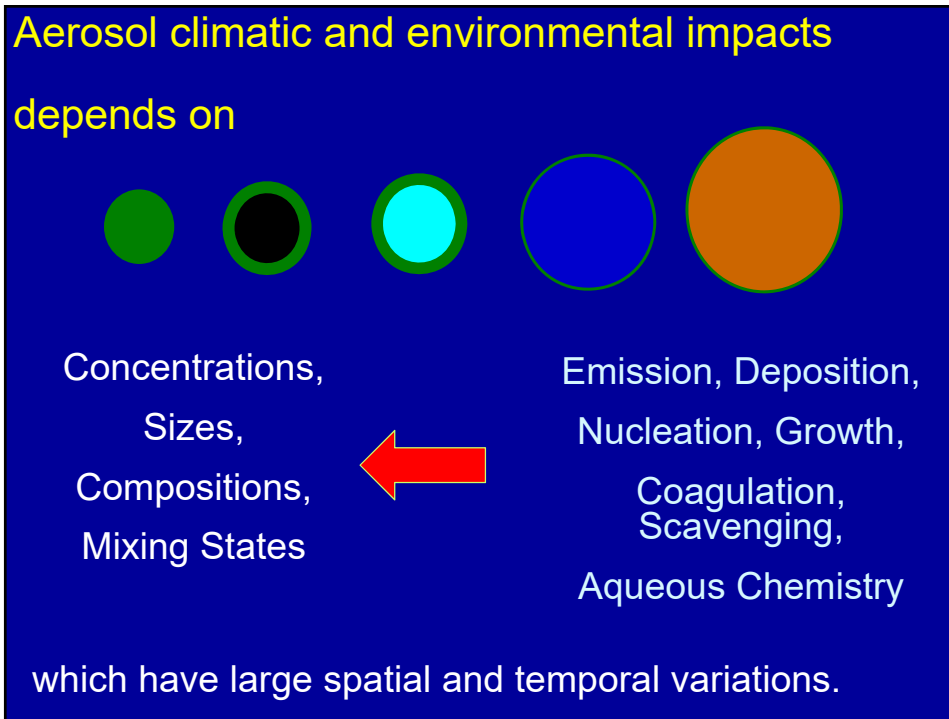
### Lecture 2:

1. Aerosol Characterization: Hands-on Exercise of Particle Size Distributions
2. Particle Microphysics Overview and Thermodynamics

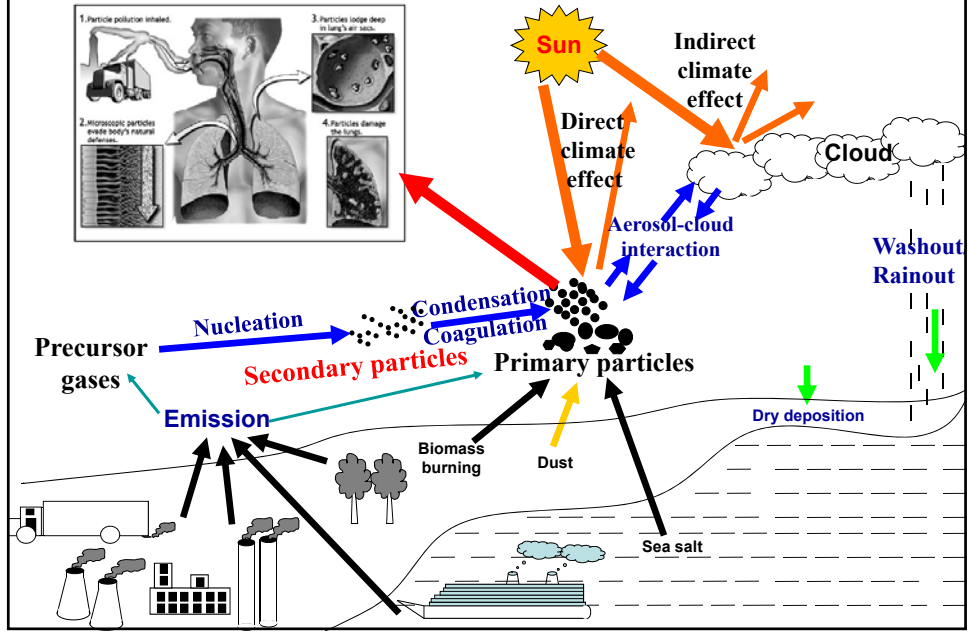
### Aerosol Characterization: Hands-on Exercise of Particle Size Distributions

Bin #	Size (diameter, Dp) Interval	Dp	dDp	dlogDp	# of particles in Interval	dNi/dDp	dNi/dlogDp	Si	dSi/dDp	dSi/dlogDp	Mi	dMi/dlogDp
i	µm	µm	µm	unitless	# cm <sup>-3</sup>	cm <sup>-3</sup> µm <sup>-1</sup>	# cm <sup>-3</sup>	µm <sup>2</sup> cm <sup>-3</sup>	µm <sup>2</sup> cm <sup>-3</sup>	µm <sup>2</sup> cm <sup>-3</sup>	µg m <sup>-3</sup>	µg m <sup>-3</sup>
1	0.010	0.020	0.015	0.010	0.301	2.00E+03						
2	0.020	0.040	0.030	0.020	0.301	3.00E+03						
3	0.040	0.070	0.055	0.030	0.243	1.20E+03						
4	0.070	0.100	0.085	0.030	0.155	1.00E+02						
5	0.100	0.200	0.150	0.100	0.301	5.00E+02						
6	0.200	0.400	0.300	0.200	0.301	1.20E+02						
7	0.400	0.700	0.550	0.300	0.243	2.00E+01						
8	0.700	1.000	0.850	0.300	0.155	1.00E+01						
9	1.000	2.500	1.750	1.500	0.398	2.50E+00						
10	2.500	7.000	4.750	4.500	0.447	3.00E-01						
11	7.000	10.000	8.500	3.000	0.155	5.00E-02						
12	10.000	15.000	12.500	5.000	0.176	1.00E-02						
16	Total											
18	Particle Density	1.500	Number Concentrations (# cm <sup>-3</sup> )				Mass Concentrations (µg m <sup>-3</sup> )					
19			CN10								PM10	
20			CN40			~ CCN0.8					PM2.5	
21			CN70			~ CCN0.4					PM1.0	
22			CN100			~ CCN0.2					PM0.1	
23			CN400									
24			CN1000									
28	PM##: Mass concentration of particles with diameter < ## µm											
29	CN##: Number concentration of particles (or condensation nuclei) with diameter > ## nm											
30	CCN##: Number concentration of cloud condensation nuclei with water supersaturation ratio = ##%											

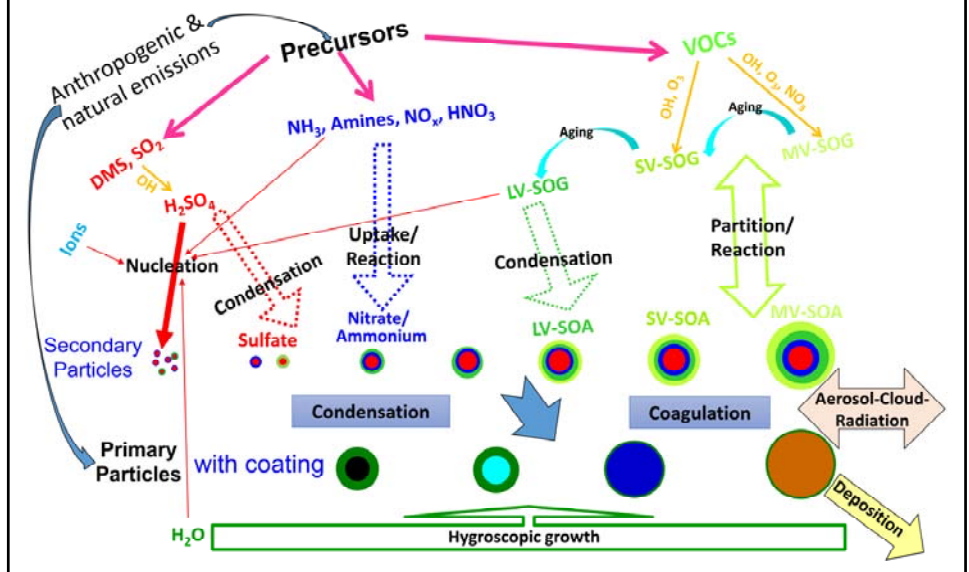
## Particle Microphysics Overview and Thermodynamics



## Physical processes controlling aerosol properties

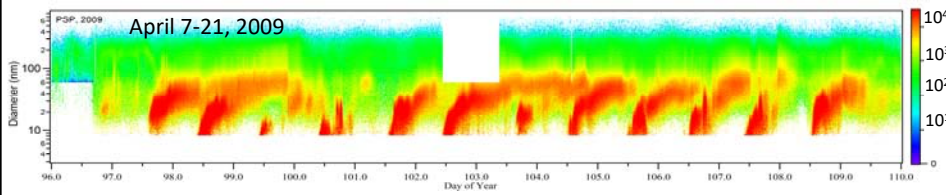


## Primary vs secondary particles



**Primary particles:** Generally dominate particle **mass** concentration  
**Secondary particles:** Generally dominate particle **number** concentration

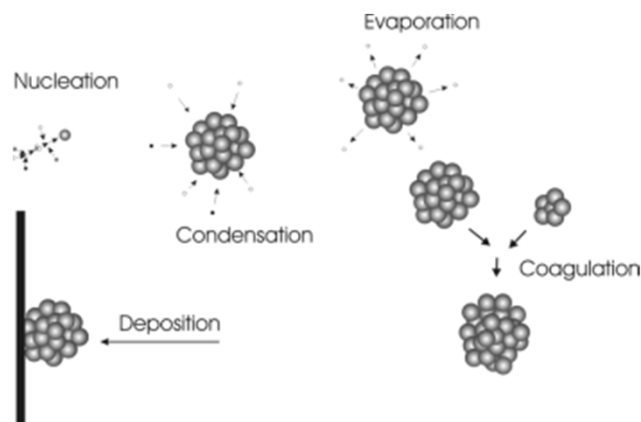
# Evolution of particle size distribution in the atmosphere



Data from James Schwab

Secondary particles dominate particle number concentrations in most part of the troposphere

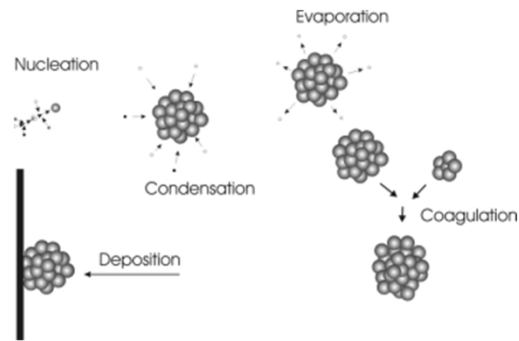
## Key Aerosol Microphysical Processes



Several important physical concepts:

- (1) Particles are suspended in gaseous medium and interact with gas molecules;
- (2) Particles are constantly moving due to Brownian motion and other forces;
- (3) A difference in chemical potential causes mass transfer from one phase to another.

## Key Aerosol Microphysical Processes



**Effect on different microphysical processes on particle number and mass concentrations: Increase, Decrease, or No Change**

	Nucleation	Condensation	Evaporation	Coagulation	Deposition
Particle Number	??	??	??	??	??
Particle Mass	??	??	??	??	??

## Thermodynamics of Aerosols

Gibbs free energy:

$$G = H - TS = U + PV - TS$$

$H$  is the enthalpy,  $S$  is the entropy, and  $T$  is the absolute temperature,  $U$  is the internal energy,  $P$  is the pressure, and  $V$  is the volume.

Gibbs free energy of a system containing  $k$  chemical compounds can be calculated by summation of the products of the chemical potentials and the number of moles of each species

$$G = \mu_1 n_1 + \mu_2 n_2 + \dots + \mu_k n_k$$

Chemical potential:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_j} \quad n_j \text{ the number of moles of system species}$$

The chemical potential has an important function in the system's thermodynamic behavior analogous to pressure or temperature.

A difference in chemical potential can be viewed as the cause for chemical reaction or for mass transfer from one phase to another.

### Conditions for Chemical Equilibrium



$\nu_i$  is the corresponding stoichiometric coefficient (positive for reactants, negative for products)

## Chemical Potentials of Ideal Gases and Ideal Gas Mixtures

### *The Single Ideal Gas*

$$\mu(T, p) = \mu^\circ(T, 1 \text{ atm}) + RT \ln p$$

where  $\mu^\circ$  is the standard chemical potential defined at a pressure of 1 atm and therefore is a function of temperature only.  $R$  is the ideal gas constant. Pressure  $p$  actually stands for the ratio ( $p/1 \text{ atm}$ ) and is dimensionless. This definition suggests that the chemical potential of an ideal gas at constant temperature increases logarithmically with its pressure.

### *The Ideal Gas Mixture*

$$\mu_i = \mu_i^\circ(T) + RT \ln p_i$$

the partial pressure of compound  $i$      $p_i = y_i p$

$y_i$  is the gas mole fraction of compound  $i$ .

## Chemical Potentials of Solutions

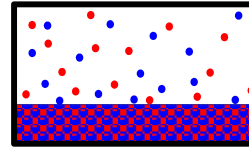
**Ideal Solutions** A solution is defined as ideal if the chemical potential of *every* component is a linear function of the logarithm of its aqueous mole fraction  $x_i$ , according to the relation

$$\mu_i = \mu_i^*(T, p) + RT \ln x_i$$

The standard chemical potential  $\mu_i^*$  is the chemical potential of pure species  $i$  ( $x_i = 1$ ) at the same temperature and pressure as the solution under discussion. Note that in general  $\mu_i^*$  is a function of both  $T$  and  $p$  but does not depend on the chemical composition of the solution.

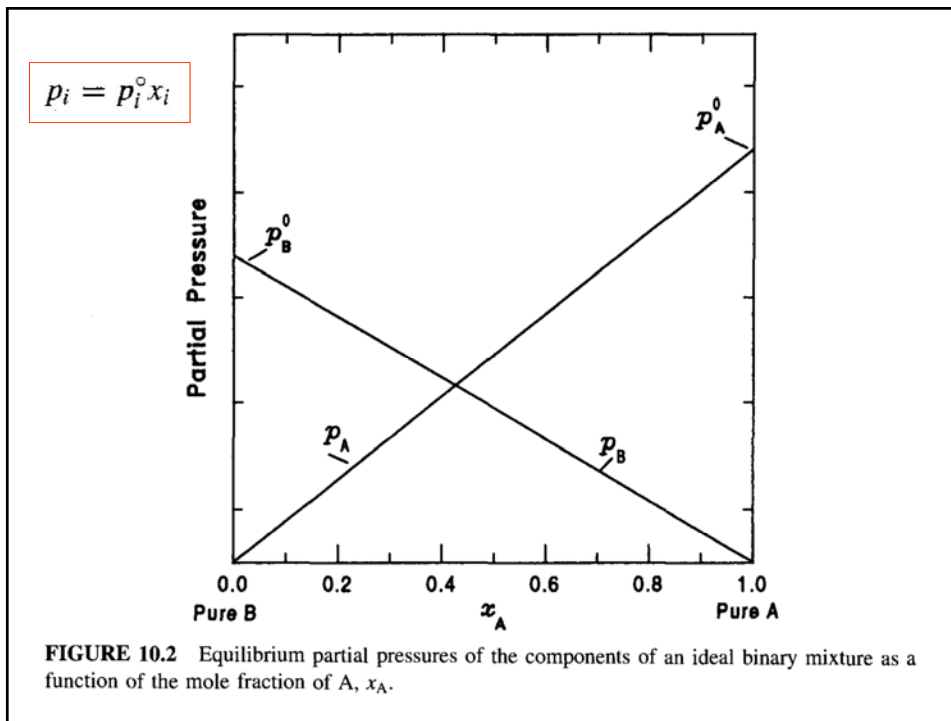


$$\mu_i(g) = \mu_i(aq) \quad p_i = \exp\left(\frac{\mu_i^* - \mu_i^\circ}{RT}\right) x_i = K_i(T, p) x_i$$



The standard chemical potentials  $\mu_i^*$  and  $\mu_i^\circ$  are functions only of temperature and pressure, and therefore the constant  $K_i$  is independent of the solution's composition.

$$p_i = p_i^\circ x_i$$



**Non ideal Solutions** Atmospheric aerosols are usually concentrated aqueous solutions that deviate significantly from ideality. This deviation from ideality is usually described by introducing the activity coefficient,  $\gamma_i$ , and the chemical potential is given by

$$\mu_i = \mu_i^*(T, p) + RT \ln(\gamma_i x_i)$$

Activity  $\alpha_i = \gamma_i x_i$

$$\mu_i = \mu_i^*(T, p) + RT \ln \alpha_i$$

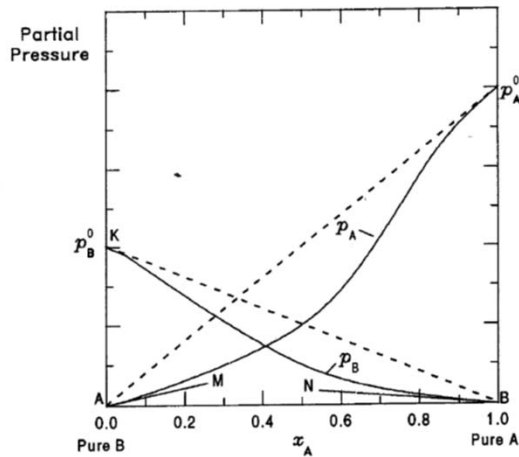
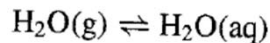


FIGURE 9.3 Equilibrium partial pressures of the components of a nonideal mixture of A and B. Dashed lines correspond to ideal behavior.

### Chemical Potential of Water in Atmospheric Particles



$$\mu_{\text{H}_2\text{O}(\text{g})} = \mu_{\text{H}_2\text{O}(\text{aq})}$$

or

$$\mu_{\text{H}_2\text{O}}^\circ + RT \ln p_w = \mu_{\text{H}_2\text{O}}^* + RT \ln \alpha_w \quad (9.61)$$

where  $p_w$  is the water vapor pressure (in atm) and  $\alpha_w$  is the water activity in solution. For pure water in equilibrium with its vapor,  $\alpha_w = 1$  and  $p_w = p_w^\circ$  (the saturation vapor pressure of water at this temperature); therefore

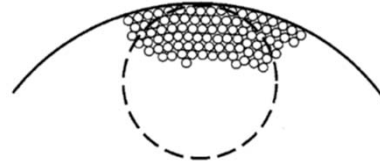
$$\mu_{\text{H}_2\text{O}}^* - \mu_{\text{H}_2\text{O}}^\circ = RT \ln p_w^\circ \quad (9.62)$$

Using (9.62) in (9.61) yields

$$\alpha_w = \frac{p_w}{p_w^\circ} = \frac{\text{RH}}{100}$$



**Gibbs free energy change for the formation of a single droplet of pure A of radius  $R_p$  containing  $n$  molecules**



$$\Delta G = G_{\text{droplet}} - G_{\text{pure vapor}}$$

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

$$\Delta G = n(g_l - g_v) + 4\pi R_p^2 \sigma$$

$$g = \left(\frac{\partial G}{\partial n}\right)_{T,P} \text{ is the chemical potential}$$

$$\Delta G = \frac{4\pi R_p^3}{3v_l} (g_l - g_v) + 4\pi \sigma R_p^2$$

Energy of converting vapor molecules to bulk liquid molecules

Energy required to maintain a liquid-gas surface boundary

$$g_l - g_v = -kT \ln \frac{p_A}{p_A^\circ}$$

$$\Delta G = -\frac{4}{3}\pi R_p^3 \frac{kT}{v_l} \ln S + 4\pi R_p^2 \sigma$$

$S$  = ratio of eq. vapor pressure around a droplet ( $p_A$ ) relative to above a flat surface ( $p_A^\circ$ )

$$R_p^* = \frac{2\sigma v_l}{kT \ln S}$$

For a droplet to exist,  $S > 1$ .  
 $p^{\text{curved}} > p^{\text{flat}}$  always

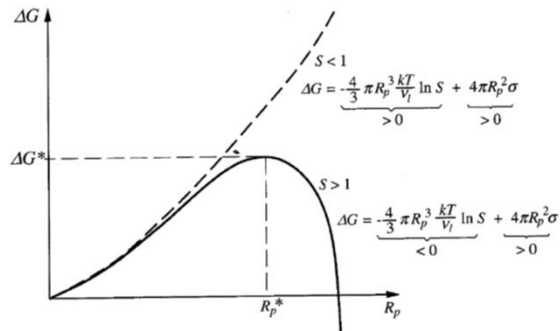


FIGURE 9.10 Gibbs free energy change for formation of a droplet of radius  $R_p$  from a vapor with saturation ratio  $S$ .

**Kelvin Equation**

How does  $S$  vary with  $R_p$ ?

$$p_A = p_A^\circ \exp\left(\frac{2\sigma v_l}{kTR_p}\right)$$

$$p_A = p_A^\circ \exp\left(\frac{2\sigma M}{RT\rho_l R_p}\right)$$

## Kelvin Effect

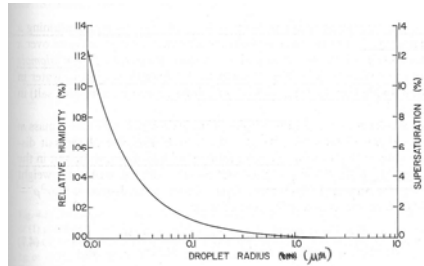


Fig. 4.11 The relative humidity and supersaturation (both with respect to a plane surface of liquid water) with which pure water droplets are in (unstable) equilibrium at 5°C.

- $R_p = 0.01 \mu\text{m}$  requires RH of 112.5%
- $R_p = 0.1 \mu\text{m}$  requires RH of 100.12%

### Questions:

- What are the typical sizes of cloud droplets?
- What are the typical size of particles that can be activated as cloud droplets?

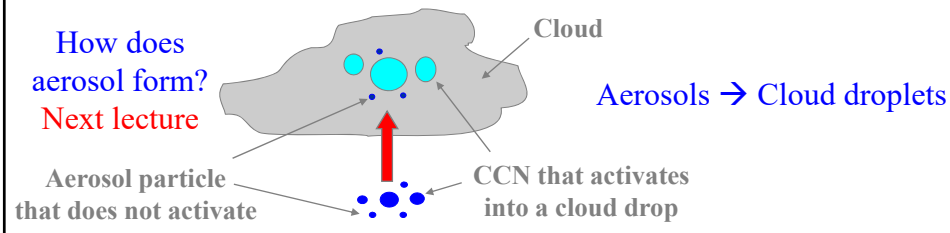
$p_A = p_A^0 \exp\left(\frac{2\sigma v_l}{kTR_p}\right)$

For pure water droplets/particles

T (K)	sigma (dyn/cm <sup>2</sup> )	Particle Radius in cm (Rp, cm)	Particle Diameter in um (Dp, um)	Water saturation ratio (S)	RH(%)	Water super-saturation ratio (SS, %)
278	76	5.00E-07	1.00E-02	1.2672	126.72	26.72
		9.00E-07	1.80E-02	1.1405	114.06	14.06
		1.62E-06	3.24E-02	1.0759	107.59	7.59
		2.92E-06	5.83E-02	1.0414	104.14	4.14
		5.25E-06	1.05E-01	1.0228	102.28	2.28
		9.45E-06	1.89E-01	1.0126	101.26	1.26
		1.70E-05	3.40E-01	1.0070	100.70	0.70
		3.06E-05	6.12E-01	1.0039	100.39	0.39
		5.51E-05	1.10E+00	1.0022	100.22	0.22
		9.92E-05	1.98E+00	1.0012	100.12	0.12
		1.79E-04	3.57E+00	1.0007	100.07	0.07
		3.21E-04	6.43E+00	1.0004	100.04	0.04
		5.78E-04	1.16E+01	1.0002	100.02	0.02
		1.04E-03	2.08E+01	1.0001	100.01	0.01
		1.87E-03	3.75E+01	1.0001	100.01	0.01

## Cloud droplet formation

- Supersaturations that develop in natural clouds due to the adiabatic ascent of air rarely exceed 1% (RH=101%)
- Consequently, droplets do not form in natural clouds by the homogeneous nucleation of pure water.
- Droplets can form and grow on aerosol at much lower supersaturations than are required for homogeneous nucleation.



## **Key knowledge points of Lecture 2:**

1. Number, surface area, and mass size distributions:

CN, CCN, PM

2. Major microphysical processes controlling particle

properties in the atmosphere

3. Key thermodynamics driving gas-particle interactions

4. Kelvin effect – importance of particle sizes