



# ΔΙΕΡΓΑΣΙΕΣ ΔΙΑΧΩΡΙΣΜΟΥ

## Μάθημα 7ο

Ακαδημαϊκό έτος 2017-2018

- The kinetics equation using the Gibbs-Thomson equation gives:

$$\ln \frac{c}{c_s^*} = \ln S = \frac{2\gamma v}{kTr}$$

$$-\Delta G_v = \frac{2\gamma}{r} = \frac{kT \ln S}{v}$$

$$\Delta G_{crit} = \frac{16\pi\gamma^3 v^2}{3(kT \ln S)^2}$$

# Crystallization from melts

$$\Delta G_v = \frac{\Delta H_f \Delta T}{T^*} \quad \text{Volume free energy}$$

where  $T^*$  is the solid–liquid equilibrium temperature expressed in kelvins,  $\Delta T = T^* - T$  is the supercooling and  $\Delta H_f$  is the latent heat of fusion. The radius of a critical nucleus is given by

$$r_c = \frac{2\gamma T^*}{\Delta H_f \Delta T}$$

and the rate of nucleation, from equation 5.9, may be expressed by

$$J = A \exp \left[ -\frac{16\pi\gamma^3}{3kT^* \Delta H_f^2 T_r (\Delta T_r)^2} \right]$$

where  $T_r$  is the reduced temperature defined by  $T_r = T/T^*$  and  $\Delta T_r = \Delta T/T^*$ , i.e.  $\Delta T_r = 1 - T_r$ . Equation 5.14, like equation 5.9, indicates the dominant effect of supercooling on the nucleation rate.

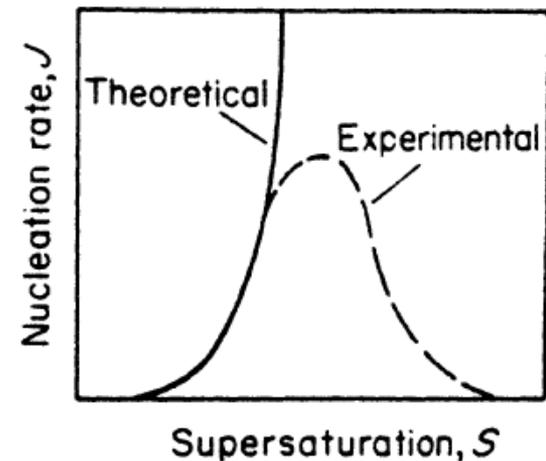
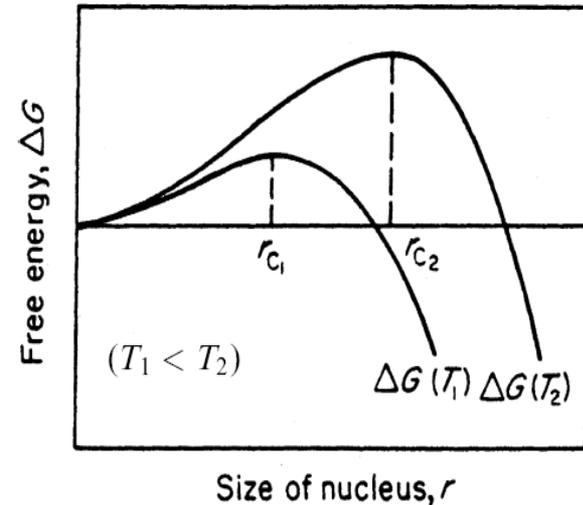
# Crystallization from melts

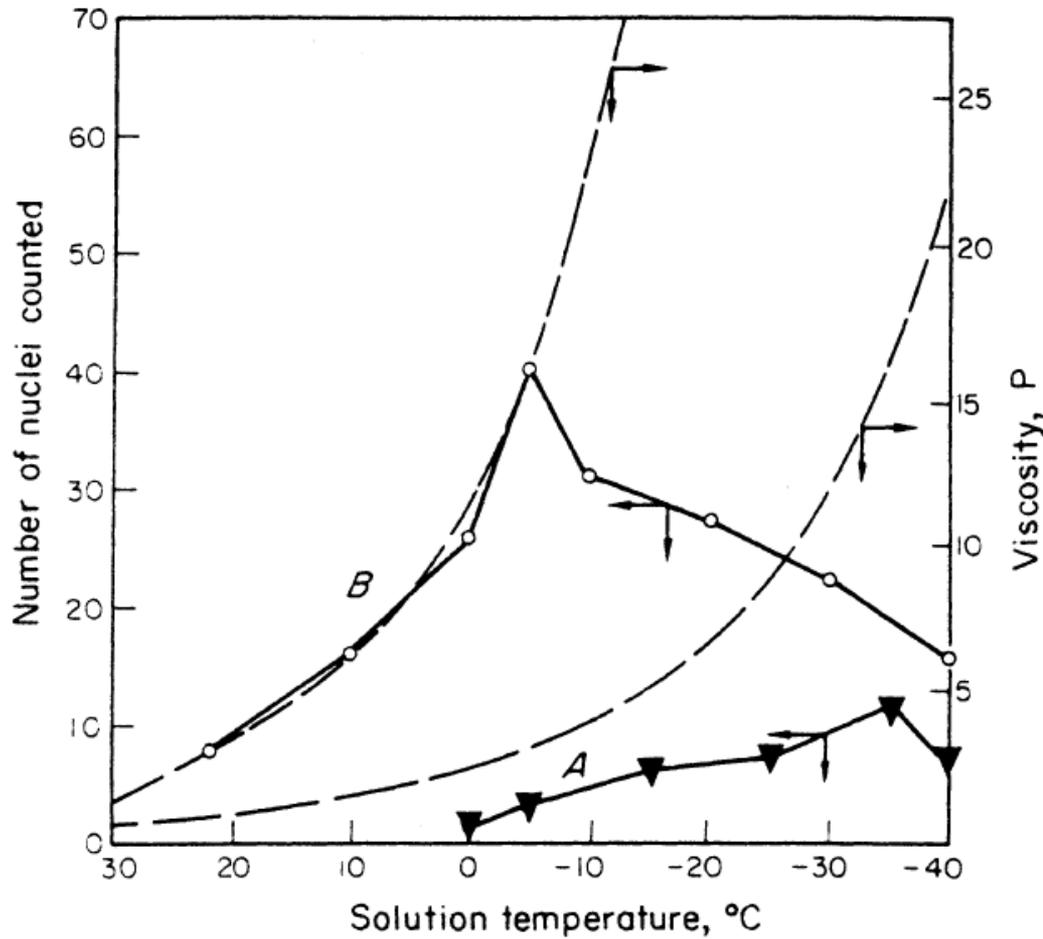
$$r_c \propto (\Delta T)^{-1}$$

$$\Delta G_{\text{crit}} \propto (\Delta T)^{-2}$$

Addition of a viscosity term

$$J = A' \exp \left[ -\frac{16\pi\gamma^3 v^2}{3k^3 T^3 (\ln S)^2} + \frac{\Delta G'}{kT} \right]$$





Increasing supercooling does not necessarily imply increase in nucleation

**Figure 5.4.** Spontaneous nucleation in supercooled citric acid solutions: A, 4.6 kg of citric acid monohydrate per kg of 'free' water ( $T^* = 62^\circ\text{C}$ ); B, 7.0 kg/kg ( $T^* = 85^\circ\text{C}$ ). (After Mullin and Leci, 1969b)

# Crystallization from melts

Rate of crystallization from melt: Depends on rate of heat transfer from crystal face to bulk liquid

Crystal at higher T than supercooled melt  
(crystallization as a rule is exothermic)

## Rate of heat transfer

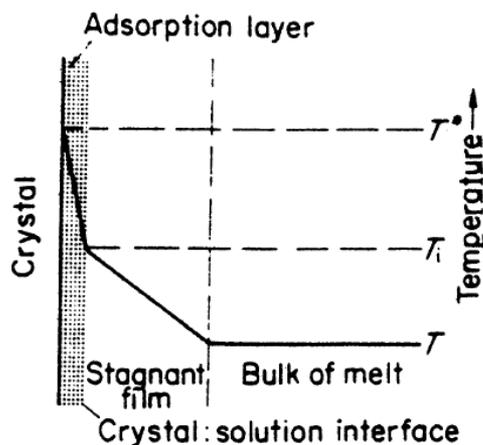
$$\frac{dq}{dt} = hA(T_i - T)$$

Thermal conductivity

Film coefficient of heat transfer

$$h = \frac{\kappa}{\delta'}$$

Effective film thickness for heat transfer



$T^*$ : melting point

Overall degree of supercooling:

$T^* - T$

*Temperature gradients near the face of a crystal growing in a melt*

The rates of crystallization from melts and from solutions are different  $\zeta$

Maximum crystallization temperature in melts:

$$T = T^* - \left( \frac{\Delta H_{\text{cryst}}}{c_m} \right)$$

$\Delta H_{\text{cryst}}$  Heat of melting

$C_m$ : Mean heat capacity of the melt

Rate of crystallization

$$\frac{dm}{dt} = K'_G A (T^* - T)^{g'}$$

Εκθέτης 1,5-2,5

Mass transfer coefficient

Total surface area of crystals

Melting cf. dissolution :

$$-\frac{dm}{dt} = K_M A (T - T^*)^x$$

$x > 1$

And because during melting we have both heat and mass transfer

$$\frac{dq}{dt} = U_M A \Delta T = -\frac{dm}{dt} \Delta H_f$$

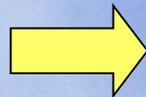


Global mass transfer coefficient

$$-\frac{dm}{dt} = \frac{U_M A \Delta T}{\Delta H_f}$$

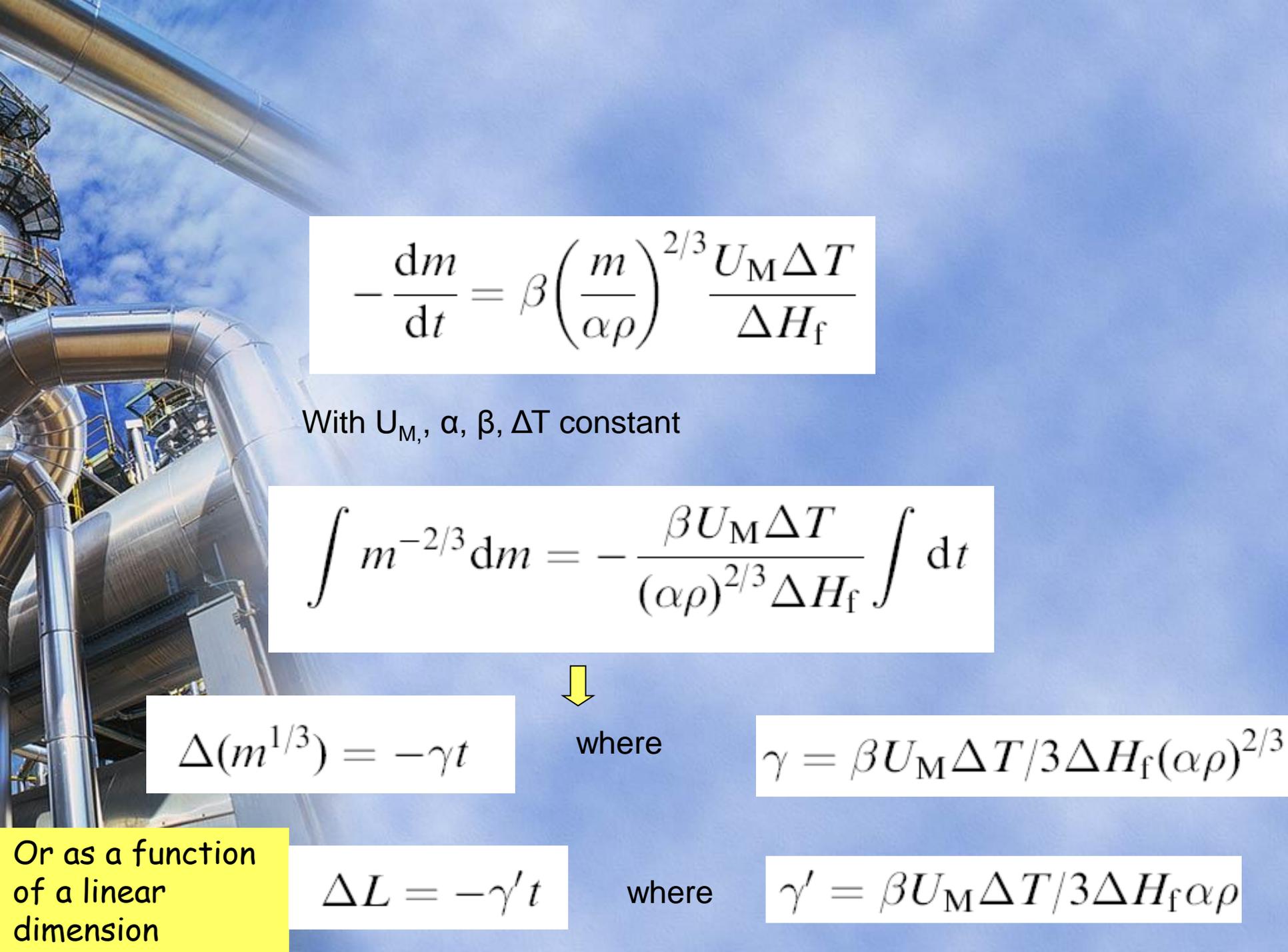
$$A = \beta L^2$$

$$m = \alpha \rho L^3$$



$$A = \beta \left( \frac{m}{\alpha \rho} \right)^{2/3}$$

$\alpha, \beta$ : shape factors


$$-\frac{dm}{dt} = \beta \left( \frac{m}{\alpha \rho} \right)^{2/3} \frac{U_M \Delta T}{\Delta H_f}$$

With  $U_M$ ,  $\alpha$ ,  $\beta$ ,  $\Delta T$  constant

$$\int m^{-2/3} dm = -\frac{\beta U_M \Delta T}{(\alpha \rho)^{2/3} \Delta H_f} \int dt$$

$$\Delta(m^{1/3}) = -\gamma t$$



where

$$\gamma = \beta U_M \Delta T / 3 \Delta H_f (\alpha \rho)^{2/3}$$

Or as a function  
of a linear  
dimension

$$\Delta L = -\gamma' t$$

where

$$\gamma' = \beta U_M \Delta T / 3 \Delta H_f \alpha \rho$$

# Measurement techniques

- Only "recently"

- Impurity free systems

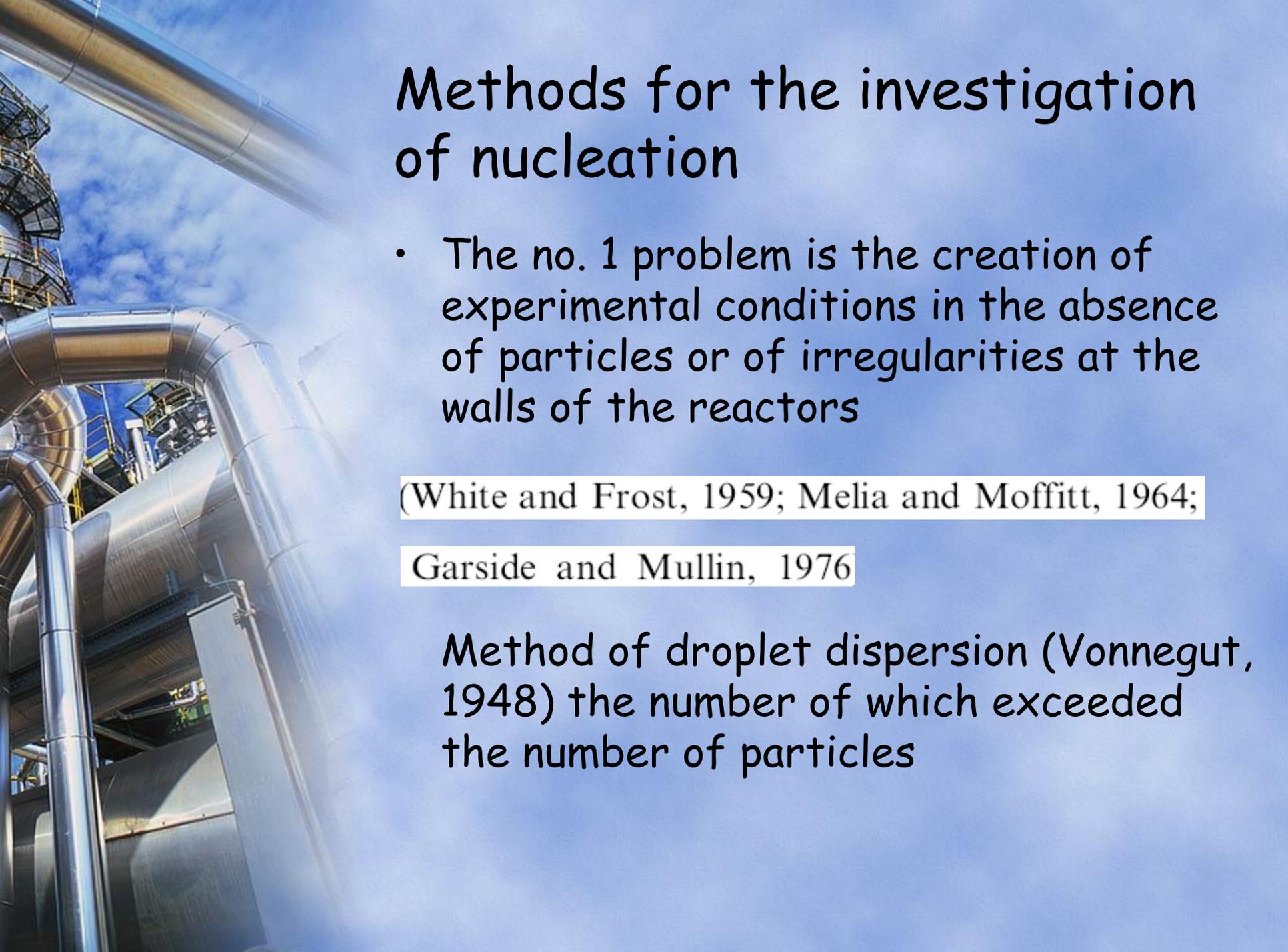
Garten, Head (1963,1966)

Crystalloluminescence during  
the formation of 3-D nuclei

$10^{-7}$  s pulses

A in the order of  $10^{25}$ - $10^{30}$   $\text{cm}^{-3}\text{s}^{-1}$

S>14 (NaCl)



# Methods for the investigation of nucleation

- The no. 1 problem is the creation of experimental conditions in the absence of particles or of irregularities at the walls of the reactors

(White and Frost, 1959; Melia and Moffitt, 1964;

Garside and Mullin, 1976

Method of droplet dispersion (Vonnegut, 1948) the number of which exceeded the number of particles

For NaCl (Garten, Head 1963, 1966)

Crystal luminescence (light pulses  $<10^{-7}$ s, nucleation events)  $10^{25}$  to  $10^{30}$   $\text{cm}^{-3} \text{s}^{-1}$  true homog.nucleation  $S > 14$

Critical nucleus made from about 10 molecules

Otpushchennikov (1962): Ultrasonic wave measurements in melts (naphtalene, phenol, azobenzene): 1000 molecules

Adamski (1963) Insoluble salts of Barium: several milion molecules

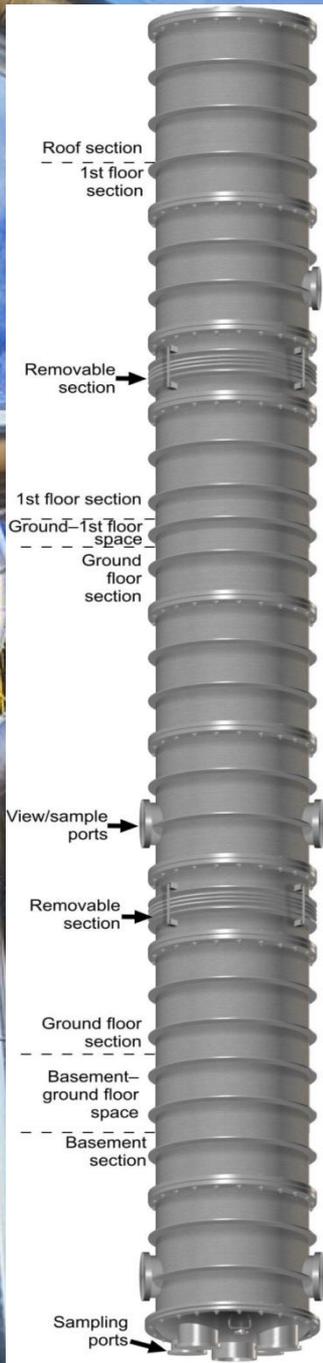
Agitation is often used to induce crystallization

0.5 °C supercooling allowed in stirred water

Very pure water has been supercooled to 40 °C

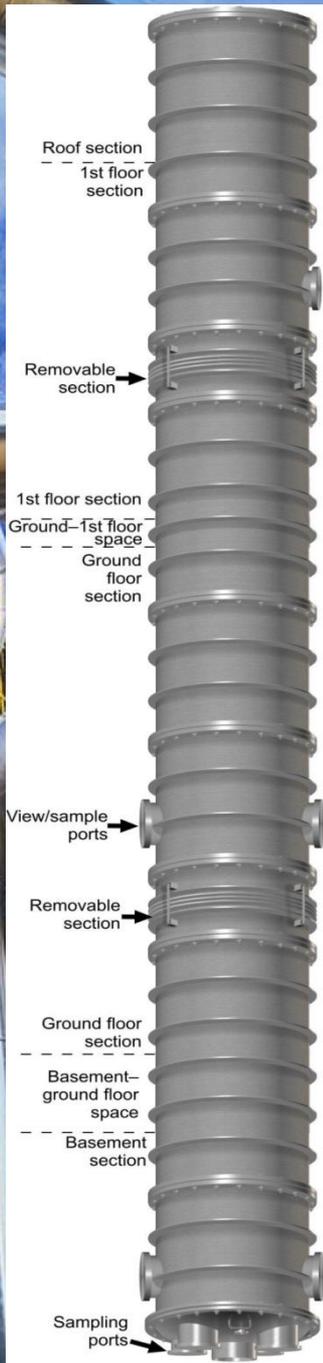
Electric and magnetic fields (D. Kaschiev, 2000)

# M.I.C.C - Manchester Ice Cloud Chamber



University of Manchester cloud chamber height of 10 m, dia. 1 m and can reach temperatures as low as  $-55^{\circ}\text{C}$ . The chamber can also be pressure sealed and evacuated to simulate conditions found in the upper troposphere. Liquid water, mixed phase, or entirely glaciated clouds can be generated in the chamber, with cloud liquid water contents ranging from zero to the highest values found in nature being reproducible. Water clouds are typically generated in two main ways. Most commonly, a water boiler is situated at the base of the chamber and boils to produce a cloud of droplets. At sub-zero temperatures, these become supercooled. Alternatively, a high power pump is used to rapidly evacuate the chamber, and the expansion of chamber air from ambient sources heterogeneously generates a cloud. Ice clouds can be formed from clouds of supercooled liquid water droplets by either heterogeneously or homogeneously nucleating clouds. Homogeneous cloud nucleation when warmer than  $-40^{\circ}\text{C}$  is achieved using one of two methods. Traditionally, a liquid nitrogen-cooled rod ( $-200^{\circ}\text{C}$ ) is inserted into the cloud to cause nucleation. Alternatively, a compressor expansion technique is used

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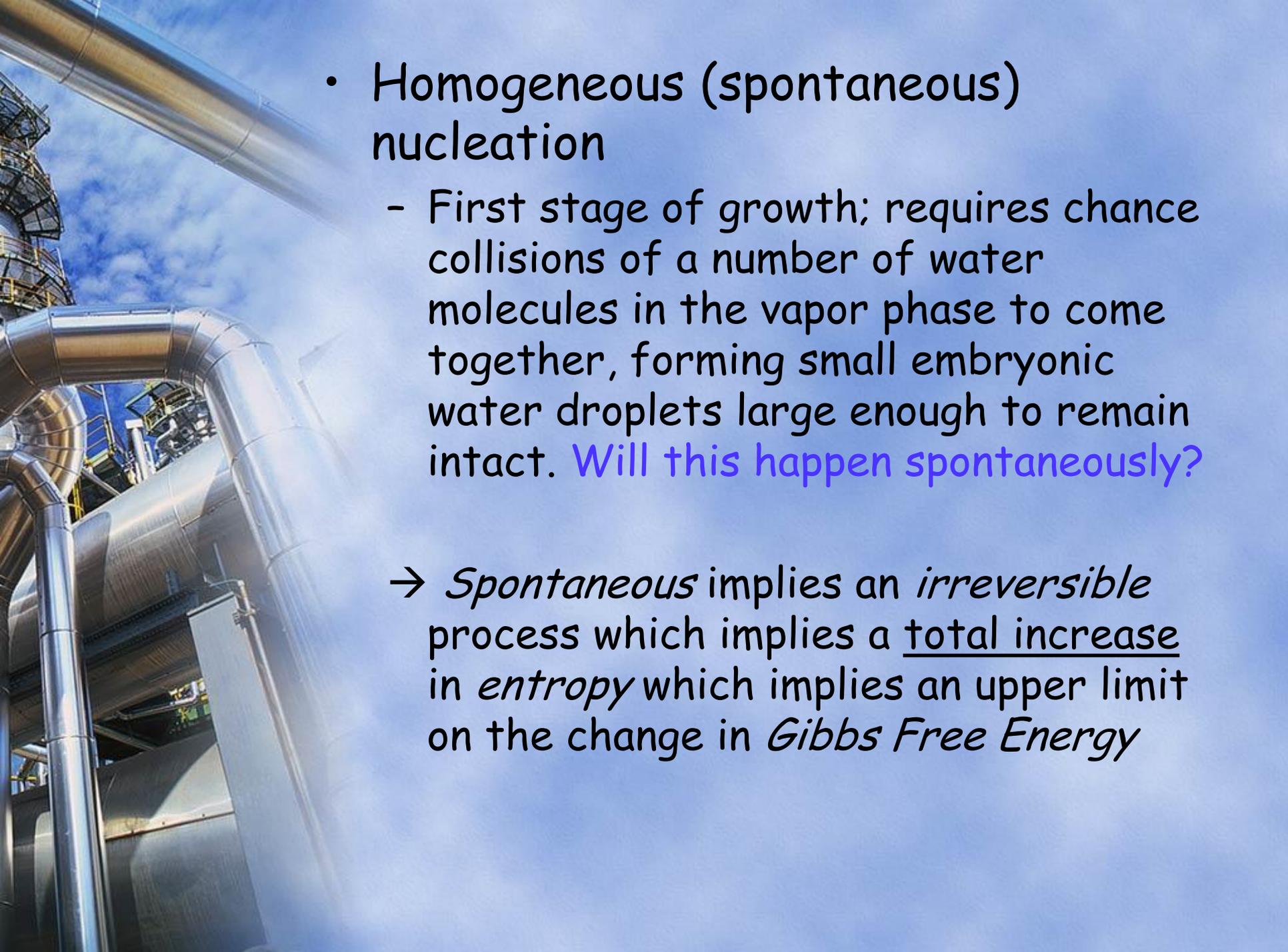


- Clouds form when air becomes *supersaturated* wrt liquid water (or ice, in some cases)
- Supersaturation most commonly occurs in the atmosphere when air parcels ascend, resulting in expansion and cooling
- Water vapor condenses onto aerosols forming a cloud of small water droplets

$$dq = du + p d\alpha$$

- 
- But do we really need aerosol to make a cloud droplet? What if we made a cloud via condensation without the aid of aerosols\*?

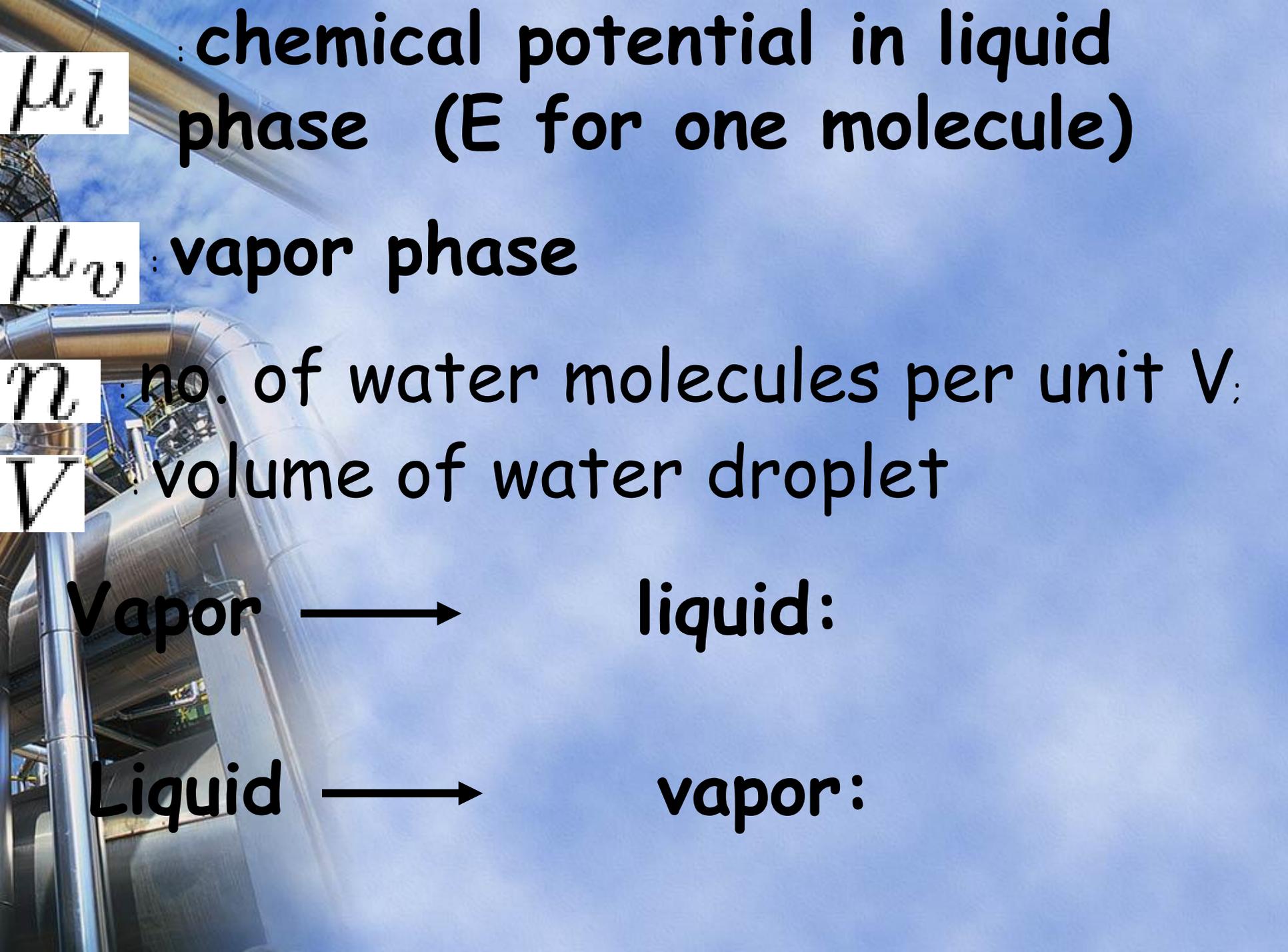
**\*homogeneous or  
spontaneous nucleation**



- Homogeneous (spontaneous) nucleation

- First stage of growth; requires chance collisions of a number of water molecules in the vapor phase to come together, forming small embryonic water droplets large enough to remain intact. *Will this happen spontaneously?*

→ *Spontaneous* implies an *irreversible* process which implies a total increase in *entropy* which implies an upper limit on the change in *Gibbs Free Energy*



$\mu_l$

: chemical potential in liquid phase (E for one molecule)

$\mu_v$

: vapor phase

$n$

: no. of water molecules per unit V:

$V$

: volume of water droplet

Vapor  $\longrightarrow$

liquid:

Liquid  $\longrightarrow$

vapor:

Vapor  $\longrightarrow$  Liquid: Energy  $\downarrow$   
Liquid:  $\longrightarrow$  Vapor: E  $\uparrow$

E decrease due to  
Condensation:

$$nV(\mu_v - \mu_l)$$

Work done to create the droplet surface:

$$A\sigma$$

$$\sigma$$

Is the work required to create a unit area of vapor-liquid interface

Total energy change in the system due to the formation of the droplet:

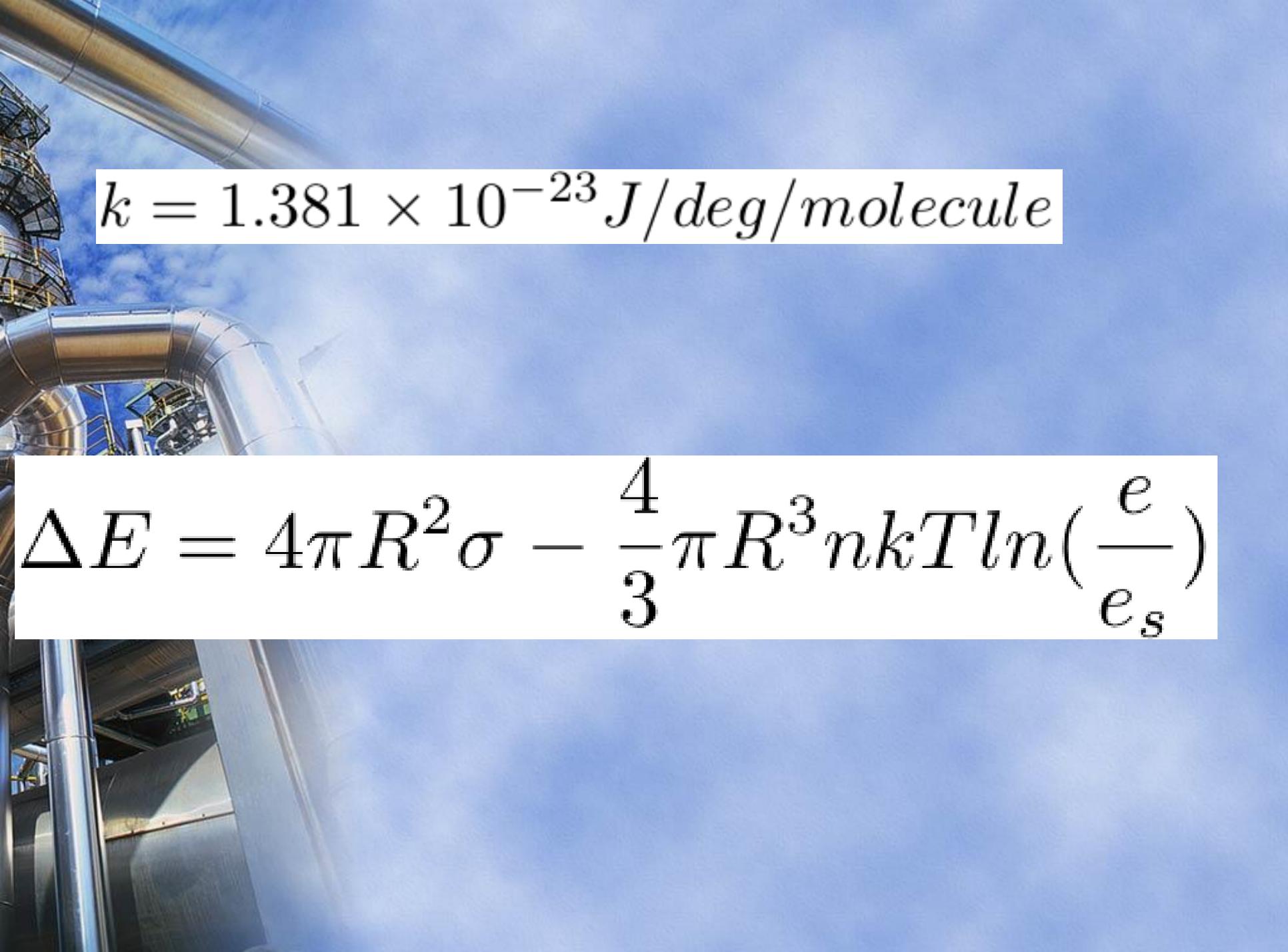
$$\Delta E = A\sigma - nV(\mu_v - \mu_l)$$

Radius:  $R$

$$\Delta E = 4\pi R^2\sigma - n\frac{4}{3}\pi R^3(\mu_v - \mu_l)$$

Since:  $\mu_v - \mu_l = kT \ln \frac{e}{e_s}$

$$\Delta E = 4\pi R^2\sigma - \frac{4}{3}\pi R^3 nkT \ln\left(\frac{e}{e_s}\right)$$


$$k = 1.381 \times 10^{-23} \text{ J/deg/molecule}$$

$$\Delta E = 4\pi R^2 \sigma - \frac{4}{3}\pi R^3 n k T \ln\left(\frac{e}{e_s}\right)$$

- Subsaturated conditions ( $e < e_s$ )

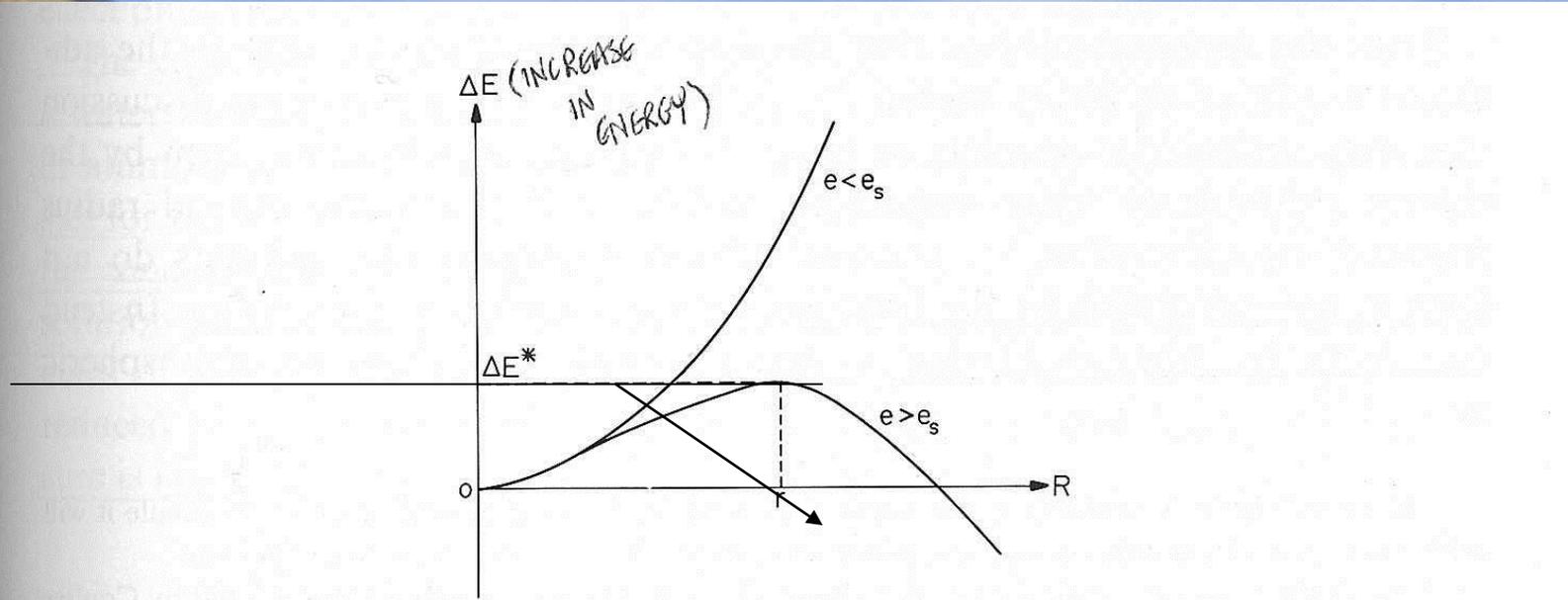


Fig. 4.10 The increase  $\Delta E$  in the energy of a system due to the formation of a water droplet of radius  $R$  from water vapor with pressure  $e$ ;  $e_s$  is the saturation vapor pressure with respect to a plane surface of water at the temperature of the system.

If droplet grows ( $R$  increases), then  $\Delta E > 0$ , this won't happen spontaneously.

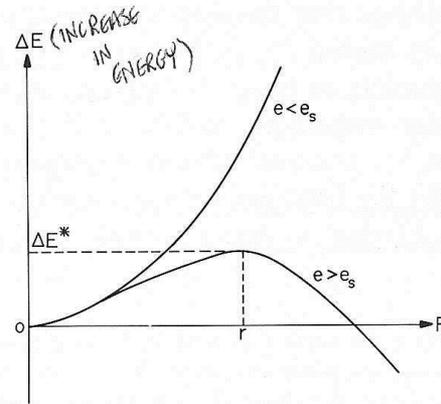


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- **Subsaturated conditions ( $e < e_s$ )**
  - Formation of droplets is not favored
  - Random collisions of water molecules do occur, forming very small embryonic droplets (that evaporate)
  - These droplets never grow large enough to become visible

- Supersaturated conditions ( $e > e_s$ )
  - $\Delta E$  initially increases with increasing  $R$
  - $\Delta E$  is a maximum where  $R = r$
  - $\Delta E$  decreases with increasing  $R$  beyond  $R = r$

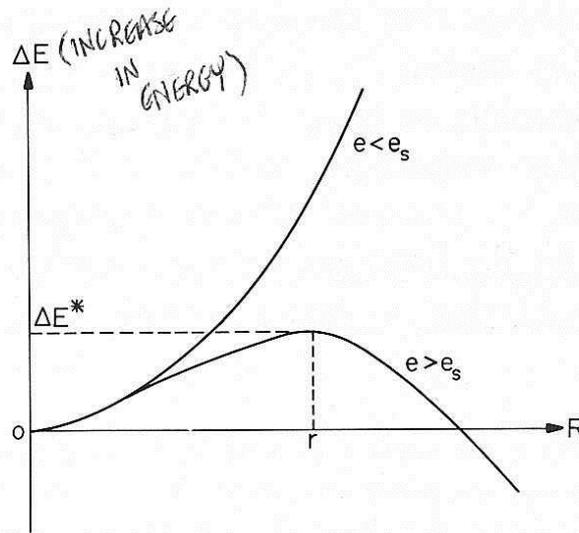


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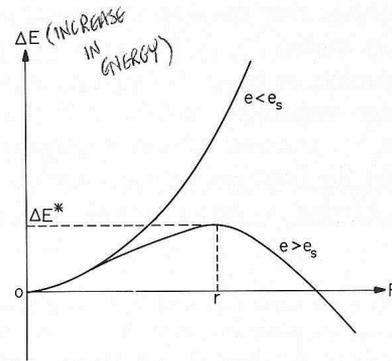
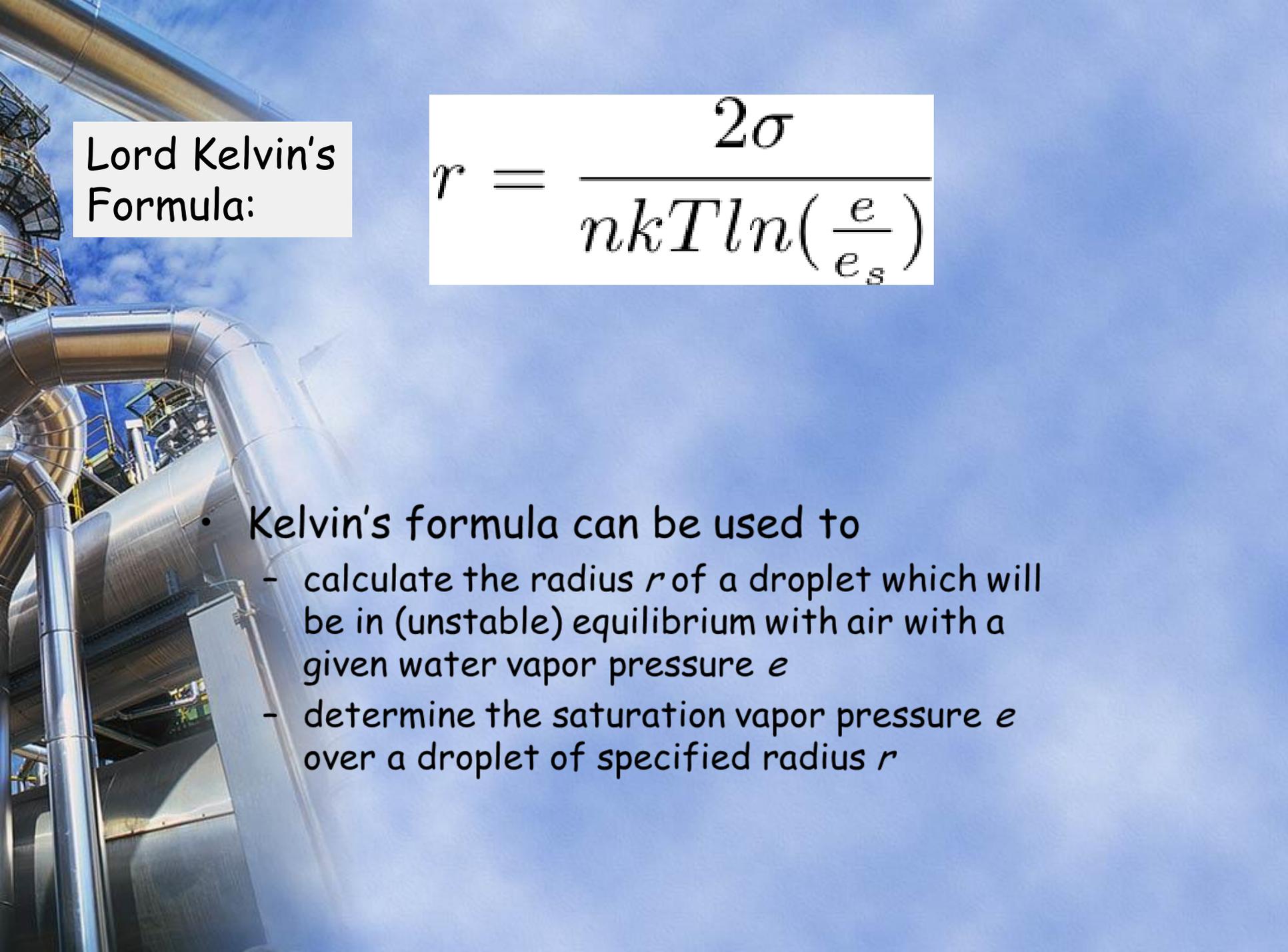


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- **Supersaturated conditions ( $e > e_s$ )**
  - Embryonic droplets with  $R < r$  tend to evaporate
  - Droplets which grow by chance (collisions) with  $R > r$  will continue to grow spontaneously by condensation
    - They will cause a decrease in the Gibbs free energy (total energy) of the system



Lord Kelvin's  
Formula:

$$r = \frac{2\sigma}{nkT \ln\left(\frac{e}{e_s}\right)}$$

- Kelvin's formula can be used to
  - calculate the radius  $r$  of a droplet which will be in (unstable) equilibrium with air with a given water vapor pressure  $e$
  - determine the saturation vapor pressure  $e$  over a droplet of specified radius  $r$

- $r = 0.01$  micrometers requires a RH of 112.5%
- $r = 1.0$  micrometer requires a RH of 100.12%

Rarely exceed 1%

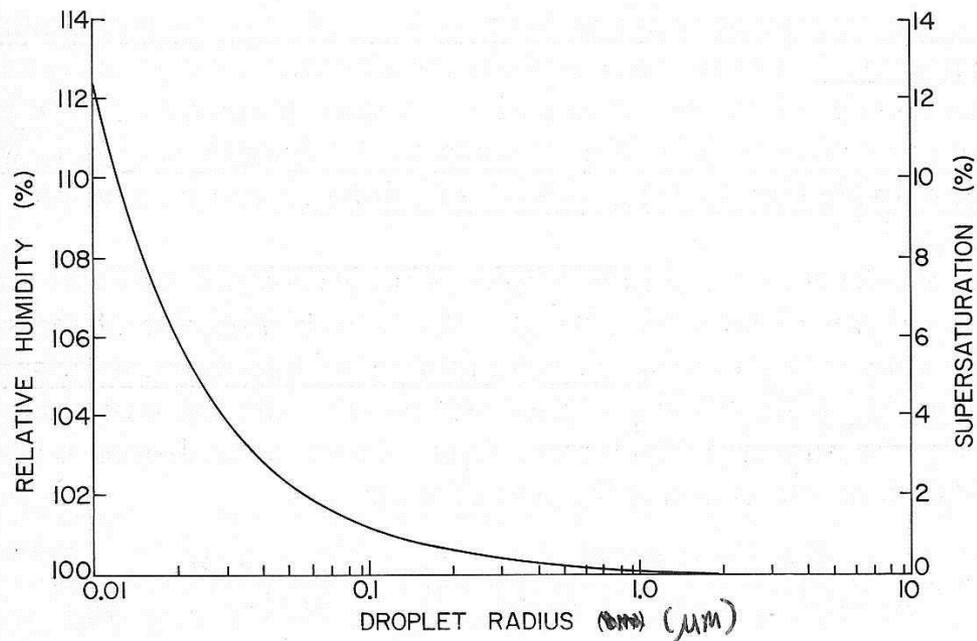
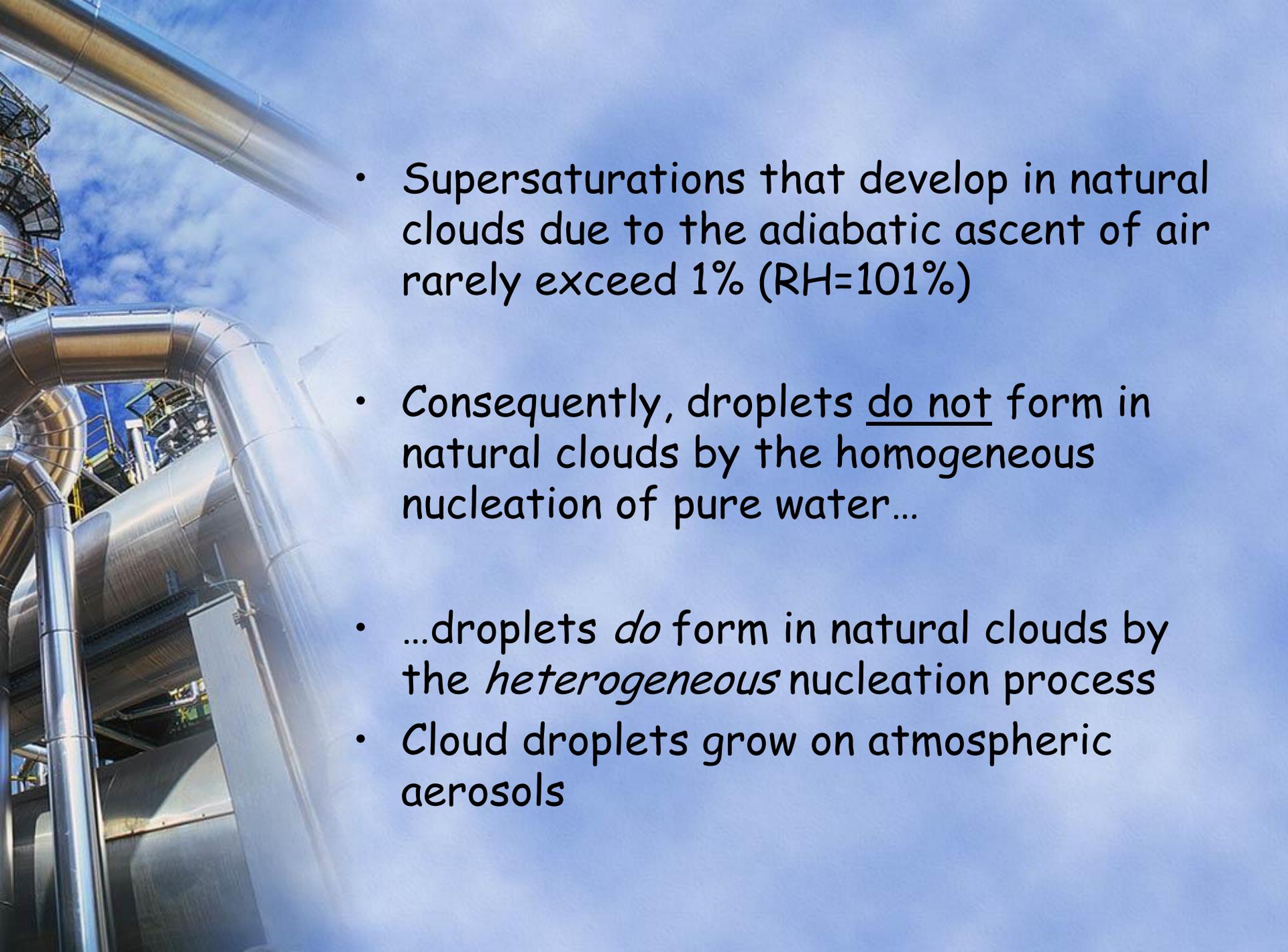


Fig. 4.11 The relative humidity and supersaturation (both with respect to a plane surface of liquid water) with which pure water droplets are in (unstable) equilibrium at 5°C.

- 
- 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 *do* form in natural clouds by the *heterogeneous* nucleation process
  - Cloud droplets grow on atmospheric aerosols

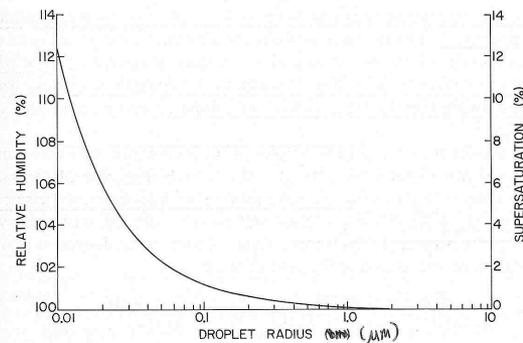


Fig. 4.11 The relative humidity and supersaturation (both with respect to a plane surface of liquid water) with which pure water droplets are in (unstable) equilibrium at 5°C.

- Droplets can form and grow on aerosol at much lower supersaturations than are required for homogeneous nucleation
  - Water vapor condenses onto an aerosol 0.3 micrometers in radius, the water film will be in (unstable) equilibrium with air which has a supersaturation of 0.4%

# Aerosols: CCN (cloud condensation nuclei)\*

- Aerosol types
  - wettable; aerosol that allows water to spread out on it as a horizontal film

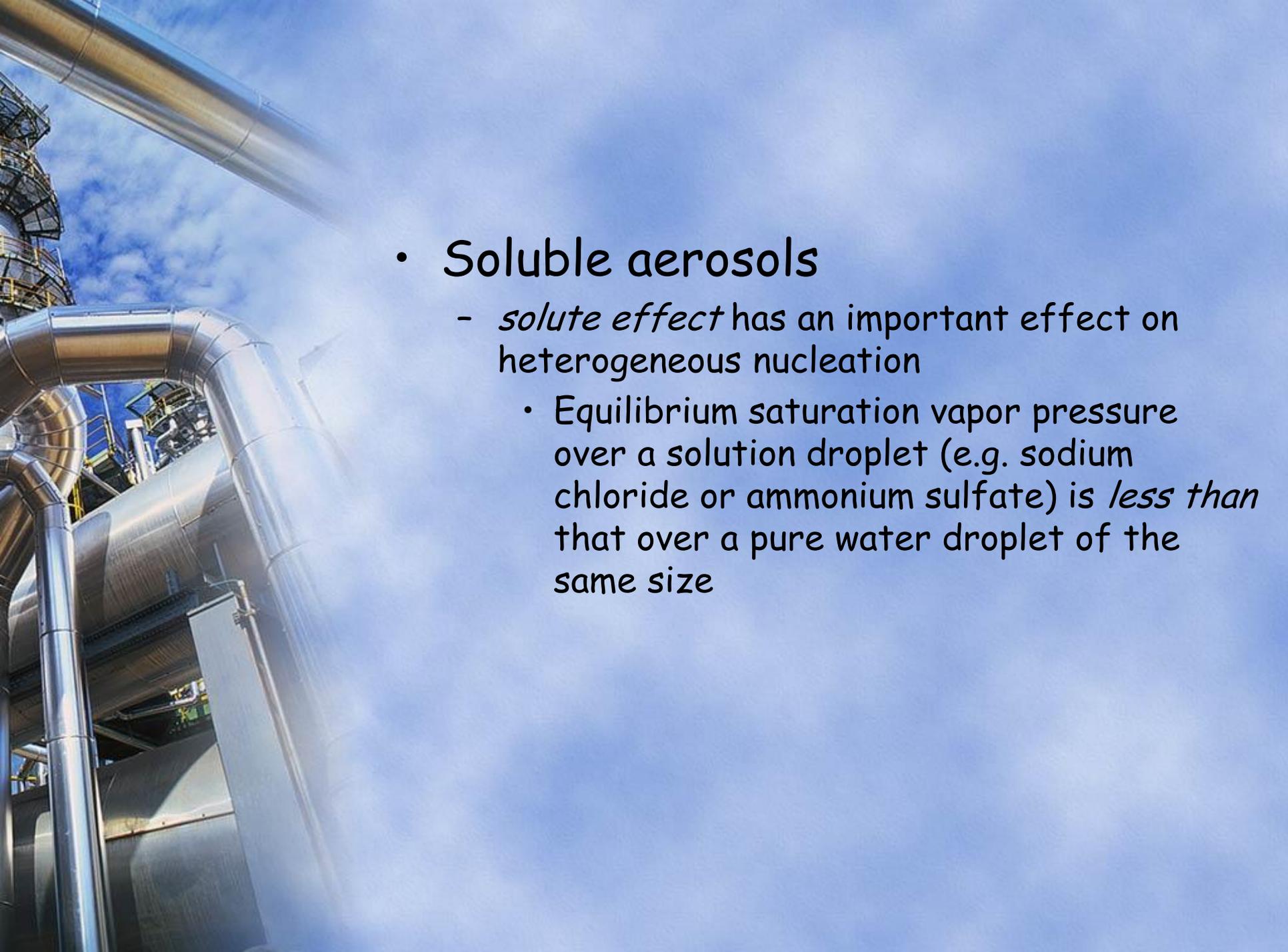
0.1  $\mu\text{m}$

- in radius; - soluble; dissolve when water condenses onto them

\*are small particles typically 0.2  $\mu\text{m}$ , or 1/100th the size of a cloud droplet on which water vapour condenses. Water requires a non-gaseous surface to make the transition from a vapour to a liquid; this process is called condensation. In the atmosphere, this surface presents itself as tiny solid or liquid particles called CCNs. When no CCNs are present, water vapour can be supercooled at about  $-13^{\circ}\text{C}$  ( $8^{\circ}\text{F}$ ) for 5-6 hours before droplets spontaneously form (this is the basis of the cloud chamber for detecting subatomic particles). In above freezing temperatures the air would have to be supersaturated to around 400% before the droplets could form.

0.01  $\mu\text{m}$

1% continental air;  
10-20% marine air;

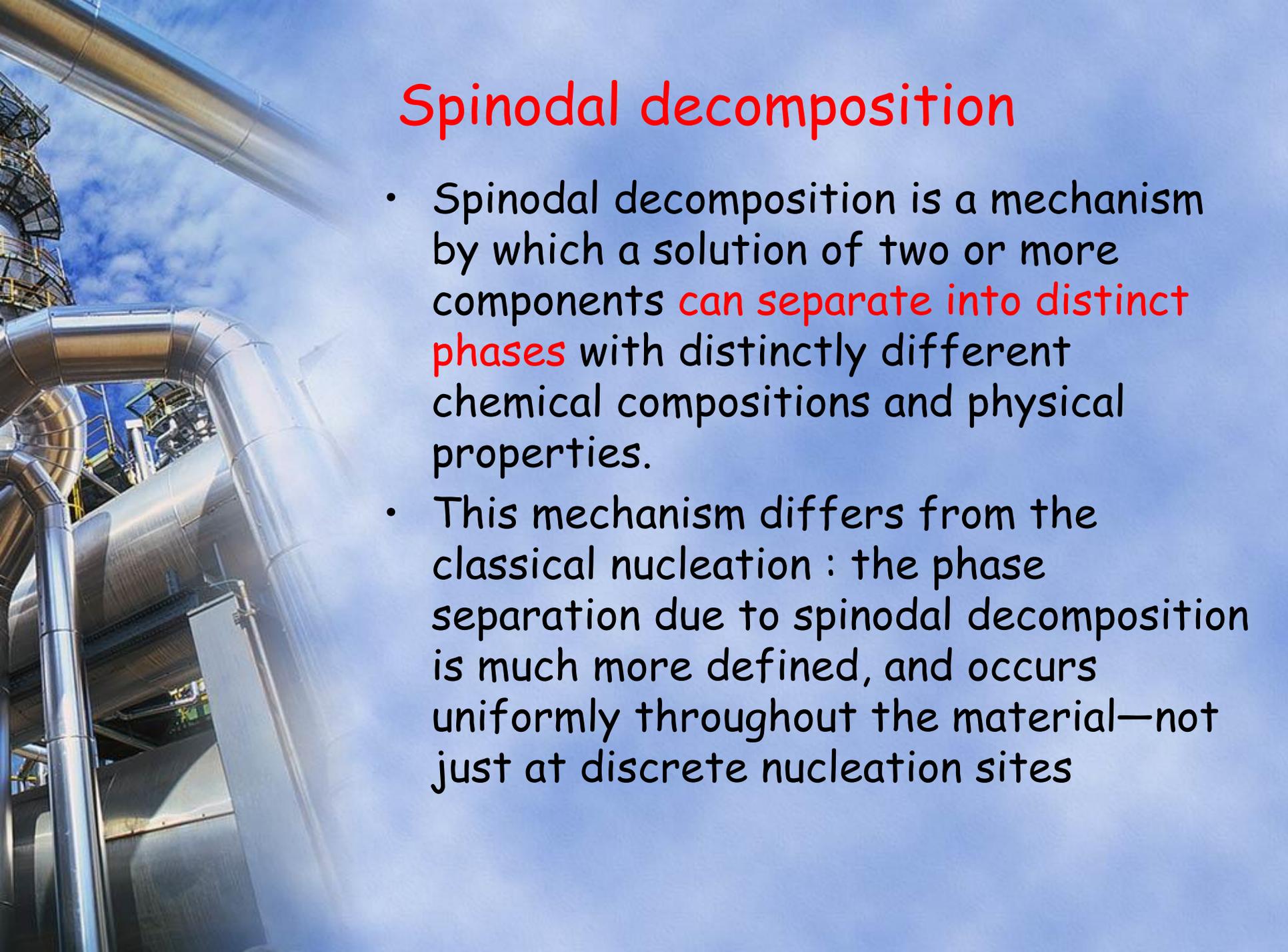


- Soluble aerosols

- *solute effect* has an important effect on heterogeneous nucleation
  - Equilibrium saturation vapor pressure over a solution droplet (e.g. sodium chloride or ammonium sulfate) is *less than* that over a pure water droplet of the same size

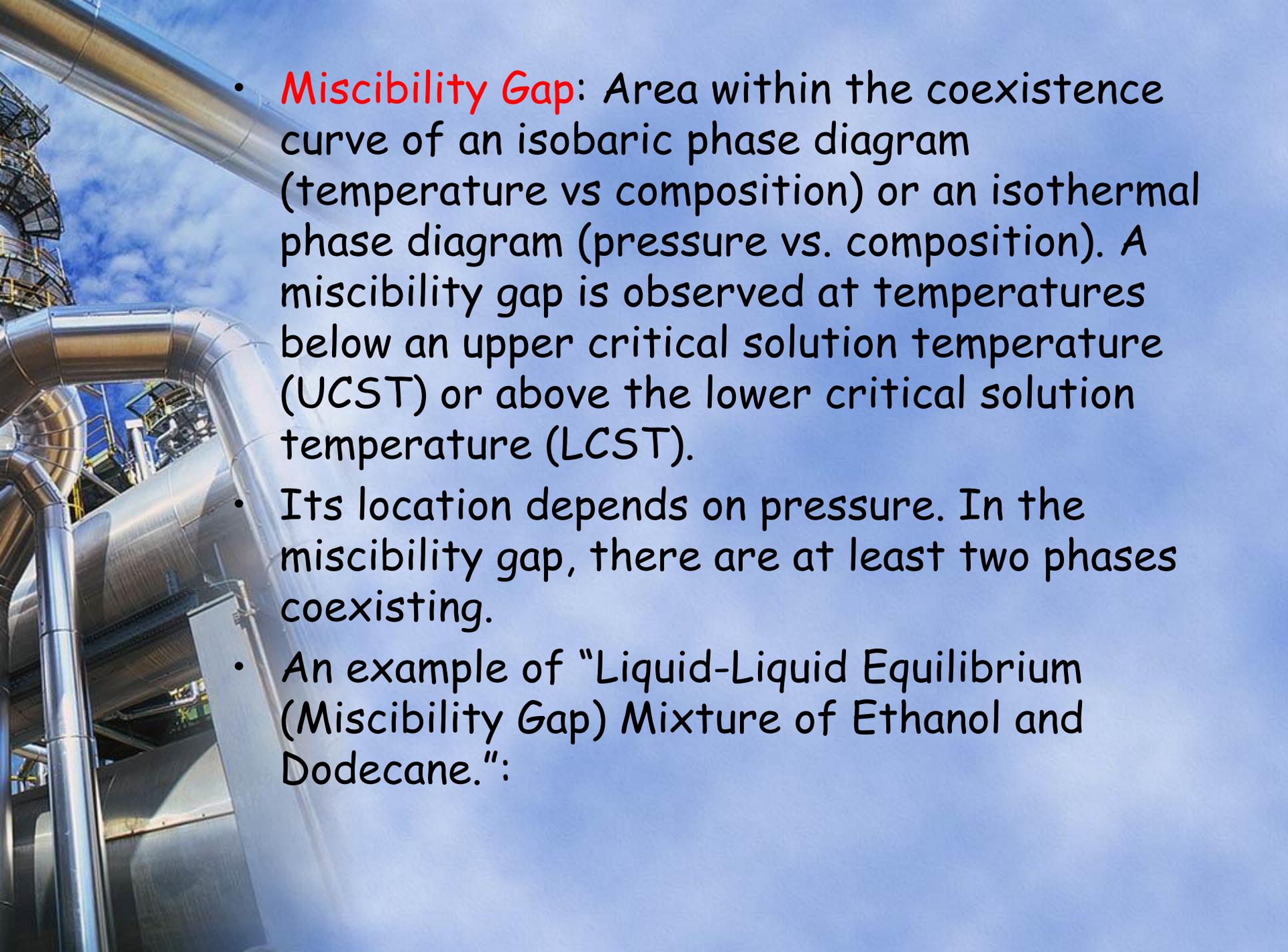
# Spinodal decomposition

- **Concentration fluctuations:**
- large degree small spatial extent (infinitesimal droplet with properties close to the supercooled phase)
- Small degree but large spatial extent (continuous change of phases)
- Classical nucleation: first concept- requires existence of a sharp interface between nucleating phase and the supercooled fluid

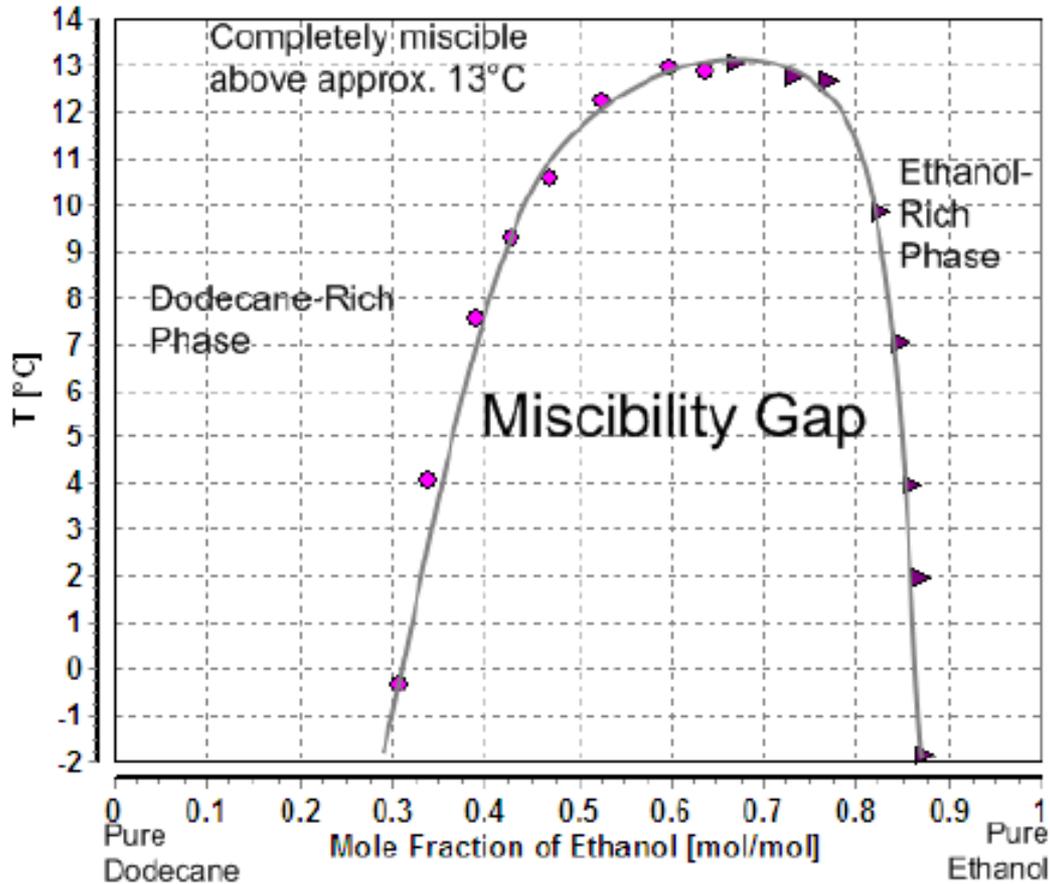
The background of the slide is a photograph of an industrial facility, likely a refinery or chemical plant. It features a complex network of large, silver-colored metal pipes and structures. The pipes are arranged in various orientations, some running horizontally and others vertically. The sky is a clear, bright blue with a few wispy white clouds. The overall scene is brightly lit, suggesting a sunny day.

# Spinodal decomposition

- Spinodal decomposition is a mechanism by which a solution of two or more components **can separate into distinct phases** with distinctly different chemical compositions and physical properties.
- This mechanism differs from the classical nucleation : the phase separation due to spinodal decomposition is much more defined, and occurs uniformly throughout the material—not just at discrete nucleation sites

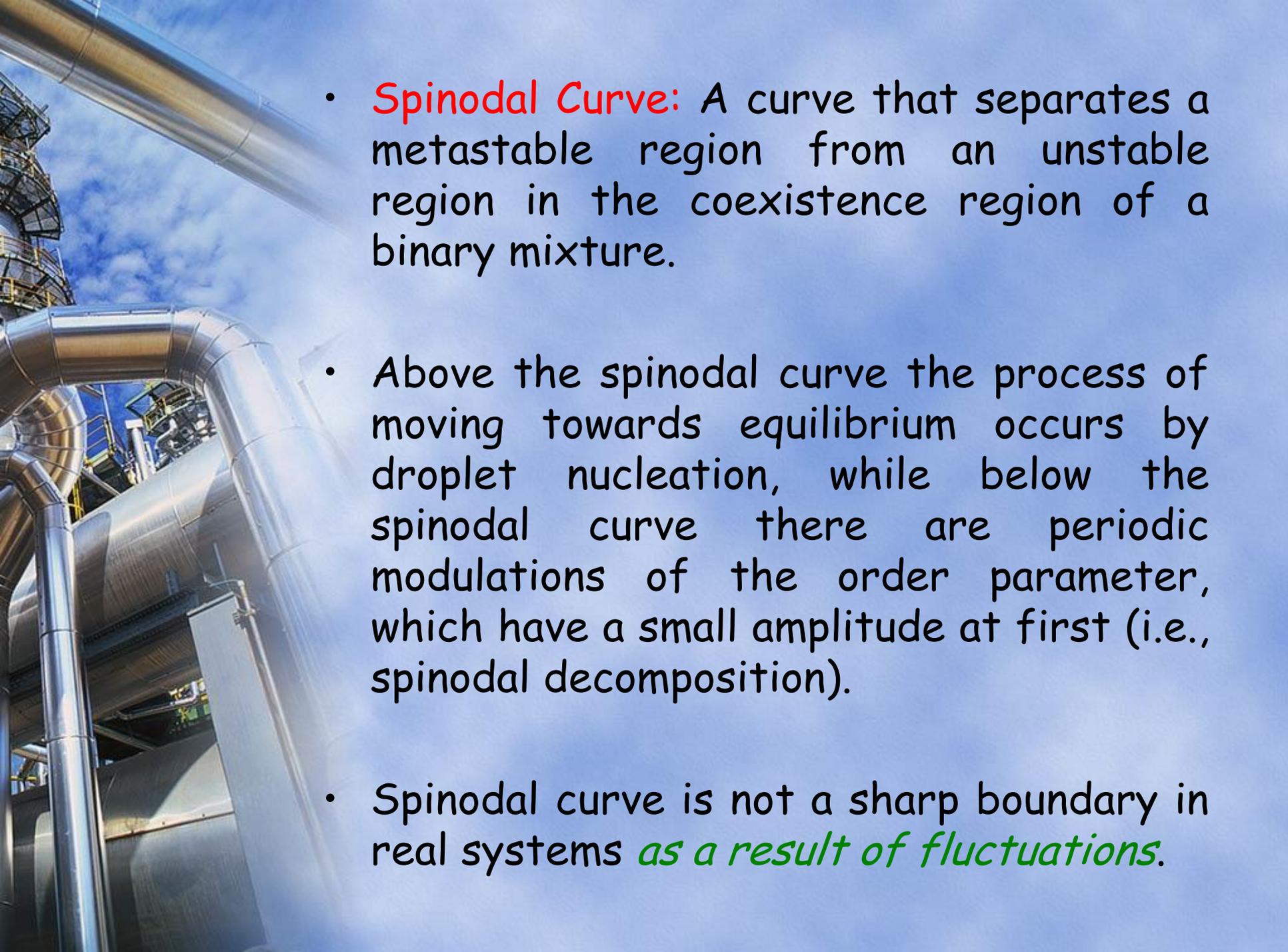
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- The background of the slide shows a complex industrial facility with numerous large, silver-colored metal pipes and structures. The pipes are arranged in a network, with some running vertically and others horizontally. The sky is a clear, bright blue with a few wispy white clouds. The overall scene is that of a modern industrial plant, possibly a refinery or chemical processing facility.
- **Miscibility Gap:** Area within the coexistence curve of an isobaric phase diagram (temperature vs composition) or an isothermal phase diagram (pressure vs. composition). A miscibility gap is observed at temperatures below an upper critical solution temperature (UCST) or above the lower critical solution temperature (LCST).
  - Its location depends on pressure. In the miscibility gap, there are at least two phases coexisting.
  - An example of "Liquid-Liquid Equilibrium (Miscibility Gap) Mixture of Ethanol and Dodecane.":

Liquid-Liquid Equilibrium (Miscibility Gap)  
Mixture of Ethanol and Dodecane

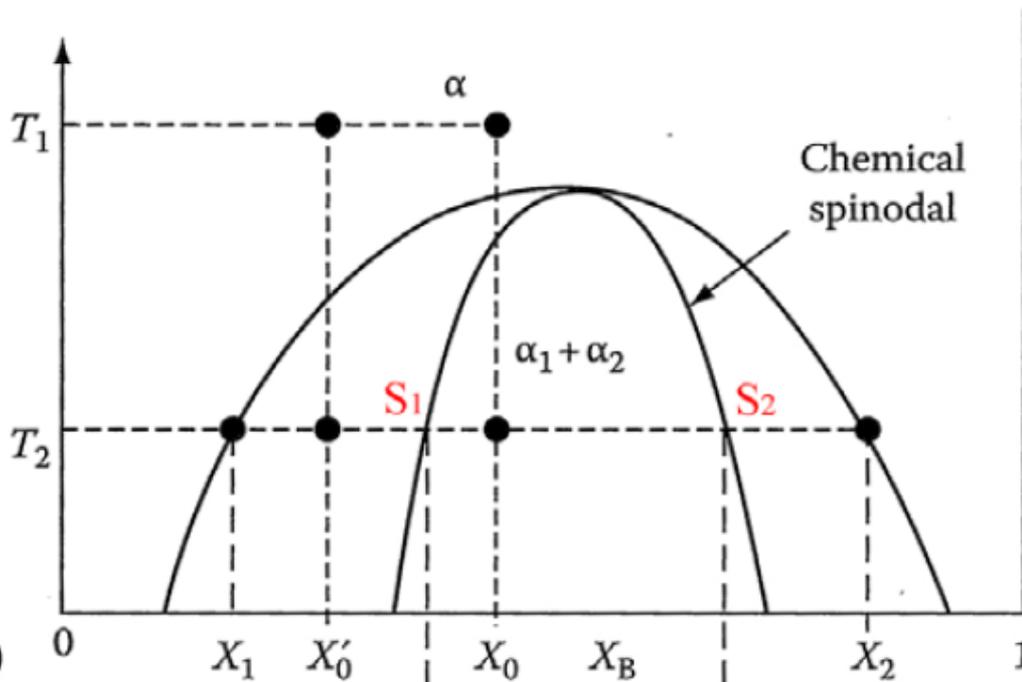


**Binodal Curve or Coexistence Curve:** It is a curve (like the bell-like one shown) defining the region of composition and temperature in a phase diagram for a binary mixture across which a transition occurs from miscibility of the components to conditions where single-phase mixtures are metastable or unstable.

**Binodal compositions** are defined by pairs of points on the curve of Gibbs energy of mixing vs composition that have common tangents, corresponding to compositions of equal chemical potentials of each of the two components in two phases.

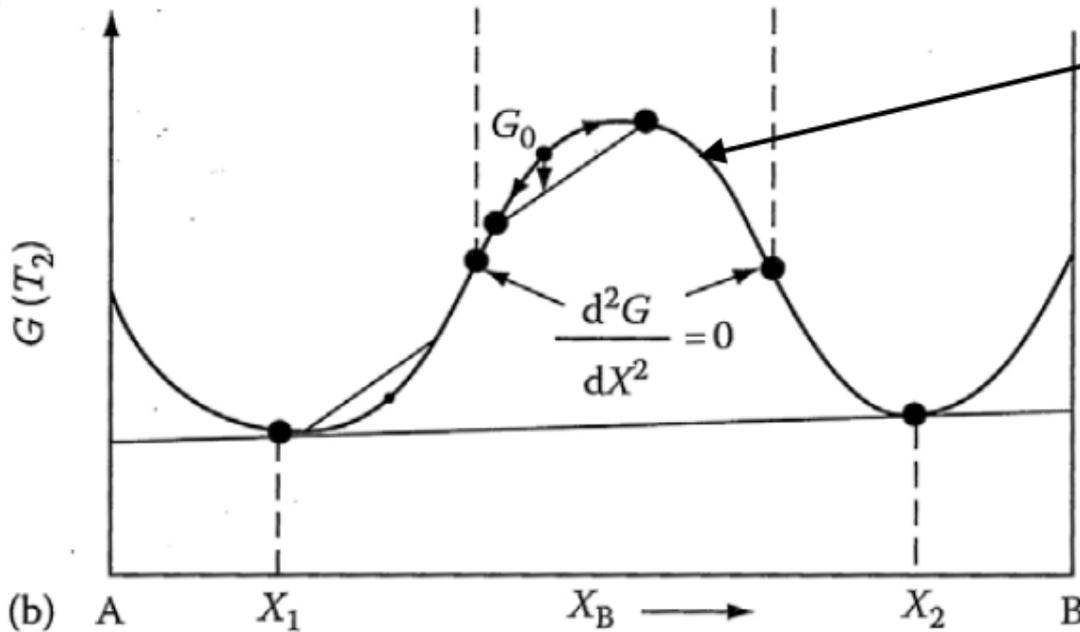
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- **Spinodal Curve:** A curve that separates a metastable region from an unstable region in the coexistence region of a binary mixture.
  - Above the spinodal curve the process of moving towards equilibrium occurs by droplet nucleation, while below the spinodal curve there are periodic modulations of the order parameter, which have a small amplitude at first (i.e., spinodal decomposition).
  - Spinodal curve is not a sharp boundary in real systems *as a result of fluctuations*.

- As a special case of phase transformation, spinodal decomposition can be illustrated on a phase diagram exhibiting a miscibility gap (see diagram). Thus, phase separation occurs whenever a material transitions into the unstable region of the phase diagram. The boundary of the unstable region, sometimes referred to as the binodal or coexistence curve, is found by performing a common tangent construction of the free-energy diagram. Inside the binodal is a region called the spinodal, which is found by determining where the curvature of the free-energy curve is negative. The binodal and spinodal meet at the critical point. It is when a material is moved into the spinodal region of the phase diagram that spinodal decomposition can occur.

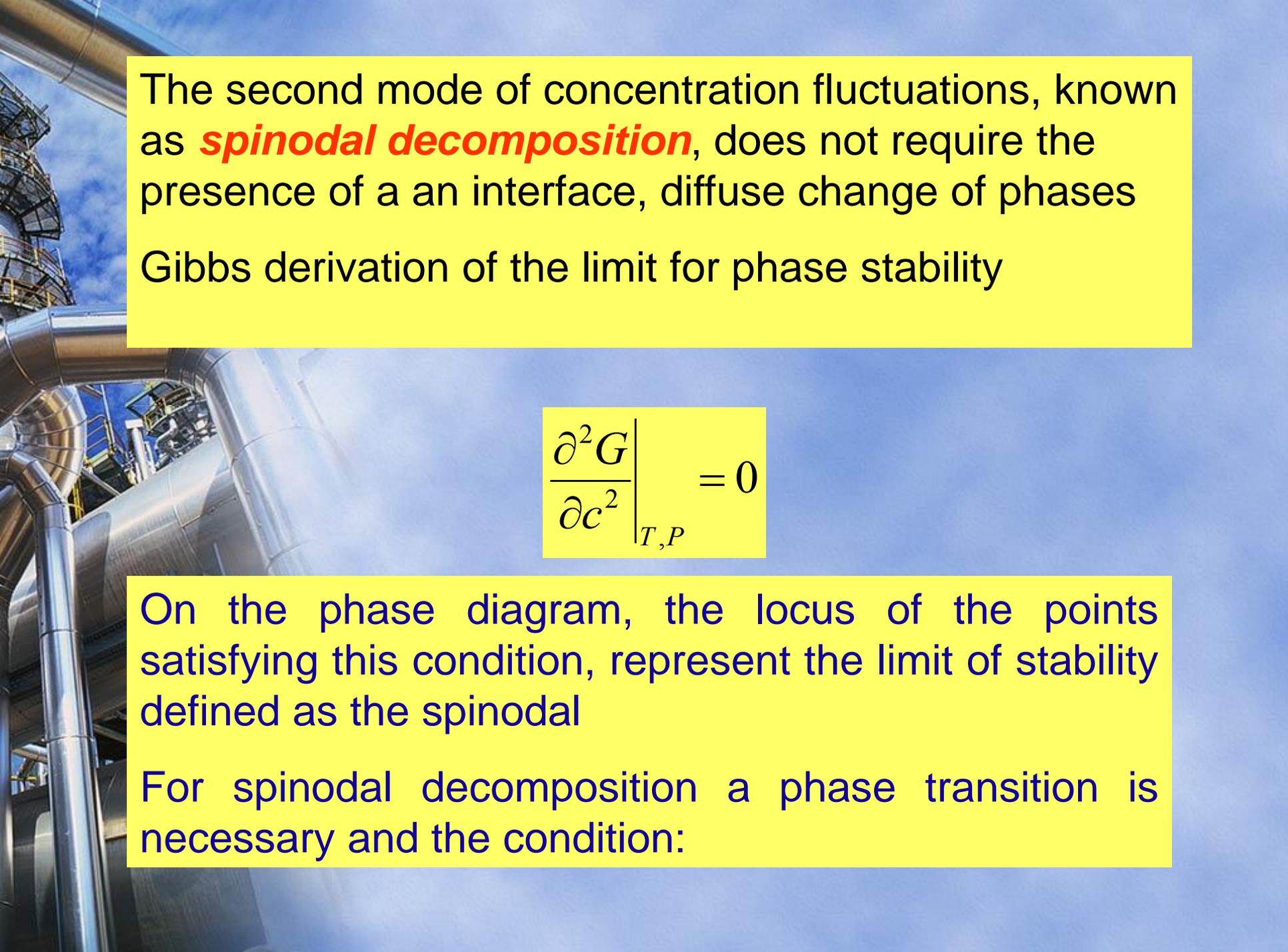


For compositions within the spinodal, a homogeneous solution is *unstable against microscopic fluctuations in density or composition*, and *there is no thermodynamic barrier to the growth of a new phase, i.e., the phase transformation is solely diffusion controlled.*

$$d^2G/dc^2 < 0$$



“c” or “X” here refers to the concentration of components.

The background of the slide is a photograph of an industrial facility, likely a refinery or chemical plant. It features a complex network of large, silver-colored metal pipes and structures, some with scaffolding, set against a clear blue sky. The perspective is from a low angle, looking up at the pipes.

The second mode of concentration fluctuations, known as **spinodal decomposition**, does not require the presence of an interface, diffuse change of phases

Gibbs derivation of the limit for phase stability

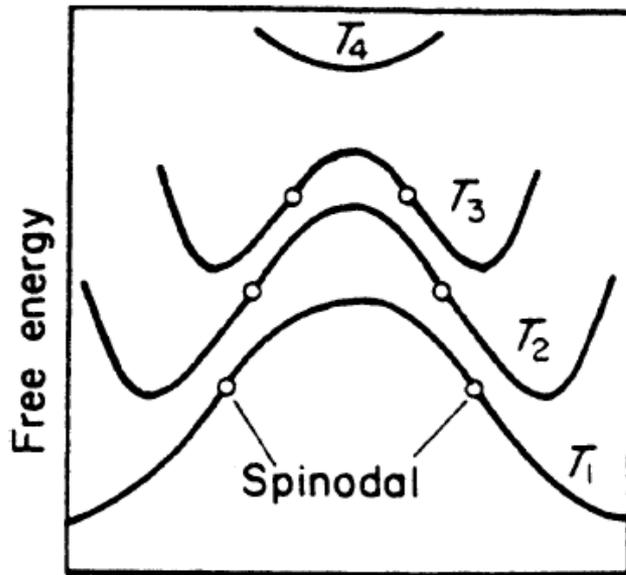
$$\left. \frac{\partial^2 G}{\partial c^2} \right|_{T,P} = 0$$

On the phase diagram, the locus of the points satisfying this condition, represent the limit of stability defined as the spinodal

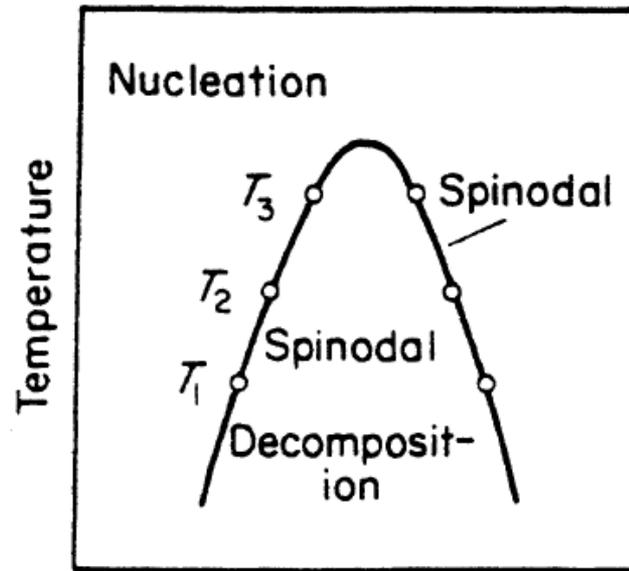
For spinodal decomposition a phase transition is necessary and the condition:

$$(\partial^2 G / \partial c^2) \leq 0$$

Should apply



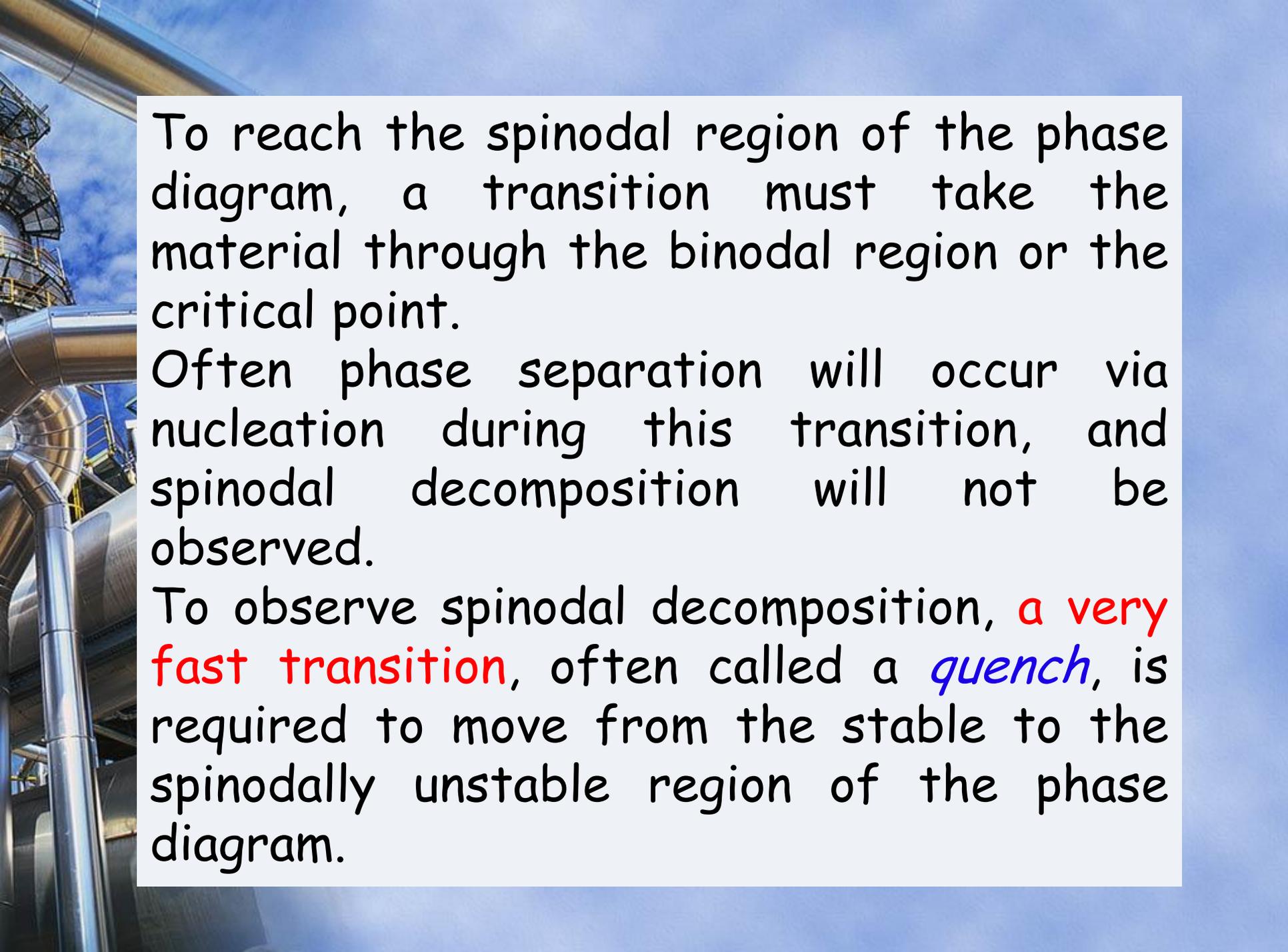
Composition  
(a)



Composition  
(b)

Within the spinodal region the energy of the system is lowered and no nucleation is needed

Condition of zero diffusivity

A photograph of industrial machinery, including large metal pipes and a complex structure, set against a clear blue sky. The image is partially obscured by a white text box.

To reach the spinodal region of the phase diagram, a transition must take the material through the binodal region or the critical point.

Often phase separation will occur via nucleation during this transition, and spinodal decomposition will not be observed.

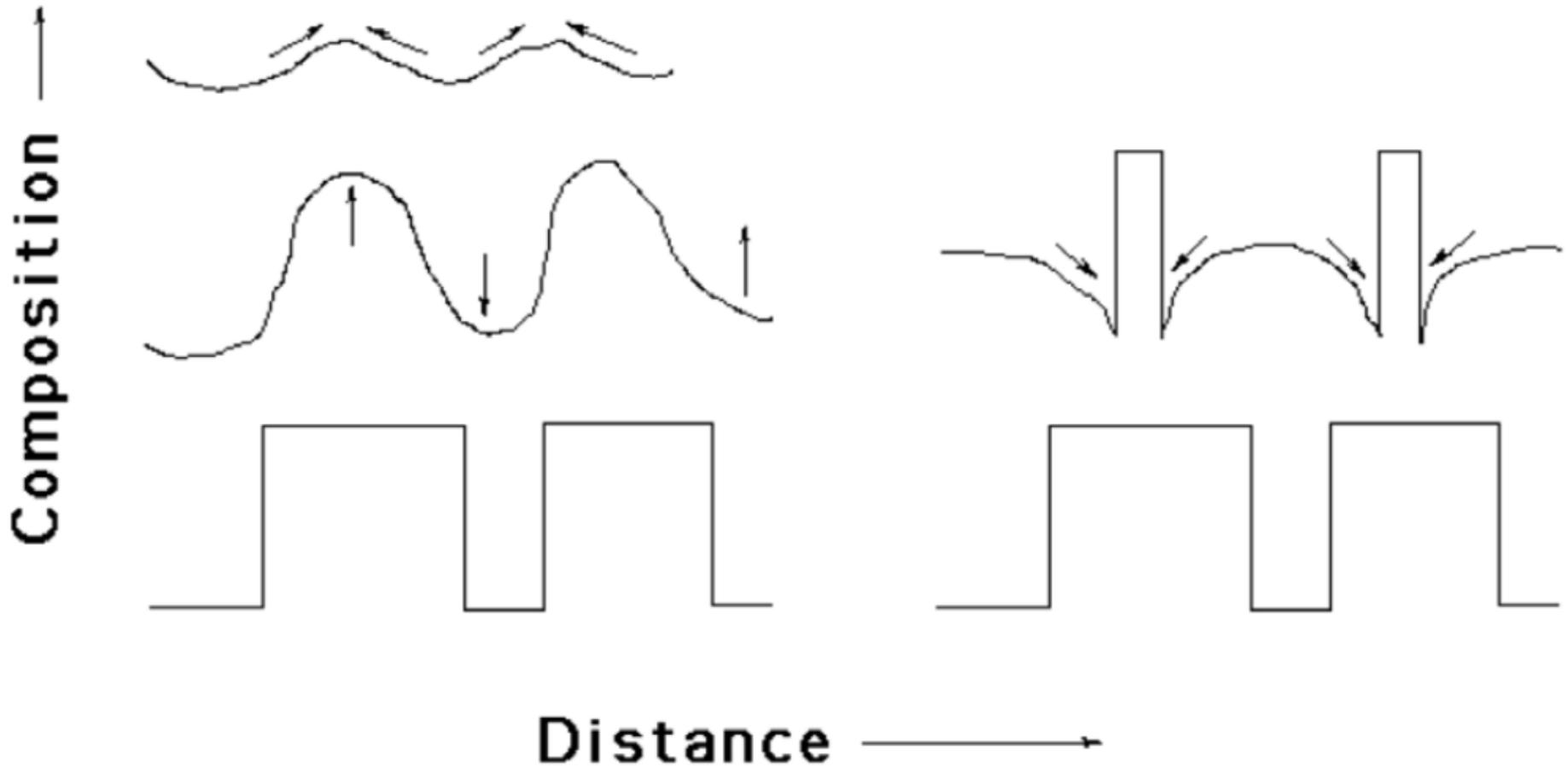
To observe spinodal decomposition, a very fast transition, often called a *quench*, is required to move from the stable to the spinodally unstable region of the phase diagram.

# Comparison between Spinodal Decomposition and Nucleation and Growth

- An initially homogeneous solution develops fluctuations of chemical composition when supercooled into the spinodal region.
- These fluctuations are at first **small in amplitude** but grow with time until there are identifiable precipitates of equilibrium composition.
- In contrast, during nucleation and growth, there is a sharp interface between the parent and product crystals; furthermore, the precipitate at all stages of its existence has the required equilibrium composition .
- Spinodal decomposition involves **uphill diffusion**, whereas diffusion is always down a concentration gradient for nucleation and growth of the type illustrated below.
- *Spinodal decomposition refers to a mechanism of phase transformation inside a miscibility gap. It is characterized by the occurrence of diffusion up against a concentration gradient , often referred as "uphill" diffusion leading to formation of a uniform-sized, periodic fine microstructure.*

## Spinodal

## Nucleation & growth

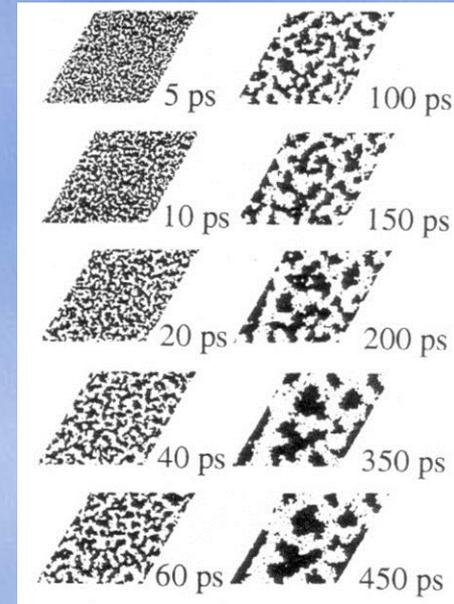
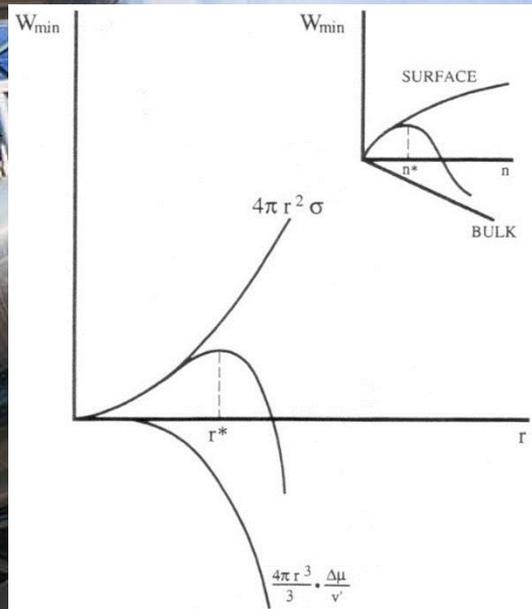


Evolution of phase separation in spinodal decomposition and during nucleation and growth. The arrows indicate the direction of diffusion.

# Phase Stability Applications

## Conclusion

- Metastable systems relax by the activated growth of localized fluctuations of large amplitude, whereas unstable systems do so by the spontaneous growth of long-wavelength fluctuations of small amplitude



Homogeneous Nucleation

Spinodal Decomposition

# Phase Stability Applications

## Homogeneous Nucleation

- Occurs in the absence of impurities and solid surfaces – small embryos of the new phase are formed within the bulk metastable phase
- It is an activated process: a free energy barrier must be overcome in order to form embryos of a critical size, beyond which the new phase grows spontaneously

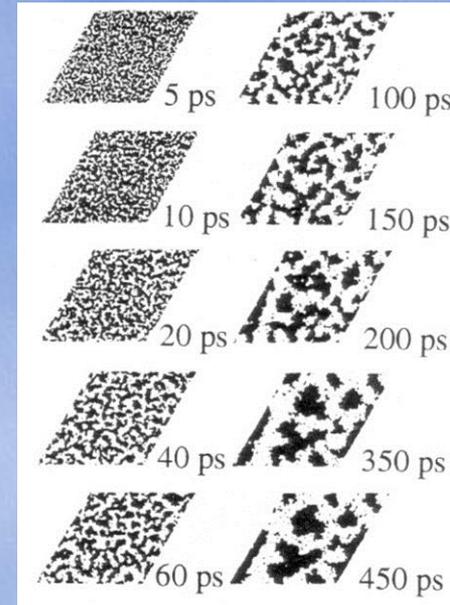
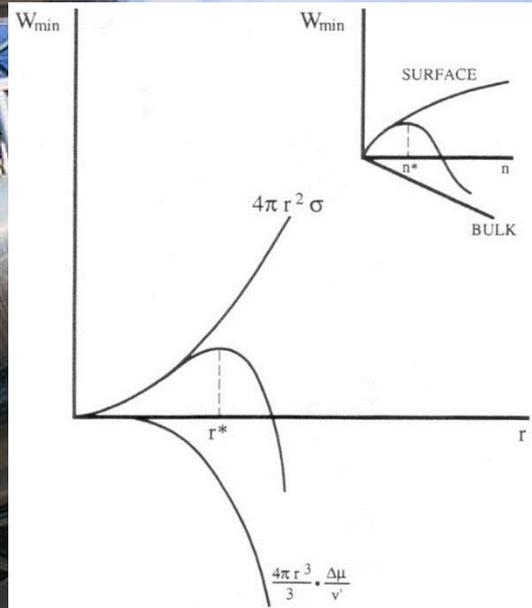
## Spinodal Decomposition

- This mechanism involves the growth of fluctuations of small amplitude that exceed a critical wavelength – the relevant fluctuating property is density for a pure substance and composition for mixtures
- Phase separation occurs spontaneously: no free energy barriers must be overcome
- E.g., when a binary mixture of near-critical composition is rapidly cooled to a subcritical temperature

# Phase Stability Applications

## Conclusion

- Metastable systems relax by the activated growth of localized fluctuations of large amplitude, whereas unstable systems do so by the spontaneous growth of long-wavelength fluctuations of small amplitude



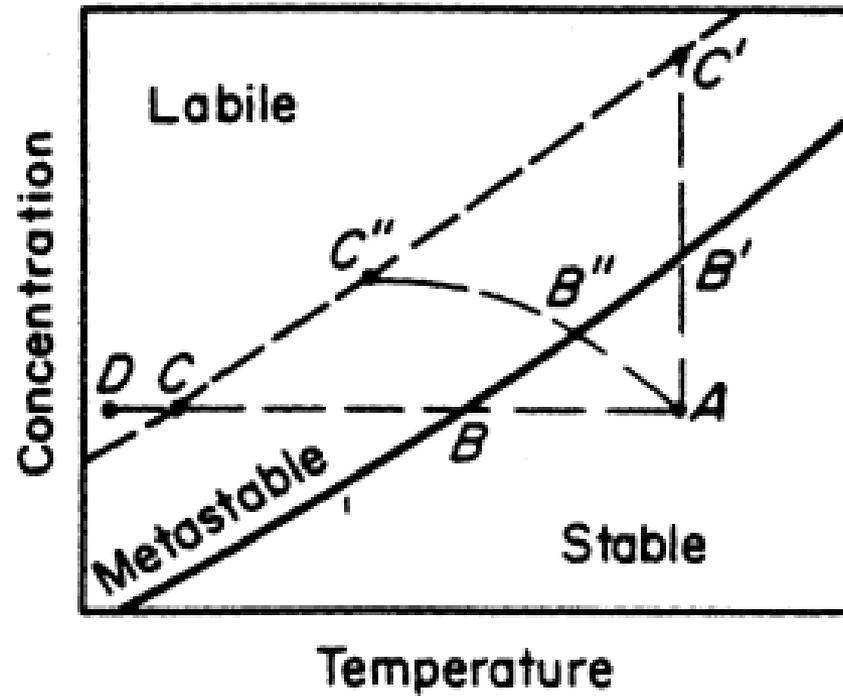
Homogeneous Nucleation

Spinodal Decomposition

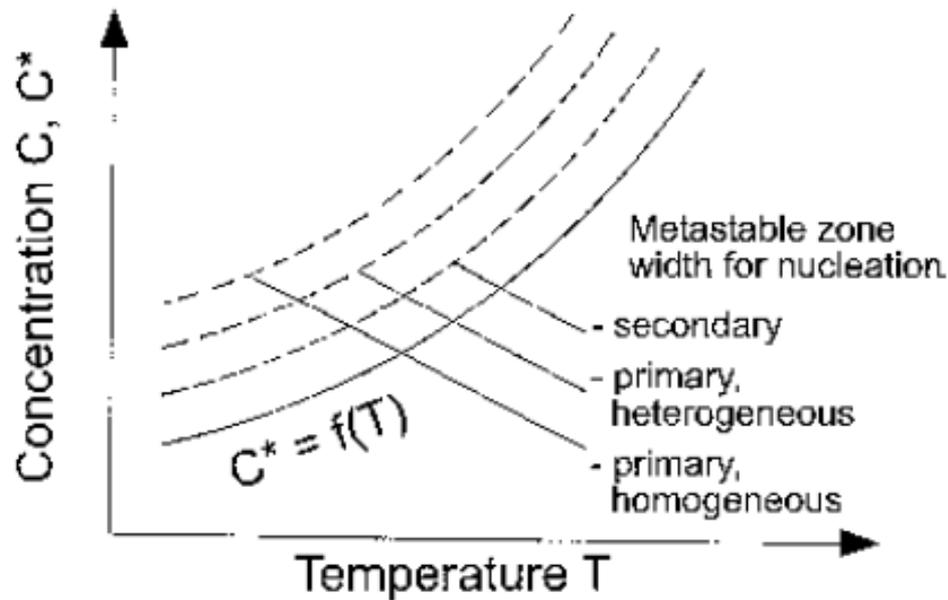
A photograph of an industrial facility with large, shiny metal pipes and structures against a blue sky with light clouds. The pipes are arranged in a complex network, with some curving upwards and others running horizontally. The background shows a clear blue sky with some light, wispy clouds.

## The industrial application

- In industrial crystallizers homogeneous nucleation is not desired
- If large crystals are desired, homogeneous nucleation has to be avoided
- Only if the formation of very fine particles are desired is this method acceptable
- Essential to know  $\Delta c_{\text{met,hom}}$  to be attained for obtaining certain number of homogeneous nuclei :  
Metastable zone width (MZW)



Spinodal: limit of metastable zone

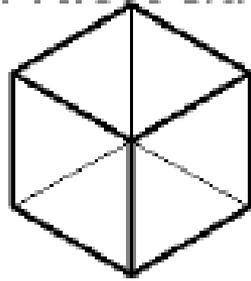


**Figure 0.2.** Metastable supersaturation against temperature for several types of nucleation process.

# Homogeneous nucleation

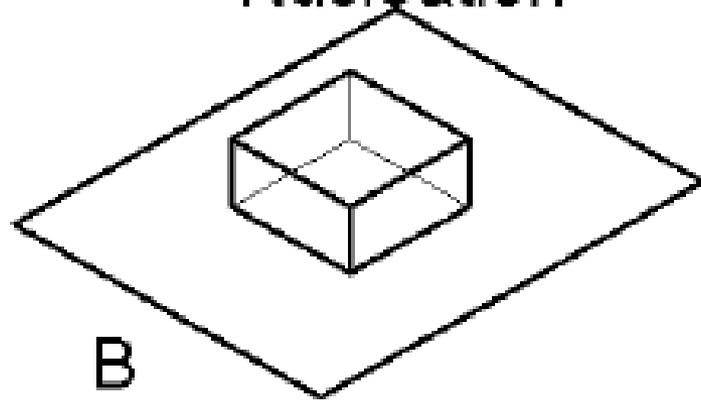
- The precise nature and way in which a nucleus is formed in a supersaturated fluid is not known
- Condensation of supersaturated vapor: formation and re-dissolution of liquid droplets
- The stable nuclei increase in size and are formed by combination of the smaller size nuclei
- 10-thousands units

Homogenous  
Nucleation



A

Heterogeneous  
Nucleation



B

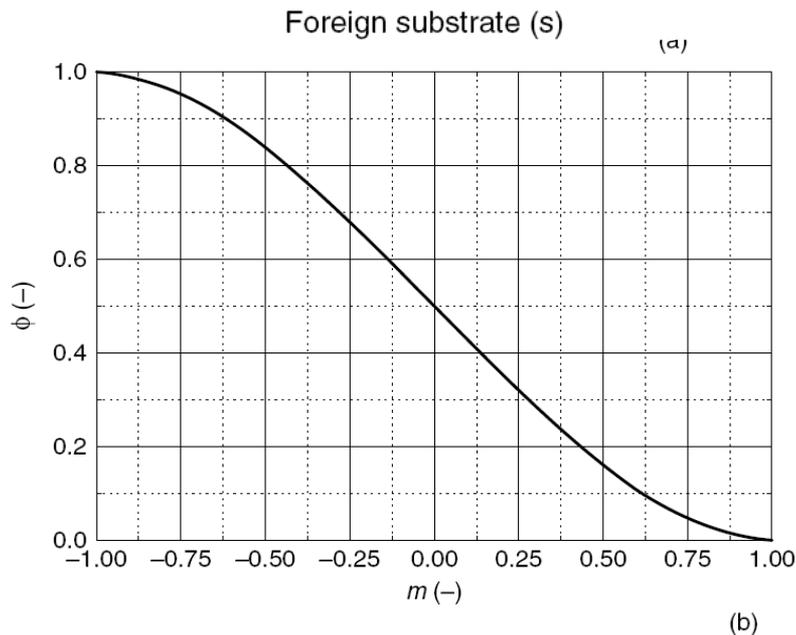
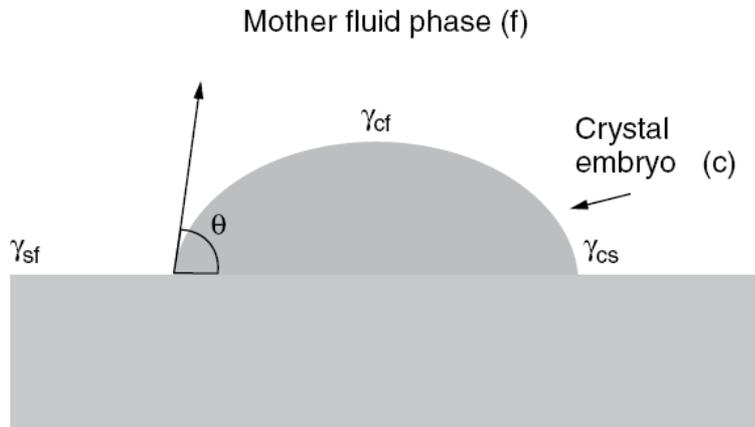
# Ετερογενής πυρηνογένεση

- Η ομογενής 3D πυρηνογένεση μπορεί να γίνει απουσία εξωτερικών παραγόντων οι οποίοι επηρεάζουν είτε την τιμή της κινητικής παραμέτρου  $A$ , είτε την διεπιφανειακή ενέργεια.

Η παρουσία ξένων σωματιδίων ή άλλων ανωμαλιών στον αντιδραστήρα καταλύουν την 3D πυρηνογένεση. Αυτού του είδους η πυρηνογένεση είναι γνωστή ως **3D ετερογενής πυρηνογένεση**.

Ανάλογα με το σχήμα των εμβρύων που σχηματίζονται στο ξένο υπόστρωμα αναπτύσσονται σε 2 ή 3 διαστάσεις. Για παράδειγμα ένα φακοειδές έμβρυο αναπτύσσεται σε 3 διαστάσεις ενώ ένα δισκοειδές σε 2.

- Η πυρηνογένεση σε ξένο υπόστρωμα μπορεί να είναι  $2\Delta$  ή  $3\Delta$  Αν το έμβρυο σχηματίζεται σε επίπεδη επιφάνεια (σχήμα σφαιρικού φακού) με γωνία διαβροχής ισορροπίας που ορίζεται μεταξύ 0 και  $\pi$



$$\cos \theta = (\gamma_{sf} - \gamma_{cs}) / \gamma_{cf} = m$$

$$\phi = (2 + \cos \theta)(1 - \cos \theta)^2 / 4$$