

Module 3: "Nucleation and Growth":

Lecture 19: ""

The Lecture Contains:

Homogeneous Nucleation

- Rate of formation of nuclei
- Nucleation in liquid

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Nucleation and Growth

Nucleation is a physical reaction characterized by localized budding of a distinct thermodynamic phase by precipitation of components from a solution in the form of nuclei inducing more precipitation. In general, a snapshot of the forming condensed phase at any time instant would consist of clusters of particles of varying sizes and numbers which might grow or shrink. Nucleation is said to take place if and only if such a cluster reaches a critical size (i.e. critical radius of nucleation) when it continues to grow rather than shrinking.

Nucleation occurs on nucleation sites contacting the vapor or liquid phases (homogeneous nucleation) or on suspended particles or bubbles (heterogeneous nucleation).

Homogeneous nucleation

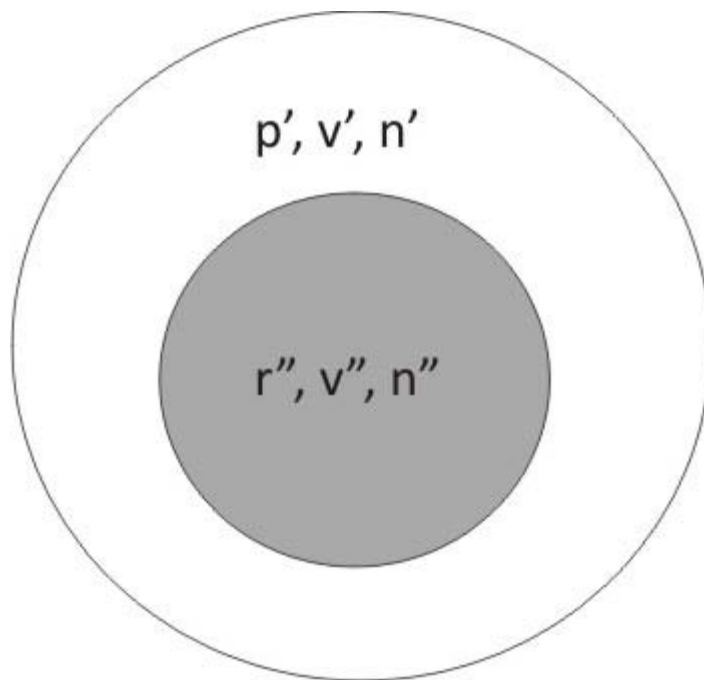


Fig.5.1: Formation of vapor nucleus

In this section we are going to discuss formation of a liquid nucleus from its vapors. When vapors are in supersaturated state they condense to form a liquid nucleus which grows till it comes to equilibrium with the surrounding vapors. Consider a liquid nucleus surrounded by its vapors as a system with a volume V .

We can assume the nucleus to be spherical in shape. For small nuclei sizes this assumption is valid as gravity effects are negligible in this case.

$$n = n' + n'' = \text{constant} \quad (\text{component which suffers phase change})$$

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At constant temperature for closed system,

$$V = V' + V''$$

$$F = U - TS = -pV + \sum n_i \mu_i$$

$$\text{Initial free energy } F_0 = n\mu_v(p'_i) - p'_i V$$

where n is the initial number of moles, p'_i is the initial pressure of the vapor and μ_v is the chemical potential of vapor at p'_i . After formation of liquid nucleus final energy of the system is given by

$$F = -p'V' - p''V'' + n'\mu_v(p') + n''\mu_l(p'') + \gamma A$$

where γA is called the energy penalty because of the formation of a new interface.

Thus the change in free energy of the system is

$$\Delta F = F - F_0$$

Substituting the values of F and ΔF we can write,

$$\Delta F = -p'V' - p''V'' + n'\mu_v(p') + n''\mu_l(p'') + \gamma A - [n\mu_v(p'_i) - p'_i V]$$

$$V' = V - V'' \text{ and } n' = n - n''$$

$$\Delta F = -p'(V - V'') - p''V'' + (n - n'')\mu_v(p') + n''\mu_l(p'') + \gamma A - [n\mu_v(p'_i) - p'_i V]$$

$$\Delta F = V(p' - p''_v) + n''\mu_l(p'') - \mu_v(p') + \gamma A + C \quad (5.1)$$

where $C = -p'V + n + \mu_v(p_v)$ which is independent of n'' .

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From thermodynamics,

$$\mu = \mu^0 + \int_{p_0}^p \bar{V} dp;$$

$$\mu_L^n = \mu_L^0 + \bar{V}^n (p^n - p_0) \quad (5.2)$$

assumption: $\bar{V}^n = \text{constant}$ (incompressible liquid)

similarly for vapor

$$\mu_V^n = \mu_V^0 + \int_{p_0}^{p_v} \frac{RT}{p} dp$$

or

$$\mu_V^n = \mu_V^0 + RT \ln \frac{p_v}{p_0}; \quad (5.3)$$

Substituting values in equation (82) we can write,

$$\Delta F = -V^n (p_0 - p_v) - n^n RT \ln \frac{p_v}{p_0} + \gamma A$$

where p_v is equilibrium vapor pressure for the system, p_0 is the equilibrium vapor pressure for the flat plate case and R is the universal gas constant, $[R = 8.314472 \text{ J. (mol. K)}^{-1}]$

First term on right hand side can be ignored in comparison to second term.

$$\left[V p' = n'' \bar{V} \frac{RT}{\bar{V}'} n' = RT n'' \frac{\bar{V}''}{\bar{V}'} < RT n'' \Rightarrow V'' (p' - p_0) < V'' p' \right]$$

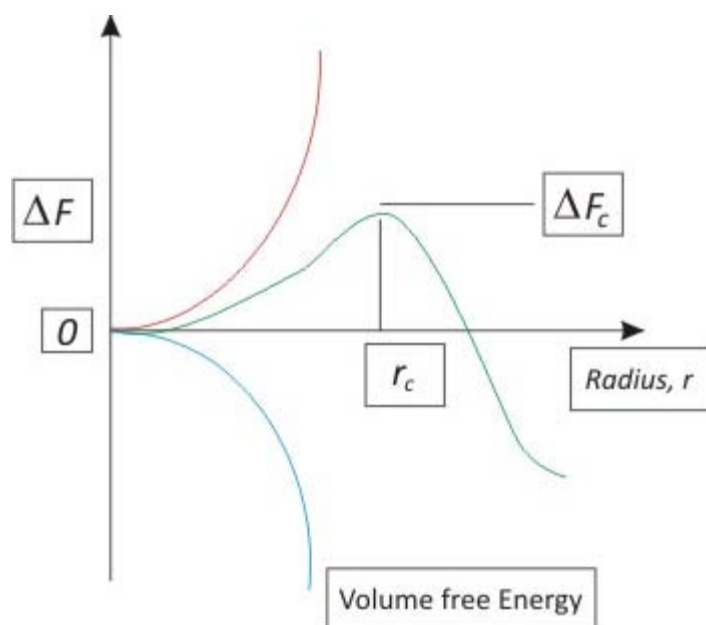


Fig.5.2: Free energy verses distance for a vapor nucleus

where, $n'' = \frac{V''}{\bar{V}''}$

Then the change in free energy is,

$$\Delta F = -\frac{4}{3} \frac{\pi r^3}{\bar{V}''} RT \ln \frac{p_v}{p_0} + 4\pi r^2 \gamma; \quad (5.5)$$

From this expression it can be concluded that the condensation is possible only when the vapors are at a sufficient degree of super saturation. If $p_v < p_0$ then condensation is not thermodynamically favorable. This expression can be expressed in more general form,

$$\Delta F = -ar^3 + br^2$$

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For critical radius (fig:5.2) we can set the $\Delta F' = 0$

or, $\frac{\partial(\Delta F)}{\partial r} = 0$; for critical condition $r = r_c$.

$$\Rightarrow -3ar_c^2 + 2br_c = 0$$

$$\Rightarrow r_c = \frac{2b}{3a};$$

$$\Rightarrow r_c = \frac{2\gamma \bar{V}''}{RT \left[\ln \frac{p_v}{p_0} \right]}; \text{ This is known as Kelvin's equation.}$$

$$\Delta F_c = \left[\frac{16\pi (\bar{V}'')^2 \gamma^3}{3(RT)^2 (\ln x)^2} \right]; \text{ where } x = \frac{p_v}{p_0} > 1$$

ΔF_c is the critical energy barrier that is required to form the nucleus. Higher the degree of super saturation(x) lesser will be the value ΔF_c . This value of ΔF_c corresponds to an unstable equilibrium because when the radius of the nucleus is less than r_c the liquid will evaporate back to form vapors, whereas when the radius is larger than r_c the radius continues to increase further.

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Rate of formation of nuclei

Rate of nucleation (I) = number of critical nucleus per unit volume per time.

$$I \propto \exp(-\Delta F_c/kT) \text{ (for single nuclei)}$$

$$I = Z \exp(-\Delta F_c/kT)$$

where Z is the collision frequency of the gas molecules which can be defined as the number of collisions per unit volume per unit area (*number of collisions/cm³.S*)

For water vapor at 0°C

$$Z = 10^{23} p_v^2 \text{ (}'p_v' \text{ is in mm Hg)}$$

$$I = 10^{23} p_v^2 \exp \left[\frac{-17.5(\bar{V}^n)^2 \gamma^3}{T^3 (\ln x)^2} \right]$$

$$\text{if } \bar{V}^n = 20 \text{ cm}^3/\text{mol}, \gamma = 72 \text{ N/m}$$

$$p_0 = 4.6 \text{ mm Hg}$$

$$p_v = x p_0$$

$$\Rightarrow x = \frac{p_v}{p_0}$$

Then the critical rate of nucleation (I_c) can be expressed as,

$$I_c = 2 \times 10^{24} x^2 \exp \left[\frac{-118}{(\ln x)^2} \right]$$

where the unit of [*# molecules/(cm³ x sec)*]

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If we calculate the values of I_c for different x values, a table can be drawn as follows,

Table 5.1: **Variation of I_c with x**

| x | I_c |
|-----|------------|
| 1 | 0 |
| 3 | 10^{-17} |
| 4 | 0.15 |
| 4.5 | 10^3 |

A graph can be plotted with these values which are shown in the Figure 5.3.

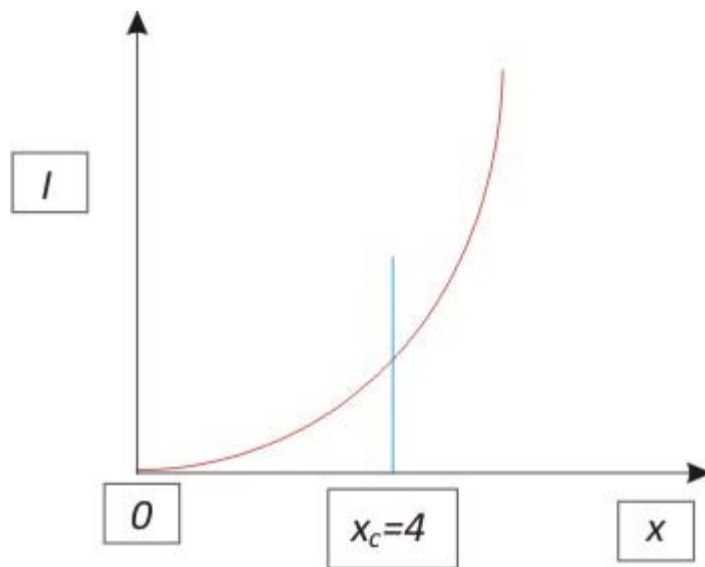


Fig.5.3: Plot of rate of nucleation versus x

As seen from the table and the above figure that for the pressure ratio (p_v/p_0) goes between 4 to 4.5 there is a sharp rise in the rate of nucleation, we can infer that for achieving a considerable degree of nucleation, a certain minimum degree of super-saturation is necessary.

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Nucleation in liquid

Crystallization of liquid to solid is initiated by cooling of the melt.

In this case, from the *Clausius-Clapeyron* relation we can write,

$$\ln x = \frac{\Delta H_v}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

where x is defined as, $x = \frac{p_l}{p_v}$; ratio of liquid to solid equilibrium vapor pressure.

T and p_l are a corresponding temperature (in units of kelvins or other absolute temperature units) and equilibrium vapor pressure of the liquid

T_0 and p_v are the corresponding temperature and pressure of the solid at another point

H_v is the molar enthalpy of vaporization

R is the universal gas constant [$R = 8.314472 \text{ J} \cdot (\text{mol} \cdot \text{K})^{-1}$]

This is valid for $T < T_0$, which indicates that subcooling is needed.

At equilibrium we can write,

$\Delta H_v = \Delta H_f$ (heat of fusion) or, molar enthalpy of vaporization.

Then we can get,

$$\Delta F_c = \frac{16\pi \bar{V}^3 \gamma^3}{3(RT)^2 (\ln x)^2} = \frac{16\pi \gamma^3 \bar{V}^3 T_0^2}{3[\Delta H_f (T - T_0)]^2};$$

where $(T - T_0) = \Delta T$ represents the degree of sub cooling, ΔH_f is heat of fusion.

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Rate of nucleation (I) in liquid depends on two phenomenon:

- Diffusion effects:

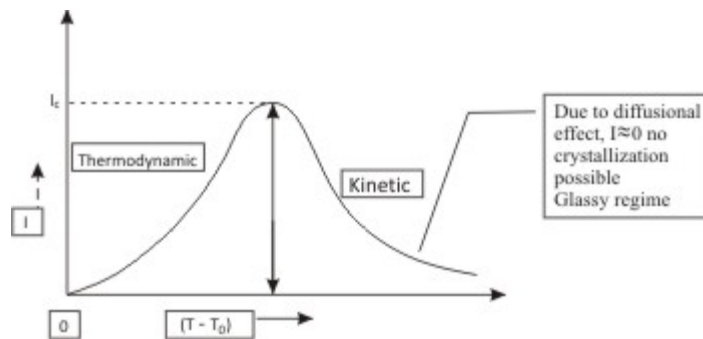


Fig. 5.4: Variation of rate of nucleation (I) with temperature

Diffusion resistance hinders the rate of nucleation. Liquid molecules add on to the solid by diffusion. If it is not an amorphous solid, but rather a crystal, there must be reorganization of molecules which can fit into a fixed place.

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- Critical energy barrier (ΔF_c)

$$I_c \propto nkT \exp\left(-\frac{\Delta F_c}{kT}\right) \exp\left(-\frac{\Delta F_D}{kT}\right); \text{ where } \Delta F_D \text{ is activation energy for diffusion}$$

And n is the number of molecules per unit volume.

This indicates that as T increases the kinetic factor increases. The simple relation for solids close to T_0 can be written as,

$$I = 10^{23} \exp\left(\frac{-\Delta F_c}{KT}\right)$$

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This can be rewritten in the following form,

$$I = cT \exp \left(- \frac{A}{kT} \right)$$

where 'A' can be written as,

$$A = \Delta F_D + \frac{4\pi\gamma}{3} \left(\frac{2\bar{V}^n \gamma T_0^2}{\Delta H_f \Delta T} \right) \tag{5.8}$$

The first half of the graph(Figure : 5.4) with increasing slope is the thermodynamic curve (ΔF_c) and the second half with decreasing slope is due to diffusion (ΔF_D) called kinetic curve. Thus when one quenches the liquid very rapidly, diffusion rate becomes high and the rate of formation of nucleus (crystal) is suppressed. Glass is formed with this technique. Equation derived for ΔF_c can also be used for supersaturated solutions where x can be written as:

$$x = \frac{a}{a_0} \tag{5.9}$$

where a and a_0 is the actual activity and equilibrium activity of solute respectively. For an ideal solution activity of the solute is same as that of its concentration. Thus we can write ,

$$x = \frac{a}{a_0} = \frac{C}{C_0} \text{ (}\neq \text{ For electrolytes)} \tag{5.10}$$