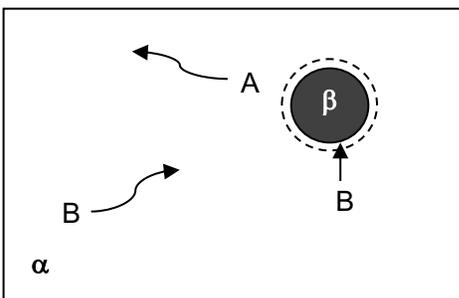


## Lecture 17: Kinetics of Phase Growth in a Two-component System:

### description of diffusion flux across the $\alpha/\beta$ interface

#### Today's topics

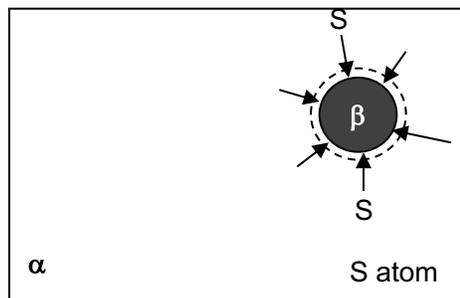
- Major tasks of today's Lecture: how to derive the diffusion flux of atoms.
- Once an incipient nucleus has reached its critical size ( $r^*$ ), the surface energy that restricts the development of the new phase become insignificant and the kinetics for growth are becoming dominated by the limiting kinetic mechanism, i.e., the migration or jumping of atoms from  $\alpha$  matrix to  $\beta$  particle.
- If the phase growth requires no long-range diffusion of atoms, then the rate of growth is controlled by the rate of atomic transfer across the growing particle interface. This is usually the case of *single-component* phase transformation as we discussed in lecture 15.
- However, for the *two-component* phase transformation (particularly in the case of dilute solution of one phase dispersed in another), growth of the minor phase usually requires long-range diffusion. In this case, the growth rate can be determined by two different rate-limiting processes: *Interface Limited Growth* and *Diffusion Limited Growth*. Both of these two processes are temperature dependent --- typically the growth rate is Arrhenius type with growth becoming very slow at low temperatures.
- Interface Limited Growth: In this case, growth is limited by how fast atoms can transfer across the  $\alpha/\beta$  interface and not the rate at which atoms can be transported to the growing interface. This is equivalent to growth where no long-range diffusion is required (like that described in Lecture 15 for the single-component system).
- Diffusion Limited Growth: In this case, the growth rate is limited by the diffusivity, i.e., how fast the necessary atoms are transfer from the  $\alpha$  matrix to the growing  $\beta$ -particles. In general, the rate of diffusion transport falls off very quickly with temperature.



Two-component system

Concentration of B atoms at beginning,

$$C_0, X_A \gg X_B$$



single-component system (Lecture 15)

The following kinetics treatment applies only to the dilute-solution of  $\alpha$  phase containing small molar fraction of  $\beta$  phase, i.e., molar fraction of B ( $X_B$ )  $\ll$  molar fraction of A ( $X_A$ ).

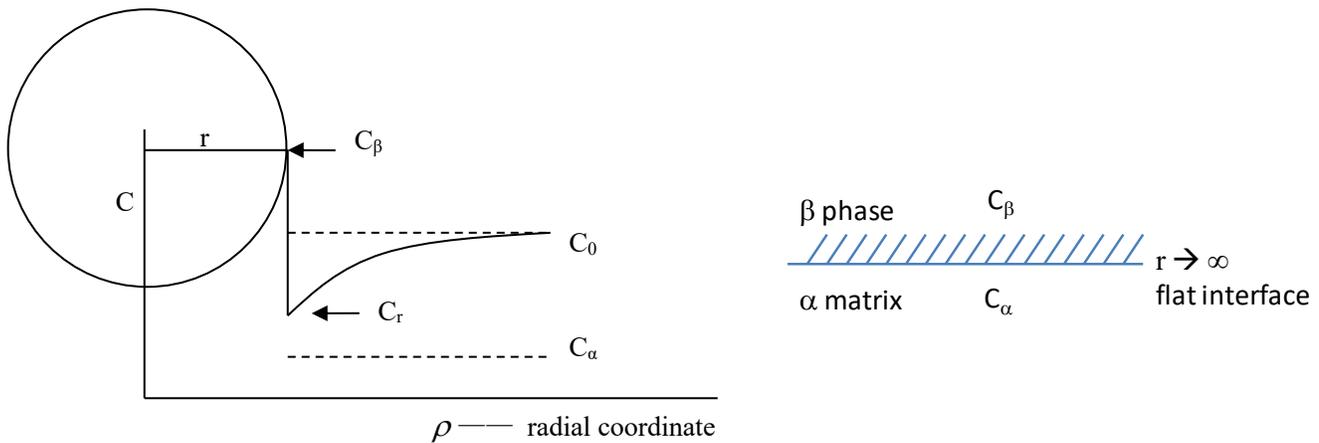
In last Lecture, we derived the diffusion flux of B atoms across the  $\alpha/\beta$  interface:

$$J = M (C_r - C_\alpha) \quad (1)$$

Where M is defined as an **interface parameter**, a measure of the transport kinetics of atoms across the  $\alpha/\beta$  interface, C has the unit of  $\#/cm^3$ , M has the unit of cm/sec.

**Deriving the diffusion flux via Fick's law:**

Here again the plot describing the concentration of B as a function of the radial coordinate ' $\rho$ ' from the center of the  $\beta$  particle of radius r:



Fick's first Law:  $J = -D \frac{dc}{d\rho}$

The pertinent diffusion equation is Fick's second law

$$\frac{\partial c}{\partial t} = D \nabla^2 C \quad (\text{Assume D is constant})$$

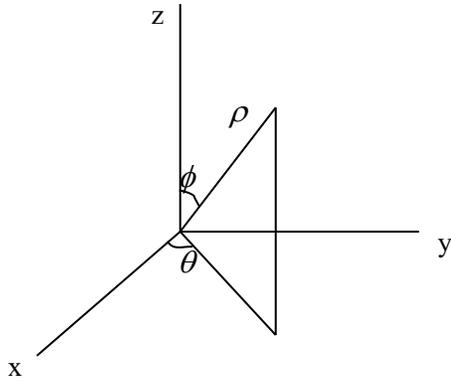
Assuming a quasi-steady state in the  $\alpha$  phase,

$$\frac{\partial c}{\partial t} = 0 \rightarrow \nabla^2 C = 0$$

In three dimensions, in Cartesian coordinates, we have

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In spherical polar coordinate:  $x = \rho \sin \phi \cos \theta$



$$y = \rho \sin \phi \sin \theta$$

$$z = \rho \cos \phi$$

For a spherically symmetric case

No dependence on  $\phi$  and  $\theta$

$$\nabla^2 = \frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho}$$

Thus,  $\nabla^2 C = 0 \rightarrow \frac{d^2 c}{d\rho^2} + \frac{2}{\rho} \frac{dc}{d\rho} = 0$

Then we have:

$$C(\rho) = \frac{a}{\rho} + b$$

Where a, b are constants.

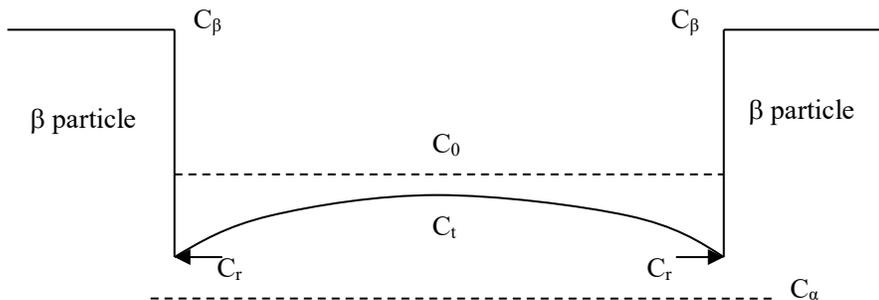
Now consider two limiting conditions:

1. As  $\rho \rightarrow \infty$ ,  $C(\rho) = C_0$ , then we have  $b = C_0$

2. As  $\rho \rightarrow r$ ,  $C(\rho) = C_r$ , then we have  $C_r = \frac{a}{r} + C_0$ , then we have  $a = (C_r - C_0)r$

So,  $C(\rho) = C_0 + \frac{(C_r - C_0)r}{\rho} = C_0 - \frac{(C_0 - C_r)r}{\rho}$ ;  $\rho \geq r$

This assumes that concentration in the matrix far away from the growing particle is  $C_0$ . In general, however, there will be other  $\beta$  particles, all competing for B atoms at same time. The net effect is that the average concentration in the bulk is lower than  $C_0$  as described in the diagram below. Also, this average concentration in the bulk is time dependent, now marked as  $C_t$ .



So the above equation can be re-written as

$$C(\rho) = C_t - \frac{(C_t - C_r)r}{\rho}$$

Then the concentration gradient in  $\alpha$  next to  $\beta$  particle is

$$\left(\frac{dc}{d\rho}\right)\Big|_{\rho=r} = \frac{C_t - C_r}{r}$$

Now, with the Fick's first Law, we have

$$J = J' = \left|D\left(\frac{dc}{d\rho}\right)_{\rho=r}\right| = \frac{D(C_t - C_r)}{r} \quad (2)$$

Here we use  $J'$  just in order to distinct the flux from the other two as deduced in Eq. (1) and (3) below.

In a quasi-steady state, the diffusion flux in bulk phase is equal to the flux as described above for the local cross-interface diffusion as shown in Eq. (1)

$$J = M (C_r - C_\alpha) \quad (1)$$

**The third way to derive the diffusion flux:**

As B atoms cross the  $\alpha/\beta$  interface, the radius of  $\beta$  increases. In time interval  $dt$ , the radius increases by  $dr$ , the volume of  $\beta$  increases by  $4\pi r^2 dr$ . The composition in this region changes from  $C_t$  to  $C_\beta$ , and the # of B atoms arrived in time  $dt$  in the volume element is

$$(C_\beta - C_t) 4\pi r^2 dr \approx C_\beta 4\pi r^2 dr, \quad \text{as } C_\beta \gg C_t$$

The area through which B atoms arrived is  $4\pi r^2$ , thus, # of B atom crossing the  $\alpha/\beta$  interface per unit area per unit time, i.e., the flux, is

$$J'' = \frac{C_\beta 4\pi r^2 dr}{4\pi r^2 dt} = C_\beta \frac{dr}{dt} \quad (3)$$

Here we use  $J''$  just in order to distinct the flux from the other two as deduced in Eq. (1) and (2)

In a quasi-steady state, all three fluxes  $J$ ,  $J'$ ,  $J''$  as deduced above in Eqs. (1)(2)(3) are equal,

$$J = J' = J''$$

or

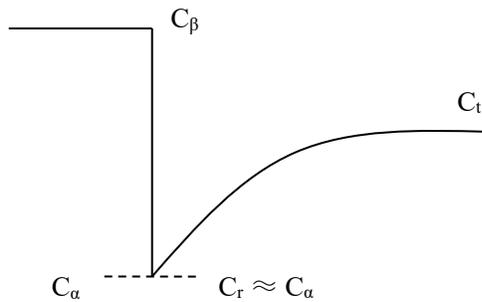
$$C_\beta \frac{dr}{dt} = \frac{D(C_t - C_r)}{r} = M(C_r - C_\alpha)$$

First, from  $\frac{D(C_t - C_r)}{r} = M(C_r - C_\alpha)$ , we have

$$C_r = \frac{DC_t + rMC_\alpha}{D + rM}$$

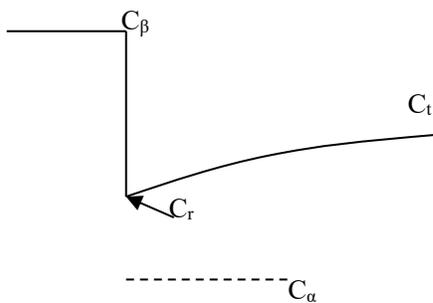
Let's examine two limiting cases:

1. when  $rM \gg D$ : Then  $C_r \approx C_\alpha$  **This is the diffusion limited case**, where the consumption of B atoms around the  $\beta$  particle is so rapid that the local concentration of B reaches the equilibrium concentration of B in  $\alpha$  phase,  $C_\alpha$ .



In this case, there is very small buildup of B atoms near the  $\beta$  particles.

2. when  $D \gg rM$ : Then  $C_r \approx C_t$  **This is the interface limited case**, where the consumption of B atoms around the  $\beta$  particle is so slow compared to the long-range diffusion flux from the bulk  $\alpha$  phase that the local concentration of B remains approximately the same as the bulk concentration of B in  $\alpha$  phase,  $C_t$ .



In this case, diffusion is fast and growth is interface-controlled. There is a large buildup of B next to  $\beta$ .

**Wert & Zener** examined diffusion limited growth, **Johnson, Mehl & Avrami** examined interface limited growth (Lecture 15).

Next Lecture, we will address the general case that considers both the two kinetics processes.