Lecture 3: Introduction to Diffusion

Mass transport in a gas or liquid generally involves the flow of fluid (*e.g.* convection currents) although atoms also diffuse. Solids on the other hand, can support shear stresses and hence do not flow except by diffusion involving the jumping of atoms on a fixed network of sites.

Assume that such jumps can somehow be achieved in the solid state, with a frequency ν with each jump over a distance λ.

For random jumps, the root mean square distance is

$$\overline{x} = \lambda\sqrt{n} \qquad \text{where } n \text{ is the number of jumps}$$

$$= \lambda\sqrt{\nu t} \qquad \text{where } t \text{ is the time}$$

diffusion distance $\propto \sqrt{t}$

Diffusion in a Uniform Concentration Gradient

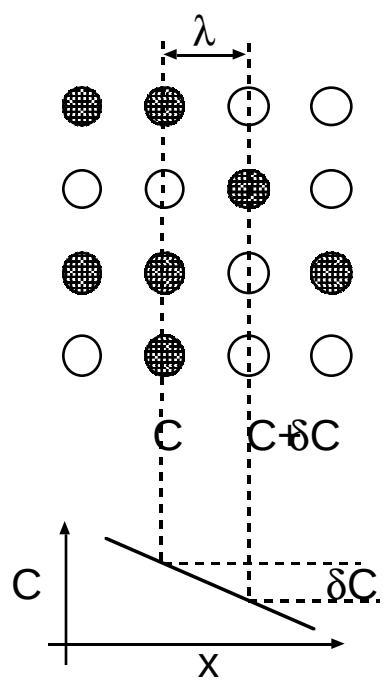

Fig. 1: Diffusion Gradient

Concentration of solute, C, number m^{-3}
Each plane has $C\lambda$ atoms m^{-2} (Fig. 1)

$$\delta C = \lambda \left\{ \frac{\partial C}{\partial x} \right\}$$

Atomic flux, J, atoms $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$

$$J_{L\to R} = \frac{1}{6}\nu C\lambda$$
$$J_{R\to L} = \frac{1}{6}\nu (C + \delta C)\lambda$$

Therefore, the net flux along x is given by

$$\begin{aligned} J_{net} &= -\frac{1}{6}\nu\,\delta C\,\lambda \\ &= -\frac{1}{6}\nu\,\lambda^2 \left\{ \frac{\partial C}{\partial x} \right\} \\ &\equiv -D \left\{ \frac{\partial C}{\partial x} \right\} \end{aligned}$$

This is Fick's first law where the constant of proportionality is called the diffusion coefficient in $\mathrm{m}^2\,\mathrm{s}^{-1}$. Fick's first law applies to steady state flux in a uniform concentration gradient. Thus, our equation for the mean diffusion distance can now be expressed in terms of the diffusivity as

$$\overline{x} = \lambda\sqrt{\nu t} \qquad \text{with} \qquad D = \frac{1}{6}\nu\lambda^2 \qquad \text{giving} \qquad \overline{x} = \sqrt{6Dt} \simeq \sqrt{Dt}$$

Non–Uniform Concentration Gradients

Suppose that the concentration gradient is not uniform (Fig. 2).

$$\begin{aligned} \text{Flux in} \qquad &= -D \left\{ \frac{\partial C}{\partial x} \right\}_1 \\ \text{Flux out} \qquad &= -D \left\{ \frac{\partial C}{\partial x} \right\}_2 \\ &= -D \left[\left\{ \frac{\partial C}{\partial x} \right\}_1 + \delta x \left\{ \frac{\partial^2 C}{\partial x^2} \right\} \right] \end{aligned}$$

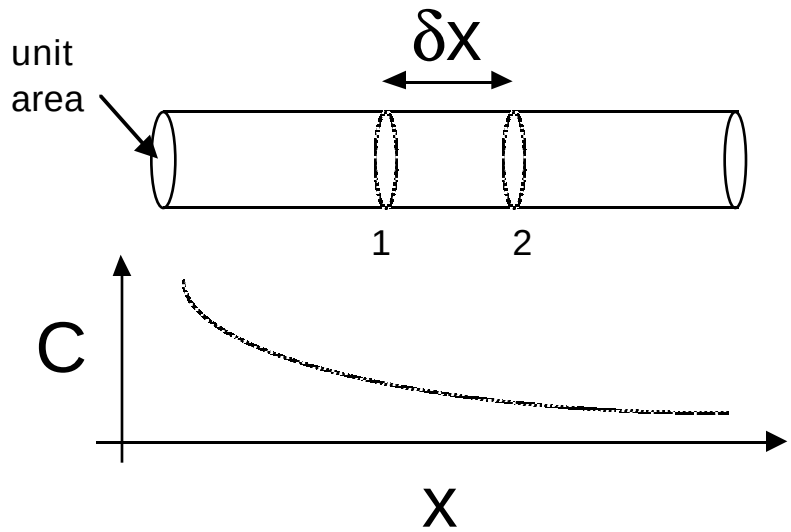

Fig. 2: Non–uniform concentration gradient

In the time interval δt, the concentration changes δC

$$\delta C \delta x = (\text{Flux in} - \text{Flux out})\delta t$$
$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

assuming that the diffusivity is independent of the concentration. This is Fick's second law of diffusion.

This is amenable to numerical solutions for the general case but there are a couple of interesting analytical solutions for particular boundary conditions. For a case where a fixed quantity of solute is plated onto a semi–infinite bar (Fig. 3),

$$\text{boundary conditions:} \qquad \int_0^\infty C\{x,t\}dx = B$$
$$\text{and} \qquad C\{x, t=0\} = 0$$

$$C\{x,t\} = \frac{B}{\sqrt{\pi D t}} \exp\left\{ \frac{-x^2}{4Dt} \right\}$$

Now imagine that we create the diffusion couple illustrated in Fig. 4, by stacking an infinite set of thin sources on the end of one of the bars. Diffusion can thus be treated by taking a whole set of the exponential

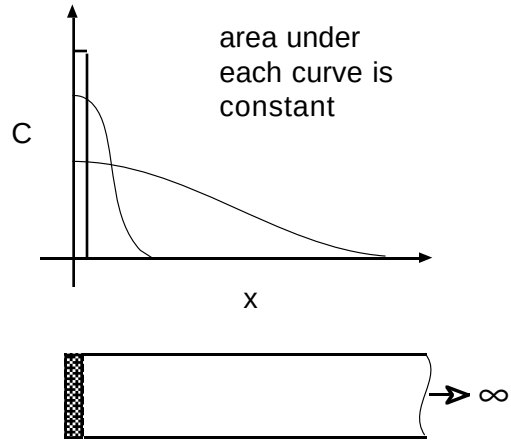

Fig. 3: Exponential solution. Note how the curvature changes with time.

functions obtained above, each slightly displaced along the x axis, and summing (integrating) up their individual effects. The integral is in fact the error function

$$\mathrm{erf}\{x\} = \frac{2}{\sqrt{\pi}} \int_0^x \exp\{-u^2\} du$$

so the solution to the diffusion equation is

$$\begin{aligned} \text{boundary conditions:} \qquad & C\{x=0,t\} = C_s \\ \text{and} \qquad & C\{x,t=0\} = C_0 \end{aligned}$$

$$C\{x,t\} = C_s - (C_s - C_0)\mathrm{erf}\left\{ \frac{x}{2\sqrt{Dt}} \right\}$$

This solution can be used in many circumstances where the surface concentration is maintained constant, for example in the carburisation or decarburisation processes (the concentration profiles would be the same as in Fig. 4, but with only one half of the couple illustrated). The solutions described here apply also to the diffusion of heat.

Mechanism of Diffusion

Atoms in the solid–state migrate by jumping into vacancies (Fig. 5). The vacancies may be interstitial or in substitutional sites. There is,

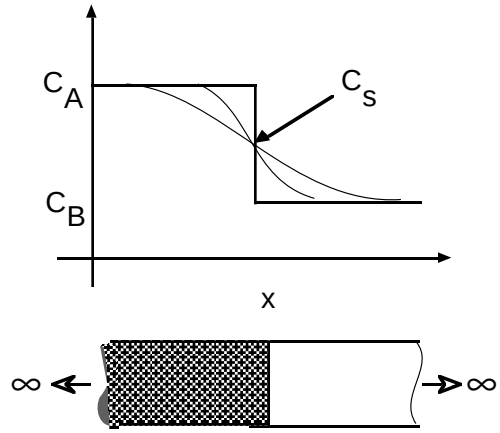

Fig. 4: The error function solution. Notice that the "surface" concentration remains fixed.

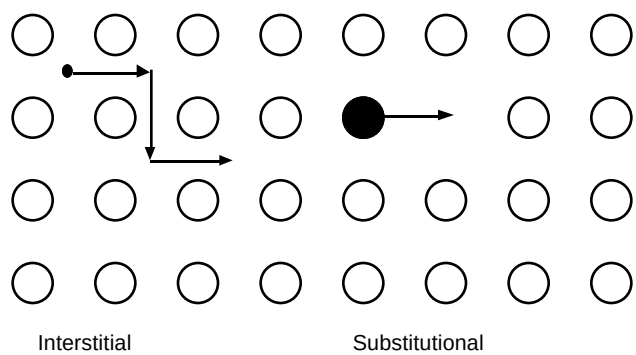

Fig. 5: Mechanism of interstitial and substitutional diffusion.

nevertheless, a barrier to the motion of the atoms because the motion is associated with a transient distortion of the lattice.

Assuming that the atom attempts jumps at a frequency ν_0, the frequency of successful jumps is given by

$$\begin{aligned}\nu &= \nu_0 \exp\left\{-\frac{G^*}{kT}\right\} \\ &\equiv \underbrace{\nu_0 \exp\left\{\frac{S^*}{k}\right\}}_{\text{independent of } T} \times \exp\left\{-\frac{H^*}{kT}\right\}\end{aligned}$$

where k and T are the Boltzmann constant and the absolute tempera-

ture respectively, and H^* and S^* the activation enthalpy and activation entropy respectively. Since

$$D \propto \nu \qquad \text{we find} \qquad D = D_0 \exp\left\{-\frac{H^*}{kT}\right\}$$

A plot of the logarithm of D versus $1/T$ should therefore give a straight line (Fig. 6), the slope of which is $-H^*/k$. Note that H^* is frequently called the activation energy for diffusion and is often designated Q.

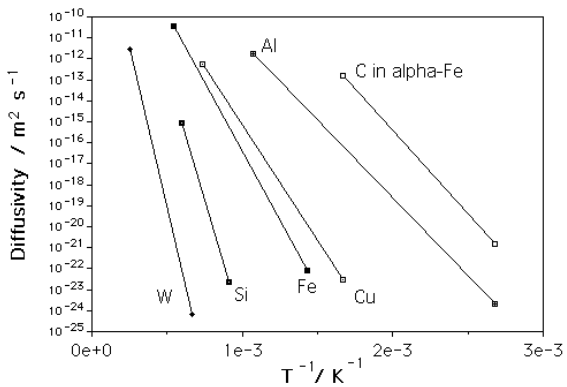

Fig. 6: Typical self–diffusion coefficients for pure metals and for carbon in ferritic iron. The uppermost diffusivity for each metal is at its melting temperature.

The activation enthalpy of diffusion can be separated into two components, one the enthalpy of migration (due to distortions) and the enthalpy of formation of a vacancy in an adjacent site. After all, for the atom to jump it is necessary to have a vacant site; the equilibrium concentration of vacancies can be very small in solids. Since there are many more interstitial vacancies, and since most interstitial sites are vacant, interstitial atoms diffuse far more rapidly than substitutional solutes.

Kirkendall Effect

Diffusion is at first sight difficult to appreciate for the solid state. A number of mechanisms have been proposed historically. This includes a variety of ring mechanisms where atoms simply swap positions, but controversy remained because the strain energies associated with such swaps made the theories uncertain. One possibility is that diffusion occurs by

atoms jumping into vacancies. But the equilibrium concentration of vacancies is typically 10^{-6}, which is very small. The theory was therefore not generally accepted until an elegant experiment by Smigelskas and Kirkendall (Fig. 7).

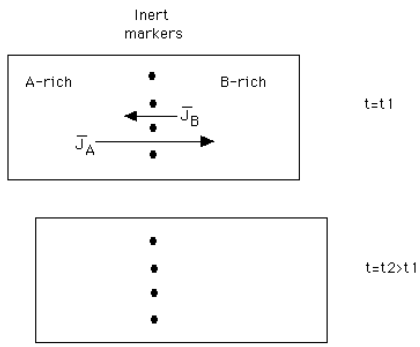

Fig. 7: Diffusion couple with markers

The experiment applies to solids as well as cible liquids. Consider a couple made from A and B. If the diffusion fluxes of the two elements are different ($|J_A| > |J_B|$) then there will be a net flow of matter past the inert markers, causing the couple to shift bodily relative to the markers. This can only happen if diffusion is by a vacancy mechanism.

An observer located at the markers will see not only a change in concentration due to intrinsic diffusion, but also because of the Kirkendall flow of matter past the markers. The net effect is described by the usual Fick's laws, but with an interdiffusion coefficient $\overline{D}$ which is a weighted average of the two intrinsic diffusion coefficients:

$$\overline{D} = X_B D_A + X_A D_B$$

where X represents a mole fraction. It is the interdiffusion coefficient that is measured in most experiments.

Structure Sensitive Diffusion

Crystals may contain nonequilibrium concentrations of defects such as vacancies, dislocations and grain boundaries. These may provide easy diffusion paths through an otherwise perfect structure. Thus, the grain boundary diffusion coefficient D_{gb} is expected to be much greater than the diffusion coefficient associated with the perfect structure, D_P.

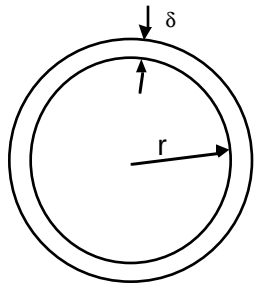

Fig. 8: Idealised grain

Assume a cylindrical grain. On a cross section, the area presented by a boundary is $2\pi r\delta$ where δ is the thickness of the boundary. Note that the boundary is shared between two adjacent grains so the thickness associated with one grain is $\frac{1}{2}\delta$. The ratio of the areas of grain boundary to grain is therefore

$$\text{ratio of areas} = \frac{1}{2} \times \frac{2\pi r\delta}{\pi r^2} = \frac{\delta}{r} = \frac{2\delta}{d}$$

where d is the grain diameter (Fig. 8).

For a unit area, the overall flux is the sum of that through the lattice and that through the boundary:

$$J \simeq J_P + J_{gb}\frac{2\delta}{d}$$

$$\text{so that} \qquad D_{measured} = D_P + D_{gb}\frac{2\delta}{d}$$

Note that although diffusion through the boundary is much faster, the fraction of the sample which is the grain boundary phase is small. Consequently, grain boundary or defect diffusion in general is only of importance at low temperatures where $D_P \ll D_{gb}$ (Fig. 9).

Thermodynamics of diffusion

Fick's first law is empirical in that it assumes a proportionality between the diffusion flux and the concentration gradient. However, diffusion occurs so as to minimise the free energy. It should therefore be driven by a gradient of free energy. But how do we represent the gradient in the free energy of a particular solute?

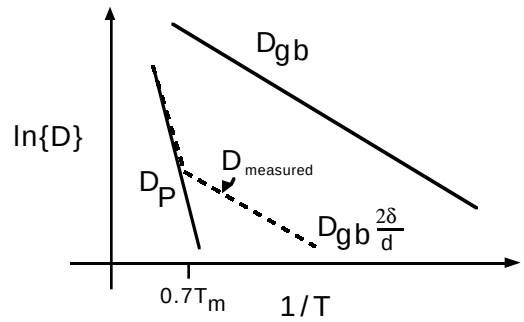

Fig. 9: Structure sensitive diffusion. The dashed line will in practice be curved.

Diffusion in a Chemical Potential Gradient

Fick's laws are strictly empirical. Diffusion is driven by gradients of free energy rather than of chemical concentration:

$$J_A = -C_A M_A \frac{\partial \mu_A}{\partial x} \qquad \text{so that} \qquad D_A = C_A M_A \frac{\partial \mu_A}{\partial C_A}$$

where the proportionality constant M_A is known as the mobility of A. In this equation, the diffusion coefficient is related to the mobility by comparison with Fick's first law. The chemical potential is here defined as the free energy per mole of A atoms; it is necessary therefore to multiply by the concentration C_A to obtain the actual free energy gradient.

The relationship is remarkable: if $\partial \mu_A / \partial C_A > 0$, then the diffusion coefficient is positive and the chemical potential gradient is along the same direction as the concentration gradient. However, if $\partial \mu_A / \partial C_A < 0$ then the diffusion will occur against a concentration gradient!