

MSE307 Unit 2—Outline of Diffusion Theory

1. Fick's first law

We will begin our discussion of diffusion in metals and alloys with the phenomenological Fick's first law,

$$J_i = -D_i \frac{dc_i}{dz} \quad (1.1)$$

This relates directly to experience and states that the flux of moles of component i , J_i , in units of mole $\text{m}^{-2} \text{s}^{-1}$ (the number of moles that pass through a unit area normal to the flow per unit time) is directly proportional to minus the gradient in concentration. Here, concentration, c_i , is the concentration of component i in moles m^{-3} . In these notes we will keep things simple and consider just one dimensional diffusion in the z -direction. In full vector notation Fick's first law is

$$\mathbf{J}_i = -D_i \nabla c_i$$

The constant of proportionality is the diffusion coefficient, or diffusivity. It has the dimensions of $\text{m}^2 \text{s}^{-1}$. These units are shared by the coefficients in the transport of heat and momentum. The thermal diffusivity, κ , is the ratio of the thermal conductivity, k , from Fourier's law and the heat capacity per unit volume; the kinematic viscosity, ν , is the viscosity, η , from Newton's law divided by the mass density. All these transport coefficients, D , κ and ν have the dimensions $\text{m}^2 \text{s}^{-1}$.

2. Mobility

At a more fundamental level, we think of the speed of a diffusing particle as the product of the force acting on the particle and its *mobility*. For example in semiconductor materials science and electronic engineering we write for the drift velocity of a carrier (electron or hole)

$$v_d = \mu_d E = \mu_d \frac{d\phi}{dz} \quad (2.1)$$

where ϕ is the electric potential, E is the electric field in V m^{-1} (or newton per coulomb, N C^{-1}) and μ_d is the *mobility* in $\text{C m}^2 \text{s}^{-1} \text{J}^{-1}$. This formula would apply also for the migration of an ion in a fuel cell. The mobility is proportional to the carrier's charge.

You know from your thermodynamics notes (**unit 2D**) that fundamentally the driving force for solid state diffusion is the gradient in chemical potential, not concentration. So to begin with we are tempted to write down

$$J_i = -c_i \mathcal{M}_i \frac{d\mu_i}{dz}$$

with \mathcal{M} having the units of mole $\text{m}^2 \text{s}^{-1} \text{J}^{-1}$. The inclusion of the factor c_i makes sense for dimensional reasons: the units of μ_d for the case of the charged carrier are

the same as those of \mathcal{M} except that the charge unit is replaced by the mole unit—each representing the amount of quantity that is responding to the force. Of course to arrive at a more standard form it is sufficient to define a new mobility, M , by

$$M_i = c_i \mathcal{M}_i \quad (2.2)$$

and then we have

$$J_i = -M_i \frac{d\mu_i}{dz} \quad (2.3)$$

But M has the crazy units of $\text{mole}^2 \text{m}^{-2} \text{s}^{-1} \text{J}^{-1}$. We would like to make contact between the phenomenological Fick's law (1.1) and the more physically motivated (2.3); in other words what is the relation between diffusivity and mobility? Recall equation (3.1) from **unit 2D** and write

$$\begin{aligned} \mu_i &= \mu_i^\circ + RT \ln a_i \\ &= \mu_i^\circ + RT \ln x_i + RT \ln \gamma_i \end{aligned}$$

Then

$$\frac{d\mu_i}{dz} = RT \left(\frac{d \ln x_i}{dz} + \frac{d \ln \gamma_i}{dz} \right)$$

and so (2.3) can be written

$$\begin{aligned} J_i &= -RT M_i \left(\frac{d \ln x_i}{dz} + \frac{d \ln \gamma_i}{dz} \right) \\ &= -RT M_i \left(\frac{d \ln x_i}{dz} + \frac{d \ln \gamma_i}{d \ln x_i} \frac{d \ln x_i}{dz} \right) \\ &= -RT M_i \frac{1}{x_i} \left(\frac{dx_i}{dz} + \frac{d \ln \gamma_i}{d \ln x_i} \frac{dx_i}{dz} \right) \\ &= -RT M_i \frac{1}{c_i} \left(1 + \frac{d \ln \gamma_i}{d \ln x_i} \right) \frac{dc_i}{dz} \end{aligned} \quad (2.4a)$$

$$= -RT \mathcal{M}_i \left(1 + \frac{d \ln \gamma_i}{d \ln x_i} \right) \frac{dc_i}{dz} \quad (2.4b)$$

If the solid solution is *ideal* or it follows either Raoult's or Henry's laws, then the activity coefficient is either one or a constant and so its derivative with respect to anything is zero and (2.4b) reduces simply to

$$\begin{aligned} J_i &= -RT \mathcal{M}_i \frac{dc_i}{dz} && \longleftarrow \text{Roultian or Henrian solid solution} \\ &= -D_i \frac{dc_i}{dz} \end{aligned}$$

This, or the more general equation (2.4), furnishes us with the relation between the fundamental formula (2.3) and the phenomenological Fick's law (1.1). D_i is called the *intrinsic diffusion coefficient* for the component i in a solid solution, and

$$\begin{aligned} D_i &= -RT \mathcal{M}_i \left(1 + \frac{d \ln \gamma_i}{d \ln x_i} \right) \\ &= -RT \mathcal{M}_i && \longleftarrow \text{Roultian or Henrian solid solution} \end{aligned}$$

3. Binary alloy—*intrinsic and chemical diffusion coefficients*

Further progress can be made in the case of a binary system. For a binary A-B alloy

$$J_A = -M_A \frac{d\mu_A}{dz}$$

$$J_B = -M_B \frac{d\mu_B}{dz}$$

To compare this with Fick's first law, again I want a relation between the derivative of μ and the derivative of c . I write, using the chain rule of differentiation, and recalling, as I did in section 2, from the properties of the logarithm that $d \ln y = (1/y)dy$,

$$\frac{d\mu_A}{dz} = \frac{d\mu_A}{dc_A} \frac{dc_A}{dz} = \frac{d\mu_A}{d \ln c_A} \frac{1}{c_A} \frac{dc_A}{dz}$$

Then

$$J_A = -\frac{M_A}{c_A} \frac{d\mu_A}{d \ln c_A} \frac{dc_A}{dz}$$

and by comparison with (1.1) and (2.2) I find that the diffusion coefficient is

$$D_A = \frac{d\mu_A}{d \ln c_A} \mathcal{M}_A$$

and similarly for component B. However the Gibbs-Duhem relation for a binary alloy leads to[†]

$$\frac{d\mu_A}{d \ln c_A} = \frac{d\mu_B}{d \ln c_B}$$

[†] For a binary alloy, $c_A + c_B$ is a constant, so we have $dc_A = -dc_B$. By the definition of the logarithm

$$d \ln c_A = \frac{1}{c_A} dc_A \qquad d \ln c_B = \frac{1}{c_B} dc_B$$

From your thermodynamics notes, equation (2.11), the Gibbs-Duhem equation for a binary alloy reads

$$n_A d\mu_A = -n_B d\mu_B$$

and if I divide through by the volume of the body under discussion then

$$c_A d\mu_A = -c_B d\mu_B$$

and this can be written using the previous identities for the binary alloy,

$$\frac{d\mu_A}{d \ln c_A} dc_A = -\frac{d\mu_B}{d \ln c_B} dc_B$$

and since $dc_A = -dc_B$,

$$\frac{d\mu_A}{d \ln c_A} = \frac{d\mu_B}{d \ln c_B}$$

and so

$$D_A = \frac{d\mu_A}{d \ln c_A} \mathcal{M}_A \quad (3.1a)$$

$$D_B = \frac{d\mu_B}{d \ln c_B} \mathcal{M}_B \quad (3.1b)$$

These are the intrinsic diffusion coefficients for the binary alloy. This means that intrinsic diffusivities in a binary alloy differ only due to the differences in mobility.

The total flux of atoms in a binary alloy is $J = J_A + J_B$. This is relative to the crystal lattice. Since there may also be vacancy flow then the flux of A atoms relative to the centre of mass of the body is J_A take away the total J times the atom fraction $x_A = 1 - x_B$; considering equations (3.1),

$$\begin{aligned} J_A^{\text{C.O.M.}} &= J_A - x_A (J_A + J_B) \\ &= x_B J_A - x_A J_B \\ &= -(x_B D_A + x_A D_B) \frac{dc_A}{dz} \\ &= -D_{\text{chem}} \frac{dc_A}{dz} \end{aligned} \quad (3.2)$$

and

$$D_{\text{chem}} = x_B D_A + x_A D_B \quad (3.3)$$

is called the *chemical diffusion coefficient*, that is the sum of the intrinsic diffusivities each weighted by the other's concentration. This exposes very nicely that in general the diffusion coefficient is a function of concentration and should not be treated as a constant in Fick's first and second laws, which consequently should be written

$$\begin{aligned} \mathbf{J} &= -\nabla (Dc) && \text{First law} \\ \frac{\partial c}{\partial t} &= \nabla \cdot (D\nabla c) && \text{Second law} \end{aligned}$$

If all diffusion is by place exchange and not by vacancy exchange then $D_A = D_B = D_{\text{chem}}$. The chemical diffusion coefficient is that which is most usually measured in an experiment. For example if a piece of pure copper and a piece of pure nickel are placed in contact with a flat and smooth interface then after placing in a furnace for some hours the two elements will be found to have inter-diffused. This is diffusion bonding. By measuring the amount of Cu on the Ni side and the amount of Ni on the Cu side at a distance z from the original interface as a function of time and temperature the diffusivity is measured. Since the two intrinsic diffusivities may be different (3.1), there may be a total flux of vacancies and so markers, such as rods of an inert metal, may be found to have moved relative to the ends of the specimen. This is called the Kirkendall effect and was used in the first instance to demonstrate that vacancies are involved in diffusion.

4. Binary alloy—tracer diffusion coefficient

If there is only one component, that is, if the metal is pure then we are interested in the *tracer diffusion coefficient*. The way this is usually measured is by a radioactive isotope tracer experiment—hence the name. If we use the subscript A for the metal atoms and a subscript A^\bullet for the isotope then the fluxes of the two types of atoms are

$$J_A = \frac{d\mu_A}{d \ln c_A} \mathcal{M}_A \frac{dc_A}{dz}$$

$$J_{A^\bullet} = \frac{d\mu_{A^\bullet}}{d \ln c_{A^\bullet}} \mathcal{M}_{A^\bullet} \frac{dc_{A^\bullet}}{dz}$$

The atom A and its isotope are chemically identical and so their chemical potentials will be the same except for differences arising from the different entropies of mixing (due to their not occurring in the same concentration). So if we put everything except for the entropy of mixing into the standard state μ° we are left with, recalling equation (3.4) from your thermodynamics notes,

$$\mu_A = \mu^\circ + RT \ln \frac{c_A}{c} \quad \text{and} \quad \mu_{A^\bullet} = \mu^\circ + RT \ln \frac{c_{A^\bullet}}{c}$$

where $c = c_A + c_{A^\bullet}$, which means that

$$\frac{d\mu_A}{d \ln c_A} = \frac{d\mu_{A^\bullet}}{d \ln c_{A^\bullet}} = RT$$

The diffusion currents must be equal and opposite and on physical grounds we expect the mobilities of the atom and its isotope to be identical. Therefore if we set $\mathcal{M}_{A^\bullet} = \mathcal{M}_A$ we see from (3.1) that

$$D_{A^\bullet} = RT \mathcal{M}_A \quad (4.1)$$

This relation between tracer diffusion coefficient and mobility is very famous indeed as it was first written down by Albert Einstein in 1905. Finally for a binary alloy we note that we have found the relation between the intrinsic and the tracer diffusion coefficients for components A and B . In view of (3.1)

$$\frac{D_B}{D_{B^\bullet}} = \frac{D_A}{D_{A^\bullet}} = \frac{1}{RT} \frac{d\mu_A}{d \ln c_A} \quad (4.2)$$

This is known as Darken's thermodynamic relation.

5. Relation between chemical and tracer diffusion coefficients in a binary alloy

So far we have defined three diffusivities: the intrinsic, the chemical and the tracer diffusion coefficient. (There is one more—the so called *self diffusivity* but we'll come to that later.) Darken's relation (4.2) expresses the connection between intrinsic and tracer diffusivities. We can also find a relation between chemical and tracer diffusion

coefficients in a binary alloy. We defined D_{chem} in equation (3.3). We can also use the Gibbs-Duhem relation to show that[†]

$$\frac{d \ln \gamma_A}{dx_A} = \frac{d \ln \gamma_B}{dx_B} \quad (5.1)$$

If I now combine (2.4) and (2.2) with (4.1) and (5.1) it follows very easily that

$$\begin{aligned} D_{\text{chem}} &= x_B D_A + x_A D_B \\ &= x_B D_{A\bullet} \left(1 + \frac{d \ln \gamma_A}{d \ln x_A} \right) + x_A D_{B\bullet} \left(1 + \frac{d \ln \gamma_B}{d \ln x_B} \right) \\ &= (x_B D_{A\bullet} + x_A D_{B\bullet}) \left(1 + \frac{d \ln \gamma_A}{d \ln x_A} \right) \end{aligned}$$

This is a very nice connection indeed as it relates the diffusivity as measured using a diffusion couple and which incorporates the Kirkendall effect with the tracer diffusion coefficients which describe the trajectories of atoms in the pure substance and finally which includes a term to account for non ideality of the solid solution. If a solid solution is ideal (or obeys either Raoult's or Henry's law) and if there is only diffusion by place exchange (that is, there is no vacancy flux) then

$$D_{\text{chem}} = D_A = D_B = D_{A\bullet} = D_{B\bullet}$$

and all diffusion coefficients are numerically equal. This would be the case for example in the diffusion of nitrogen or carbon in ferrite or in reasonably low concentration in austenite. It should also hold for hydrogen or oxygen diffusivity in titanium alloys and many other cases of the diffusion of interstitial impurities.

6. Atomistic aspects

At the atomic scale diffusion is thought to take place either by a vacancy exchange, in the case of substitutional elements, or by the movement of interstitials. In the first case there is a severe restriction that for a particular atom to be able to jump it must have at least one neighbouring site vacant, while in the case of interstitials, as long as these are sufficiently dilute then we can assume that each neighbouring site is vacant. This means that for interstitial diffusion the rate is principally determined by the probability that the atom will jump over the activation barrier; while in the substitutional case this probability must, roughly speaking, be multiplied by the probability that the site in

†

$$x_A d\mu_A = RT(dx_A + x_A d \ln \gamma_A) = RT \left(1 + \frac{d \ln \gamma_A}{d \ln x_A} \right) dx_A$$

which when put into the Gibbs-Duhem equation becomes

$$RT \left(1 + \frac{d \ln \gamma_A}{d \ln x_A} \right) dx_A = RT \left(1 + \frac{d \ln \gamma_B}{d \ln x_B} \right) dx_B$$

and since for a binary alloy $dx_A = -dx_B$, (5.1) is proved.

the direction of jumping is vacant. This second probability is actually extremely small in metals given that even near the melting point the vacancy concentration is usually smaller than 10^{-5} . This is why diffusion of substitutional elements, such as Mn, Ni, Mo, in steel is orders of magnitude smaller than interstitials such as C or N. The diffusion of hydrogen in ferrite is probably the fastest known in the solid state. However there are more exotic possible processes for diffusion that have been proposed, illustrated in figure 1. Apart from those already discussed there are direct exchange and ring diffusion and diffusion via substitutional or host atoms temporarily occupying interstitial positions; this is usually regarded as rare since the formation enthalpy of an interstitial defect is very large—much larger than the vacancy formation energy. But an interstitial may have quite a low formation energy if one atom is placed between two atoms belonging to a row of atoms in a close packed lattice direction: the row of atoms can all move a little to accommodate the interstitial. This row of atoms containing one additional atom is called a “crowdion”. Crowdions in the $[111]$ direction in the bcc lattice can move rather easily—but only in the particular $\langle 111 \rangle$ direction, the crowdion cannot turn corners!

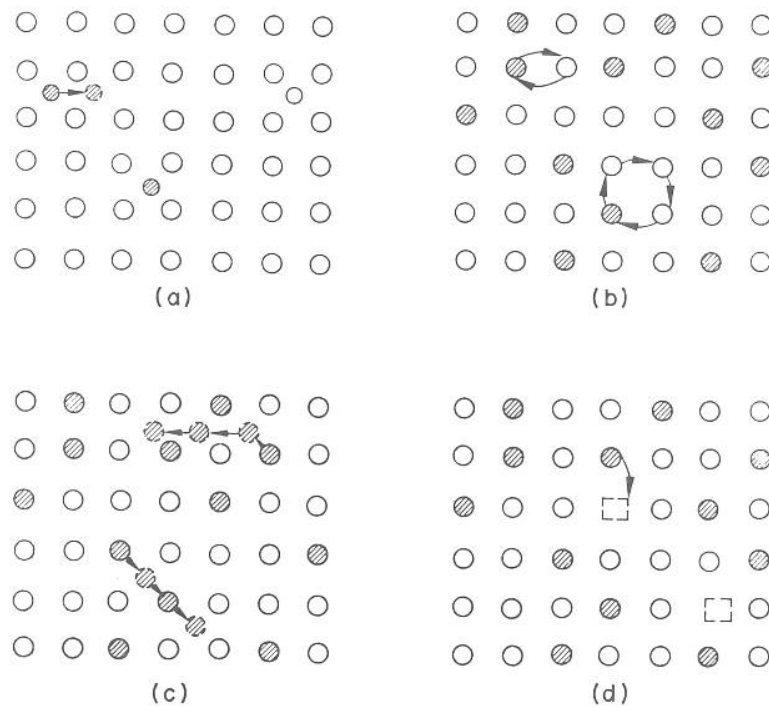


Figure 1: Cartoon illustrating possible diffusion mechanisms at the atomic scale. (a) Interstitial solid solution, (b) place exchange and ring diffusion (no vacancies needed), (c) diffusion of substitutional atom by an interstitialcy mechanism (the lower inclined line shows a crowdion), (d) vacancy diffusion.

6.1 Equilibrium concentration of vacancies

Since the probability that a substitutional site is vacant is central to the diffusivity we'll need to calculate it. It is the same as the fraction of sites that is vacant, namely the equilibrium concentration of vacancies. I can create a vacancy by removing an atom from the interior of a crystal and placing it on the surface.[†] Suppose the crystal has N_L lattice sites of which N_V are vacancies. Since the vacancies can be arranged in a large number of ways, whereas there is only one distinguishable way to arrange the atoms in a perfect lattice, the configurational entropy is increased from zero to S_c . We calculate this from Boltzmann's famous formula (it's engraved on his tombstone),

$$S_c = k \ln W$$

k is the Boltzmann constant and W is the number of ways of arranging N_V vacancies among N_L sites,

$$W = \frac{N_L!}{N_V!(N_L - N_V)!}$$

As usual we use Sterling's approximation for $\ln x$ when x is very large. For us it's on the order of the Avogadro number so it's very large indeed, so this is not really an approximation:

$$\ln W = N_L \ln N_L - N_V \ln N_V - (N_L - N_V) \ln (N_L - N_V)$$

The mole fraction of vacancies is

$$x = \frac{N_V}{N_L}$$

so that

$$1 - x = \frac{N_L - N_V}{N_L}$$

Using the last three equations and after some algebra we get

$$\ln W = -N_L (x \ln x + (1 - x) \ln (1 - x))$$

Then the configurational entropy of the crystal containing N_V vacancies is

$$S_c = k \ln W = -k N_L (x \ln x + (1 - x) \ln (1 - x))$$

This is not the total change in entropy. When I remove the atom this changes the vibrational frequencies of the surrounding atoms and so it changes the total vibrational entropy, S_ν (also called thermal entropy) of the crystal. Assuming that making further vacancies simply increases S_ν additively (that is, that the change in vibrational frequencies is *local*) then the total increase in entropy due to the creation of N_V vacancies is

$$\Delta S = N_V \Delta S_\nu + S_c$$

[†] This need not affect the surface energy since I can place the atom at a kink along a terrace edge—this doesn't change the surface energy.

There is also a change in enthalpy at the creation of each vacancy. At the simplest possible level this is because, say, z bonds are broken when I wrest the atom from the interior, but some fewer than z (roughly $z/2$) bonds are remade when I attach it to the surface. Hence in the zeroth approximation the enthalpy of formation of one vacancy, ΔH is roughly the cohesive energy per atom of the pure solid. The change in free enthalpy on the introduction of N_V vacancies is therefore

$$\begin{aligned}\Delta G^{\text{cryst.}} &= N_V \Delta H - T \Delta S \\ &= N_V \Delta H - T N_V \Delta S_\nu - T S_c \\ &= N_V \Delta G'_V + kT N_L (x \ln x + (1-x) \ln (1-x))\end{aligned}$$

where $\Delta G'_V = \Delta H - T \Delta S_\nu$ is the total change in free enthalpy per vacancy having taken away the configurational entropy contribution. I divide through by N_L and I get the change in free enthalpy per lattice site

$$\frac{\Delta G^{\text{cryst.}}}{N_L} = \Delta G_L = x \Delta G'_V + kT (x \ln x + (1-x) \ln (1-x))$$

I can find the equilibrium concentration of vacancies, x^{eq} , by finding the value of x that minimises ΔG_L . I take the derivative of ΔG_L with respect to x and set the result to zero. After rearranging the result I get

$$\frac{x^{\text{eq}}}{1-x^{\text{eq}}} = e^{-\Delta G'_V/kT} = e^{\Delta S_\nu/k} e^{-\Delta H/kT} \approx x^{\text{eq}}$$

The last approximation follows because you find in any metal below the melting point that $1-x^{\text{eq}} \approx 1$.

You can use this procedure to find the equilibrium concentration of any point defect. If you care to ignore the, possibly small, change in vibrational entropy on the creation of the defect and in addition neglect the $\Delta(pV)$ term in the enthalpy then you have

$$x^{\text{eq}} \approx e^{-\Delta U/kT}$$

and these days you can calculate ΔU using first principles quantum mechanics.

6.2 Random walk

Even if there is no gradient in chemical potential the atoms are still jumping from site to site in a solid under the influence of thermal excitation and the collective action of phonon wavepackets. The simplest example is a dilute interstitial impurity all of whose z neighbouring interstices are empty. It can choose to jump to any one at random and it will jump on average at a rate of Γ jumps per unit time. In any case, including the case of vacancy or other mechanisms we expect that we can assert that

$$\Gamma = Pz\nu$$

where P is the probability that the site in the direction of the jump is vacant, z is the coordination number or number of neighbours, and ν is a rate coefficient for the activated jump process: it is the frequency with which an atom makes a unit jump (see section 7, below).

If an atom starts out at the origin at time $t = 0$ and it makes n jumps, and if at the j^{th} jump it moves a vector distance \mathbf{s}_j then after the n jumps it has arrived at a position vector from the origin given by

$$\mathbf{S} = \sum_{j=1}^n \mathbf{s}_j$$

The square of the distance that it has jumped is $S^2 = \mathbf{S} \cdot \mathbf{S}$. This is

$$\begin{aligned} S^2 &= \sum_{j=1}^n \mathbf{s}_j \cdot \mathbf{s}_j + 2 \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \mathbf{s}_i \cdot \mathbf{s}_{i+j} \\ &= \sum_{j=1}^n s_j^2 + 2 \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} s_i s_{i+j} \cos \theta_{i,i+j} \end{aligned}$$

where $\theta_{i,i+j}$ is the angle between the vectors belonging to the i^{th} and the $(i+j)^{\text{th}}$ jump. This formula makes no approximations concerning the randomness of jumps, lengths or angles between jumps, or even the dimension (whether this is 3D, 2D or 1D movement). In the more usual cases, certainly in fcc metals and almost certainly in bcc metals, and certainly for interstitial jumping in these metals, the jump distances are all equal, call it the distance a . (You would have to be careful in hcp metals.) In those special circumstances, and we will assume such cases from now on)

$$S^2 = na^2 + 2a^2 \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \cos \theta_{i,i+j}$$

We now take a statistical average over the trajectories of many atoms (some small fraction of an Avogadro number in a typical diffusion experiment) and we write,

$$\overline{S^2} = na^2 + 2a^2 \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \overline{\cos \theta_{i,i+j}} \quad (6.1.1)$$

where the overline indicates an average, and $\overline{\cos \theta_{i,i+j}}$ is the average value of the cosine of the angle between the directions of the i^{th} and j^{th} jumps. This is a very important term because it embodies all the *correlations* that are present in the jumping process. The trajectory of an atom is not usually even approximately a random walk. This is particularly true for the jumping of substitutional impurities, since these impurities will have different interaction preferences with vacancies than the host atoms. Also in general for the case of vacancy diffusion: if an atom exchanges places with a vacancy, at the next jump by far the most likely probability that it will reverse that jump because

that is where the nearest vacancy is. However if the direction of each jump is selected entirely randomly then $\overline{\cos \theta_j} = 0$ and

$$\overline{S^2} = na^2 \quad (6.1.2)$$

According to a kinetic argument for a cubic lattice the diffusivity is

$$D = \frac{1}{6t} \overline{S^2} \quad (6.1.3)$$

(an argument first put forward by Einstein in 1906). After n jumps in a time t the rate of jumping must have been $\Gamma = n/t$, or $t = n/\Gamma$ and so for the diffusivity we have

$$D = \frac{1}{6} \Gamma a^2 = \frac{1}{6} P z \nu a^2 \quad (6.1.4)$$

This truly only applies to interstitial dilute impurity diffusion in fcc and bcc metals, for which we will have $P = 1$, $z = 12$ for fcc and $z = 4$ in bcc metals. ν is unknown and can only be measured indirectly, but it is possible nowadays to calculate rate coefficients to good precision using first principles quantum mechanics—even in the case of hydrogen in steel where quantum mechanical tunnelling is involved.

6.2 Non random walk

We should modify the equation (6.1.4) for the diffusivity to account for the correlation and other effects neglected thus far. A sensible modification is to write,

$$D = \frac{1}{6} f (sa_0)^2 \nu P P' j z \quad (6.2.1)$$

Here, a_0 is the lattice parameter and sa_0 is the distance actually jumped in the direction of atom flow. P as before is the probability that the site in the direction of travel is available for a jump, *i.e.* vacant, and P' is the probability that the atom is residing on its site just prior to the jump. ν is the rate coefficient, or the number of events per unit time, for the atom and vacancy to exchange places. z is the atom's coordination number and j is the fraction of its neighbours which are placed in the intended direction of travel. Finally, f is the “correlation factor” which account for the non randomness of the walk. We'll come back to how to work out f shortly. First let's look at the example of vacancy diffusion in a pure fcc metal. Consider diffusion along a [001] direction: atoms will jump a distance $a_0/2$ between successive (002) planes so $s = 1/2$. We assume all sites are occupied so $P' = 1$ and the probability that a site in the next (200) plane is vacant is x^{eq} as we discussed in section 6.1. $z = 12$ in the fcc lattice but only a third of the neighbours are in the next (002) plane and so $j = 1/3$. The diffusivity is hence

$$D = \frac{1}{6} f \left(\frac{1}{2} a_0 \right)^2 \nu x^{\text{eq}} \frac{12}{3} = \frac{1}{6} f a_0^2 x^{\text{eq}} \nu$$

A useful general definition of f comes about in this way. Consider the difference between the trajectories of a vacancy and of an atom that has been harmlessly tagged in some

way. The ornithologist tags a bird by attaching a ring to its leg and hopes that this will in no way affect its behaviour. We could tag an atom by replacing its nucleus with an isotope of the same metal. Its diffusivity is $D_{A\bullet}$ as we saw in section 4. The trajectory of a vacancy, at least in a pure metal, is truly a random walk—its diffusivity is called the “self diffusivity” D_{self} , of the metal. Self diffusivity is what is measured in gasses and liquids, or in Brownian motion, in which each particle or molecule, before jumping, has no memory of where it came from and chooses each available direction in which to jump with equal probability. The same applies to dilute interstitials in metals as we have seen. Conversely a substitutional atom is very biased in choosing the next direction in which to jump: the greatest likelihood is that it will jump straight back again into the site it just vacated; but occasionally that vacant site will become occupied by another of its neighbours and our atom will have to stay put until another vacancy drifts into a neighbouring position. So the tracer diffusivity is *essentially* different to the self diffusivity in vacancy diffusion and we can define the correlation factor as

$$f = \frac{D_{A\bullet}}{D_{\text{self}}} = \lim_{n \rightarrow \infty} \frac{\overline{S_n^2(A\bullet)}}{\overline{S_n^2(\text{vac.})}}$$

the ratio of the mean square displacements of the tracer and vacancy after n jumps. Since $\overline{S_n^2(\text{vac.})} = na^2$, equation (6.1.3), we have

$$f = 1 + \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \overline{\cos \theta_{i,i+j}}$$

which follows from (6.1.1). Actually the memory is not that long term: the atom only remembers its previous jump and so the direction of the next jump is only correlated with the immediately preceding jump. Put another way the geometry of the problem concerns tracer-vacancy pairs and these are all identical except for their orientation. In that case $\overline{\cos \theta_{i,i+j}}$ is independent of the index i and we define $\overline{\cos \theta_j}$ as the average value of the cosine of the angle between the directions of the i^{th} and j^{th} jumps and is independent of i . In fact

$$\overline{\cos \theta_j} = \overline{\cos \theta_{j-1}} \overline{\cos \theta_1} = (\overline{\cos \theta_1})^j = (\overline{\cos \theta_1})^j$$

so it's just the angle of the first jump raised to the power j . This leads to

$$f = \lim_{n \rightarrow \infty} \left(1 + \sum_{j=1}^{n-1} (n-j) \overline{(\cos \theta)^j} \right)$$

and θ is the angle between successive jumps as there's nothing special about the first jump. The limit can be taken and the series summed analytically. The result is

$$f = \frac{1 + \overline{\cos \theta}}{1 - \overline{\cos \theta}}$$

The calculation of f is dreary and difficult and involves some probability theory. A number of people have kindly done this for us and found that correlation factors for fcc

and bcc pure metals are 0.781 and 0.727 respectively. So they are not very close to one and cannot really be ignored.

7. Rate theory aspects

I'll take you through a simplified and not very rigorous "derivation" of the well known formula for the diffusivity,

$$D = D_0 e^{-Q/kT}$$

We want to know the frequency, ν , at which an atom will exchange places with a vacancy. Put another way, if an atom and a vacancy are neighbours, what on average is the time $\tau = 1/\nu$ that I have to wait before the atom and the vacancy change places? This is a standard question in materials science and chemistry. The event is an "activated process". Think of the atom as it is dragged from its lattice and taken adiabatically into the empty neighbouring site. During this procedure the total energy of the crystal must increase until a maximum is reached, probably when the atom is half way along its journey. This arrangement of atoms is called an activated complex in chemistry; the configuration of all the atoms is at a saddle point in the energy landscape. At any point in time and at any temperature in a crystal of metal that has an equilibrium concentration, x^{eq} , of vacancies, there will also be an equilibrium concentration of these activated complexes. By exactly the same argument that we used in section 6.1 we can take it that the equilibrium concentration of these is

$$e^{-\Delta G'_M/kT}$$

where, by analogy with $\Delta G'_V$, $\Delta G'_M$ is the free enthalpy of formation of one activated complex take away its configurational entropy contribution. So the frequency of jumping is this concentration times the frequency, ν_0 , at which an atoms attempts the jump. Approximately speaking we take it that ν_0 is the vibrational frequency of the collection of atoms in that particular mode of vibration which drives the atom in the direction of the saddle point configuration[†] What's causing this to happen is the system of phonons whose amplitude depends on temperature. This gives us

$$\nu = \nu_0 e^{-\Delta G'_M/kT}$$

which we can put into our formula (6.2.1)

$$D = \frac{1}{6} f j z a^2 \nu P j z \quad (6.2.1)$$

along with the equilibrium vacancy concentration that we obtained in section 6.2,

$$P = x^{\text{eq}} = e^{\Delta G'_V/kT}$$

This results in

$$\begin{aligned} D &= \frac{1}{6} f j z a^2 x^{\text{eq}} \nu = \frac{1}{6} f j z a^2 \nu_0 e^{-(\Delta G'_M + \Delta G'_V)/kT} \\ &= \frac{1}{6} f j z a^2 \nu_0 e^{(\Delta S'_M + \Delta S'_V)/k} e^{-(\Delta H^M + \Delta H^V)/kT} \\ &= D_0 e^{-Q/kT} \end{aligned}$$

[†] Statistical mechanics arguments can be used show that $\nu_0 = kT/h$, where h is the Planck constant.

which is the desired result. Here, ΔS_ν^M and ΔS_ν^V are respectively the vibrational entropies of formation of the activated complex and an isolated vacancy: these reflect changes in the phonon spectra when these defects are created. Similarly, ΔH^M and ΔH^V are the respective enthalpies of formation.

$$D_0 = \frac{1}{6} f j z a_0^2 \nu_0 e^{(\Delta S_\nu^M + \Delta S_\nu^V)/k}$$

is defined by the above formula; note that it has the expected dimensions of a transport coefficient: length squared over time, or $\text{m}^2 \text{s}^{-1}$.

$Q = \Delta H^M + \Delta H^V$ is called the “activation energy” and note that is is an enthalpy, not a free enthalpy—the configurational entropy is already included in ν as we saw in section 6.1, and the remaining entropy terms are included in the D_0 “prefactor”. The activation energy is relatively easy to calculate using first principles quantum mechanics. ΔH^M can be calculated using a computational technique called the “nudged elastic band” in which we drag the atomic configuration up the saddle point as it were with an elastic band which confines images of the system to the reaction coordinate. Total energies are calculated using the density functional theory. If we are happy to neglect thermal entropy terms then we can find a reasonable estimate of the diffusivity. On the other hand the whole estimation can be done using a computer method called molecular dynamics; this will in principle include entropy and finite temperature terms, but it has other attendant problems, mostly connected with not having fast enough computers and thereby having to throw away the proper quantum mechanical theory in favour of very approximate so called “classical potentials.”

Sources

1. J. W. Christian, *The theory of transformations in metals and alloys*, Third edition (Pergamon, 2002)