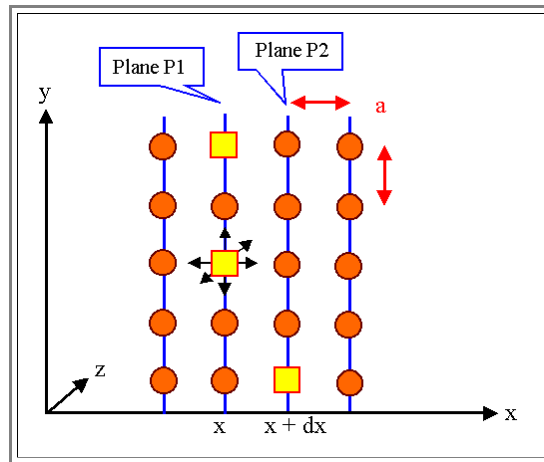


Diffusion Coefficient and Atomic Mechanisms

Basics

- ▶ We are looking for an equation that links the diffusion current j of Ficks 1st law with the individual atomic jumps of a particle like an interstitial atom or a vacancy.
 - For simplicities sake we only consider vacancies in a primitive cubic lattice. The extension to interstitials is rather trivial.
 - We only consider a one-dimensional geometry.
 - Extensions to three dimensions, real crystals and exotic atomic mechanisms, albeit not necessarily easy, do not give new insights and will not be covered.
- ▶ Lets look at two lattice planes of a simple cubic crystal which are perpendicular to the x -direction considered and which contain the diffusing particles - here vacancies.



- ▶ We are only interested in the flux of vacancies in the x -direction, the **diffusion current j** of the *vacancies*. The flux or diffusion current of *atoms* that move via a vacancy mechanism, would have the same magnitude in the opposite direction.
 - We do not assume equilibrium, but a space-dependent vacancy concentration $c_V(x, y, z)$. Being one-dimensional, we only assume a concentration gradient in the x -direction, $c_V(x, y, z) = c_V(x)$.
 - On any lattice plane perpendicular to x we have a certain number of vacancies per unit area (the area density in cm^{-2}), which is computable by $c(x)$. We distinguish this particular concentration with the index of the plane; i.e. P_1 is the number of vacancies on 1 cm^2 area on plane No. 1, etc.
 - We then have

$$P_1 = a \cdot c_V(x)$$

$$P_2 = a \cdot c_V(x + dx)$$

- With $dx = a = \text{lattice constant}$, because smaller increments make no physical sense, we obtain

$$P_2 = a \cdot c_V(x + a)$$

- ▶ Next we consider the jump rates in x -direction, i.e. that part of all vacancy jumps out of the plane that are in $+x$ -direction. We define

$$r_{1-2} = \text{jump rate in } x \text{ - direction from } P_1 \text{ to } P_2$$

$$r_{2-1} = \text{jump rate in } -x \text{ - direction from } P_2 \text{ to } P_1$$

- We obtain for our geometry:

$$r_{1-2}(T) = r_{2-1}(T) = \frac{1}{6} \cdot r(T)$$

- This means that **1/6** of the total number of possible jumps of a vacancy is in the **+x** or **-x** direction, the other possibilities are in the **y**- or **z**-direction.

The jump rate itself is given by the usual Boltzmann formula

$$r = v_0 \cdot \exp - \frac{H^M}{kT}$$

- With v_0 = vibration frequency of the particle, H^M = enthalpy of migration.

We obtain for the number of vacancies per **cm²** and second, which jump from **P₁** to **P₂**, i.e. for the component of the diffusion current **j₁₋₂** flowing to the right (and this is *not* yet the diffusion current from Ficks law!):

$$j_{1-2} = P_1 \cdot r_{1-2}$$

- This is the current of vacancies flowing **out** in **x**-direction from **P₁**. This current will be compensated to some extent by the current component **j₂₋₁** which flows **into** **P₁**. This current component is given by

$$j_{2-1} = P_2 \cdot r_{2-1}$$

- With the equation from above we obtain for the two components of the current

$$j_{1-2} = \frac{r}{6} \cdot a \cdot c(x)$$

$$j_{2-1} = \frac{r}{6} \cdot a \cdot c(x + dx)$$

The net **j_x** current in **x**-direction, which *is* the current in Ficks laws, is exactly the difference between the two partial currents, we obtain

$$j_x = j_{1-2} - j_{2-1}$$

$$= - \frac{a \cdot r}{6} \cdot \{c(x + dx) - c(x)\}$$

- If we now multiply by **dx/dx = a/dx** we obtain directly [Ficks first law](#) for one dimension:

$$j_x = - \frac{a^2 \cdot r}{6} \cdot \frac{c(x + dx) - c(x)}{dx} = - \frac{a^2 \cdot r}{6} \cdot \frac{dc(x)}{dx}$$

- All we have to do is to indentify **(a² · r)/6** with the diffusion coefficient **D** of Fick's first law; we then have it in full splendor:

$$j_x = -D \cdot \frac{dc(x)}{dx}$$

➤ Ficks first law thus can be deduced in an unambiguous and physically sensible way for primitive cubic crystals in one dimension. (Mathematicians may have problems with the equality $dx = a$; but never mind).

- We also obtain an equation for the *phenomenological* diffusion coefficient D in terms of the *atomic parameters* lattice constants and jump rate (for the simple cubic lattice).

➤ Considering arbitrary crystals now is easy.

- The only parameters different in different crystal systems are the factor **1/6** and the jump distance, which does not have to be only a , but, in general, for jump type i will be Δx_i . With i we enumerate all geometrically different variants of jumps and take into account that the x -component may depend on i .
- The diffusion coefficient then is given by

$$D = g \cdot a^2 \cdot r$$

- And g is a constant which is specific for the lattice under consideration, it is the so-called **geometry factor** of the lattice for diffusion.

➤ If we reconsider how we obtained the factor **1/6** for the cubic primitive lattice [used above](#), it is clear that in a general case the geometry factor is defined by the equation

$$g = \frac{1}{2} \cdot \sum_i \left(\frac{\Delta x_i}{a} \right)^2$$

- The factor **1/2** takes into account that only **1/2** of all possible jumps must be counted, because the other half would be the jumps back. $\Delta x_i/a$ simply expresses the component of the jump in x -direction in units of a .
- For simple lattices g is easily calculated; for the **fcc** and **bcc** lattice we have $g = 1$.

➤ Taking into account three dimension is easy, too:

- In isotropic lattices (which, besides the cubic lattices, covers all poly-crystals) no direction is special, the above equations are equally valid for the y - and z -direction. We obtain then a vector equation for Ficks first law

$$j(r) = -D_0 \cdot \exp\left(-\frac{E_M}{kT}\right) \cdot \nabla c(x,y,z)$$

➤ In anisotropic crystals things are messy. Every direction has to be considered separately, the so far *scalar* quantity D evolves into a second-rank *tensor*. Fortunately, we do not have to consider this here.