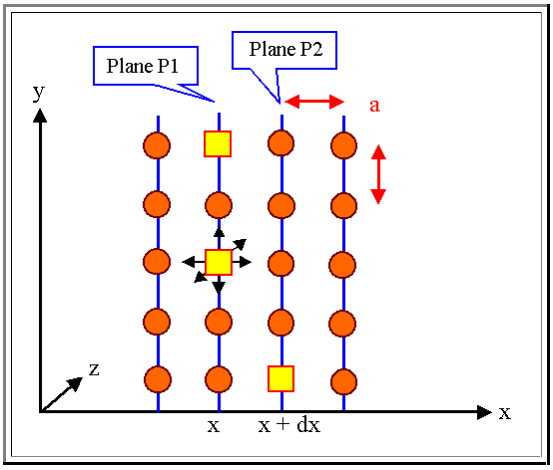
Diffusion Coefficient and Atomic Mechanisms

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 $\mathbf{cm^{-2}}$), 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 cm²** 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 **d*x*** **= *a* =** *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} = **jump rate in *x* – direction from P_1 to P_2**

r_{2-1} = **jump rate in – *x* – direction from P_2 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

$$r = \nu_0 \cdot \exp - \frac{H^M}{kT}$$

- With ν_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 P_1 to P_2, i.e. for the component of the diffusion current j_{1-2} 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 P_1. This current will be compensated to some extent by the current component j_{2-1} which flows **into** P_1. 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 **d*x*/d*x* = a/d*x*** 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 $(a^2 \cdot r)/6$ 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

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

  - 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

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

- 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.