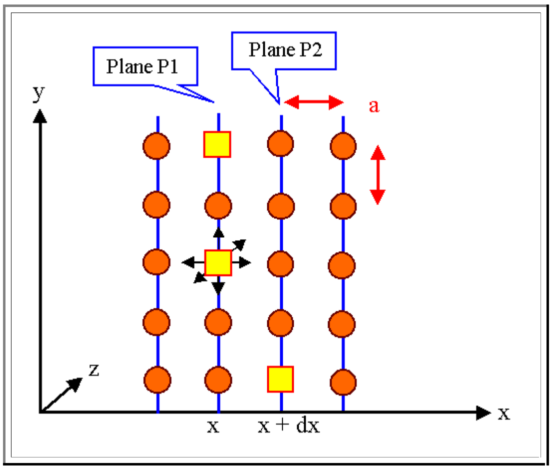
Diffusion Coefficient and Atomic Mechanisms

- 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.

Basics

- 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 $\mathbf{1\ cm^2}$ 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 $dx = a =$ *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

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

  - With ν_0 = vibration frequency of the particle, H^M = enthalpy of migration.

- We obtain for the number of vacancies per cm^2 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

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

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

- 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

$$\begin{aligned} j_x \;&=\; j_{1-2} \;-\; j_{2-1} \\ &=\; -\frac{a \cdot r}{6} \cdot \{c(x + \mathrm{d}x) \;-\; c(x)\} \end{aligned}$$

  - If we now multiply by **d*x*/d*x* = *a*/d*x*** we obtain directly Ficks first law for one dimension:

$$j_x \;=\; -\frac{a^2 \cdot r}{6} \cdot \frac{c(x + \mathrm{d}x) \;-\; c(x)}{\mathrm{d}x} \;=\; -\frac{a^2 \cdot r}{6} \cdot \frac{\mathrm{d}c\,(x)}{\mathrm{d}x}$$

  - 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.