

### 3.2.2 Self-Diffusion

We ask ourselves how the regular atoms of a crystal diffuse. In the case of crystals with two or more different atoms, we have to answer this question for each kind of atom separately.

The answer is easiest for a simple (mono)vacancy mechanism in simple elemental cubic crystals. The **self-diffusion coefficient** is given by  $g \cdot a^2$  times the number of jumps per sec that the diffusing particles make.

Since only lattice atoms that have a vacancy as a neighbor can jump, or, in other words, the number of lattice atoms jumping per sec is identical to the number of vacancies jumping per sec, we obtain for the diffusion coefficient of self-diffusion by a simple vacancy mechanism the following equations:

$$D_{SD} = c_v \cdot D_v$$

$$D_{SD} = g \cdot a^2 \cdot n_0 \cdot \exp\left(-\frac{G_m}{kT}\right) \cdot \exp\left(-\frac{G_f}{kT}\right)$$

$$D_{SD} = g \cdot a^2 \cdot v_0 \cdot \exp\left(-\frac{S_m}{k}\right) \cdot \exp\left(-\frac{H_m}{kT}\right) \cdot \exp\left(-\frac{S_f}{k}\right) \cdot \exp\left(-\frac{H_f}{kT}\right)$$

$$D_{SD} := D^* \cdot \exp\left(-\frac{H_m + H_f}{kT}\right)$$

$G_m$  is the free enthalpy for a jump, i.e. the free enthalpy barrier that must be overcome between two identical positions in the lattice.

In words: All the material dependent constants (including the migration and formation entropy) have been lumped together in  $D^*$ ; and the exponential now contains the **sum** of the migration and formation energy of a vacancy.

Lets discuss this equation a bit:

As mentioned before, we need an entropy of migration as a parameter of a point defect. In summary we need four parameters correlated with an intrinsic point defect to describe its diffusion behavior (if we discount the vibration frequency).

But only two parameters, the formation energy and the migration energy are of overwhelming importance.

Everything else may be summarized in a (more or less) constant pre-exponential factor  $D^*$  which contains the entropies. Since the entropies may be temperature dependent (for **Si** this is probably the case), you must look at bit closer at your calculations if you are interested in precise diffusion data.

An **Arrhenius-representation** ( $\lg D$  vs.  $1/T$ ) will give a straight line, the slope is given by  $H_m + H_f$ . The pre-exponential factor determines the intersection with the axis and is thus measurable.

Since it is much easier to measure diffusion coefficients compared to point defect densities, the **sum**  $H_m + H_f$  for point defects is mostly much better known than the **individual** energies. Some **values** are given in the link.

Self-diffusion via self-interstitials follows essentially the same laws.

For self-diffusion in **Si**, we find the following (rather small) values :  $D_{SD} = (10^{-21} \text{ — } 10^{-16}) \text{ m}^2/\text{s}$  in the relevant temperature regime. [Detailed data in an Arrhenius plot for for self-diffusion in Si](#) can be found in the link; some numbers for **Si** self-diffusion as well as the migration parameters of vacancies and interstitials and a few elements are [also illustrated](#).

Now for an exercise. Self-diffusion means that the atoms in a crystal change their position. After some time **all** atoms will have changed their positions at least once.

Our crystal just lying there, somehow changes identity. What does it mean? How long does it take? Do the exercise **3.2-1**!

#### Exercise 3.2-1

Crystal Identity

#### Exercise 3.3-1

Quick Questions to 3.