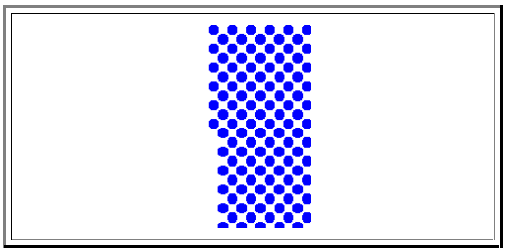
3.2 Diffusion Mechanism

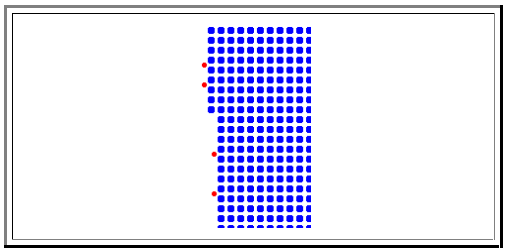
3.2.1 Atomic Mechanisms

- There are several atomic mechanisms that lead to the movement of atoms. By far the most prominent are the vacancy mechanism and the direct interstitial mechanism. How they work can be seen in the animations:

Simulation of the vacancy mechanism

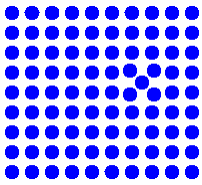


Simulation of the direct interstitial mechanism



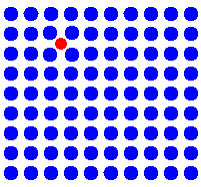
  - Note a fundamental difference! If you consider the diffusion of a *particular* atom (any blue one of your choice for the vacancy mechanism, any one of the red ones for the interstitial mechanism), your selected atom *always* moved a bit in the second case, but *may not have done anything in the first case*. The diffusion of a particular lattice atom by a vacancy mechanism, while inextricably linked to the movements of vacancies, is not the same as vacancy diffusion, but something different!
  - In other words: if a vacancy has made ***N*** jumps by moving around in the lattice, ***N*** atoms will also have made a jump. However, not necessarily ***N*** *different* atoms, because some *individual* atoms may have made more than **1** jump. If we look at any *particular* atom, there is no way of telling if ti has made a jump or not. At best we can give some probability.
  - This leads to a major conclusion: While the diffusion of a *particular* lattice atom by a vacancy mechanism is inextricably linked to the movements of *many vacancies*, its specific movement is principally different from the movement of a single vacancy.
- Other mechanisms which are quite rare but nonetheless potentially important in semiconductors are:

Indirect interstitial mechanism
for self-interstitials



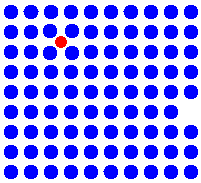
  - The simulation shows the elementary step: A self-interstitial (shown in light blue for easier identification) pushes a lattice atom into the interstitial lattice. The net effect is the migration of an self-interstitial from one interstitial site to an different one.
  - The mechanism is totally different from the regular interstitial mechanism. If in a thought experiment you mark a *specific* self-interstitial atom (paint it red), it will move a lot with the direct interstitial mechanism, but hardly at all with the indirect one.

The **"kick-out" mechanism**
for impurity atoms



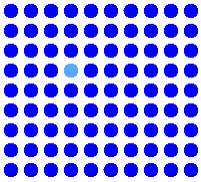
  - Interstitial impurity atoms move rather fast by a direct interstitial mechanism, until they eventually displace a lattice atom. This is shown in the simulation. We now have a self-interstitial (that may or may not be very mobile) and a rather immobile substitutional impurity atom, which may now diffuse with one of the other (slow) mechanisms.
  - The total effect of the diffusion now is caused by the superpositon of *two* (usually very different) mechanisms. **Au** in **Si**, and possibly some other impurities, diffuse in this fashion.

The **Frank-Turnbull mechanisms** (or **dissociative mechanism**).



- This is the pendant to the kick-out mechanism. Here the diffusing impurity atom does not dislodge a lattice atom, but gets trapped in a vacancy, whereupon it is almost immobile. The total effect may be quite similar to the kick-out mechanism.
- Which mechanism - Frank-Turnbull or kick-out - is operative, is difficult to find out. We must expect that in materials containing predominantly vacancies, the Frank-Turnbull mechanism will occur for some impurities, while the kick-out mechanism may be operative in materials with sizeable concentrations of interstitials.

Various direct diffusion mechanisms



- Shown is *one* variant, a direct exchange of places between two atoms. Other variants are exchanges involving more that **2** atoms (a whole "ring" that "rotates").
- Direct mechanisms are every now and then suggested in the literature to account for some new diffusion phenomena, but so far do not seem to occur in crystals.
- They may, however, play a role (in analogous form) when considering diffusion in amorphous materials.

Then we *could* have:

- The **"Extended interstitial" mechanism**
  This is a possibility not yet discussed or observed. It is mentioned just to show that there might be more atomic mechanisms than have been discovered so far. Imagine an extended interstitial moving through a crystal. The **10** or so atoms "inside" the extended interstitial move around a bit while the interstitial passes through and may end up on lattice places different from the ones where they were - they have moved! It is totally unknown if this effect plays a role in **Si**, but it well might occur at high temperatures.
- And, maybe, there could be more?

Again, it is important to keep in mind that you must clearly keep apart the movement of the "vehicle" - the vacancy, interstitial, etc. - and the movement of the atom(s) whose diffusion is of interest to you!

Exercise 3.3-1

Quick Questions to 3.