5.2.2 Defects that Get Around

Point defects are the easy-going defects in our defect zoo. They can *move* around in the crystal *easily* in contrast to the two and three-dimensional defects which are almost immobile and move rather slowly if at all. I've introduced you to this already in the preceding chapter. Here I'm gong to get serious about *diffusion*, as we called it.

Only one-dimensional defects or *dislocations* can also move around in a crystal, moving atoms in the process. They do that in a way completely different from that of point defects, as we will see shortly.

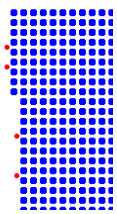
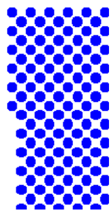
All interstitial atoms—extrinsic or intrinsic—as we cursorily call all the fellows sitting on interstitial places, can move around *randomly* as shown below. All they need to do is to squeeze from wherever they are to one of the neighboring places. Which one of the eligible places they pick for their move is completely random. So interstitial atoms, in contrast to proper lattice atoms, don't need vacancies as vehicle if they want to move; they just jump from one place to a neighboring one, see the animated figure below.

All they need for jumping around is a bit of energy=temperature. Make your crystal hot and its *interstitials* will get around. The proper atoms of the crystal, however, are not involved in all that interstitial frolicking. They stay where the are—except if a vacancy drops by.

We have essentially the same thing for the *vacancies*. They can hop around at random like interstitials, see the figure below. But there are major differences to the interstitial jumping mechanism, too:

1. *First*, interstitials are usually more lively than vacancies. They jump far more frequently at a given temperature than vacancies.
2. *Second*, if a vacancy moves by jumping to some neighboring place, it was really an *atom* of the crystals that has jumped

Jumping is what interstitials and vacancies actually do. It is a good word for the mechanism by which atoms move but it is a bit too simple for scientific purposes. The word "jump", after all, might stem from Gallo-Romanic dialects of southwestern France: "jumba", meaning "to rock, to balance, swing" or even "to do the sex act with" (or bump). We scientists certainly don't want to get mixed up in that; it might have prevented us from becoming scientists, for God's sake!
So we came up with a serious word and called the random jumping around of atoms "**diffusion**" and the mechanisms by which they do it "**diffusion mechanisms**".
The word "diffusion" comes from the Latin "diffusionem", meaning "pouring forth," "scatter", "apart, in every direction" and thus is much more high-browed than the lowly "jump" or "jumping mechanism".

	
Direct interstitial diffusion	Diffusion via vacancies
Animated diffusion mechanisms	

Diffusion or the random movement of atoms is an extremely important major point for sword making—that's why I have introduced it before. In case you forgot, here is the quote from chapter 4.4.2:

> **The major reason why we heat up our iron and steel a lot during sword making is the *need to make vacancies* so we can move atoms around.**

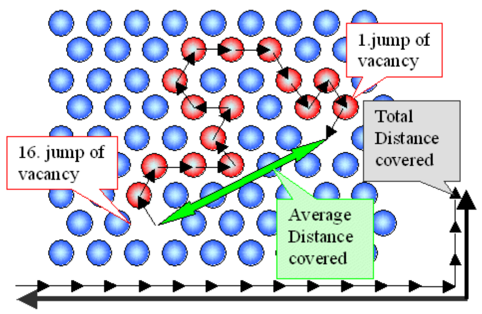
Diffusion of atoms thus can happen in two ways:

- Diffusion of interstitial atoms or **interstitial diffusion mechanism**.
- Diffusion via vacancies or **vacancy diffusion mechanism**.

- Either mechanism moves atoms around in a *random* fashion, and moving atoms around is what is needed if we do something to our steel - you know that by now.
  Like it or not, the **diffusion of carbon interstitials** in the iron crystal and the **diffusion of the iron atoms** themselves are the *major* reason why we heat (or cool) our steel during forging a sword.
  In consequence, we really need to understand diffusion if we want to tackle the big "why" questions.

Let's start by considering how far a diffusing entity—a vacancy or an interstitial—has moved after it jumped around *randomly* for some time in its crystal lattice. That's not an academic question at all, it has straight bearings to real life.

- Imagine a crowded bar somewhere in the desert, discharging rather drunken but happy regulars all the time. They will stumble around at random in two dimensions: one step forward, two steps to the left, another step forward, a step to the left, two steps back, ... For *perfect* model drunks it is equally likely that their next step will go forward, backward, left or right. They are doing what is called a **random walk** in sober science. Now comes the decisive question:
  You know where the bachelor party took place. Where are you going to look for ~~your husband~~ the helpless persons after they left the party, did 1.000 random steps, each on average 50 cm long, and then decided to lie down and go to sleep?
  You're not going to look for that slimeball? I can understand this. So let's assume that you are the owner of the bar who depends on the business of those random walkers and goes out to collect them.
  Let's look at the figure below to get an idea of what it is all about. Instead of your drunken spouse, I have a vacany move about, it is far easier to draw.



Random Process of Vacancy Diffusion and Distances Covered.

The *average* distance covered by the vacancy or the *diffusion length* is far smaller than the *total* distance covered or the **path length**. The arrows show the jumps of the atoms into the vacancy.

The figures above and below show it all schematically in *two* dimensions (you're welcome to supply a good and clear drawing of these processes in three dimensions. If it is really good, I will use it in the next edition of the hyperscript). Right now you must imagine what it looks like in three dimensions.

- Hint: In bird heaven there is a bar, discharging rather drunken but happy birds all the time. They will fly around at random in three dimensions: one step up, one to the right, two down, one to the left, ... For *perfect* model drunken birds it is equally likely that their next swoop will go forward, backward, left, right, up or down.
  You also can imagine drunken sharks if you are fearless.
  If you want it easy on your (by now drunken?) brain: just watch a single fly in one of those swarms of flies hanging around my and your garden in late summer, buzzing around apparently at random in three dimensions.
- All those random walker, flyers or swimmers cover some total distance or *path length* that is simply given by the number of steps time the average step length. But that was not the question. The question can be phrased in several ways; in what follows I'm going from the specific to the general:

  - Where are you going to look for ~~your husband~~ the helpless persons after they left the party, did 1.000 random steps, each on average 50 cm long, and then decided to lie down and go to sleep? That was the original question.
  - Where are you going to look for a random walker who did ***N*** random steps, each on average ***a*** cm long, and then decided to lie down and go to sleep? That is the original question rephrased and generalized
  - How far, *on average*, does a random mover in 1, 2, or 3 dimensions move away from its starting point?
  - What is the radius of the circle (sphere), drawn around the origin of a random mover, where it is *most likely* to find the mover after ***N*** steps?
  - What is the **diffusion length** of some random movement?

- When a smith case hardens a sword, he *diffuses* carbon atoms from the surface of the blade into the interior of the blade. We know that carbon hardens steel (we still don't know why, however), and *now* we know that the thickness of the hardened part is given by the *diffusion length* of the randomly diffusing carbon atoms. That's the distance they go on average into the blade from their starting point somewhere on the surface of the blade.
  So it would be neat to be able to calculate the diffusion length. Can we do it? Well, I don't know about you, but I certainly can.

How long is the diffusion length of some randomly perambulating particle about which we know a few things? You probably wouldn't guess that it was **Albert Einstein** who first figured that out. The extremely simple answer to the rather tricky question is:
The diffusion length ***L*** of randomly moving objects scales with the (average) *width* ***a*** of one step and the *square root* of the number of steps ***N*** they made; ~~$L=aN^{1/2}$~~. Sorry, I almost forgot my promise (too many beers at the bar).

- Let me give you an example: Your drunken spouse, after doing 1000 steps with an average lenght of 0,5 m will *on average* have covered a distance of $(1000)^{1/2} \times 0{,}5$ m=15.81 m from the bar.
  There is no square root sign in HTML, so I will always use the mathematically equivalent "power of ½" notation.
  $\sqrt{x} = x^{1/2}$
  Just to be on the safe side, let's emphasize an extremely important, if obvious, point. You will, for almost sure, *not* find your spouse at a distance of 15.81 m from the bar, just as you for almost sure will *not* find a women, who delivered her baby exactly at the predicted distance in time. Try to find the guy who personally has exactly the *average*income for your peer group. You can be almost sure that *individual* incomes are never the same amount as the *average* income. Same for diffusion lengths.
- Below you can watch what getting away by random walk looks like. Just imahine that we start a lot of random walkers at some place in a street and watch their progress. They will ony be be able to go left or right (it's a very narrow street). Just press "Run", pick your favorite red dot, and see how it does in the race of drunken red dots.

The great drunkards race
Details here.

Ignore everything except the "Run", "Stop" and "Reset" buttons.

- How is it done? Your PC flips a coin for evey red dot. Head means "go left", tail means "go right". The PC can do this rather fast for a lot of red dots, and it can keep track of what is going on. That allows to display the distribution of the red dots and to produce the bar chart, telling you how many red dots you will find in the interval given (the "distribution function"). I hope it doesn't come as a big surprise that eventually the typical bell-shaped curve emerges, also known as "Gaussian distribution", that you find for many statistical phenomenae.

Now let's make a little table to see what happens if your spouse keeps stomping around for longer and longer times:

Number Steps	Diffusion Lenght [m]	Path Lenght [m]
10	1.58	5
100	5	50
1.000	15.81	500
10.000	50	5.000
100.000	158	50.000
The step width is 50 cm=0,5 m		

This makes rather clear that you don't get all that far with random walking. After he has covered a total length of 5 km, he just will be 50 m away from his starting point - on *average*! Ten times that distance - 50 km, hard to do in one fell swoop even when sober - and he will just be 158 m away.
So keep in mind that average distance covered and now called a *diffusion length* increases only slowly with the time or number of steps our random walker or flyer is able to do.

Now let's turn the question around. We want a 10 µm thick outer layer of our blade case-hardened by diffusing carbon into the steel. 10 µm is about a quarter of the thickness of a hair, so it is not very much. The step width of carbon atoms is about 0.3 nm or 0.0003 µm. How many jumps are needed? And how long is the path length, the total distance a carbon atoms covers?
Sounds suspiciously like one of those dreaded math problems (one banker can embezzle 50 Mio Dollars in three hours. How much money can 3,5 bankers destroy in 3 month?). Try nevertheless - or look at the answer:

- It takes 1 110 000 000 or $1.1 \cdot 10^8$ or 111 Mio jumps. The jumping atoms covers a total distance of 33 000 000 nm or 33 000 µm or $3.3 \cdot 10^4$ µm or 33 mm or 3.3 cm or somewhat more than an inch!
  We are getting dangerously close to using equations and thus math, and that I promised not to do. So look up the "**random walk**" science module if you are interested in a bit more of that.

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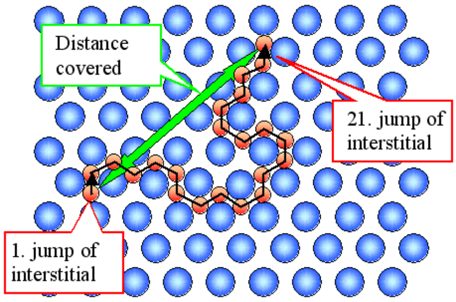
Science Link
Random Walk

Now let's look a bit more closely on how those *interstitials* move about:



Random Process of Interstitial Diffusion and Distances Covered

The *average distance covered* or *diffusion length* obviously follows the same rules we had for the vacancy movement.

- It's essentially the same picture as for the vacancy movement, and all statistical rules apply just as well. We used that already in the hardening example above.
  There is a big difference, however: the crystal atoms do *not* move.

To make things more realistic, I will now give you a few **numbers** for vacancy concentrations. There will be more later on, after we learned that iron comes in more than one structure.

Vacancy concentration	
Close to melting point at 1811 K (1538 °C, 2800 °F)	**10^{-5}** =1 out of 100 000 atoms is missing =0,001 %=10 ppm
Around 1.000 K (727 °C, 1340°F)	**2×10^{-8}** or 20 ppb
At room temperature 300 K	**$1{,}5 \cdot 10^{-29}$** or simply zero because there are less than 10^{29} atoms

- A concentration like 2×10^{-8} seems to be negligible, too, but that is *wrong*. Just as a tiny percentage of the population, take terrorists or scientists, for example, can cause a lot of pain or joy, respectively, to the rest of the huge population, just a few vacancies make a world of difference to a crystal.
  Here are a few more numbers:

Moving Things		
Time	**Diffusion length** @ 700 °C	
	Carbon interstitial	**Vacancy**
1 s	25 µm	2 nm
100 s	250 µm	20 nm
1.000 s	800 µm	65 nm

- Now that is interesting if you compare that to the example from above. The carbon atom had to cover a huge distance for a lousy diffusion length of 10 µm. Here we get substantially large diffusion lengths and that's because a carbon interstitial actually makes about 300 million jumps *per second* at 1000 K! The total distance covered, the path length in other words, is then 80 mm.

- The *vacancies*, in comparison, are rather sluggish. At 1000 K they jump just a few times per second. It needs higher temperatures to get them going.
  At room temperature, our carbon atoms still make one jump or two per second, while the iron atoms are not doing anything anymore (except vibrating a bit).
  More to that in the science super link.
  We'll have a little break now. I will be back shortly

Link Hub
Diffusion

I'm back. I hope you checked out the super science module in the meantime. It's a "super" module because it acts as a hub to more modules.
But even if you're the type who ignores commercials and rather uses the time to drink beer or to make room for more beer, we can arrive at a simple conclusion as far as sword making (and about making everything else) is concerned:

We need to heat up our steel for diffusion to happen! Things speed up a lot ("exponentially") with increasing temperature.

- We need diffusion so atoms can move. We need to move atoms so things change. We just have answered one of the "why" questions: Why do we almost always need to heat things to make things? Edible food, pottery, fire, metals, microelectronic chips, and so on. Now you know.