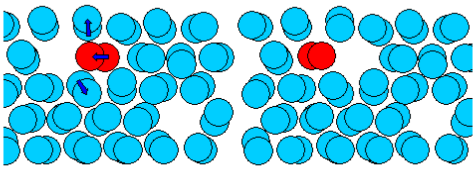
4.4.2 Moving Atoms Around

- Why do vacancies relate in some important way to making a sword?
  - The answer is simplicity in itself! If we have vacancies, we have the "vehicles" that we need to **move atoms** .



Atom about to jump

Atom has jumped

At the particular instance in time shown here, the red atoms happens to move to the left while it *oscillates*, and the two neighbors to its left happen to move up or down, respectively, as indicated by the arrows. The red atom then can move unhindered into the vacancy to its left.	The situation after the red-marked atom has jumped. The net result is that an atom has moved one atomic step to the *left*, and the vacancy has moved one atomic step to the *right*.

How atoms *in a crystal* move

- Vacancies are *extremely* important since moving atoms is a big deal, just wait. The major reason why we heat up our iron and steel a lot during sword making (or Si for making microchips, or most everything else for making most everything else; excluding babies), is the *need to make vacancies* so we can move atoms around.
  - It's a good bet than whenever a (crystalline) material is heated up to a temperature higher than, let's say, half of its melting point (as measured in Kelvin), you do it because you need vacancies. By heating you *produce* vacancies. It's unavoidable, the second law will see to that.
    My buddies and I, by the way, know *exactly* how many vacancies you will produce in a given material at a given temperature.
    It's quite easy to calculate (with a bit of calculus, logarithms and combinatorics, involving factorials), the link shows how. Even so the math may look a bit involved, it is about the most simple calculation you can do when invoking the second law with Boltzmann's super-famous formula. Calculating vacancy concentrations is a kind of paradigm for statistical thermodynamics.

    Please look it up! Like Wagner's music1), it is better than it appears.

Science Link

Making vacancies

- Now let's deal with that big "*why*" question you have on your mind:

Why do I need to move atoms around in order to make a sword?
(or a microprocessor?)

- Because whatever you do to make something, you *must* change the way the atoms are arranged in your material. You must rearrange the atoms in your crystal somehow, and for that you need to *move atoms around*.
  If you don't move atoms around when you try to do something to your material, it is *exactly* what it was before you did something to it—so why bother? That's so important that I will repeat it in huge letters:

If after some processing no atom has moved, then nothing has changed!

- If you think about that for a moment, you will realize that there aren't so many ways to move atoms around in a crystal without invoking vacancies. Let's look at some options that may occur to you:

  1. You can scrape some atoms off the surface of your steel (with a file, for example). The atoms inside then won't even notice that something has happened. Well - yes, you can do that! And you don't need to invoke vacancies for that. But you *only* changed the *shape* of a material by reducing its volume in this way, but not its properties.
  2. You can bang your material with a hammer. The material will crack it if it is brittle or changes its shape *without* loosing volume if it is ductile.
     Changing the shape of a crystal without changing the number of its atoms can *only* happen if some atoms are now somewhere else. So *plastic deformation* is indeed the *other* major way to move atoms. We will see presently how that is done without vacancies.
  3. You might corrode your iron by throwing it in acid or just by letting nature takes its course. It will certainly change. But that's once more doing things at the surfaces like in item 1, and we already covered that.
  4. Then you could — Yes? Any suggestions? I bet you are at the end of your tether now because *I* am (almost). If *you* find another way to move atoms around without using vacancies, let me know. I'm really curious. I will present your idea as my own and get the Nobel prize.

I'm going to assert that insight with a big green box:

Moving atoms in a crystal *randomly* is done via vacancies !

- Note the "*randomly*" in the statement above. Moving atoms via plastic deformation (No. 2 above), from the viewpoint of the afflicted atoms, is not a jolly, free-spirited, hopping-around-at-random thing but an orderly and forceful process - and that's why we are going to call it "military movement" later on.

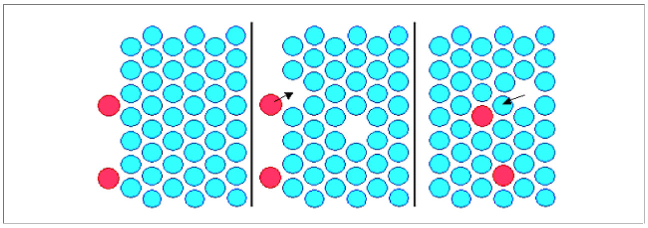
It is easy to see how the vacancy mechanism of atom movement works. One of the atoms bordering a vacancy jumps into the empty space that is the vacancy, see the figure above, or the more schematic figure below. As a result, one atom has moved and is now somewhere else, and so has the vacancy.

- *Which* one of the neighboring atoms will jump into the vacancy, and *when* it's going to do this, is a purely statistical or *random* event. Randomness always means that you can simulate what is going on by casting dies and following some simple rules. For example, get a 12-sided die, make the rules like: 1 = atom on top moves, 2 = atoms on the upper left moves, …) and you now can cast a die to determine which one of the 12 neighbors to a vacancy in an fcc or hcp crystal is going to jump. For a bcc element crystal you need a 8-sided die. Of course it is far easier and faster to your program your computer to simulate those dies. Just utilize its "random number" generator.
- Again, even so it gets a bit repetitive: we can calculate precisely what will happen on **average**. It's not called "**statistical thermodynamics**" just for fun; there is an awful lot of chance, randomness, and statistics involved. But "**stochastics**", to give it its proper name, is a precise mathematical discipline and we know precisely how often, *on average*, atoms jump around in their crystal or, same thing, vacancies jump around in their crystal.
- For example, in pure iron at 900 °C (1652 °F), just below the temperature where it turns into a bcc crystal, a vacancy will jump about *100 million times per second*, while at room temperature it essentially *sits still*. That means that at the high temperature about 100 million atoms per vacancy in there will be somewhere else after just one second.

The whole process of atoms moving around randomly is called "**diffusion**". Diffusion happens naturally all the time in liquids and gases because there the atoms move randomly by definition. It is the reason why you might smell your Beloved before you see him—the smell "molecules" just move or diffuse faster than he moves. But diffusion of gases or liquids is not of much interest to us here.
Diffusion in crystals via vacancies is at the root of changing properties of solids, and that's what we are actually discussing, remember?

- Let's look at the importance of diffusion via vacancies in the light of modern technology. Let's make a **microchip** and not a sword for a change.
  The basic task is to take a perfect silicon (Si) crystal and to replace a few of its atoms (one out of 10 million, let's say) by Arsenic (As) atoms in a certain region. That's called "**doping**" the silicon, and *doping* is the process at the very heart of microelectronics.

How are you going to do this? You only can "go in" via the surface, so let's put some arsenic atoms on the surface of the silicon crystal. This is shown schematically on the right-hand side in the figure below; the arsenic atoms are colored red.



Diffusion and the making of a chip

- If you have some arsenic on the surface at room temperature, you're not getting anywhere. The arsenic atoms would be sitting on the silicon surface forever, give or take a small eternity.
  - What you are going to do now is to produce some *mobile vacancies* as shown in the middle picture. For that you must *heat* your silicon to a sufficiently large temperature (at least 800 ^{0}C (1472 ^{0}). In the picture we have generated two vacancies. The vacancies move around at random because silicon atoms are jumping into them all the time. Eventually, as shown in the middle figure, one vacancy happened to move next to an arsenic surface atom, giving it a chance to make a first jump into the silicon. And so on.
    The picture on the right shows the two arsenic atoms now inside the crystal. Most of the time they are just sitting there, waiting for vacancies to come by. If that happens, they might make another jump, always provided if they can beat the silicon atoms that are competing for a jump into the vacancy. If they jump, they might make it deeper into the crystal or back to the surface; it's all equally likely, after all.
- This looks like some truly awkward process for going places. Well, it is—but it works. It works quite nicely, in fact.
  - Look into your silicon microprocessor with your brain microscope. The structures you will find *inside* the silicon are far more complex then you could imagine in your wildest dreams - but they were produced mainly by this vacancy diffusion process.
    The vacancy diffusion process also works for iron. It is the cornerstone of iron and steel technology, and of any other "crystal changing" technology.
- By the way, how fast do you think those atoms *oscillate*? What's your guess?
  Back-and-force a few hundred times per second like a tuning fork? A few thousand, million, billion, … times per second? Well, you either know or you don't. You can't really guess that number intelligently. If you don't know it, you must do some calculations. Since we don't do calculations here, I will tell you.
  - Those atoms are small and nimble; they actually oscillate with a **frequency** of about 10^{13} Hertz (Hz) or 10^{13} times back and forth per second. In other words: 10 billion times per second in Europe, or 10 trillion times in the USA. By the way, that's about 1 % of the frequency of light if you consider it to be an electromagnetic wave.
    What that means is that all this jumping around can be quite fast. An atom next to a vacancy "tries" 10 trillion times per second to move over to the vacancy position. So even if the probabilities for making that big jump are very low, it still could happen rather often per second.
    All in all, atoms can move around quite swiftly at high temperatures despite single jumps being very small (about 1 nm; remember?).
- Let's summarize:
    - A perfect element crystal is an ordered assembly of one kind of atom (for example iron). Its lattice type (bcc for iron at room temperature) is the one belonging to its "nirvana" state.
    - The atoms oscillate around their basic lattice position with a rather high frequency. The energy contained in these oscillations we call "*temperature*". When the temperature increases, the amplitude of the oscillations increases.
    - Depending on temperature, a certain number of **vacancies** *must* also be present and their concentration increases sharply (a better word is: *exponentially*) with increasing temperature.
    - Oscillating atoms and vacancies exist because the *second law* commands with absolute authority that by increasing temperature, things *must* become more disorderly; the entropy must increase. And that is good! Being perfect all the time is boring.
    - The vacancies can move around and that provides for movement of the atoms, something we call *diffusion*. Diffusion is the key to processing crystalline materials.
  - Now read out loud to yourself:

If my steel changed - from soft to hard or the other way around, whatever - the internal atomic structure must have changed. This means: atoms must have moved. Diffusion via vacancies provides one of the two ways to move atoms in a crystal.

- So far, so good. But we still have a major *why* question open that has no obvious relation to vacancies and diffusion:

Why does pure iron change its phase from a bcc crystal to an fcc crystal at precisely 911 °C (1.672 °F)?

- This question applies equally well to *all* elements that change their crystal structure upon heating (or cooling), for example like Cobalt (Co), Strontium (Sr) and carbon (C) – look up the table with the list to find more.
  - We might ask just as well *why* elements like Ag (silver), Au (gold), Al (aluminum), Cu (copper), Si (silicon), and so on, do *not* change their structure at some temperature?
- The answer is simple in principle. In practice it will provide work for generations of materials scientists to come. Here it is: A crystal of any material can be considered to be an extremely powerful analog computer that at any instant in time assesses the following items:

  1. The present situation, including, for example, the actual temperature, pressure and the availability of foreign atoms.
  2. Its actual structure, including the actual crystal structure, the number of vacancies and other defects we will encounter later.
  3. The balance between energy and entropy for the present situation and the *actual* structure.
  4. The balance between energy and entropy for the present situation and *any* conceivable *possible* structure.

  - If one of the conceivable states is nirvanawise better than the actual state, the crystal implements all the measures at its disposal to change its present state to that more desirable state. And that may be a different crystal structure at some changed temperature.
- Of course, the crystal does not really compute. It is mathematically just as challenged as your average banker or politician; it might just be a little bit ahead when it comes to large numbers.
  - The crystal just does whatever it does because every atom simply does what comes naturally, like an ant in an anthill. All the possible structures are continuously tried out on a very small scale. Some atoms just assume some state, purely at random, and if it "feels good", it spreads. All possible states always "compete" with each other, and the winner takes all.
    Only if you look at the *big* picture with regard to crystals or ant colonies, something meaningful emerges that is not visible on the atom or single ant level.
  - It's only us curious humans who have to go through an algorithm (in the form of a computer program) as outlined above to figure out what is going on. The four-step procedure above is simple enough in principle but outrageously difficult in detail. What are the *possible* potential structures? If challenged, you probably could come up with a few—but rest assured that there are far more than you could imagine in your wildest (Material Science) dreams. The link gives an example of what previously unimaginable wonders we have already encountered.
- So, to answer the question, it just so happens that in iron, cobalt, and few other metals it is necessary to change the crystal structure at some temperature for achieving nirvana, while for aluminum gold, and so on it's not.
  - Simply speaking, the crystal has one more trump card up his sleeve for balancing energy and entropy than just adjusting atomic vibration amplitudes and vacancy concentrations. It can also change its basic crystal lattice structure. Doing that also changes vibrations and vacancy numbers. That makes it a bit difficult for us to *compute* if changing the basic structure, meaning to initiate a *phase transition*, would be a good move.
    Now for the good news. Being engineers, we don't have to compute all that! The crystal, after all, can and will do that for us. We just have to *measure* what it is doing by designing some suitable experiments.
  - What we will note already here is that the fcc phase that iron assumes at high temperatures is actually only a *little bit* closer to nirvana than the bcc phase, while at low temperatures the bcc phase is *a lot* better than the fcc phase.
- Come to think of it, we actually know about this already. Pretty much *all* crystals change their basic structure at a very special temperature that we call **melting point**. This particular **phase transition** just looks more dramatic compared to changing from one crystal lattice structure to another one, but in essence it is the same thing.

  - If an element crystal undergoes one or more phase transitions before the final big one called *melting*, and at what temperature this happens, we know from experiments. But not only did we measure it in great detail, we can actually (almost) calculate it. Essentially we know how to calculate it (see above), and we get good approximate numbers. Getting precise numbers is still beyond our ken (but not for much longer) because you need to do extremely tricky math and that's not only tough but needs more computing power than we command right now.
- Not many elemental crystals undergo a phase change in the solid state, and very few do it more than once like iron. Now you have a first indication why iron is just about the most complicated crystal among the major metals. Its bag of tricks for achieving nirvana is rather larger than that of most other crystals.
  - Iron is also **magnetic** in its bcc state—but not in its fcc state. This provides for a few more tricky ways to play with energy and entropy. Being (ferro) magnetic is a rare treat among elements. Only nickel (Ni) and cobalt (Co) are ferromagnetic, too! I won't go into this here because it is not very important for sword making.
    There is a science module about magnetism, however.
    All things considered, iron is just a rather special material, already in its ideal form as perfect "brain" crystal.

Science Link

Magnetism

- In reality, however, there is no such thing as a *perfect* iron crystal in a state of nirvana, utterly at peace with itself and the world.
  - There are only *real* iron crystals out there, not brain crystals, and none of them can ever achieve perfect nirvana, just like you and me. They only can get close. Their desire to get as close as possible is what makes things happen.
  - So we now need to look inside a *real* iron crystal and see what happens there.

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1) "Wagner's music is better than it sounds", Mark Twain