8.1.2 A Closer Look at the Second Law

- The second law tells us how things should be for the coveted state of nirvana. What the actual structure will be is a different kettle of fish.
 - Your mother, your teacher, your priest and so on told you many times what you should be; now consider what you are. You probably are not the president, a Nobel Prize winner, or the pope (me neither). But perhaps you are a teacher, a (rich) plumber, a real estate agent, or a professor. Not so bad either. And I can still win the Nobel price even so it's highly unlikely.
 - The second law does tell a crystal what it should be—in precise equations. Your mother told you what you should be in countless words, and your priest, imam, rabbi etc. threatened you with eternal fire and brimstone etc., if you didn't heed their ideas about what you should be. I prefer equations by far. The second law also relates to crystals what the second-best structure would be, the third-best, and so on. If the

very best structure is unattainable, the crystal is smart enough to go for the second best, third best and so on. Can you match that?

Unfortunately, while the *crystal* always seems to know precisely what is best under given circumstances, we do not always know it for sure, neither for the crystal nor for ourselves. The second law doesn't tell us all these alternatives straight away but hides the answers in so-called differential equations or other tough math. We can't always find the solutions—in contrast to the crystal.

If you have not yet achieved nirvana or a good approximation thereof, you must do something. Doing anything means to move some atoms around. That is true for you and for a dumb crystal. The crystal usually does it by some of the diffusion mechanisms we already discussed. If the crystal wants to form a big precipitate with, say, a million impurity atoms inside, it must gather this number of impurity atoms from a largish volume that contains enough of the stuff, and send them all to the place where the precipitate is to be located.

How, I ask you, can a rather dumb crystal, consisting of not-so-smart atoms, know about this and then actually do it?

There can only be one answer: the crystal "knows" nothing whatsoever. It happens all by itself, without purpose and intent!

Out of the pure chaos of impurity atoms and vacancies running about at random, order, in the form of neat precipitates embedded in the crystal, will arise all by itself if the conditions are right.

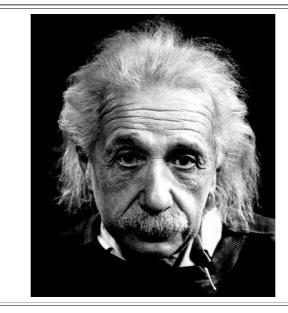
How does that happen? Roughly like this: Two impurity atoms jumping around at random in their host crystals, meet accidentally somewhere, and since they like each other to some extent, stick together for some time. Then they break up again, resume their random walk, and meet some others, or maybe meet some threesome that has formed accidentally somewhere else.

As the temperature goes down, their movement becomes more sluggish and they tend to stick together for a longer time. Precipitates start to form and grow as soon as more atoms stick to it per second than atoms leaving it again.

Look at your bank account. The amount of money in your account starts to grow as soon as more money comes in per month then flows out. If your account balances, you are at equilibrium: nothing changes anymore (on average). Change the average stream of money flowing in or out ever so slightly, and your precipitate of money localized in your account gets larger or smaller.

The second law (and some other quite exciting stuff) comes right out of "statistical thermodynamics"; that part of physics that describes what temperature actually is. We always deal with huge numbers of atoms and that's why we can only deal with statistical entities like averages. Temperature, in case you forgot, is just another word for "average energy contained in the random movement of elementary things like atoms or molecules". You see there are good reasons to call it statistical thermodynamics.

By the way, the first scientist who explained phenomena like diffusion in terms of atoms jumping around at random was no less than Albert Einstein. With that he also established the reality and existence of atoms. Later he got a Nobel Prize for explaining the so-called "photo electric effect", essentially establishing the photon . He should have obtained at least *five* more Nobel prices, definitely another one for explaining (in terms of equations) the phenomena of diffusion of atoms in solids.



Albert Einstein

Born in Ulm / Suebia / Germany. One of the many
achievements of Suebians

- Since you asked: Nobel prices should have been awarded to Albert for:
 - 1. Explaining the phenomena of diffusion in terms of atoms.
 - 2. Explaining the photoelectric effect. (This one he got).
 - 3. Special theory of relativity (worth about 5 regular Nobel prizes).
 - 4. General theory of relativity (worth about 10 regular Nobel prizes).
 - 5. Describing (in equations of course) the so-called "stimulated emission of photons", the very foundation of Lasers, about 50 years before the first Laser went operative.
 - 6. Predicting the so-called "Bose-Einstein condensation" a strange thing that matter does at very low temperatures. The "Bose-Einstein condensation" was found experimentally not so long ago, and that did provide for Nobel prizes.
- But despite Einstein's involvement with what we now call statistical thermodynamics, the supreme price for that, in my opinion, goes to Ludwig Boltzmann (1844 1906) and <u>Josiah Willard Gibbs</u> (1839 1903), who put the <u>second law</u> as we use it here on firm footing just about before the turn of the 19th century.
 - The (very short) equation on Boltzmann's <u>tombstone</u> (S = klog w) ranks up there with the very well-known short equation from **Newton** (F = ma), Einstein (E = mc²) or Max Planck (E = hv). I promised that I would abstain from equations here, what you see above are just quotes.
 - Boltzmann not only did not receive the Nobel prize; he finally was driven to suicide by some of his dear colleagues who ridiculed him for proposing that things like atoms did actually exist. "Can you see them" he was asked, "if not, shut up". He couldn't see atoms then—but we can <u>see atoms now</u>. Grave injustice has been done to a hero of physics and materials science once more!
- The long and short is that neither crystals nor atoms are smart. They just do at random what circumstances permit them to do, just like some American presidents.
 - Boltzmann and others were smart. They could predict what the nirvana states (best, second best, ...) would be and how it can be achieved by atoms running around. Let's be smart, too and see what we can do.