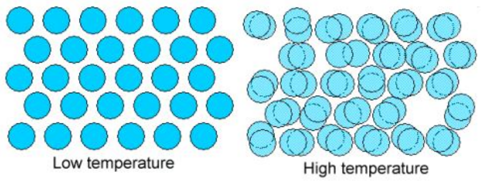
4.4 Inside a Perfect Crystal

4.4.1 Perfect Crystals and the Second Law

- Let's take a hypothetical *perfect* iron crystal (a brain crystal, in other words), or just any perfect crystal, for finding out what crystals will do when you heat them up.
  - No real *iron* crystal will ever come close to being perfect, but the *silicon* crystals grown for microelectronics actually are not so bad. Whatever, it's no problem for us here. We work with a "brain-and-paper crystal" and it's ridiculously easy to keep those perfect.
- First we look at our crystal at very low temperatures, close to absolute zero (=0 K). It's not so easy to do this in reality but it's no real problem either if you have the right equipment.
  - Disorder then hardly counts for achieving niravana. Whatever disorder or entropy S you have, the product TS at very small temperatures close to zero is always very small; for T=0 K it would be zero, no matter how large S would be
  - So coughing up some energy to produce disorder doesn't make any sense when it's really cold. The return on that investment cannot be large. It is thus clear that whenever it's *very* cold, you thrive for *perfect order* as shown on the left in the (schematic!) figure below.



Law and order for crystals	
Schematic drawing of a perfect crystal at very low temperature. Perfect order, with atoms sitting (almost) still.	Same crystal at high temperature. Atoms are vibrating wildly (hard to draw) and two *vacancies* have formed.

- Now we increase the temperature a *little* bit. What is our crystal to do?
  - To answer that question, we first have to answer that particular question that kept nagging you subconsciously all this time, giving wild dreams about hot things and keeping you from sleeping well:

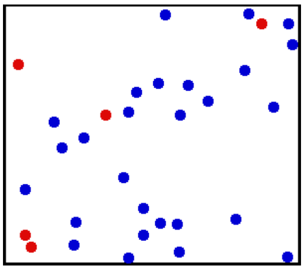
What, exactly, is TEMPERATURE ?

- You think that is an easy question? You think that any idiot can tell the difference between hot and cold water, or a hot and cold day? Allright. Tell me about it!
  - Aha. Hot water is hot because you burn your fingers when you stick them in. And it's a cold day when your a.. freezes off, and hot day when you get a sunburn.
    Fine, but how can your a.. tell that it's freezing? And I hope you will excuse my saying so, but science doesn't give a fart about how your fingers or your a.. *feels* about temperature.
    Considering that you consist mostly of water (and some beer and red wine in my case) the question is: how do the water molecules in your a.. know that it's cold enough to start freezing?
  - Remember, *all* we have so far are atoms, molecules, crystals and whatever else you can make from atoms, plus photons (the particles of light), and the first and second law.
    Maybe there is something like a "temperature particle"? Let's call it **phlogiston** (ancient Greek of course; phlogistón="burning up"), so we have a name and feel better about it. Having invented phlogiston makes things simple: shove some phlogiston around and things get hotter or colder. You could also call it "caloric" and assume it is an element like carbon, if that makes you feel better. The eminent **Antoine Lavoisier**, the "father of modern chemistry", did that in 1789, not all that long ago.
    Tough luck! There is no phlogiston, or caloricum, or any *substance* of heat—notwithstanding the fact that a large part of humankind believed that for quite some time; use the links for details. Atoms, molecules, crystals and whatever else you can make from atoms, plus photons (the particles of light) is the complete list. No phlogiston, caloricum, heatstuff or whatever.

- Looking at a perfect crystal you see atoms, and *nothing but atoms*! The question then must be: What is different in the *arrangement* of atoms at low and high temperature? The arrangement is the only thing that could be different!
  Please commit to memory:

**Temperature is just another word for
"average energy contained in the
random movement
of elementary things
like atoms or molecules".**

- Let's whip out your brain microscope and give the air around you a close look. Ready? Then you should see a lot of nitrogen and oxygen molecules (N_2 and O_2, respectively) flitting around at high speed and bumping into each other all the time.
  - The animated figure below shows schematically at very high magification (around 10.000.000×) and in very slow motion what you are supposed to see:



The air as seen with your brain microscope

Colors are only used to make it easier for you to keep track of some particle. In real air the spheres would be (elongated) oxygen or nitrogen molecules, there would be far more of them then shown here, they move on average with the speedof sound, and they would move in three dimensions.

Source: English Wikipedia, author A. Greg

  - The molecules bump into each other (and into the atoms of the wall) all the time, and that makes their motion rather *random*. Their total energy then is just the *average* kinetic energy of *one* molecule times the *number* of molecules. Their *average* kinetic energy, of course, is determined by their mass and average speed *squared*.
    The *average* random energy of those atoms or molecules is exactly what we call *the temperature* of the gas, it just happens to be measured on a different scale for historical reasons.
    Note that the gas molecules in your car, traveling along with you at whatever speed you are driving at, also have some *additional* kinetic energy because of the car motion. This is, however, not a *random* motion. All molecules travel with the same speed you are traveling with *on top* of their random motion—and this does not count!
- We can measure this kind of energy in "Kelvin" (we never say "degree Kelvin, by the way), "degree Celsius", "degree Fahrenheit", or whatever temperature scale you prefer. The numbers are quite *different* but it is always the *same* energy. This might be a bit confusing but it is nothing new.
  - You can measure your wealth in Dollars, Pounds, Euro, or the number of Ferraris it can buy. You will produce quite different numbers for each scale, but it is the *same* wealth and you can always switch from one number into the other one.

    Converting energy measured in barrels of oil, British thermal units (btu) Joules (J), kilowatt-hours (kWh), electron volts (eV), or temperature (T) produces quite different numbers too, but it is the same energy and ~~you~~ I can easily convert from one unit to another one. It's just as easy as switching from one currency to another one, with the additional advantage that the exchange rates never change.
- By the way, how fast on average are the molecules of air at room temperature? What's your guess? Faster or slower than your Ferrari at top speed?

Guess! Do try!

- Here is the answer: they run around with the *speed of sound*, about 330 m/s.
    - It can't be otherwise because sound is a local disturbance in the running–around pattern of the gas molecules, and this disturbance cannot possible mover faster than its parts, the air molecules.
- Now whip out your brain microscope once more and look at *molten steel* . At the magnification required this can actually *only* be done with a brain microscope. It will be rather hot work so, for starters, let's look at a more convenient liquid like water at room temperature. Beer or red wine is just as good, if that helps your looking.
  What are you going to see?
    - Water molecules in liquid water are flitting around randomly and bumping into each other all the time! The bumping into each other makes their motion random, and so on. *Schematically* it looks exactly as in the animation above. The animation above could also be used to *schematically* illustrate water *vapor* , a gas. It is pretty much fine for all liquids and gases.
      So what is the difference between a **liquid** like water and a *gas* like water vapor?
      In a liquid the atoms or molecules are closer together and still stick to each other a bit. If given more room, they would not thin out like water vapor or any gas but still occupy the same volume. Nevertheless they move around freely but always feel some attraction to the other guys, not unlike people at a party in a crowded room. They move around freely but also stick together.
    - If we extend the analogy from a a party to a crowded movie theatre where people sit on the same chair all the time, we changed from *liquid* to a **crystal**. Nobody is running around, everybody, including you, sits at a fixed position. All you can do is to wiggle around that position a bit. Only people with a **vacancy** (=unoccupied seat) next to them can move—one place at a time.
- Now back to our *perfect crystal*. In contrast to gases or liquids, the crystal atoms *cannot* move around to acquire some of the energy we call temperature. All they can do is to wiggle around their position. They do that very quickly so we don't call it "wiggle" but **oscillating** or *vibrating* . Those atoms or molecules thus oscillate around their proper position a bit.
  The maximal deviation from their position at rest we call **amplitude**. The rest is easy:

        - *Low* temperatures=small amplitudes.
        - *High* temperatures=large amplitudes.
    - Oscillations or vibrations are hard to draw. I did the best I could in the figures here and there. What we can see, however, is that the hot crystal above, with its atoms oscillating wildly, would look a lot less orderly than the cold one next to it—even if there weren't any vacancies.
      Vibrations of the atoms evidently induce disorder or, as we agreed to say, *entropy* .
    - Here we have the full answer to the question from (far) above! When we raise the temperature, the energy goes up, yes - but so does the entropy. At the raised temperature we can always find a proper balance of energy and entropy and achieve nirwana again. Everybody is happy.
- Now we get our crystal going and raise the temperature *a lot*. We give more **thermal energy** to the crystal, to introduce a new buzz word.
    - The atoms now must vibrate wildly, with large amplitudes, and that is part of the reason why the crystal becomes a bit larger by **thermal expansion**.
      Entropy increases too, but not enough for nirvana purposes. There is only that much disorder you can make by keeping things not exactly at their proper place but always nearby. Think of your **spice rack**. Not having the spices in alphabetical order but still on the rack produces *some* disorder or entropy. Allowing some spice containers to be off the rack for good (they might now be in the refrigerator, the underwear drawer, or God knows where; it doesn't matter) offers *far more* possibilities for making things messy.
- In very hot crystals we need more massive disorder for achieving nirvana than we can make with vibrations, and for that we have to misplace things.
    - The only things we can misplace are the atoms; we have nothing else. So let's misplace atoms and create **vacancies**—it was done already in the figure above. I have misplaced two atoms. They are gone, no longer with us. They might now be in the refrigerator, the underwear drawer, or God knows where; it doesn't matter. In their place we now have our first *crystal defect*, the *vacancy*. We are going to become very familiar with these little nothings because they are important for sword making.
      Since we cannot really loose atoms completely, you might wonder were they *really* are now. Well, consider for the time being that they went to that mysterious place where the **missing single socks** go. Like those socks our atoms have not really disappeared into thin air. Your wife could find your single socks for you, I could find the missing atoms for you. I will eventually—but you don't need to care about that here; it is irrelevant for what I want to get across here.
    - Our crystal looks really messy now and we have plenty of entropy. For making the *vacancies*, as we will call the **missing atoms** now, we had to invest some energy but as a return on the investment we got substantial entropy. If we invest just right, we make exactly the right amount of vacancies to give the best balance between energy and entropy for the temperature we have chosen. We have achieved nirvana once more.
- "What the hell", you might be inclined to yell out now. "Wen I drive around with my girl friend in search of a vacancy in some motel, I might care about vacancies. This here looks like some crazy little game for academically inclined eggheads but certainly does not relate in some important way to my girl friend or to making a sword."

Well, you're wrong. Utterly wrong.

- Without **vacancies in crystals** you would not drive in a car. You might not even exist, because Columbus would not have discovered America. The likes of you would live in what we call the stone age.