# 1. Global and Local Equilibrium for Point Defects

Science

Phase Transformations, Supersaturations and Equilibrium

Phase transformations are everyday stuff. A new phase must form whenever something freezes or melts, evaporates or condenses, dissolves or precipitates. This new phase must *nucleate* - it must start somewhere and sometime as a cluster of just a few atoms or molecules. Let's look at a few examples; the first ones are the every-day kind:
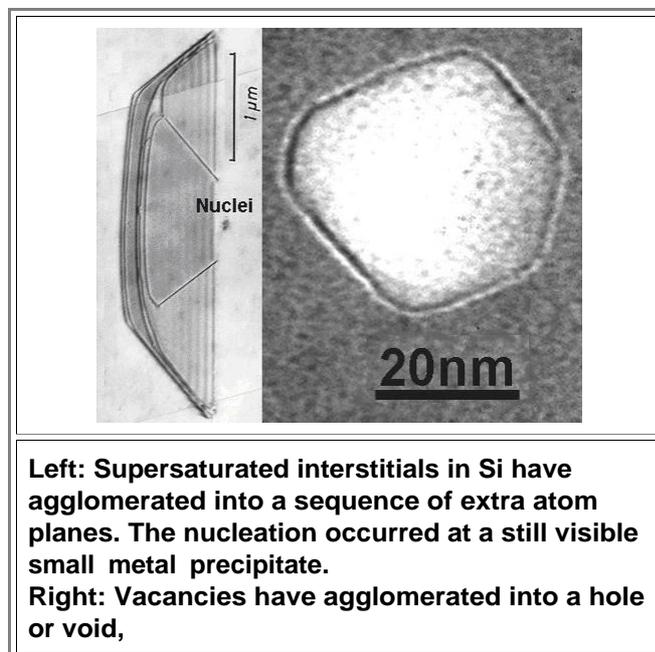
- Liquid water evaporates, the resulting water vapor is dissolved in the air and invisible. Water vapor in *supersaturation* eventually condenses to water droplets. Now you can see it - it's a cloud. The water droplets grow and eventually rain will fall. If the droplets freeze, we have hail or snow. There are two phase transformations in there (solid ⇔ liquid; liquid ⇔ vapor).
  The nucleation of the first tiny droplets needs some help, e.g. by suitable "dirt particles". That's why "**rain making**" is possible to some extent.

- Salt or sugar dissolves in water because at the beginning the water is *undersaturated* with salt or sugar components. The solids now have "disappeared", you can't see them anymore. In the sun the water evaporates, the solution becomes *supersaturated*, and salt / sugar crystals "appear" again because they precipitate out of the liquid solution.
  The process is far easier and produces better crystals if some nucleation help is provided, e.g., by inserting a toothpick into the solution:

Sugar crystallized around a toothpick
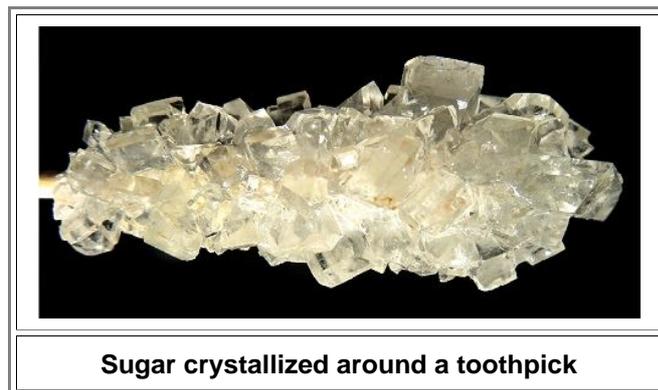
- Water freezes. Watch a frozen puddle or any ice surface closely, and you see that freezing tends to start at some special points where first nucleation occurred.

- Water boils. The steam bubbles never appear just somewhere in the water but always at "favored" nucleation points. Usually a (tiny) flaw at the pot bottom acts as nucleation center, but but also any implement you stick into the hot water will do. Rough surfaces (wood) are better than smooth surfaces (glass).

Now a few examples of the not-so-everyday kind:

- Vacancies or interstitials in some crystal become *supersaturated*. They "condense" or agglomerate into a small void or into discs of interstitials, producing "stacking faults", respectively. Below are two examples from transmission electron microscopy.

Left: Supersaturated interstitials in Si have agglomerated into a sequence of extra atom planes. The nucleation occurred at a still visible small metal precipitate.
Right: Vacancies have agglomerated into a hole or void,

- Carbon atoms dissolved in steel become *supersaturated* . The condense or precipitate into **Fe₃C** cementite particles.

- **A**-type atoms / molecules in **B**-type materials (crystal / glass / polymer, you) become *supersaturated*. The precipitate into some **AB** kind of material like cementite or kidney stones.

The key word above is "**supersaturation**". What does it mean? Well - go back to the "making vacancies" module to get a first idea. Now let's go on.

- What we do here is to look at the basic equation for point defect equilibrium once more:

$$c_{PD} = c_0 \cdot \exp - \frac{E_F}{kT}$$

c_{PD} = equilibrium ("nirvana") concentration of some point defect **PD**,
c_0 = "pre-exponential factor roughly = **1**,
E_F = formation energy of the **PD**; roughly around **1 eV**,
kT = Boltzmann constant **k** times absolute temperature T = thermal energy = **1/40 eV** at room temperature.

- This little beauty tells you exactly how many point defects you need for equilibrium at some specific temperature T. Chances, however, are that you have a concentration quite different from the equilibrium or "nirvana" concentration. This leaves two possibilities:

  1. **Supersaturation**: The actual concentration is *larger* than the equilibrium concentration.
  2. **Undersaturation**: The actual concentration is *smaller* than the equilibrium concentration.

- In both cases you are not in *global equilibrium* , the smallest value of the free energy that can possibly exist.

We have two basic kinds of point defects: intrinsic PD's, meaning essentially vacancies, and extrinsic PD's, meaning foreign atoms. The crystal can somehow make *and* get rid off vacancies (and interstitials as far as some are present), so there is a general possibility that equilibrium can be attained. Nevertheless, we might have supersaturations or undersaturations of vacancies, too. Let's look at that possibility first.

- When you *heat up* a crystal, the equilibrium concentration of vacancies is going up exponentially. Since the production of vacancies takes some time, chances are that the *actual* concentration is lacking behind the one needed. We have *undersaturation*.
However, since heating up means it gets hotter and hotter and everything needing some energy becomes more likely to happen, it takes less and less time to produce enough vacancies for reaching equilibrium.
In other words: you cannot maintain undersaturation for very long. Nirvana is easy to reach and will eventually prevail.

- *Cooling down* is entirely different. Things get sluggish, vacancies cannot disappear as fast as needed, and eventually you are going to "freeze in" a supersaturation of vacancies that might be with you forever.
  Nirvana or global equilibrium, the very best state of being, is unreachable *forever*. The time has come to look for the second-best state of being. For example, if *you* can't achieve nirvana, you still can hope for being reborn as Material Scientist. Send me large amounts of money and I will hope with you.

The choices for the second-best option for vacancies are a bit more limited:

- *Undersaturation:*
  Do nothing. There aren't enough vacancies around, alright, but anything you could do with those vacancies makes it worse. Your only option is to be patient and make more vacancies as fast as you can.
- *Supersaturation:*
  Try to get rid of the surplus. If there aren't any "sinks" around into which you can dump the surplus vacancies (for example grain boundaries, dislocations, impurity precipitates), imprison as many vacancies as needed in some vacancy agglomerates or clusters. In other words: make vacancy "precipitates".

The catch is that precipitates of all kinds cannot spring into full-grown existence just so. The need to grow bit by bit - and this is a torturous process in the beginning and possibly in the end.
In the beginning the vacancies are highly mobile but need to find a hard-to-get nucleus, where agglomeration can start. In the end there are enough precipitates to go to, but you can't move anymore.

- It's a bit like the (old-fashioned) boys chase girls. In the beginning the boys are highly mobile, able and motivated, but they need to find one of those elusive girls before clustering can start. In the end, there are plenty of "girls" or nuclei (woman still live about 7 years longer than men) but the ability of the few remaining unattached men has sadly deteriorated.
  But enough foreplay by now. Let's gird our loins and look at the most simple case first: a perfect crystal with nothing but vacancies.

Vacancies and Supersaturation

We are looking at a *hypothetical* case. We start with a *perfect* crystal at nirvana, i.e. a crystal with no dislocations, grain boundaries etc., but with the global equilibrium concentration of vacancies, since this is part of being perfect, i.e. at nirvana. We neglect self-interstitials here for simplicies sake and because they do not figure prominently in metals.
Then we make the crystal a bit less perfect. We do this by still having only vacancies as defects, but now with concentrations that are *not* the nirvana concentration. This is not a very realistic case (we only do that in our brain, after all) but it will teach us a thing or two that we can carry over to realistic cases.
Let's now make a clear distinction of what we are going to find *on average* at equilibrium or non-equilibrium conditions, and on what is actually going on.

- *First*, let's look at bit more closely at what is going on while we have nirvana conditions. So we have *exactly* the right amount of vacancies on average - but that doesn't mean that nothing is happening! Quite the opposite:

  - The vacancy concentration has the nirvana or equilibrium value $c_{eq} = c_0 \cdot exp-(E_F/kT)$. All those vacancies are running around at random with a "speed" or *mobility* relating to their diffusion coefficient $D_V = D_0 \cdot exp-(E_M/kT)$.
  - Occasionally, two vacancies run into each other, bond, and form a **di-vacancy**. The probability that this happens scales with the *concentration* and the *mobility* of the vacancies.
    Bonding releases some **bonding energy E_{2B}** since "making" a *di-vacancy* costs less formation energy $E_F(2V)$ than making two single ones (fewer bonds need to be "cut"). We have $E_{F(2V)} = 2E_{F(1V)} - E_{2B}$.
  - The vacancy concentration now has decreased a little bit - 2 vacancies are missing. The di-vacancy concentration has gone up a little bit - there is one new pair now.
  - Once in a while, a di-vacancy dissociates again into two single vacancies. The probability for that process is given by the Boltzmann factor for overcoming the energy E_{2V}.
    The vacancy concentration then has gone up a bit, the di-vacancy concentration went down.
  - Nirvana implies that (on average) nothing changes anymore. This requires that the rate for di-vacancy *formation* is identical to the rate of *dissociation* . If this is the case, the two concentrations stay constant on average.
    If we do not have this conditions, the concentrations change as much as it takes to arrive at values where the two rates are equal. Now we have equilibrium again.
  - Running through the numbers for the rates gives for the equilibrium (= nirvana) concentration c_{2V} of di-vacancies, and by implication for clusters of *n* vacancies, gives us the following relations.
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Di-vacancies	c_{2V} =	$\exp - \dfrac{E_{F(2V)}}{kT}$ =	$c^2_{1V} \cdot \exp + \dfrac{E_{2B}}{kT}$
n-vacancies	c_{nV}	=	$c^n_{1V} \cdot \exp + \dfrac{E_{nB}}{kT}$

Pre-exponential factors are omitted for simplicity.

For perfect equilibrium or nirvana we always have $c_{1V} << 1$, and that implies that $c_{2V} << c_{1V}$ obtains at all temperatures. Since c_{1V} decreases with decreasing temperature, c_{2V} decreases even faster.

- Exactly the same reasoning goes for tri-, quadro-, or simply *n*-vacancies (called voids if *n* is large enough). They will be there in some equilibrium concentration that decreases rapidly with increasing *n* - we actually asserted that before. In our standard Arrhenius plot this is easy to show:

Global equilibrium concentration of vacancies and vacancy agglomerates.
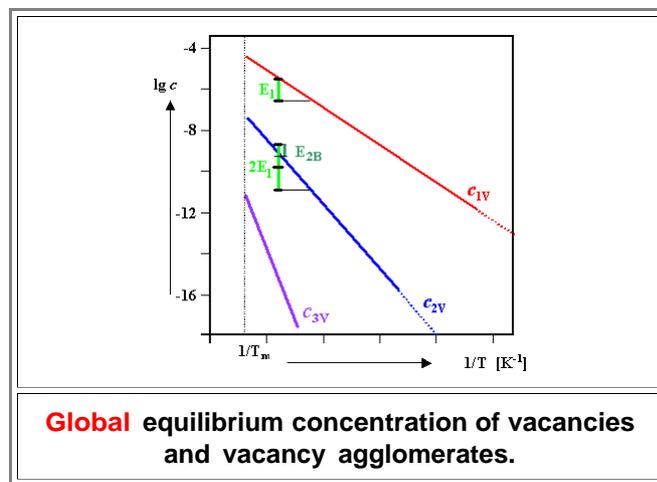
- The slope, as always, gives the formation energy. It is $nE_1 - E_{nB}$. The concentration of *n*-vacancy agglomerates are always much smaller than those of agglomerates with (*n* -1) vacancies. For *n >> 5* or so, the concentration is zero for all practical purposes.

The essential message is:

Even at nirvana we have some small vacancy "precipitates" because there is a dynamic equilibrium between single vacancies and vacancy clusters of all kinds

- Multiple vacancies (also called vacancy agglomerates or clusters) exist even in global equilibrium. Their concentration is very small, however.
An essential insight we gained is:

Clusters absorb *and* emit vacancies all the time. In equilibrium, the absorption rate is equal to the emission rate.

Now let's look at what happens if we generate a *vacancy supersaturation*. All we need to do in an otherwise perfect crystal is to cool it down not too slowly. The surplus vacancies can only disappear at the surface and for that they must diffuse quite a distance. This takes time, and a supersaturation will built up, at least for some time.

- What happens when we have a supersaturation? Vacancies are still running around and bumping into each other to form di-vacancies and so on. The rate for this still scales with the vacancy concentration and their mobility. The dissociation into di-vacancies, however, scales with their concentration and the Boltzmann factor; in the beginning of a vacancy supersaturation it is essentially the same as before.
  As an immediate consequence, the di-vacancy concentration now goes up and the single vacancy concentration goes down until a new *local* equilibrium is reached.

- We can deduce that easily from the equations above for what we now will call **local equilibrium**. We are no longer going for global or universal equilibrium but only for what can be done *locally*, the second-best state of being under conditions where some insurmountable constraints are present. The constraint we made up here is that we cannot get rid of vacancies as quickly as we would like.
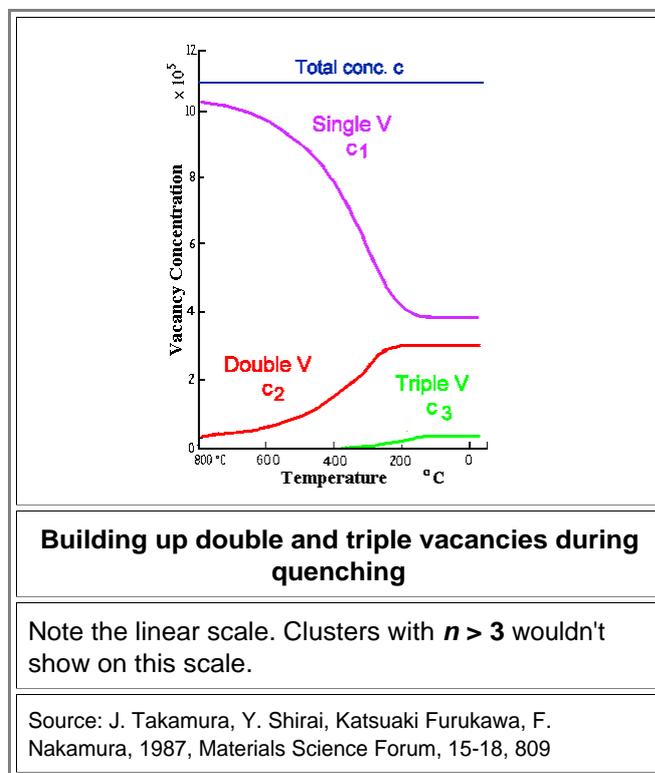
All we need to do is to assume that the movement of the vacancies below some temperature T_1 becomes so sluggish that it takes a long time to change their concentration. Somewhat idealized, we simply assume that from some temperature T_1 downwards, the concentration of single vacancies stays (approximately) *constant*. This will then produce a supersaturation that increases with declining temperature.

- What is going on is still described by the equations above. The only difference is that c_{1V} stays *constant* now. That demands that all c_{nV} values must now increase with decreasing temperature $T < T_1$. Below T_1 we have
  $c_{nV}(T < T_1) =$ **const · exp+**(E_{nB}/kT)!
  In the Arrhenius plot this looks like this:

Local equilibrium concentration of di-vacancies if the vacancy concentration stays constant.
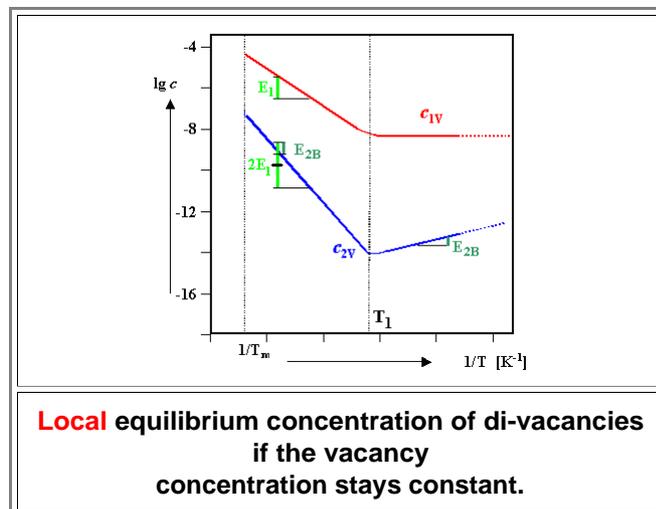
- Of course, the concentration is not coming down smoothly and then suddenly stays constant when T_1 is reached. It's a continuous process. Nevertheless, the point made is valid. What happens doesn't change *in principle*, just the details get more complicated if we make the situation more realistic.

Here is a calculation for the case of a perfect crystal and a constant over-all concentration of the vacancies for a large and constant cooling rate (i.e. for rapid quenching) *and* with realistic diffusion behavior used for the calculations. You still get an increase of *n*-vacancy cluster.

Building up double and triple vacancies during quenching

Note the linear scale. Clusters with $n > 3$ wouldn't show on this scale.

Source: J. Takamura, Y. Shirai, Katsuaki Furukawa, F. Nakamura, 1987, Materials Science Forum, 15-18, 809

🔵 Note that the the di-vacancy concentration and so on would keep growing according to our simple *equation*. In the not-so-simple computer simulations, everything peters out below about 200 °C because nothing can move anymore.

Impurity Atoms and Supersaturation

Looking at impurity atoms, the situation is entirely different. The over-all concentration has a more or less constant value, given by the history of the material. Equilibrium with respect to atomically dissolved impurity atoms would only be reached at some particular temperature if at all.
For pretty much all temperatures, atomically dissolved impurities are therefore either undersaturated or supersaturated.

🔵 What is the crystal going to do about that? For *small* impurity concentrations it follows pretty much the same strategy it used for vacancies:

- It does *nothing* in the case of undersaturation in the bulk of the crystal.
  If more of the impurity atoms are sitting at the surface, they will be "encouraged" to diffuse into the material.
- *Precipitates* are formed in the case of supersaturation. That might be more involved in detail than vacancy agglomeration because more complex entities are formed, e.g. **Fe₃C**. Nevertheless, the general reasoning still follows what I've outlined for vacancies, just the numbers can be quite different. The global equilibrium concentration, for example could be much higher than that of vacancies, and the "bonding energy" needs to be considered in the context of what kind of precipitate actually form.
  In regions close to the surface (and possibly also at some interface like a grain boundary), the surplus atoms are "encouraged" to leave the crystal since these interfaces can absorb the point defects.

🔵 The remarks to what could happen at interfaces are important for what we do with steel. What is really going on at the surface can be rather complicated. The word "encouragement" here simply refers to rates again. If there are more impurity atoms inside the crystal than required for happiness, the rates with which they reach the surface is simply larger than the rates with which they go in again. The net effect is that the concentration in surface-near region goes down. For undersaturation, it is the other way around.
The complications come from the fact that a lot of things are usually going on at the surface; we don't have just some impurity atoms sitting there. For example, if carbon atoms from the interior are immediately burnt off upon reaching the surface because your iron is kept in the oxidizing part of a flame, the concentration will always go down, we have *de-carburization*. If the iron is kept in the reducing (CO-rich) part of a flame, the opposite will happen. The surface near regions become richer in carbon and we are now setting the stage for *case hardening*.

What Did We Learn?

What did we learn by all of this for our nucleation? Admittedly not much by this module alone - but quite a bit as soon as we put it in perspective with what is to follow. The messages (to get a little bit ahead of myself) are:

- Even equilibrium thermodynamic teaches us that a supersaturation of point defects encourages the formation of point defect clusters. We knew that qualitatively all along - but now we have *numbers*.

- Equilibrium - global or local - results from some competition of (at least) two competing processes. In the example here it is rate of vacancy generation by the decay of vacancy clusters, and the rate of vacancy removal be the forming of those clusters. Equilibrium is just another word for the equality of the two rates.
  If one or both of those rates changes for some reason, the concentrations change until a new equilibrium is reached. This happens as long as not everything is just "frozen in" because it gets too cold.

- The shortcoming of the brain model here is that we kept the total vacancy concentrations constant. That allows for easy math but is not realistic. The crystal, in fact, wants pretty much *all* of its vacancies gone for good at some lower temperatures.

- Moreover, we conveniently forgot about a *new* energy term that must come into consideration as soon as we don't just have di- or triple-vacancies but real voids with an internal *surface* and thus a surface energy.

It is time for the **Homogeneous Nucleation** module.

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- **3. Heterogeneous nucleation**
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- **5. Precipitation and structures**