Science

2. Homogeneous Nucleation

In the preceding module we have looked at a *constant* but supersaturated concentration of vacancies or impurity atoms. That taught us a few important things that we are going to need here - but the whole approach was unrealistic. The crystal, after all, wants to get rid of the supersaturation and that involves that the concentration comes down. We need to make a "big" precipitate with lots of point defects in it, not just tiny clusters.
As in the preceding module, we assume a crystal that is absolutely perfect except for some supersaturated point defects. The crystal has to do whatever needs to be done all by itself, in particular it must make the nuclei required to start precipitation without external or extrinsic "help". It would thus be logical to call that process "*intrinsic*" nucleation. I won't, however, because it has always been called "*homogeneous nucleation*" for historical reasons. Since this is also a good term, let's go with the flow here.

- Let's assume that the precipitate is spherical, with a diameter of ***r***. The basic problem in making precipitates is simple:
  - Putting atoms *inside* the precipitate leads to a *gain* in energy. This is good.
  - The interface precipitate - matrix has some interface energy. If the precipitate grows because we keep putting atoms inside, the interface area increases. This *costs* energy and that is bad.
- To get a feeling of what is involved, let's look at some numbers. We have the following relations for the surface area ***S*** and the volume ***V*** of the spheres, the number ***No. V*** of atoms or vacancies contained in the sphere, the number ***No. S*** of atoms or vacancies sitting on the surface of the sphere, and the ratio between atoms in the bulk and on the surface in percent.

Radius *r* nm	**Surface *S* nm^2**	**Volume *V* nm^3**	***No. V* atoms**	***No. S* atoms**	**Relation**
r	$4\pi r^2$	$\frac{4\pi r^3}{3}$	$\frac{V}{(0.3\ \text{nm})^3}$	$\frac{S}{(0.3\ \text{nm})^2}$	$\frac{\text{No. V}}{\text{No. S}}$
0.3	1,131	0.1131	4	-	100 %
0.5	3,14	0.523	19	-	100 %
1.0	12,56	4.187	155	140	90 %
1.5	28,27	14.137	523	313	60 %
3	113,1	113.04	4.187	1.256	30 %
10	1257	4.189	155.184	13.967	9 %
20	5.026	33.510	$1.24 \cdot 10^6$	55.844	4,5 %

Some numbers to precipitates

The size (= diameter) of a vacancy or atoms is assumed to be **0.3 nm** but details don't matter much.

- Of course, clusters smaller than 8, 9, or 12 atoms for bcc, prim. cubic or fcc crystals, respectively, have all of their atoms or vacancies at the "surface".

What we see very clearly is that the energy gained by putting atomic defects into "prison" is pretty much lost again by having most atoms or vacancies at the surface for *very small* clusters or the *nuclei* of precipitates. Only for clusters larger than 10 nm or so, the volume will win.

- We knew that all along. "*You get more potato peel from 20 small potatoes than from one big one!*" is stated in the backbone right about here.
  True enough. But now we will *calculate* exactly how much more potato peel we are talking here.

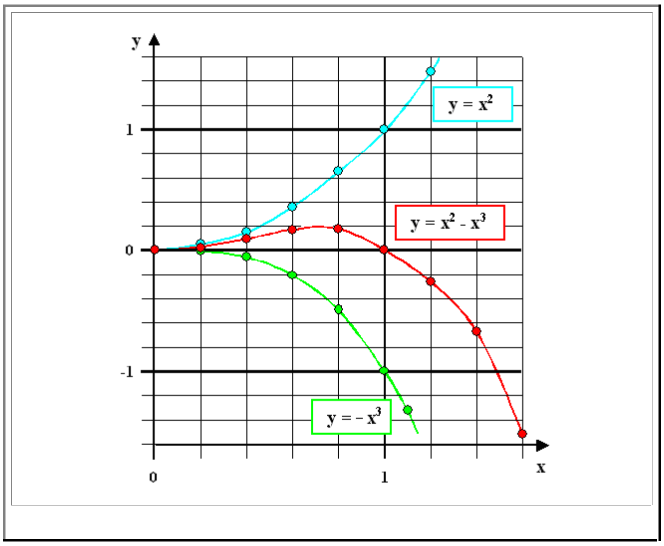
Essentially, whenever we consider to produce a precipitate with radius ***r*** by agglomerating particles like impurity atoms, vacancies, interstitials or any mix thereof, we need to figure out if the balance $\Delta G(r)$ of the energies involved makes the investment worthwhile. Only if the making of a precipitate offers a solid chance for *decreasing* the free energy ***G*** of a crystal with a supersaturation of something, the investment would make sense. Note that I'm not saying that there must be an *immediate* or direct return on investment!
We have only two energy terms to consider:

1. The **surface energy** E_S that we have to invest for making a precipitate with a certain surface, or better interface area. E_S is quite simply given by the area $4\pi r^2$ of the surface, times the specific interface energy γ of the interface in question. Its sign is always positive; we have to "pay".
2. The (free) energy gained by imprisoning one surplus particle in the precipitate. This energy is given by the volume $4/3(\pi r^3)$ of the precipitate times the energy Δg gained per particle volume. Its sign is negative since we gain energy.

The energy balance thus quite simply writes

$$\boxed{G(r) \;=\; 4\pi r^2 \cdot \gamma - 4/3(\pi r^3) \cdot \Delta g}$$

This is a simple function of the type $y = ax^2 - bx^3$. No matter what values of **a** and **b** you enter, the general behavior is always as shown below for the most simple case.
In other words, our ***G*(*r*)** curve looks exactly the same - just change the scales to ***G*** and ***r*** and provide the right numbers on the scales. With increasing radius ***r***, starting from $r = 0$ **nm**, the energy balance always increases, reaches a maximum, and then decreases, eventually becoming negative as desired.



What can we learn form this? *Two* things:

1. There is a **critical radius** r_{crit} for a viable nucleus, given by the *maximum* of the ***G*(*r*)** curve. A nucleus (or tiny precipitate) with this size will *not* yet have provided a lower free energy for the crystal but will produce a net return if it grows beyond that critical size. It then will tend to *grow*. Precipitates smaller than the critical radius would tend to *shrink*.
The critical size is easy to calculate from setting the differential quotient $dG(r)/dr = 0$. We have

$$\frac{dG(r)}{dr} \;=\; 8\pi \cdot \gamma \cdot r_{crit} \;-\; 4\pi \cdot \Delta g \cdot r^2_{crit} \;=\; 0$$

$$r_{crit} \;=\; 2\gamma/\Delta g$$

2. I derived that result for the clustering of something like vacancies or impurity atoms inside a solid crystal. Let's now look at the solidification of a liquid. Look, or even better, *think*. Did you get it?

All phase transformations need nuclei with a critical radius for starters!

- When a liquid solidifies, you need to start somewhere to put the atoms together in crystalline form. There is some energy gain for temperatures below the melting point if atoms are put into the system, and there is some solid - liquid interface with some interface energy γ. Same thing as before. Just the numbers for γ and Δg are different.
  You do all the other examples.

- Actually, looking at freezing offers a little bonus: We know something about Δg! We know that in order to melt a certain amount of a solid, you must invest a defined amount of energy. When the liquid solidifies, you get exactly that energy back. It is called the "**heat of fusion**" H_F, and is rather easy to determine. In contrast, the Δg from above, describing properties of particles like vacancies or impurity atoms and their temperature dependence is not all that easy to get.
  - For the critical radius of a nuclei for **solidification** we get:

$$r_{crit}(\text{solidification}) = \frac{2\gamma \cdot T_M}{H_F \cdot (T_M - T)}$$

  - We have $H_F \cdot (T_M - T)/T_M$ instead of Δg.
    The quantity $T_M - T$, i.e. the difference between the melting point temperature and the actual temperature at which the material is still liquid, is called "**supercooling**" or undercooling. Supercooling and supersaturation are closely related; they simply describe how much a system deviates from equilibrium.
  - The critical radius scales directly with the interface energy γ. The interface energy is pretty much a constant, independent of temperature or supersaturation, and thus easy to assess.
    The critical radius scales inversely with the energy Δg that is to gain, and we if we generalize a bit, with the supersaturation / supercooling.
    So the critical radius does decrease for small interface energies, large energy gains, and with increasing supersaturation. That makes sense.
- But let's not dawdle any more. Let's look at numbers for critical radii. There is, of course, a large spread of possible γ, H_F and Δg values for whatever possible process, supercooling or supersaturation you look at, but no matter:

The critical radius is almost always
far too large to enable precipitation, solidification, and so on.

- What does "*far too large*" mean? Well, let's first consider what we could have in terms of small nuclei. We did that already in the "Global and Local Equilibrium for Point Defects" module.
  - We might get a very few clusters with more than 5 or 6 vacancies / impurity atoms in it, but that will be clusters with nominal radii well below **1 nm**. And we need *much more* for most cases - **5 nm** or **10 nm**! Nuclei with such a critical radius carry far more energy E_n around than a typical vacancy or impurity atom, and the probability for having clusters or nuclei with such a high energy is given by the ubiquitous Boltzmann factor **exp-E_n/kT** - and is zero for all practical concerns!
- What that means is simple:

Homogeneous nucleation never happens!

- Well, *almost* never. Solidification, for example, would require undercoolings of up to 100 K before the critical radii required are small enough to initiate freezing, and that's just not what we observe. Typically, undercoolings of at most a few degrees will do the trick. Only ultra-clean liquids under tightly controlled laboratory conditions can be supercooled to a large extent, i.e. stay liquid well below their freezing point.

Where does that leave us? Well - obviously there is another, more efficient nucleation mechanisms. Yes, there is! It is called *heterogeneous nucleation* (surprise!), and it utilizes defects.

- That will be the topic of the next module in this series.

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