3. Heterogeneous Nucleation

Heterogeneous nucleation simply makes the best out of a not-so-good situation. You're a crystal full of defects that you do not like but can't get rid off. So who said "if you can't beat 'em join 'em"? Nobody seems to know (in contrast to the German version[1]). Crystals followed that particular strategy for as long as they exist (age of universe minus a few billion years).

If a crystal contains defects like grain boundaries, it will not be at global equilibrium or nirvana, and it will not be able to get rid of those defects completely. So how about using those grain boundaries to get at least rid of some *point defects* that are in supersaturation? Maybe grain boundaries can help to make nuclei having the required "critical radius"?

Yes, grain boundaries (and other defects) can do that - and it is easy to see how. Let's just make a precipitate containing some N_{Prec} particles right on a grain boundary and see what happens:


Heterogeneous nucleation at a grain boundary
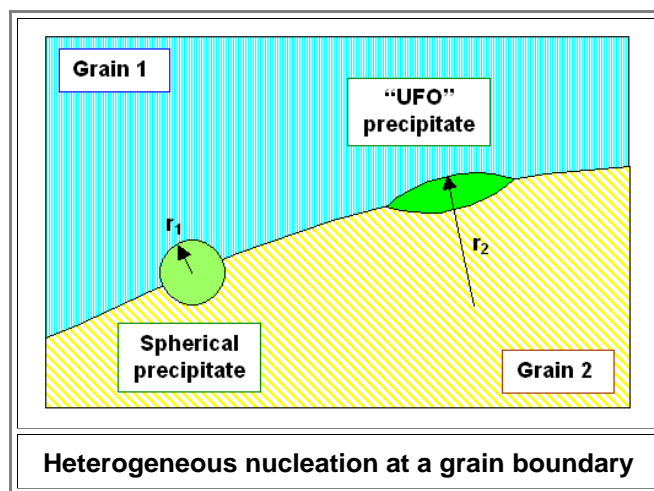
First let's consider the energy balance for a spherical precipitate with radius *r* and interfacial energy γ_{prec} sitting smack at a grain boundary with a grain boundary energy γ_{GB} as shown in the schematic drawing:

1. *Invest:* Interface energy of precipitate: $+ 4\pi r^2 \cdot \gamma_{prec}$.
2. *Return on invest 1:* Volume energy of precipitate: $- (4\pi/3)r^3 \cdot \Delta g = V_{prec} \cdot \Delta g$.
3. *Return on invest 2:* $- \pi r^2 \cdot \gamma_{GB}$

The first two terms are identical to those of homogeneous nucleation. The third term is new and good news: we gain some energy because we erase part of the grain boundary. Since grain boundary energies are often larger than interface energies of precipitates and matrix, this is a win-win situation for all concerned.

And we can do even better. It might pay to increase the surface of the precipitate while keeping its volume V_{prec} constant by making it "UFO" or lentil shaped as shown.

This certainly increases the surface area of the precipitate but also the area of the "cancelled" grain boundary. The gain in cancelled grain boundary energy might well be worth the increase in precipitate area. That's what is going to happen. And you know it because you have seen it many times.

Ever watched a drop of water settle on some smooth surface? What's it doing?

Water droplet in various shapes
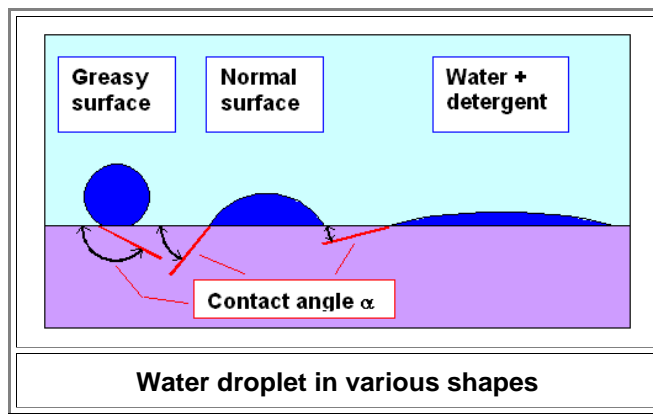
On a greasy surface it tends to ball up. On a clean surface it spreads out some, and if you add a minute amount of detergent it spreads out a lot. The "*contact angle*" α decreases.
The key word here is "**surface tension**", an abbreviation of "*interface energy of water with minute amounts of something and air*".

What you witness while watching your water droplet is an interplay of three interface energies:

1. Interface energy γ_S of the surface and air.
2. Interface energy γ_W of the water (+ minute amounts of something) and air.
3. Interface energy γ_{SW} of water (+...) and the surface.

A water droplet takes out some of the surface-air interface energy, substituting it with the water-surface interface energy. The final shape, characterized by the contact angle α , once more minimizes the total energy of the system. If some detergent (otherwise known as "**surfactant**") decreases the water-air interface energy a lot, it costs little to increase the water surface by spreading out. The return of that investment can be substantial, however, since the high energy of the interface surface-air is reduced.

It is very easy calculate the water example. What one gets is

$$\cos\alpha \; = \; \frac{\gamma_S - \gamma_{SW}}{\gamma_W}$$

Forming a precipitate of any kind on a grain boundary follows exactly the same principles. It will spread out into an "***UFO***" or lens shape if that lowers the balance of all the energies involved. Can we calculate it?

Of course. But what exactly is "it"? Well, we can describe the shape of a lens by the radius *r* of curvature of one of its spherical caps (see the figure) and the total thickness *d* of the lens. Volume V_L and surface area S_L of the lens then are given by the well-known (consult Wikipedia if in doubt) formula

$$V_L \; = \; \frac{\pi d^2}{12}(3r - d/2) \qquad\qquad S_L \; = \; \pi r\, d$$

That's all you need for writing down the energy terms, and for finding the minimum of the energy as done before for the more simple case of homogeneous nucleation. Get to it!

Actually, it gets a bit messy. I spare you the gruesome details and only give you the result, which is simplicity in itself!

- The critical radius r_{crit} is the same as before for homogeneous nucleation.
- But since we now have a lens-shaped precipitate, the volume is much smaller and a hell of a lot less particles are needed to form such a precipitate.
- Since the probability of finding such clusters goes with the *volume*, they are now far more likely to occur!

The following figures make that abundantly clear (I hope). No more needs to be said about this.

**Comparison of homogeneous and
heterogeneous nucleation
for the same critical radius.**
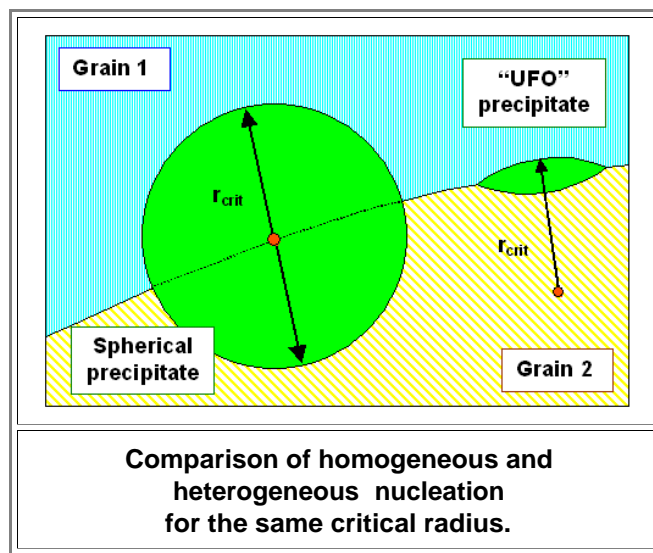
What needs to be said, however, is that *all* defects could act as nucleation sites. Why it is typically more favorable to nucleate something heterogeneously at a dislocation instead of homogeneously in the crystal is perhaps not quite as obvious as in the case of grain boundaries. It is nevertheless the case, just trust me on this.

Same thing for other precipitates, phase boundaries, stacking faults - you name it. The whole arsenal of defects discussed in chapter 5 may help to nucleate a new phase.
To be sure, exactly how that works and under what kind of circumstances it will happen, depends very much on the details.
Anyway, the thing to remember is:

**All phase transformations need nuclei.
The nuclei are (almost) always some
defects like grain boundaries
or dislocations**

Time to look at the next module of this mini series: Size and Density of Precipitates.

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[1] "Immer strebe zum Ganzen, und kannst du selber kein Ganzes Werden, als dienendes Glied schließ an ein Ganzes dich an". (Goethe / Schiller: Xenien, in: Friedrich Schiller, Sämtliche Werke, Bd. 1, München 1962, S. 305.)

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