Science

2. Constitutional Supercooling
and Interface Stability

Non-equilibrium and How to Deal With That

We have a binary alloy, e.g. iron plus some carbon, in the liquid state, i.e. at temperatures above about 1.500 °C (2.732 °F) . Our system is perfectly happy because it has achieved nirvana; i.e. it is in equilibrium.
Now some mischievous individual turns off the furnace and the temperature goes down to room temperature. If that happens very slowly (taking a week, for example), the system will feel a bit challenged but will be able to do most if not all of what the phase diagram requires at the high temperatures where solidification takes place, and thus stays relatively happy.
If the mischievous individual does not just turn off the furnace, but takes out the vessel with the liquid steel and throws it into a swimming pool full of cold water, cooling down will be rapid and the system will be in serious trouble. It's easy to do this in a thought experiment. If somebody does something like that in real life, it is advisable to run like hell, though.
Somebody less mischievous and more sensible might take the liquid and pour it into some cold mold to form a cast object, for instance a sword blade. The cooling rate then is rather fast at the beginning but eventually slows down because the mold heats up. It is nevertheless far too large to allow near-equilibrium conditions at all times.
In both cases the system will be far away from equilibrium. That's not good from a systems-like-nirvana point of view. The system thus will not just take that crap - it will fight back! Let's just look at casting in what follows, that will be hard enough. Let's also call the minority constituent an "impurity", just to keep the language simple.

What kind of options for fighting back does a binary system have? Or a ternary system, or just about any system? It *cannot*, for example, change its shape because that is firmly given by the mold (as long as it doesn't explode, as we sincerely hope). It cannot change the diffusion coefficients and thus influence how fast atoms move either, because that is controlled *only* be the temperature. It also can't do much about the temperature gradient since the low outside temperature (= room temperature) is more or less given, and, together with the shape and mass of the mold, determines how *global* cooling down will proceed. All it can do, perhaps, is to play a bit with the fine adjustment of *local* temperatures. Some parts might be a bit hotter, and some parts a bit cooler than the average, for example. More to the point, the melting temperature might be different in different parts because it depends on the impurity concentration in the liquid, which is not necessarily constant.
Before we turn to the question of what the system *can* do to fight back, let's find out exactly what the system *wants* to change or optimize by putting up a fight. The answer is:

> **The system wants to make the currents flowing through, from or towards the interface as large as possible!**

Energy and particle currents *only* flow through or from the interface because the system is *not* in equilibrium. The currents transport whatever needs to be transported to establish equilibrium again. The larger the currents, the sooner we have equilibrium. I have reasoned like that and given examples in the preceding module already.

The equations for the heat and atom current *densities* j_H and j_A, respectively, were:

$$j_H(x, y, z, t) \;=\; -\kappa \cdot \nabla T(x, y, z, t)$$

$$j_A(x, y, z, t) \;=\; -\nabla\{D(T(x, y, z, t)) \cdot c(x, y, z, T(x, y, z, t))\}$$

These equations are tied to the **thermal conductivity** κ and the diffusion coefficient **D**, respectively, and the system has to work with whatever values they have locally. They are also tied to the gradients ("∇") of the temperature and the concentrations. Since the system wants to get rid of these gradients by producing currents, it would be foolishto increase the gradients in order to increase the currents.
It sure looks like there are no options left?

Not true. The interface doesn't know anything about **currents**, it only knows about **current densities**, the current per area. When it rains in Schleswig-Holstein (it rains a lot!), a current of raindrops falls on the country that we can measure in liters per second. Personally, I don't' care about that number. What I do care about and know, is how man liters per second and *square meter* hit my garden. In other words, I know and care about the rain current *density* at my particular place at the total solid-liquid interface. I don't give a damn about how much rain falls twenty kilometers away. I don't even know about this. The total rain current (= total amount of rain) doesn't concern me at all.
Same thing about those atoms in the interface. They are affected by the *local* current *density* and neither know nor care about the total current. The local current density is still proportional to the gradients, which the crystal wants to be as low as possible.
Now there is an option: Increase the interface area **A** and down go the current densities **j** and the gradients - while the total current $I = \int j dA$ can still be large.
Doing that brings you locally closer to equilibrium - and that's what you want.

That's the long and short of it. The system actually can fight back. It can, as the first option, turn the solid -liquid interface into complex shapes with areas far larger than a planar interface. Small current densities and gradients everywhere but still a large over-all current.
If that helps to stay closer to equilibrium, the concomitant gain in energy may well be worth the prize that must be paid: the increase in total interfacial energy; also given by the interface area times the *specific* interface energy per **cm^2** .
The system has yet another option, mentioned already above. It can change the local melting point by changing the local composition. Increase the carbon concentration *locally* in some molten carbon steel composition, and the melting point will *locally* go down. The local mix then stays liquid at temperatures where the nominal composition would be solid.

How does the system exercise these options? In a rather specific way. What will happen are more or less sudden transitions from one interface morphology to another one, as the deviation from equilibrium increases. In the end, the interface may assume rather bizarre shapes, looking like the interface of a pine forest with the air or *dendritic* (Greek for "looking like an interface of a pine forest with the air").

It might surprise you that it is relatively simple to derive a criterion for the conditions that induce such a change from a planar to a dendritic interface. The magic word is:

Constitutional Supercooling

Let's start by defining " **supercooling**". Water and other simple liquids with only one component usually freeze at a precisely defined temperature. Take a measure of regular water and cool it. At exactly **0 ºC (32 ºF)** ice crystals will form and grow: the water freezes.
If you try to cool down your water suddenly by putting it into a freezer (typically running at **-18 ºC (-28ºF)**, the water will stay liquid for a while since it takes time to transport the heat of solidification out of it. The temperature of the liquid part, however, will not go below exactly **0 ºC**.

No go and visit your friendly scientist who has access to a good lab. Induce her to borrow you some very clean glass ware with perfect smooth walls and some "semiconductor grade" water, i.e. extremely clean stuff. Fill the water into the glass (best done in a clean room) and then put the water into your freezer.
Surprise! You will now be able to reach water temperatures far below the freezing temperature! At **-18 ºC (-28ºF)** the water might stay liquid, no matter how long you wait. This is what we call *supercooling*: having a liquid at a temperature smaller than the nominal freezing temperature of that liquid.
If you keep lowering the temperature of your supercooled water, crystallization will eventually occur (at the latest around -48 °C (-55 °F)) and then proceed very quickly and violently. You can also induce sudden solidification by shaking the glass or bumping it on the table.

Now why is that? Easy. Being very clean and gentle, you just do not supply nuclei for the normal heterogeneous nucleation of the first ice crystals. The system has no choice but to go for homogeneous nucleation, always a difficult thing to do. Actually, in the "Homogenous Nucleation" module , I already introduced this kind of "***normal*** " **supercooling** - together with the equations that allow you to calculate the temperature shown above.

OK - so now we know what supercooling is. But what is *constitutional* supercooling?

Well, obviously it is supercooling that relies on the *constitution* of the melt. So what the hell is constitution? How should I know, I'm only an ignorant German after all, always having trouble with those English words that have a lot of different meanings. So here is what the dictionary proclaims.
Constitution is:

- The fundamental political principles on which a state is governed.
- A statute embodying such principles, e.g.: "We the People of the United States, in Order to form a more perfect Union, establish Justice, insure domestic Tranquility, provide for the common defence, promote the general Welfare, and secure the Blessings of Liberty to ourselves and our Posterity, do ordain and

establish this Constitution for the United States of America".
What a surprise: "defence" is the only goal that is not written with a capital first letter. I would never have guessed!
- The act of constituting, or state of being constituted.
- A person's disposition of mind; temperament.
- *The way in which a thing is composed; physical make-up; structure*

Obviously we go with "the way in which a thing (*the liquid*) is composed", an so on. So why isn't it called *composition*? Because that word has already been taken. The composition of the liquid is given by the state point on the liquidus line that we get when the system decomposes into solid + liquid, like the points 1 and 2 in our example.

Constitution thus refers to the *local* composition in the vicinity of the solid liquid boundary. Since in a binary system the concentration of the minor component or *constituent* (sic!) in the solid is always smaller then in the liquid, the solid-liquid interface, while moving into the liquid, must reject atoms of the minor constituent (or impurity), which means that the concentration close to the interface goes up. The surplus atoms will diffuse into the bulk of the liquid and are carried away by convection - but that takes some time

It is not very difficult to calculate the concentration profile for simple assumptions. We will do that because that will lead us straight to "constitutional supercooling".

We consider a (planar) solid-liquid interface that moves with a velocity **v** into the liquid region. We use two coordinate systems: a fixed one with coordinate **x**, and a moving one, tied to the interface with coordinate **z** as shown in the drawing below.
We assume a *steady state*, meaning that we will have no changes as seen from the interface. In other words: the concentration profile around the interface doesn't change anymore as the interface moves into the liquid. That is not overly realistic but never mind - it will work for us!
The differential equation for the impurity concentration in the coordinate system moving with the interface then is simply:

$$D \frac{d^2 C}{dz^2} + v \frac{dC}{dz} = 0$$

The first term is the change of concentration due to the diffusion current from Fick's second law; by itself it gives dC/dt; the change of the concentration in time, and leads to a *decrease* of the concentration. We have postulated steady state, however, and that means that $dC/dt = 0$. We must thus have another mechanism that cancels the effects of diffusion. That other mechanism is the movement of the interface, of course, that drives more impurities into the melt next to the interface and thus *increases* the concentration.

We don't have to worry about exactly how that happens because in *steady state* we simply know that after a differentially small time dt, the interface has moved the distance $dz = vdt$. For the change in concentration we have $dC/dz = dC/vdt$ or $dC/dt = v(dC/dz)$. Both terms for the change in concentration must add up to zero and that gives the differential equation above.

We need a boundary condition to arrive at a solution of the problem. This is were it gets a bit complicated. The boundary condition always used simply states that the impurity concentration C_i in the liquid right at the interface must be

$$C_i = C(z = 0) = \frac{C_\infty}{k}$$

$$\text{with} \quad k = \frac{C_S}{C_L} = \text{segregation coefficient}$$

$$C_\infty = \begin{array}{c} \text{Concentration in L far} \\ \text{away from interface} \end{array} = C_0 = \text{composition}$$
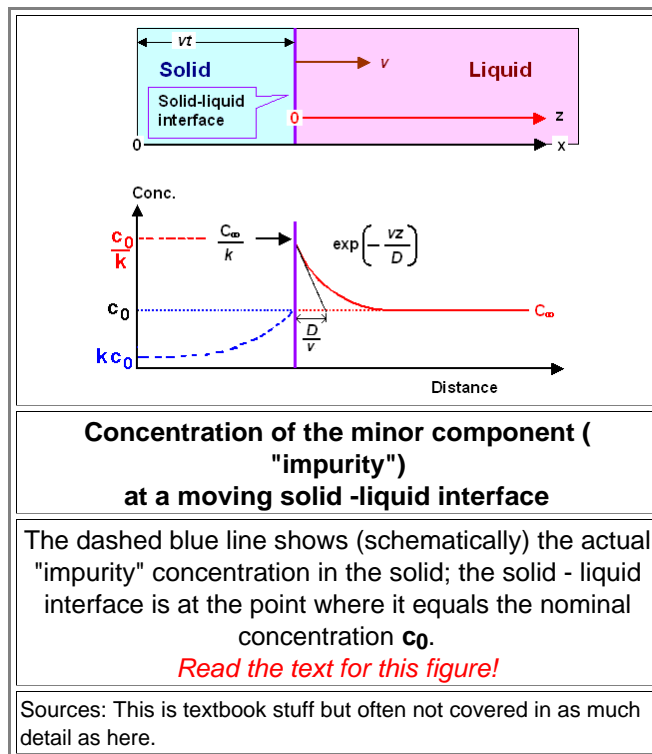
In other words: we assume some special concentrations as visualized below. This is justified to some extent because a moving solid-liquid interface can only exist in non-equilibrium and needs a temperature gradient with a cool end at the solid side and a hot end at the liquid side. Far away it is very hot and we have the pure liquidus phase with the original composition, or $C_\infty = C_0$. Moreover, if some stuff has already solidified, we will be around $C_S = C_0$, too.

The problem is simply that there is no real stationary state. In the beginning of solidification, the solid will have a composition with $C_S < C_0$; as solidification progresses, C_S increases and eventually becomes larger than C_0. It never stays *exactly* the same, so we never have exactly steady state. Around $C_S \approx C_0$, however, changes are small and the situation is as close to being stationary as it will ever get.

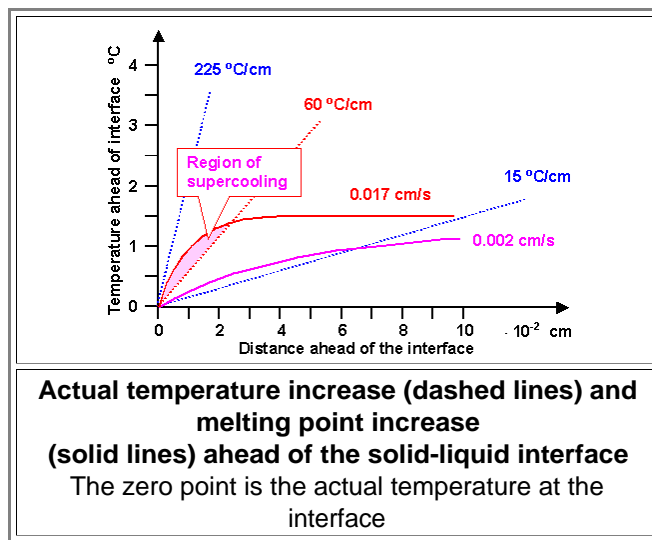The solution of the differential equation becomes simple with the boundary conditions from above; we obtain:

$$C(z) = C_\infty + C_\infty \left(\frac{1}{k} - 1 \right) \cdot \exp{-\frac{vz}{D}}$$

The following figure shows it all. The essential part is the red curve in the liquid region; it simply is the graph of what we just calculated. Note that the quantity D/v has the dimension of a length; its numerical value gives roughly the distance over which the concentration decreases.

Concentration of the minor component ("impurity") at a moving solid -liquid interface

The dashed blue line shows (schematically) the actual "impurity" concentration in the solid; the solid - liquid interface is at the point where it equals the nominal concentration c_0.
Read the text for this figure!

Sources: This is textbook stuff but often not covered in as much detail as here.

This is all rather simple minded (it's one-dimensional, for example) and not very realistic. Nevertheless, it will become quite powerful as soon as we take the next step. What we do *first*, is to calculate the *melting point* of a liquid with the kind of composition shown above.

Or rather, we just look at the result, it's easy to guess, anyway. We know that the melting temperature comes down with increasing impurity concentration. It is thus *lowered* close to the interface in comparison with the rest of the melt. Curves of the melting point vs. distance from the solid-liquid interface thus must look as shown below for the red and mauve solid line, which have been calculated for the interface velocities indicated.

Actual temperature increase (dashed lines) and melting point increase (solid lines) ahead of the solid-liquid interface
The zero point is the actual temperature at the interface

- We assume that at the interface we have the actual solidus temperature, i.e. things freeze. Relative to that the melting point increases upon going into the liquid; by how much depends on the velocity of the interface. The increase iis shown for two values of the interface velocity.
  This is still textbook stuff but often not covered in as much detail as here. Very interesting in this context are the recollections of **Ken Jackson** [2], the prime guy here, who described how he and the others "invented" constitutional supercooling in the early fifties:

- In a *second* step we give some thought to the *temperature gradient* in the liquid. For the reasons mentioned above, it must be hotter far away from the interface. The easiest way to take care of that is to assume a linear increase in the temperature as we move away from the interface. This is shown by the dotted lines in the figure above.
  If you wonder about the large gradients with, e.g., 225 °C temperature change over just 1 centimeter, consider: You pour extremely hot melt into a cold mold - there is no way you can avoid rather large temperature gradients from the outside to the inside at least at the beginning.

Now we will have a climax: The figure makes clear that for *some* combinations of melting point curves and temperature gradient curves, e.g. for the two red curves above, the *local* temperature in the interface-near region is *smaller* than the melting temperature! This is always the case if the straight line denoting the temperature as one "goes" into the liquid is below the lines denoting the melting point. Since we are by definition in thee liquid, this means:

The liquid close to the solid-liquid interface is (constitutionally) supercooled! The interface morphology is unstable!

Before I deal with the second statement from above, you need to note that increasing temperature gradients for a *given* interface velocity will eventually lead to curves that do *not* intersect with the melting point curves. This happens as soon as the slope of the melting point curve at the origin is identical to the slope of the temperature curve. In other words: constitutional supercooling only happens for certain combinations of interface velocity and temperature gradients.
That is easy to calculate. Supercooling will occur if:

$$\left(\frac{dT}{dz}\right)_{z=0} = G \; < \; mC_\infty \left(\frac{1}{k} - 1\right)\frac{v}{D}$$

G = temperature gradient at the interface
m = constant (given by phase diagram), relating concentration to melting point (essentially the slope of the solidus line)

🔵 It is advantageous to rewrite that equation in terms of more convenient quantities. Useful parameters are:

- The concentration difference right at the interface: $\Delta c_0 = C_0/k - C_0$
- The temperature difference ΔT_0 between the liquidus and solidus line in the phase diagram for the composition C_0

Juggling the terms shows that supercooling occurs as soon as the ratio of temperature gradients and interface velocity becomes smaller that a critical value

$$\left(\frac{G}{v}\right)_{crit} = \frac{\Delta T_0}{D}$$

🔵 If G/v is larger then the critical value, the interface is stable and planar growth results. While G and v are both parameters that are determined by what we *do* with the system, the diffusion coefficient D and the temperature difference ΔT_0 are intrinsic parameters that describe what the system *is*. I'll get back to this with illustrations later.
It should be noted that the relation breaks down and is not valid for very large values of v.

This is not a good equation for producing reliable numbers. For that it is too imprecise, given the simplicity of the **model** used for the derivation.
However, in the words George Box: "All models are wrong, but some are useful". How true! The one-dimensional constitutional supercooling model is extremely useful because, as you may have realized by now, details don't matter *at all* for the basic insight that can be gained from it: close to the moving solid-liquid interface the liquid might be supercooled under certain circumstances!

🔵 Details still don't matter for some general relations we can extract from the model and that obviously will still hold for more complex situations encountered in in reality:
The tendency to encounter supercooling increases if:

- Temperature gradients G get smaller
- Interface speeds v get larger
- Diffusion coefficients are larger.
- Solidus / liquidus lines are steeper,
- And so on.

🔵 Of course, large temperature gradients will cause large interface speeds, so the two variables up there are related, making things a bit more complicated. Nevertheless, the model gives clear guide lines for constitutional supercooling to occur or to be absent.

Why is (constitutional) supercooling so important? Because, as already claimed, it causes *interface instability*.

Constitutional Supercooling, Interface Stability and Dendritic Growth

As pointed out a couple of times before, we expect that the solid-liquid interface is planar with an area as small as possible. There are good reasons for that, it minimizes the energy. Interfaces, however, tend to be a bit on the stupid side: they don't know this! They actually try to break up into more complex shapes *all the time*. Usually the second law acts as the drill sergeant who whips aberrant parts of the interface back into shape again.
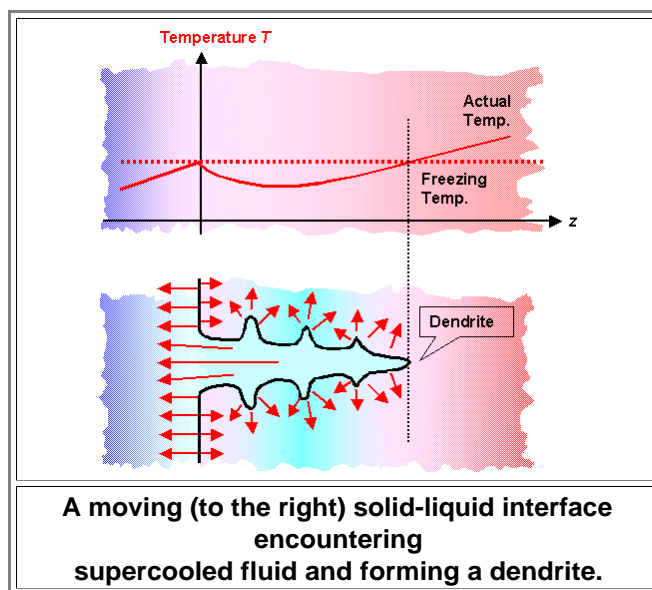Let's see how that works under normal circumstances, and why discipline breaks down as soon as constitutional supercooling occurs.

🔵 The first figure below shows the normal situation where the temperature increases monotonously from the solid to the liquid and there is *no* undercooling! If some enterprising part of the interface tries to run a bit ahead by forming a bump as shown below, it encounters hotter liquid than the rest of the interface.

**A moving (to the right) solid-liquid interface with a "fluctuation"
under normal circumstances (no supercooling)**
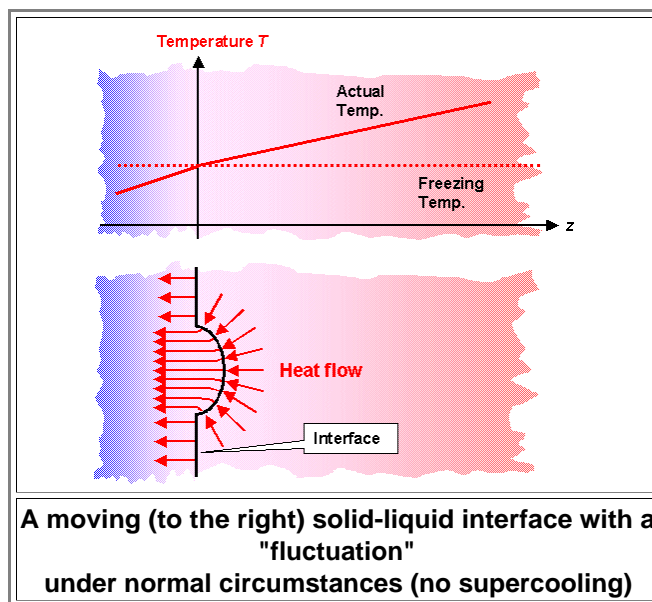
- *More* energy has to be removed through the bump compared to a normal part of the interface. First the heat needed to cool down the liquid to the melting point must get out, and second, the heat of crystallization need to be removed. As the figure schematically shows, behind the bump the heat flow density back into the solid must now be *larger* than in other planar areas - and that is simply not possible because the heat flow density in the regular parts is already as large as it could be. Otherwise the interface would simply speed up.
  In other words, local attempts of interface portions to break out and get ahead of the crowd will simply not get very far or last very long. We say the interface is *stable* with respect to small fluctuations.

The situation changes completely if undercooling occurs. This is schematically shown below.

**A moving (to the right) solid-liquid interface encountering
supercooled fluid and forming a dendrite.**

A small fluctuation or "bump" of the interface now encounters a supercooled liquid, ready to freeze quickly. While there is still the heat of solidification that needs to be removed, the necessary energy flow doesn't have to go exclusively to the solid part. Heat can now also flow into the supercooled liquid. All that happens is that the liquid heats up somewhat but that doesn't matter as long as the temperature stays below the melting point. Freezing can still occur.

- In other words: it is now favorable for protrusions generated by some fluctuations to grow into the supercooled melt, and a randomly formed small bump may quickly grow into a needle. The needle will sprout secondary needles as indicated above, tertiary needles (not shown) and so on - as long as it encounters supercooled fluid. The structure then resembles a kind of tree and that's why our highly educated forebears, who spoke Latin and ancient Greek as a matter of course, in contrast to you and me (but not one of my daughters), called it **dendrite** or tree-like.

My drawing skills are limited, so please realize that there is not just *one* dendrite, but lots of them, all over the place. They also don't grow just *perpendicular* to the the old interface but also at inclined angles. The ones that are nearly at right angles and crystallographically favorably oriented (some crystal planes can grow faster than others) will soon crowd out the less fortunate ones, and in the end it looks like the picture shown in the backbone, or like this one:
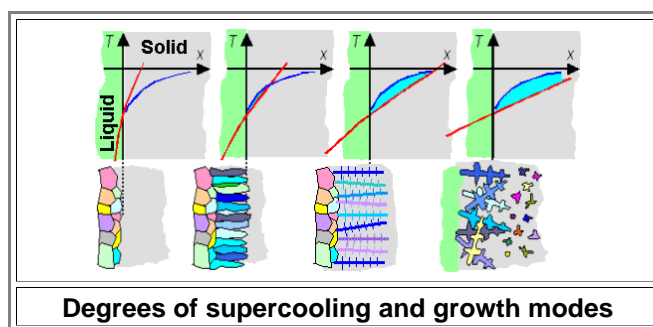

Dendrites

Source: Internet at large
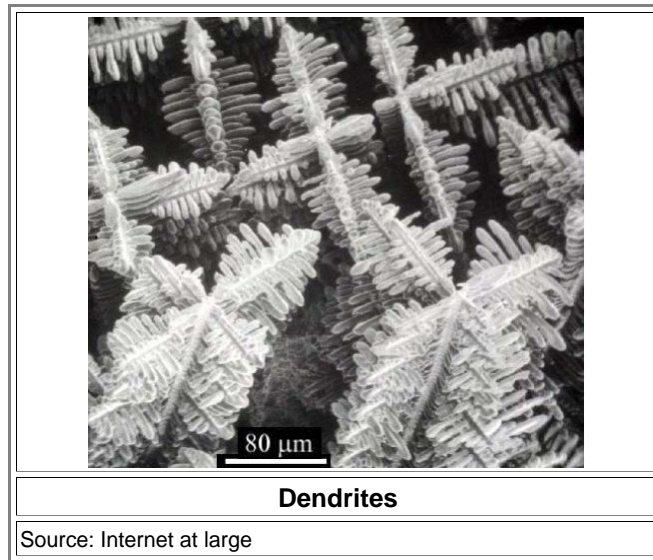
So everything is clear now. Alas! It ain't that easy! Constitutional supercooling does lead to interface instability, yes. And interface instability does mean that a planar minimal-area interface is no longer the best way to make the system happy, indeed. It does *not* mean, however, that one and the same dendritic interface is now the *only* way to produce a better interface. There might and will be be other ways, too. There are many reasons for this. Let's look at a few:

First, there are many ways that constitutional supercooling could occur. If you look at the decisive figure above, you can appreciate that large temperature gradients together with large interface velocities lead to much larger differences between the actual temperature and the melting point than combinations of small temperature gradients and interface velocities. Moreover, the width of the supercooled zone will be quite different, too. It is larger for the second case.
The first case is encountered when we pour liquid iron or steel into a cold mold. The second case corresponds rather to the making of *wootz steel*, where the hot liquid steel cools very slowly and with small temperature gradients in its crucible.
It would be foolish to assume that dendrite formation as shown above is the only possible answer to these rather different conditions. What we get, very schematically, looks like this:

Degrees of supercooling and growth modes

Moving from no undercooling via small undercooling to large undercooling, we encounter planar interfaces, cellular interfaces, small dendrites growing directional, and large dendrites growing haphazardly.
While the figure speaks for itself, the growth modes shown here will become clearer in what follows.

- *Second*, constitutional supercooling arises because of an inhomogeneous distribution of minor constituents ("impurities") in the melt, caused be a moving solid-liquid interface. The break-down of the planar interface into dendrites, or whatever, changes the situation very much. What happens to the surplus impurities ahead of the planar interface, that caused supercooling in the first place, while a dendrite sweeps through the supercooled region? Some will be found in the solid because they were caught by the now rapidly advancing interface. The solid will now have a concentration that is too large compared to what it should be at those places. Most impurities, however, escape into the area *between* the dendrites where thing are less hectic, and are eventually incorporated (at too high concentrations) into the crystal as soon as these regions eventually solidify, because they cannot escape into the now far-away major liquid reservoir. Some other do manage to diffuse into the liquid, and some more are swept away by currents and eddies developing in the liquid. All in all, the impurity concentration in the melt changes considerably as a function of time and location, and thus also the supercooling.

  In other words, there is a complex and (horror!!) non-linear feed-back loop, and it is far from clear that some steady state can be achieved at all. Steady state, once more, would mean that no matter when and where you look, you always see on average the same kinds of dendrites.

- *Third*, the melt is not just sitting there, doing nothing. Temperature gradients in the melt mean density gradients, too. Liquids, like solids, normally expand when they get hotter, and hot melt is less dense then "cold " melt close to the freezing point. The denser melt than sinks to the bottom of the mold were it heats up, the hotter melt moves to the top where it cools down, and the liquid simply starts moving around. This process is called "**convection**". It often takes place in a self-organized orderly fashion by the formation of **convection cells**. Heat some oil in a pot and you can actually see it: cells are forming, with hot oil from the bottom of the pan moving up in the center of a cell, cooling on the surface and moving down in the walls of what we call " **Benard cells**" or convection cells.

Benard cells; also known as convection cells.

Source: Internet; from A U.S. Department of Commerce | National Oceanic & Atmospheric Administration | NOAA Research site.
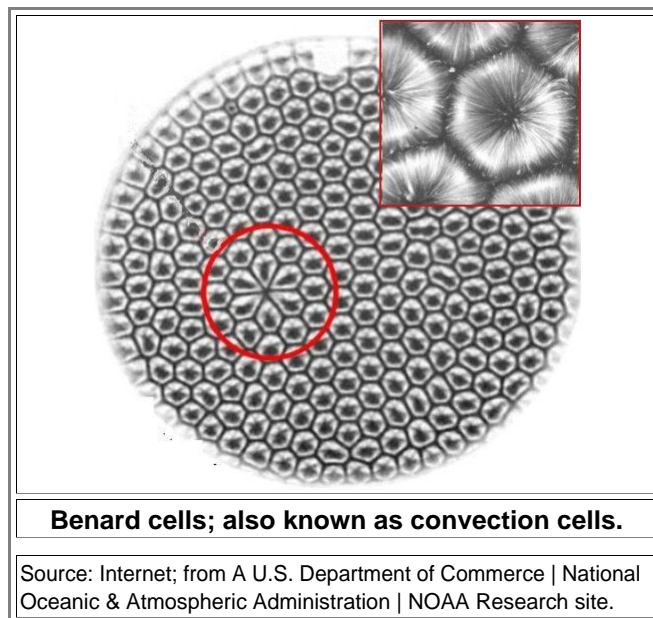
- Some "dust" was mixed into the oil to make the structure better visible. The red circle shows a defect in the otherwise perfect hexagonal arrangement of the cells. It is caused be a flaw in the pot bottom, showing that what you get depends sensitively on small distortions. The inset shows the flow pattern in one cell: up in the center and down at the walls.

- *Water* in a pot, of course, does exactly the same thing as oil; its's just not so easy to see because hot water looks pretty much the same as cold water. Liquid iron / steel in a mold does pretty much the same thing, too, and it is just almost impossible to see if you treasure your eyesight and life.

  In essence, we have yet another interface instability but now on the liquid side, driven by the temperature gradient, but also by surface tension and God knows what else. The important thing to realize is that :

Convection in a liquid moves atoms far more efficiently than diffusion!

The kind of convection we have in the liquid during freezing either sweeps impurity atoms away from the interface (easing or even preventing constitutional supercooling) or towards the interface (you guessed it), interfering very much with what is going on there.

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Time out for silent contemplation
of all that complex stuff
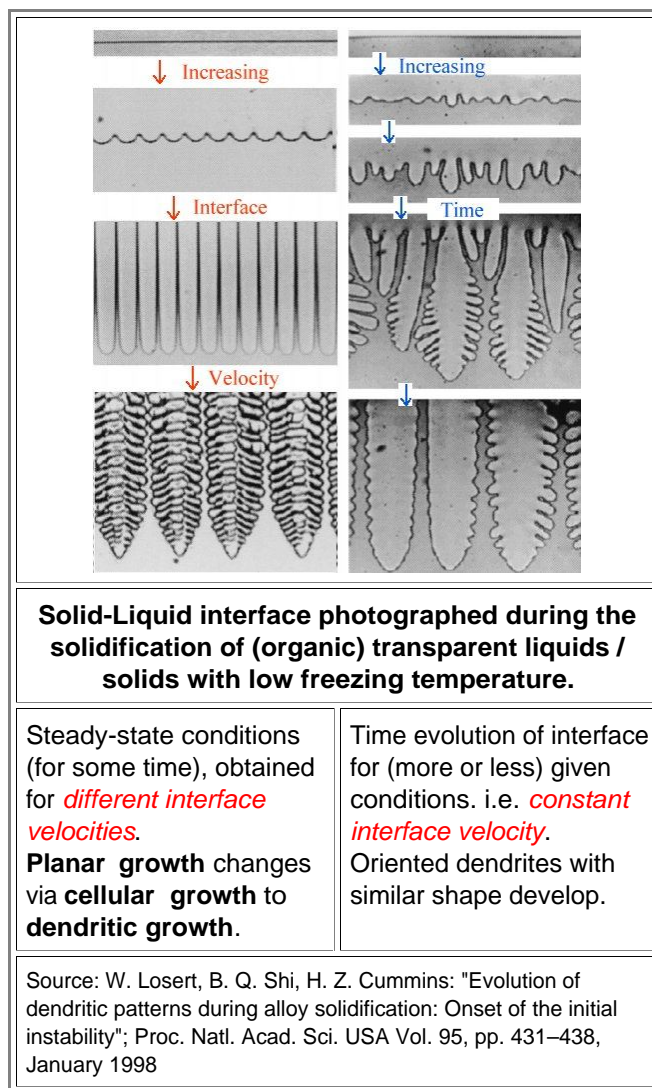(or for getting a bottle of your favorite poison).

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The long and short of this is that there are far more growth modes than just a "uniformly moving planar interface" or "dendritic interface". What we might have, for example, are

- Cellular interface structures, looking pretty much like the Benard cells above.
- Interfaces - straight or dendritic - that are not moving with constant speed but in a "stop and go" fashion.
- New interfaces coming up by growing crystallites that were nucleated somewhere inside the supercooled liquid. Either supercooling is so large that homogeneous nucleation becomes possible, or broken off parts of dendrites floating around in the liquid serve as heterogeneous nucleation centers. As some crystallite grows in the liquid, it will tend to sink to the bottom and merge with the solid there.
- And so on...

The last spelled out point gives a first hint that we also have *plain* supercooling as needed for homogeneous nucleation in pure liquid metals, just as in the example with the pure water all the way above.
I'm going to stop here - even so the list could go on. Once more we realize:

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Calculating the (micro) structure of a cast object (not to mention segregation in that microstructure) is exceedingly difficult!

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Nowadays, with the help of huge digital computers, the task can be tackled but is still not easy. In the old days, all one could do was to use one of Mother Natures analog "computers": the system itself. After all, you can look at the microstructure *after* the object has been cast. Then you might see dendrites or other stuff left over from the solidification.

It just doesn't get you very far with, e.g., iron or steel. The microstructure present after the first solidification is certainly *not* the microstructure you will find at room temperature! Look at the phase diagram ! You have at least to more phase transitions before you reach room temperature. These phase transformations will tend to wipe out the grain structure of the first solidification. Moreover, impurity atoms distributed inhomogeneously due to to segregation may equalize their concentrations if cooling is not very fast, and that is particularly true for fast diffusers like carbon. I will dedicate a whole module to what happens during casting and enlarge on all of this there.
On the other hand, slow diffusers like vanadium (V) or titanium (Ti) contained as impurities at low concentrations may still be distributed pretty much as they were after the first solidification, since they just can't run off very far. Normally, however, you are not going to see that because a sprinkle of those impurities does not influence the microstructure very much. However, with luck and tricky processing, they might give cause to the **wootz pattern** we admire so much!

So we must call ourselves lucky that a major experimental breakthrough occurred in 1965, when Jackson and Hunt realized[2] that certain transparent organic materials effectively solidify like metals, just at much lower temperatures. This allows to watch the whole thing in an ordinary optical microscope. Here are some examples.

Solid-Liquid interface photographed during the solidification of (organic) transparent liquids / solids with low freezing temperature.

Steady-state conditions (for some time), obtained for *different interface velocities*. **Planar growth** changes via **cellular growth** to **dendritic growth**.	Time evolution of interface for (more or less) given conditions. i.e. *constant interface velocity*. Oriented dendrites with similar shape develop.

Source: W. Losert, B. Q. Shi, H. Z. Cummins: "Evolution of dendritic patterns during alloy solidification: Onset of the initial instability"; Proc. Natl. Acad. Sci. USA Vol. 95, pp. 431–438, January 1998

Where does this leave us concerning steel swords? At this stage, two points can be made:

- Even if our forebears could have melted iron and steel a few thousand years ago, casting would not necessarily have produced a better sword than forging. Casting, as you now realize, is a tricky business.
- Wootz swords, while forged and not cast, where made from steel that was molten once. Segregation must have happened in such a way that some special impurities (so-called carbide formers like vanadium (V), titanium (Ti) or chromium (Cr)) where segregated in such a way that the typical wootz pattern would eventually result - provided the steel artificers and the smith did everything *just right*.

Now comes the test:

> **Did you realize that I have not yet covered the statement made just above concerning the "segregation of so-called carbide formers like vanadium (V), titanium (Ti) or chromium (Cr) in such a way that the typical wootz pattern would eventually result"?**

I bet you did not realize this. Wootz steel, as you probably know, has a rather large carbon content up to **2 %**. The carbide formers, that supposedly nucleate the large cementite precipitates that you see in those striations that produce the wootz pattern, are present in concentrations around **0.02 %**, far smaller than the carbon concentration. It is thus safe to assume that constitutional supercooling, dendritic growth, and whatever else might go on, will be caused by the carbon and *only* the carbon. The vanadium (V) in there will simply *not* be able to noticeably change whatever is going on. It thus cannot produce its own segregation.

- However, it can respond to whatever effects the carbon produces. Decisive for this is the local interface velocity and the convection in the liquid. Wherever and whenever the interface moves fast, more carbon / vanadium will be incorporated than when it is slow. Wherever and whenever the liquid moves quickly along the interface, concentration gradients get smaller and less carbon / vanadium will be incorporated compared to a stagnant liquid.

  We thus can have some vanadium segregation, and it will always be coupled somehow to carbon segregation, right after solidification.

  During cooling, however, this relation breaks down. While the phase transitions on the way to room temperature will affect the vanadium distribution to some extend, the effect is minor - the carbon distribution is far more affected. Not only will carbon as a fast diffuser equilibrate its distribution far easier than the slow diffuser vanadium, it also participates in cementite formation. However, cementite formation might be nucleated by the vanadium and thus occurs more likely in regions with a high vanadium concentration.

- This starts to sound like:
  So nat'ralists observe, a flea
  Hath smaller fleas that on him prey,
  And these have smaller fleas that bite 'em,
  And so proceed ad infinitum."
  (Jonathan Swift).
  So let's stop here and go on to see what really happens.

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1) Kenneth A. Jackson: "Constitutional supercooling surface roughening", Journal of Crystal Growth **264** (2004) 519–529.

   The original publication is: W.A. Tiller, K.A. Jackson, J.W. Rutter, B. Chalmers, Acta Met. 1 (1953) 428.

2) Jackson, K. A. & Hunt, J. D. (1965) Acta Metall. 13, 1212–1215.

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