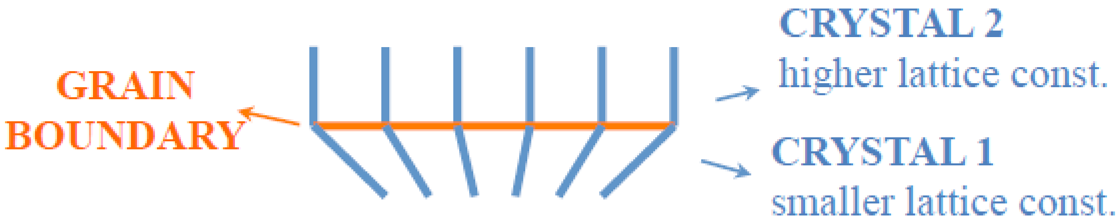
Planar defects
and
Phase transformations

GRAIN BOUNDARY

i.e., the interface between two crystalline grains (possibly different)

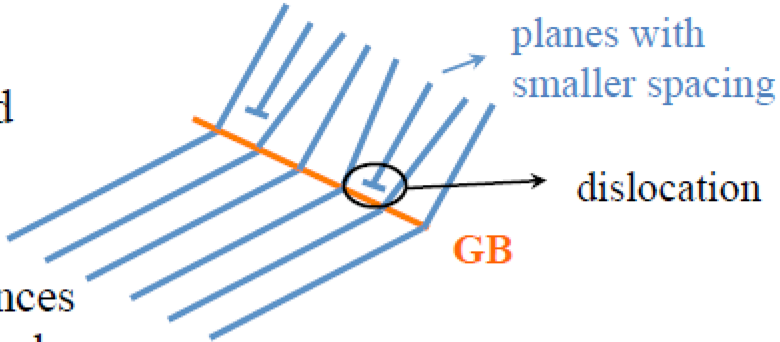
The most important issues are:

- chemical matching
- elastic matching

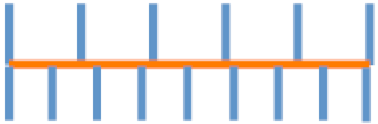


This happens where at interface { **elastic:** bad, **chemical:** good }

⇨ We know this leads to **misfit dislocations.**



However, clearly for large sizes, and due to differences in the thermal expansion coefficient, boundaries can be **incoherent** (partially).



{ **elastic:** good, **chemical:** bad } ⇨ Grain boundaries generally host impurities

Degrees of Freedom to identify a GB:

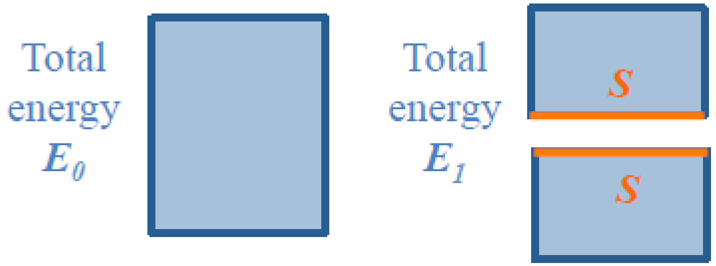
- first lattice is fixed → 0
- second lattice orientation → 3
- plane between two angles → 2

⇨ **5 degrees of freedom** in total

SURFACE ENERGY

$\gamma \quad \frac{[Joule]}{[m^2]}$ “The energy of forming the surface”

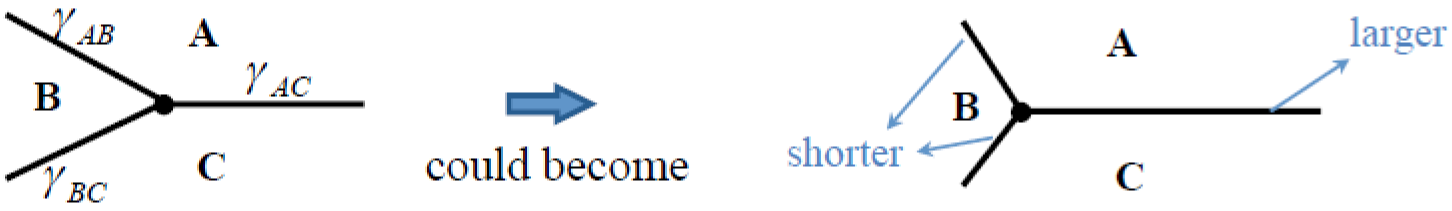
it can be defined (and calculated) as the energy of forming the surface from a bulk specimen. It is often called cleavage energy.



$$\frac{(E_1 - E_0)}{2S} = \gamma$$ **“cleavage energy”**

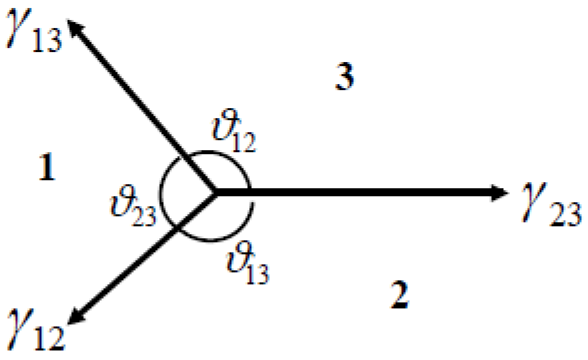
Similarly for grain boundary energies.

Looked at from the side, the G.B. “looks” like a segment, consider e.g. a triple junction



SURFACE ENERGY

From this point of view, there is a “force” aligned with the G.B., pulling the triple point:



Equilibrium:

$$\gamma_{13}\sin\vartheta_{12} = \gamma_{12}\sin\vartheta_{13}$$

so that does not exist a force orthogonal by the 23 plane.

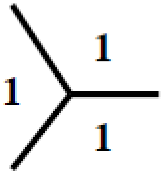
$$\therefore \boxed{\frac{\sin\vartheta_{12}}{\gamma_{12}} = \frac{\sin\vartheta_{13}}{\gamma_{13}} = \frac{\sin\vartheta_{23}}{\gamma_{23}}}$$

Equilibrium Law

because of symmetry

of course, if there is **one** material only and we set all *γ*’s to the same value*****:

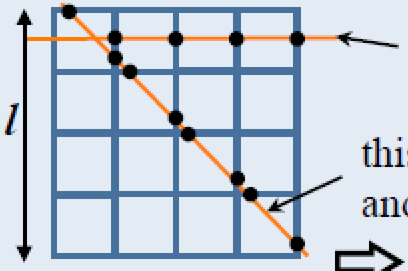
$$\sin\vartheta_{12} = \sin\vartheta_{13} = \sin\vartheta_{23} \Rightarrow \vartheta = 120°$$



“triple point”

The interesting case is, however that of **two phases**. But we still do not know if 4-ple points are possible. Let’s look at this problem first.

*Note: in reality *γ* does depend on the orientation. Let’s see it for a cleavage energy.



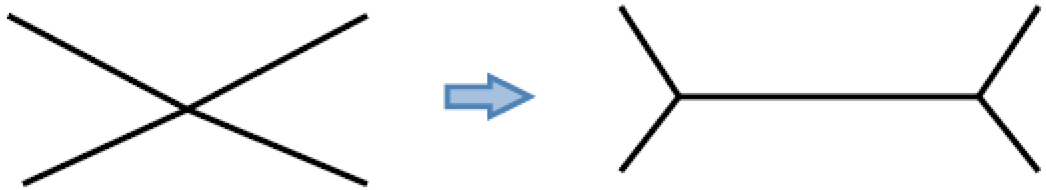
this breaks 4 bonds and has length = l

this breaks 8 bonds and has length= $l\sqrt{2}$

⇨ clearly, higher *γ*

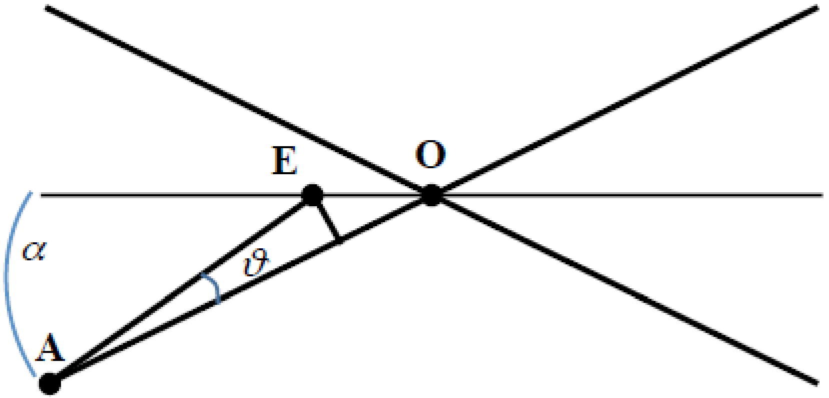
SURFACE ENERGY

We next show that a 4-point joint cannot exist, as they would be unstable



This “reaction” always shortens the total GB surface (and energy, since $\gamma > 0$).

Proof:



We arrange this so that $\alpha < \pi/4$

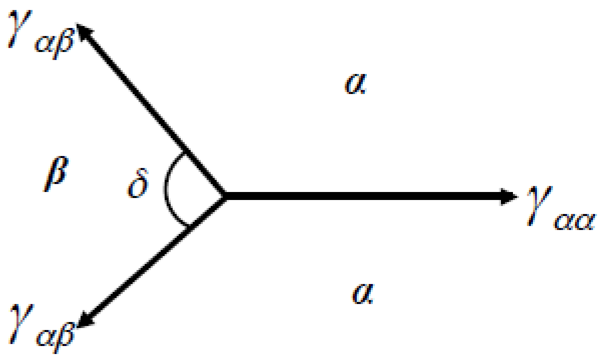
$$AO = \underbrace{AE\cos\vartheta}_{1-\frac{1}{2}\vartheta^2} + EO\,\underset{\substack{\downarrow \\ >\frac{1}{2}\ (\text{actually} > \frac{\sqrt{2}}{2} = 0.707\,!)}}{\cos\alpha} > AE + \frac{1}{2}EO$$

(for EO small enough ***$\vartheta \rightarrow 0$*** as a 2nd order term, while ***EO/2*** goes to ***0*** as a 1st order term)

⇨ The complete proof is achieved by just multiplying the above by 4.

GRAIN BOUNDARY PRECIPITATION

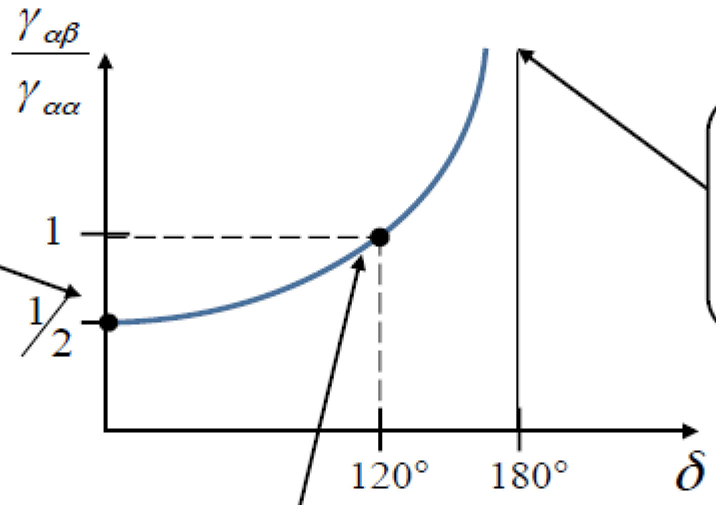
We next discuss the inclusion of $\boldsymbol{\beta}$ at an $\boldsymbol{\alpha\alpha}$ Grain Boundary.



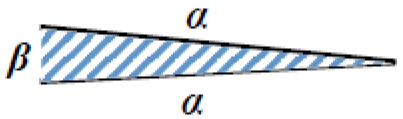
$$\frac{\gamma_{\alpha\alpha}}{\sin\delta} = \frac{\gamma_{\alpha\beta}}{\sin{}^{\delta}/_{2}}$$

but: $\sin\delta = 2\cdot\sin{}^{\delta}/_{2}\cos{}^{\delta}/_{2}$

$$\therefore\ \gamma_{\alpha\alpha} = 2\cdot\gamma_{\alpha\beta}\cos{}^{\delta}/_{2} \Rightarrow \frac{\gamma_{\alpha\beta}}{\gamma_{\alpha\alpha}} = \frac{1}{2\cos{}^{\delta}/_{2}}$$



$$\gamma_{\alpha\beta} \le \frac{1}{2}\gamma_{\alpha\alpha}$$

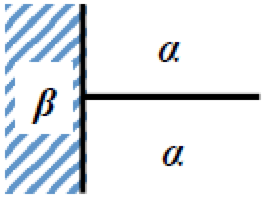


Complete "wetting" of $\boldsymbol{\beta}$, which substitutes the $\boldsymbol{\alpha\alpha}$ GB, since $\boldsymbol{\alpha\beta}$ GB is "cheaper".

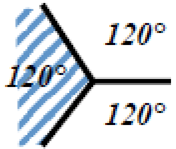
Divergence,

$\gamma_{\alpha\beta} >> \gamma_{\alpha\alpha}$

$\delta \to 180°$



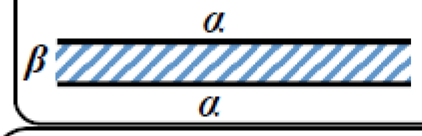
$$\cos\left(\frac{120°}{2}\right) = \frac{1}{2} \rightarrow \gamma_{\alpha\beta} = \gamma_{\alpha\alpha}$$



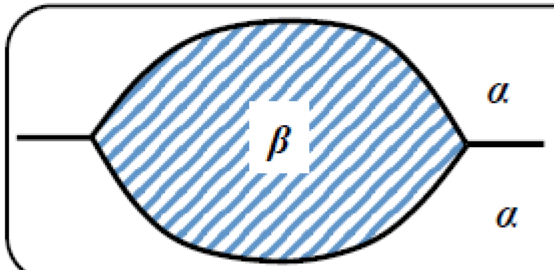
from the point of view of the GB energy, the two materials are equivalent

GRAIN BOUNDARY PRECIPITATION

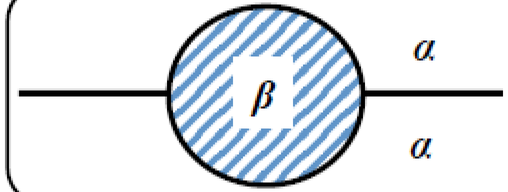
To recap:



for $\gamma_{\alpha\beta} \leq \frac{1}{2}\gamma_{\alpha\alpha}$

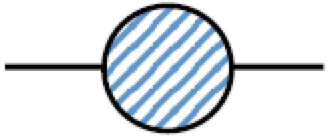


for $\gamma_{\alpha\beta} \cong \gamma_{\alpha\alpha}$

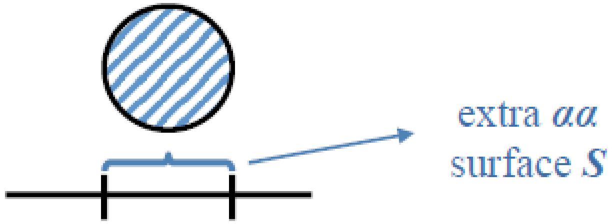


for $\gamma_{\alpha\beta} >> \gamma_{\alpha\alpha}$

note: in all cases

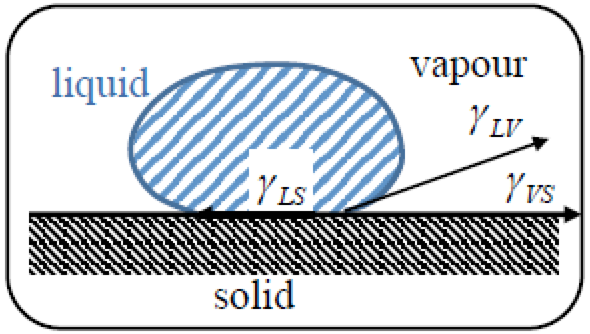


is more stable then



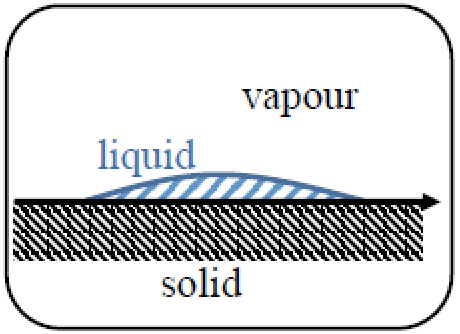
So that is the “grain boundary segregation” source! It’s independent of phase **β**, since $\Delta E = \gamma_{\alpha\alpha}S$.

Wettability



if $\gamma_{SL} > \gamma_{LV} + \gamma_{VS}$

⇨ “**Lotus Leaf**” effect



if $\gamma_{VS} > \gamma_{LV} + \gamma_{LS}$

⇨ complete “**wetting**”

The two conditions cannot coexist! By adding: $\gamma_{SL} + \gamma_{VS} > 2\gamma_{LV} + \gamma_{SL} + \gamma_{VS} \rightarrow \gamma_{LV} < 0$ (clearly wrong)

GRAIN GROWTH

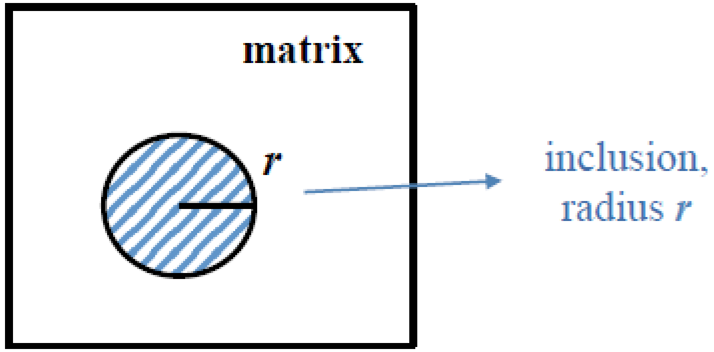
This is an internal pressure issue controlled by the surface/volume ratio ~*1/r* taking into account that creating a surface costs γ (per m^2).

Question: What's the pressure due to the γ cost?

$$\delta L = p \cdot dV = p \cdot 4\pi r^2 dr$$

$$\delta E_{surface} = d\left(4\pi r^2 \gamma\right) = 8\pi r \cdot \gamma \; dr$$

Equating: $$\boxed{p = \frac{2\gamma}{r}}$$



A more general Law, for elliptic inclusions with 2 different radii is:

$$\boxed{p = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)}$$

Gibbs Thomson Equation

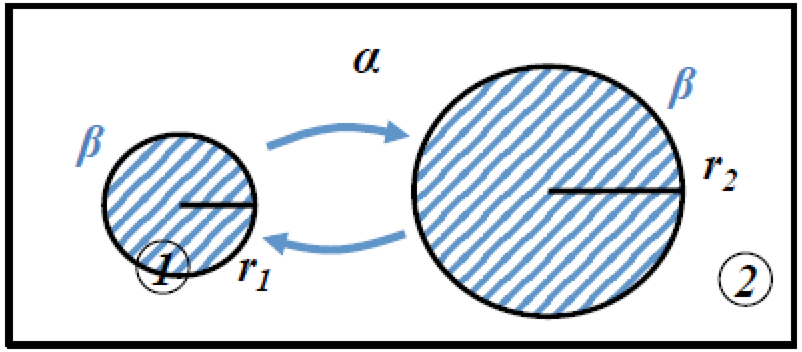
Note that p is in fact the difference between the internal and external pressure if the latter is not zero

→ The atoms inside the grain are "under pressure" due to the surface

Example: γ for H_2O is **a lot** but adding soap it gets lower. So that soap bubbles are possible even with gravity switched on… (no problem with pure water bubbles on the space station..!)

OSTWALD RIPENING

Consider two inclusions of material ***β*** in the matrix ***α*** exchanging atoms ***β*** (**slow**: diffusion).



Maintaining everything else the same, going from ① to ② an atom of volume ΔV yields the enthalpy gain (negative variation):

$$\Delta H = \left[p_2 \Delta V - p_1 \Delta V\right] = -2\gamma \Delta V \left(\frac{1}{r_1} - \frac{1}{r_2}\right)$$

and if $\boldsymbol{r_2 >> r_1}$ (say $r_2 = 100\mu m,\ r_1 = 1\mu m$) ⇨ $\Delta H \cong -2\gamma \Delta V \frac{1}{r_1}$

for $\begin{cases} \gamma \cong 0.5\ J/m^2 \\ \Delta V = 10^{-30} m^3 \\ r_1 = 10^{-6} m \end{cases}$ ⇨ $\Delta H = -\dfrac{2 \cdot 0.5 \cdot 10^{-30}}{10^{-6}} = -10^{-24} J \cong -10^{-5} eV$ → Very small!!

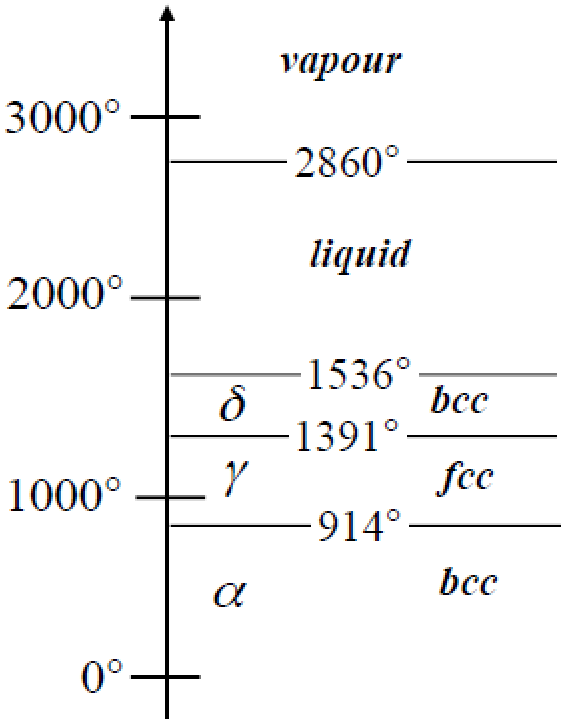
($k_b t \cong 0.02 eV$ at room temperature)

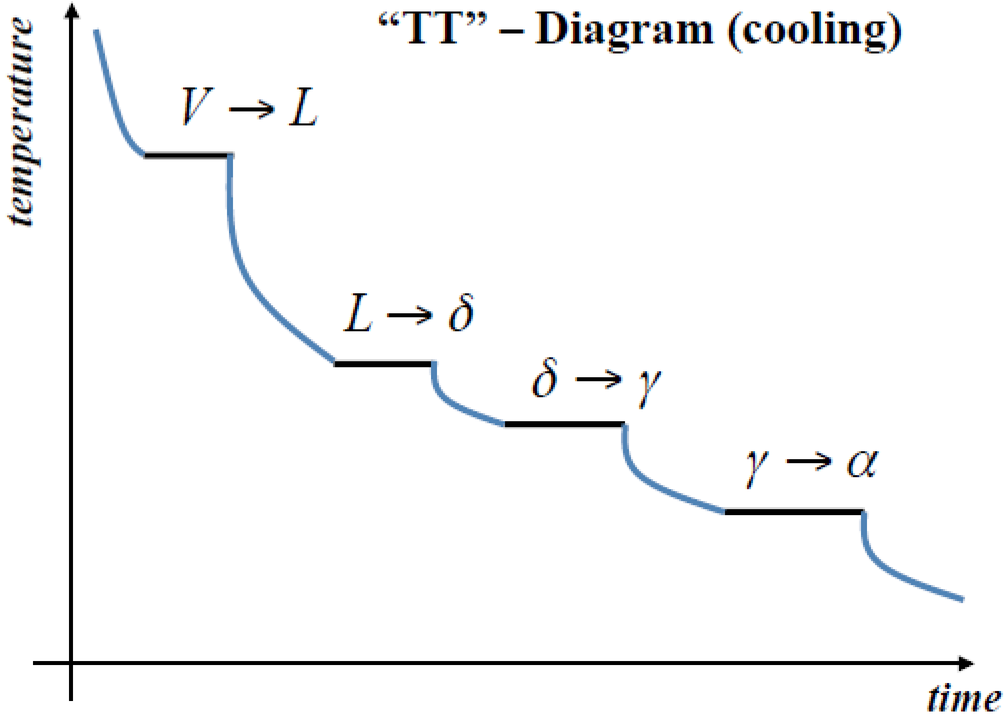
→ grain growth is thus **very slow,** in practice most materials (e.g., metals) are polycrystalline

Example: cf. tungsten grain growth in light bulbs (helped by temperature)

PHASE TRANSITIONS

An empirical example, for iron

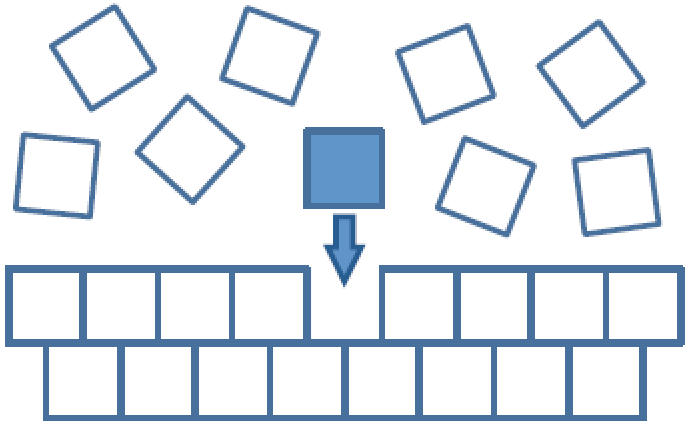



"TT" – Diagram (cooling)

Clearly, while two phases coexist, the temperature is "pinned" at the coexistence value

PHASE TRANSITIONS

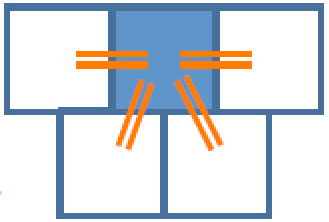
Here, for example, the L → δ-iron transition. Although the system overall is loosing energy to the rest of the world, the temperature remains fixed at 1536° until there is only solid iron



LIQUID (only slightly less dense than the solid, but there are exceptions e.g., water)

CRYSTAL

When the atom ■ falls in place it forms four " **bonds**" with the growing solid, while its freedom is largely diminished.



➡ **Energy got lower!** (ok, enthalpy, which is ~ the same as $p\Delta V \cong 0$).
Entropy got lower as well, and the two effects *compete*

$\Delta G = \Delta H - T\Delta S$ Overall it must be $\Delta G < 0$ for the reaction to proceed.

PHASE RULES

It concerns the equilibrium state of a heterogeneous system.

$$\boxed{\nu = C - F + 2}$$

ν = # of degrees of freedom (P,T, and concentrations)

C = # of components (e.g., different chemical species)

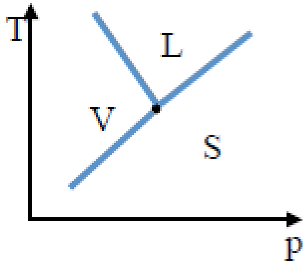
F = # of phases (e.g., liquid, solid, …)

- if all components vary their concentration by chemically transforming into each other, the C concentrations will provide (C-1) degrees of freedom for every phase: **+ F (C - 1)**
- pressure and temperature are free: **+2**
- However, every one of the C components must have the same μ_0 for every phase present at **the considered** phase diagram point: **- C(F-1)** degrees of freedom from the constrains

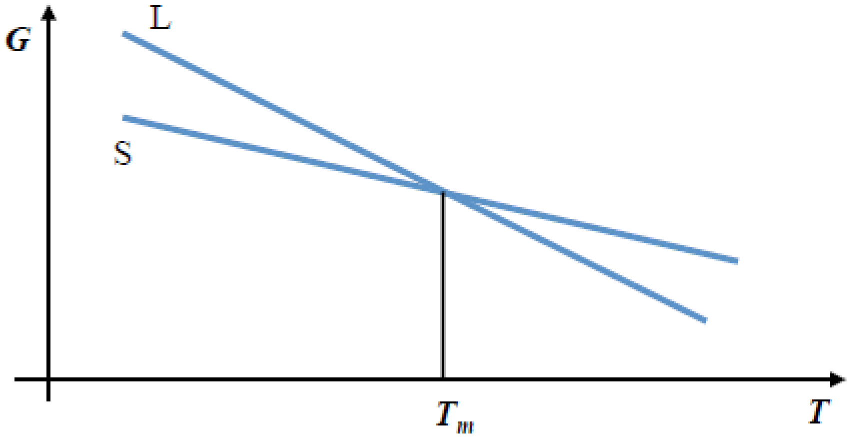
$$\nu = F(C-1) + 2 - C(F-1) = C - F + 2$$

Example: triple point of water

$C = 1 \qquad F = 3 \quad \rightarrow \quad \nu = 0$ (a phase diagram *point*)



PHASE TRANSITIONS



typically, the G of a particular phase (e.g., S) becomes equal to that of another phase (e.g., L) at some transition temperature (e.g., the melting temperature T_m)

$$G = H - TS \quad \rightarrow \quad \Delta G = \Delta H - T_m \Delta S = 0 \quad \text{so that} \quad \frac{\Delta H}{T_m} = \Delta S \quad \text{at} \quad T = T_m$$

Now, we can hope that $\Delta H = T_m \Delta S$ also for $T \approx T_m$ since $\begin{cases} H \cong H_m + c_p \Delta T \\ S \cong S_m + c_p \dfrac{\Delta T}{T_m} \end{cases}$

$$\therefore \quad \frac{\Delta H}{\Delta S} \cong \frac{\Delta H_m + \Delta c_p \Delta T}{\Delta S_m + \Delta c_p \dfrac{\Delta T}{\Delta T_m}} = T_m$$

$$\boxed{= \frac{\Delta H_m}{T_m}}$$

so, for $T \cong T_m \rightarrow \Delta G = \Delta H - T\Delta S$

$$= \Delta H \left(1 - \frac{T}{T_m} \right)$$

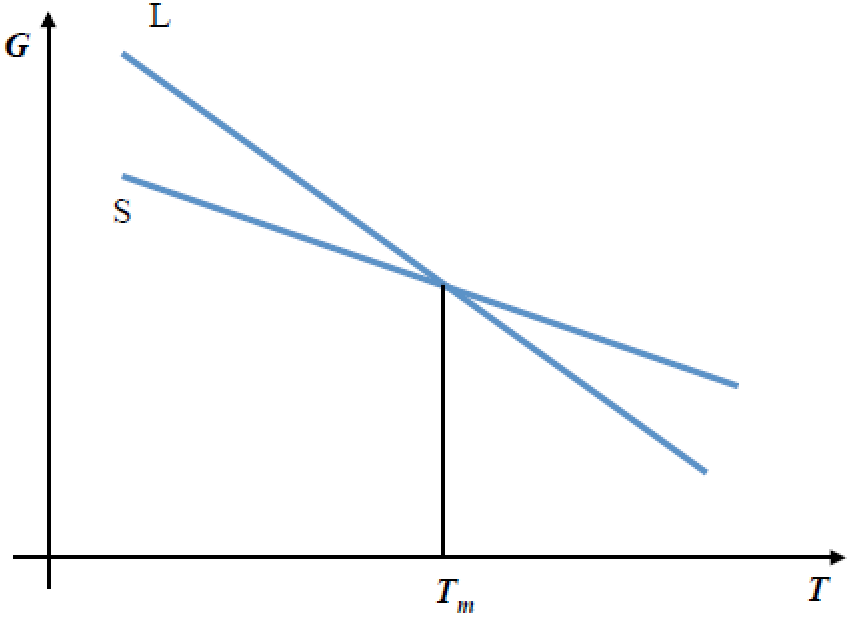
PHASE TRANSITIONS

For example if $T < T_m$,

the $S \rightarrow L$ transition $(\Delta H > 0)$ will have

$$\Delta G = \underbrace{\Delta H}_{\boxed{>0}}\underbrace{\left(1-\frac{T}{T_m}\right)}_{\boxed{>0}} > 0$$

and will **not** happen spontaneously



But for $T > T_m$, $\Delta G = \underbrace{\Delta H}_{\boxed{>0}}\underbrace{\left(1-\frac{T}{T_m}\right)}_{\boxed{<0}} < 0$ will happen spontaneously

Note that, typically $T_m >> |\Delta T|$, so $|\Delta G| << |\Delta H|$, i.e.: large, almost equal enthalpic and entropic variations, leaving just a small driving force

PHASE TRANSITIONS

Example: water at *1 atm*

$\Delta H = 334\, kJ/kg$ for ***ice → water***
$\Delta H = 2263\, kJ/kg$ for ***water → vapour*** (much bigger)

The entire budget to boil a kg of ice is:

$$334 + 100 \cdot 4.187 + 2263 = 3016\ kJ$$

→ sufficient for lifting 300 tons by 1 metre !

Note that $1\ kWh = 3600$ kJ

Since, however $T_m \cong 300°K\ \ (273.15°C)$ ⇨ $\Delta G = \Delta H\left(\frac{\Delta T}{T}\right) \cong 1\ kJ/\text{kg}$ for $\Delta T = 1°K$
which is 300 times less…

it looks like we would need ~100 *W* for 1 hour to melt a kilo of water and 1000 *W* for 1 hour (1kWh) to boil it away, but the **net** "driving force" ΔG for melting ice at 1°C is ~1 *kJ/kg*.

Q: can we relate the *~3000 kJ/kg with* the total chemical bond energy in 1kg of water?

A: $1\ kg \cong 50\, mol$ (as the atomic weight of H_2O is about 20 (just rough estimates here!))

so $\Delta H_{S \to V} \cong \frac{3000}{50} \cong 60\ \ kJ/mol$

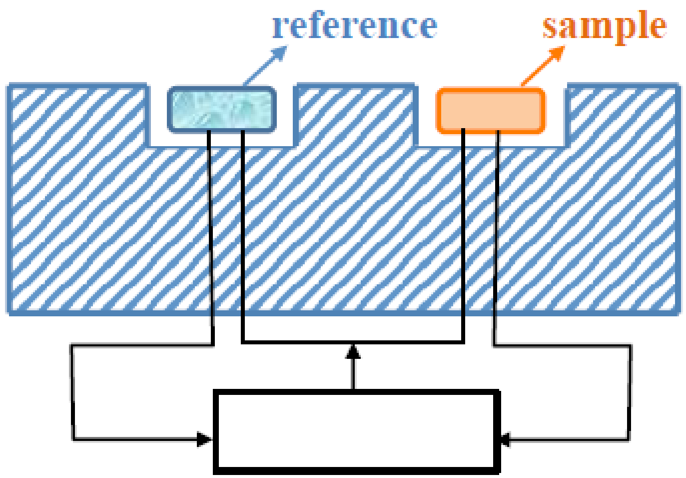
Now $1\ \ eV/molecule \cong 96\ \ kJ/mol$ (since $N_a \cong 6 \cdot 10^{23}$ and $1\ eV = 1.6 \cdot 10^{-19} J$)

So $0.6\, eV/molecule$ seems sufficient to vaporize ice, which is ok since for every molecule there are 4 bonds (but they are across 2 molecules, so we only count two)

OK! A hydrogen bond is indeed $\cong 0{,}25\ eV$ → $0.5\, eV/molecule$

THERMAL ANALYSES

Similar evidence is given by the
- ThermoGravimetric Analysis (TGA)
- Differential Thermal Analysis (DTA)



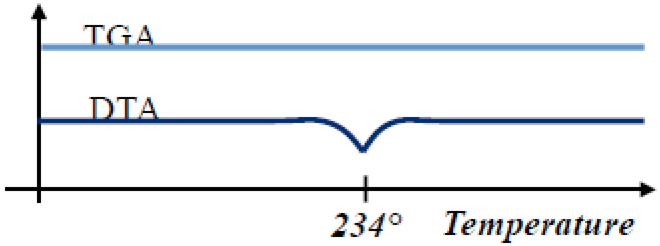
DTA

The two thermocouples will record any ΔT between the sample and the reference (stable) material while the block is slowly heated up

TGA

Just weighs the sample at all times

Example: melting pure tin



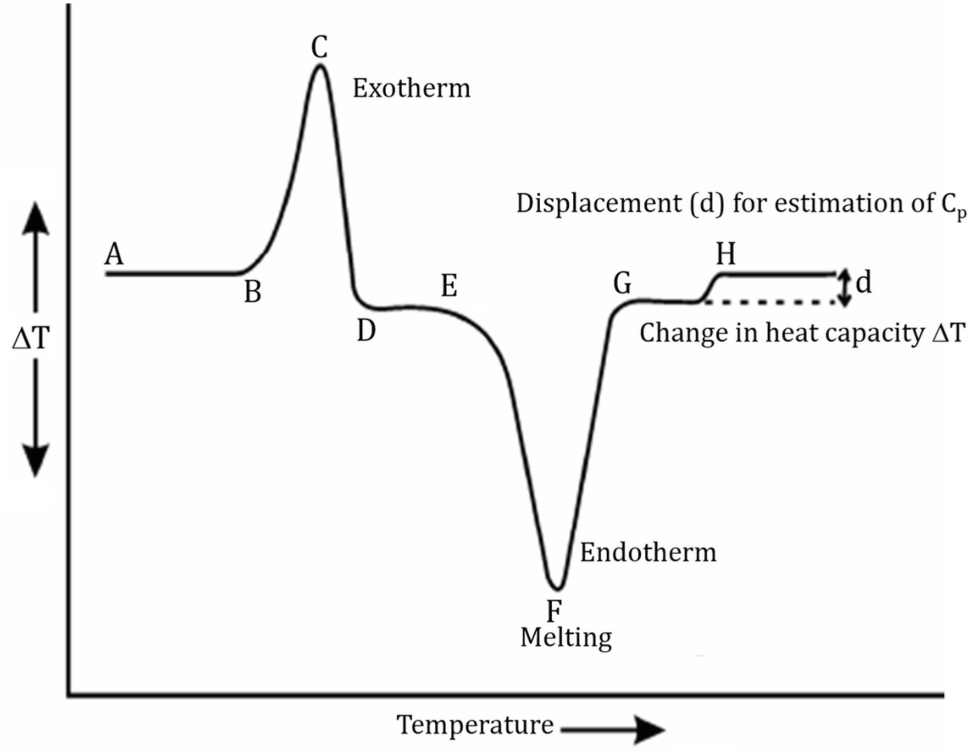
TGA stable (liquid tin does not evaporate)

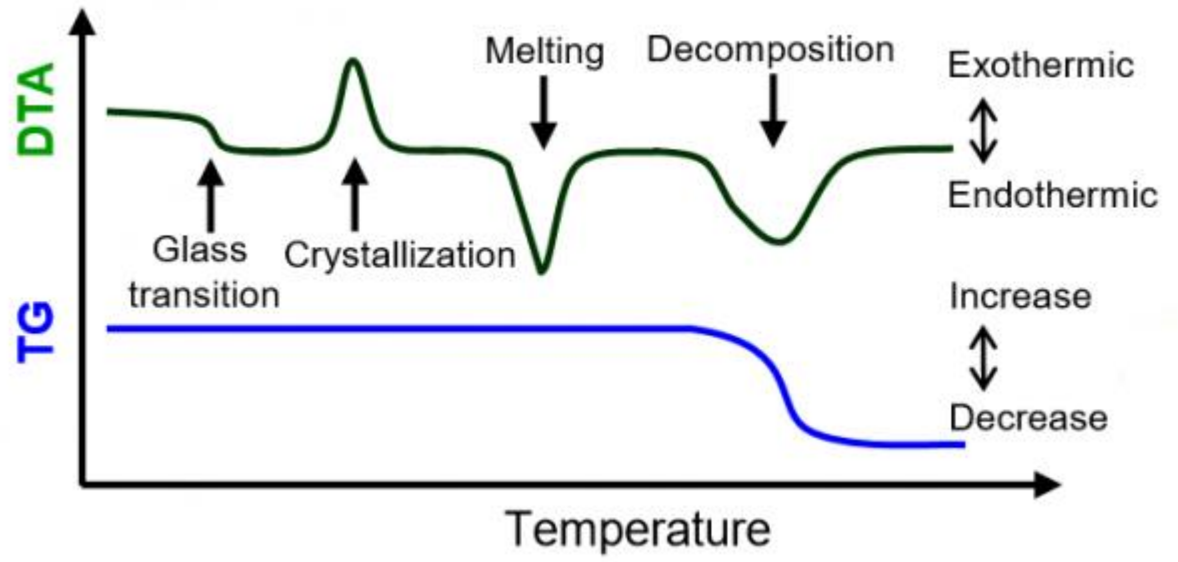
Tin “**lags behind**” while the enthalpy of melting is produced (and the temperature is pinned at T_m)

Flame - retardant materials:

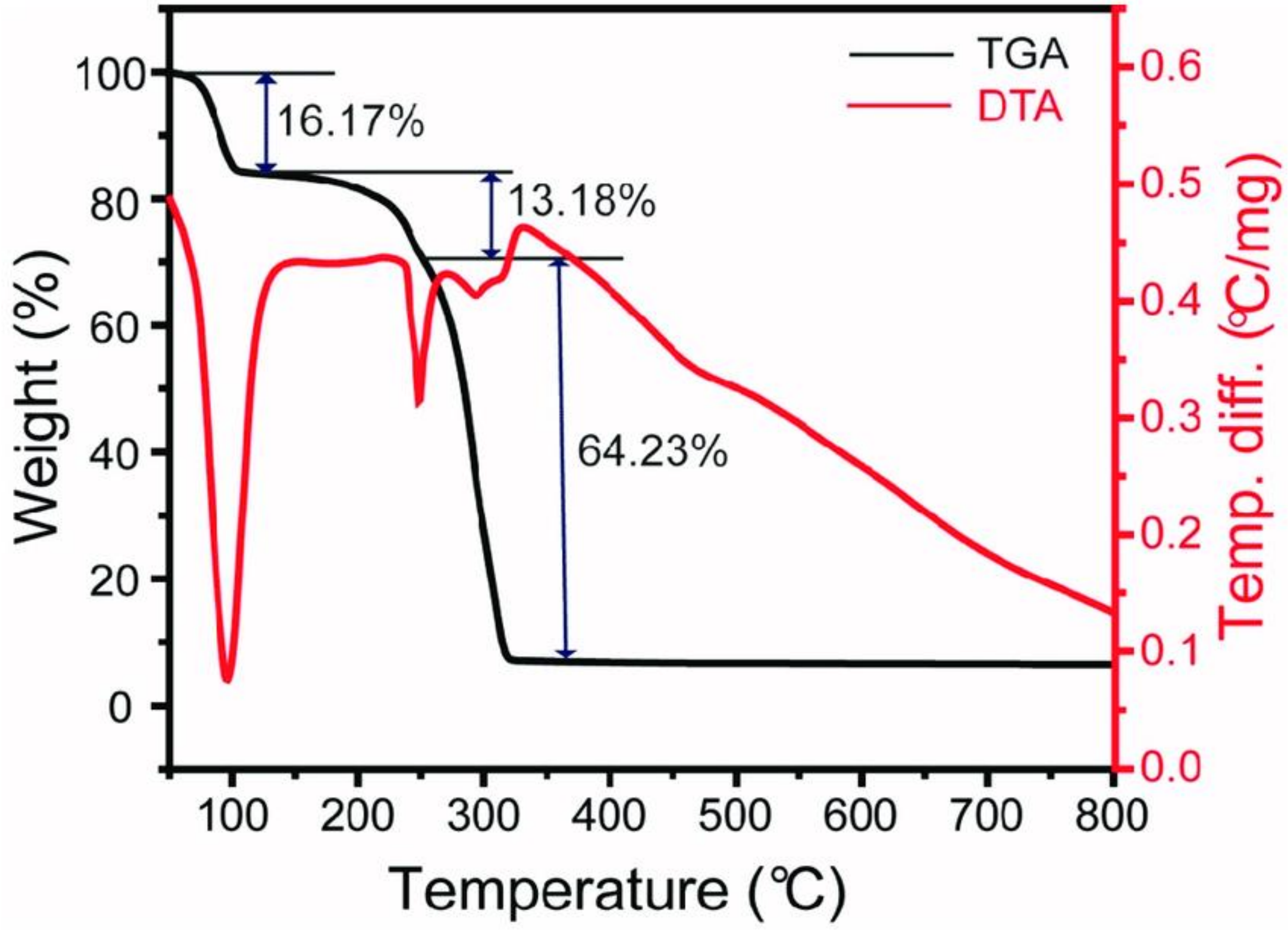
They can be Mg-Al silicates, mica structures, …, with adsorbed interlayer water.
They will imply a large ΔH of vaporization while heating up, and thus require significant energy to be heated up to flame temperatures

Main features in DTA-TG

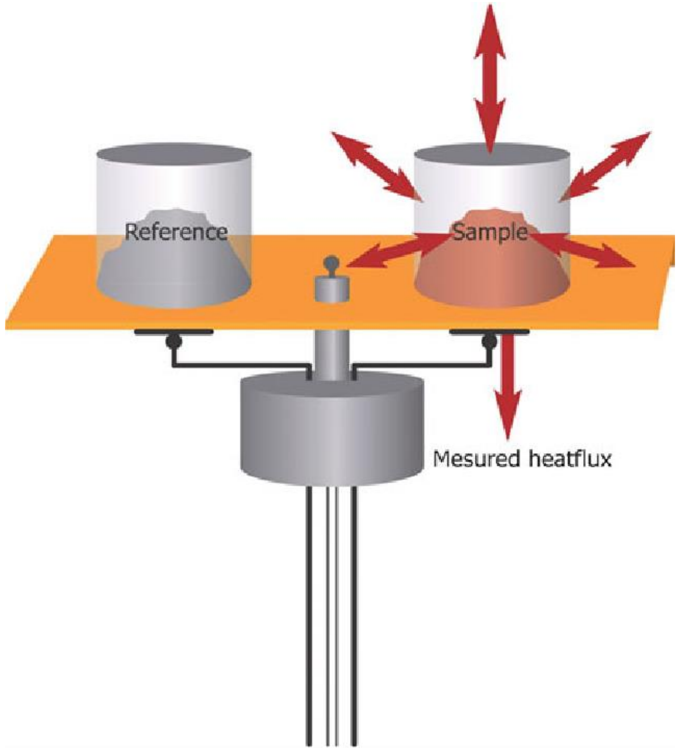


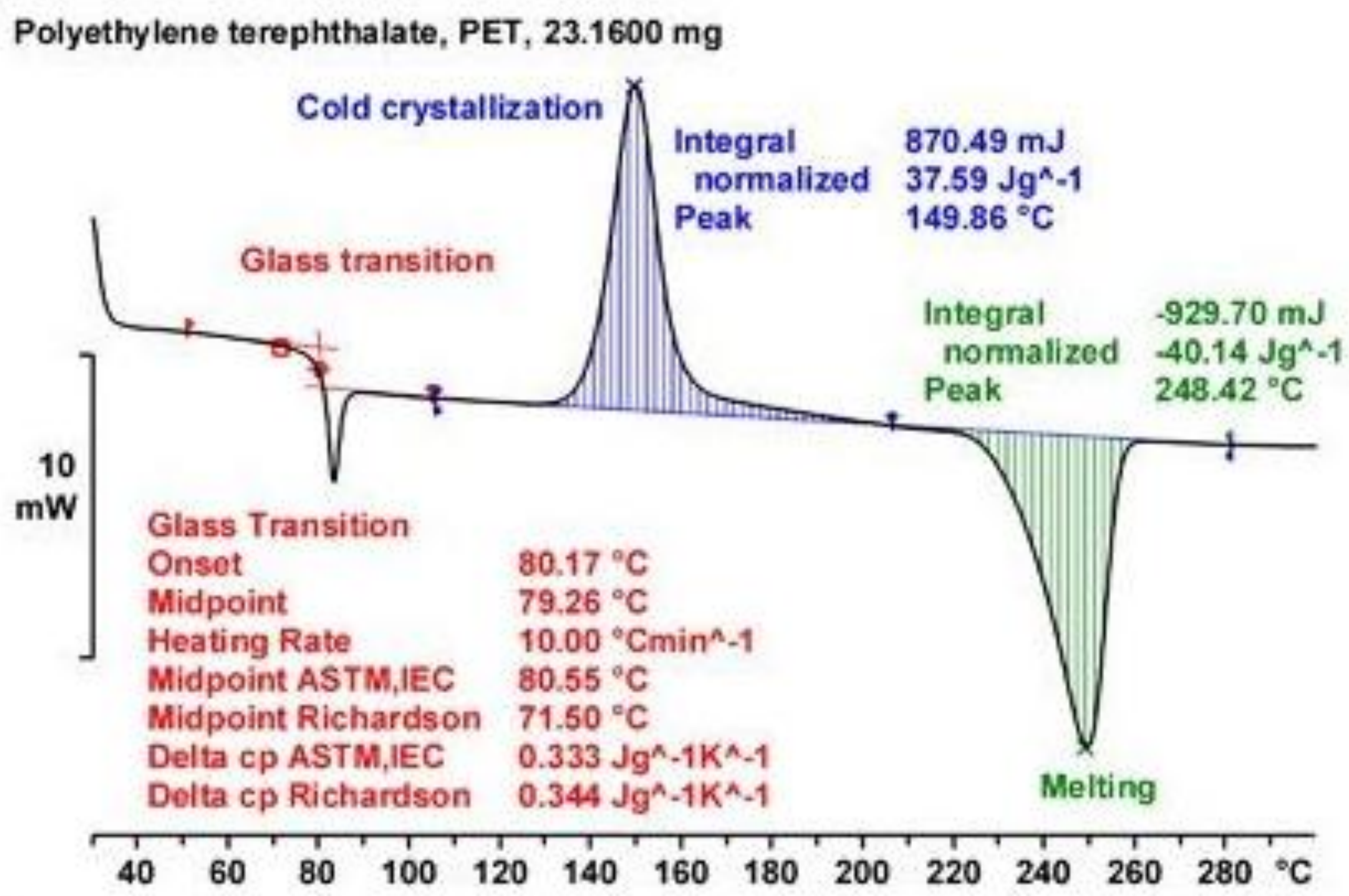


Example of DTA-TG data



Differential Scnning Calorimetry

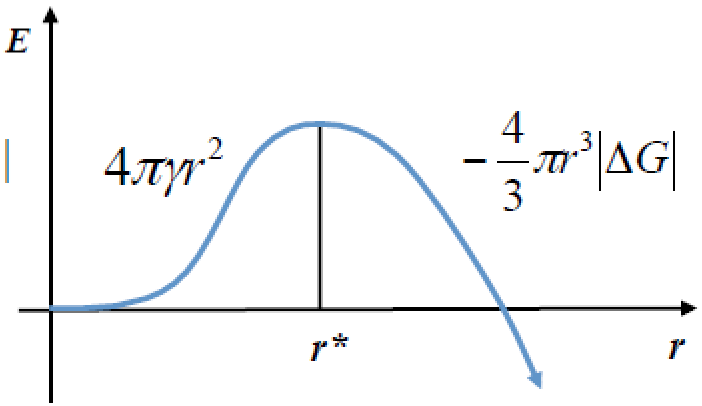




HOMOGENEOUS NUCLEATION

…or "how impossible it really is"

imagine you wish to form a spherical nucleus of a new phase, of radius *r*. There exists a driving force |ΔG| (volumic, i.e. in *J/m*³), but also a cost $4\pi\gamma r^2$ to create the interface.



$$E = 4\pi\gamma r^2 - \frac{4}{3}\pi r^3|\Delta G|$$

The radius beyond which a fluctuation will progress is:

$$\frac{\partial E}{\partial r} = 0 \quad 8\pi r\gamma = 4\pi r^2|\Delta G| \to r^* = \frac{2\gamma}{|\Delta G|}$$

$$E(r^*) = 4\pi\gamma\frac{(2\gamma)^2}{\Delta G^2} - \frac{4}{3}\pi\left(\frac{2\gamma}{\Delta G}\right)^3|\Delta G| = 16\pi\frac{\gamma^3}{\Delta G^2}\left(1-\frac{2}{3}\right) = \frac{16}{3}\pi\frac{\gamma^3}{\Delta G^2}$$

Example: let's try to see how much this is for water

$$\Delta G = \frac{334}{273} \cong 1\frac{kJ}{kg} = 10^6\frac{J}{ton} = 10^6\frac{J}{m^3};\ \gamma = 0.5\frac{J}{m^2} \Rightarrow \frac{16}{3}\pi\frac{\gamma^3}{\Delta G^2} \cong 2\cdot\frac{1}{10^{12}} = 2\cdot 10^{-12}J \cong 10^7 eV$$

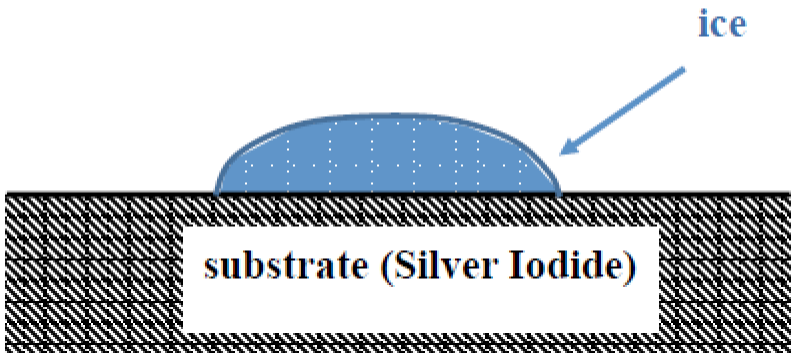
also $r^* = \frac{2\gamma}{|\Delta G|} = \frac{1}{10^6} = 10^{-6} = 1\mu m$

enormous!
(try $e^{-10^7\cdot 40}$)

… in practice, nucleation almost always heterogeneous!

HETEROGENEOUS NUCLEATION

Example: nucleating ice from a vapour phase



if the substrate is "like" ice:

$$\gamma_{ice,sub} \cong 0$$

$$\gamma_{ice,vap} \cong \gamma_{sub,vap}$$

since the ice lower and upper surfaces have about the same area, the surface energy cost of creating the ice nucleus drops drastically from its value in pure vapour, and it is much more likely to form an ice nucleus

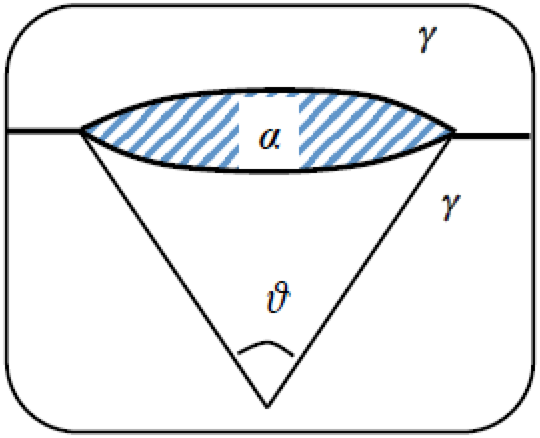
$$4\pi r^2 \cdot \gamma \;\; \rightarrow \;\; Surf \cdot \left(\gamma_{ice,vap} + \overset{\cong 0}{\gamma_{ice,sub}} - \gamma_{sub,vap} \right)$$

equal

See Ashby & Jones's book for some consequences of this…

NUCLEATION RATE GRAPH

We now want to describe the nucleation and growth of materials phases into one another. We can take for example, the $\gamma \rightarrow \alpha$ transition in pure iron at 914°C



Iron α can nucleate at grain boundaries between γ (e.g.), giving heterogeneous nucleation

In all cases

$$r^* = \frac{2\gamma}{|\Delta G|} \quad \text{and } E^* = E(r^*) = \alpha(\vartheta)\left(4\pi\gamma r^{*2} - \frac{4}{3}\pi r^{*3} \cdot G\right)$$

a factor which depends on the angle ϑ on both sides

$$\Rightarrow \quad E^* \propto \frac{1}{G^2}$$

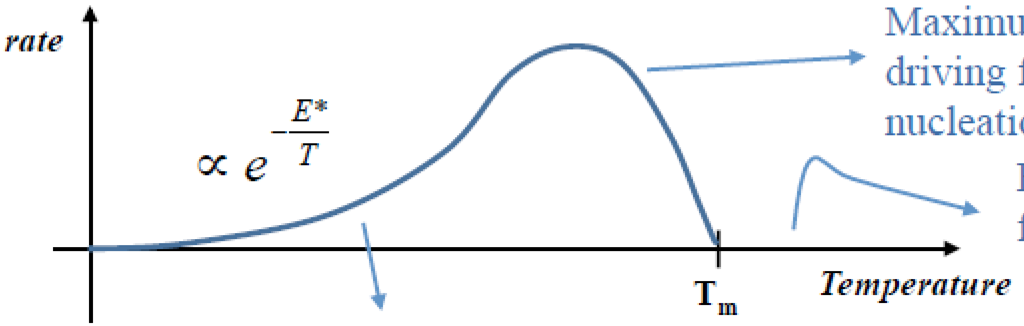
And we know that:

$$|G| = \Delta G = \Delta H\left(1 - \frac{T}{T_m}\right) = \Delta H\left(\frac{\Delta T}{T_m}\right) \propto \Delta T$$

so, sizeable ΔTs will yield smaller radii (undercooling and overheating).

NUCLEATION RATE GRAPH

We can also have a look again at the nucleation rate of a solid vs. temperature:



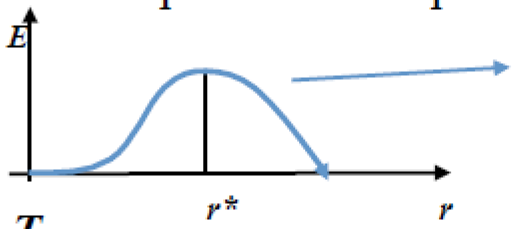
Maximum rate is at T low enough to have a driving force, but high enough that nucleation is allowed

For $T > T_m$ there is no driving force for the reaction.

The driving force grows, however the barrier is more difficult to overcome at lower T.

we can consider again the energy in the nucleation process at temperature $T \rightarrow T_m$:

$$E^* \rightarrow \infty \left(\text{since} \propto \frac{1}{\Delta T^2} \right) \text{ because } r^* \rightarrow \infty$$

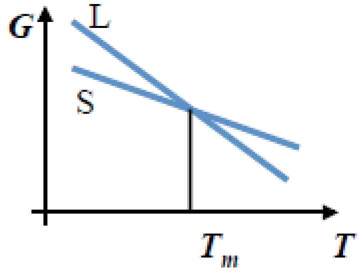


This moves to the right and up: it takes more for the volume effect since the driving force is vanishing.

so $\frac{dN}{dT} \propto e^{-\frac{E^*}{kT}}$ quenches the rate for $T \rightarrow T_m$.

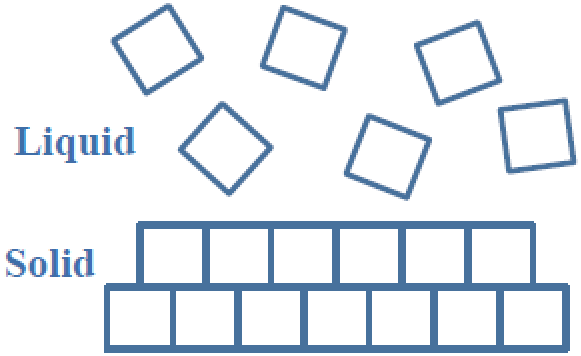
For $T \ll T_m$ the driving force |ΔG| will grow (see below) but the kinetics will slow the nucleation exponentially since $e^{-\frac{E^*}{kT}}$.

just the finite diff. between two phases ← $\boxed{\Delta H} - \boxed{T\,\Delta S}$ → vanish for low T



REACTION PROGRESS RATE

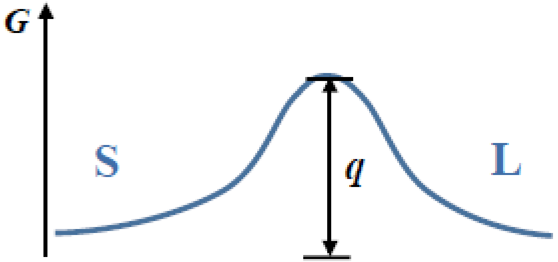
So suppose we now grow a solid nucleus inside a liquid, for $T < T_m$



We could ask ourselves what's the rate of conversion

$$J_{L\to S} = \nu_L \cdot n_L \cdot e^{-\frac{q}{kT}}$$

density of liquid at the interface, trying to become solid

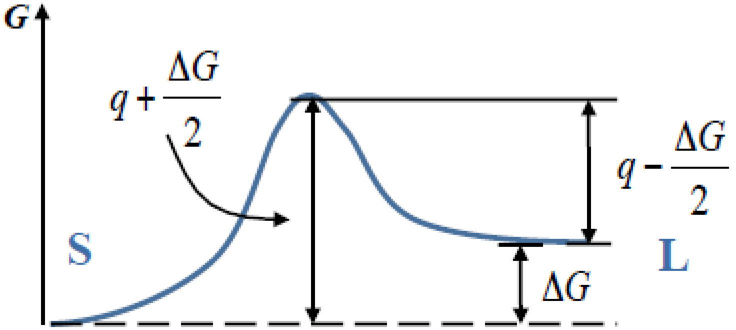


$\nu_L \cdot n_L = \nu_S \cdot n_S$ and $J_{S\to L} = \nu_S \cdot n_S \cdot e^{-\frac{q}{kT}}$

is the same at equilibrium (at T_m).

But if $T < T_m$ → there will be a driving force $\Delta H\left(1-\frac{T}{T_m}\right) = \Delta H\frac{\Delta T}{T_m}$ so that:

where $\Delta G = G_L - G_S > 0$



REACTION PROGRESS RATE

So we have a total current:

$$J_{tot} = \nu \cdot n \cdot \left(e^{-\frac{q-\frac{\Delta G}{2}}{kT}} - e^{-\frac{q+\frac{\Delta G}{2}}{kT}} \right) = \nu \cdot n \cdot e^{-\frac{q}{kT}} \left(e^{\frac{\Delta G}{2kT}} - e^{-\frac{\Delta G}{2kT}} \right) =$$

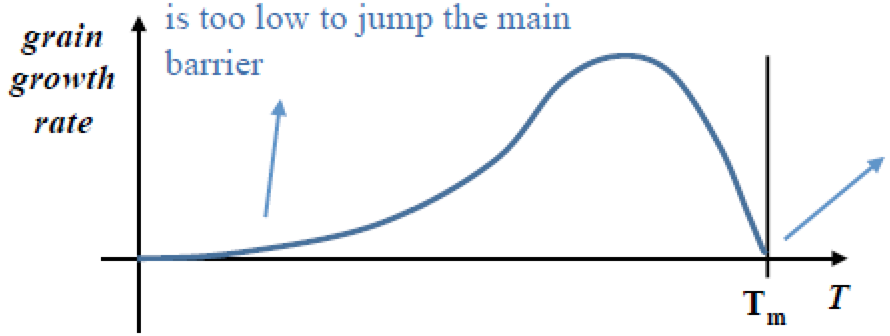
for a small ΔG > 0 we have

$$= \nu \cdot n \cdot e^{-\frac{q}{kT}} \left(1 + \frac{\Delta G}{2kT} - 1 + \frac{\Delta G}{2kT} \right) = \nu \cdot n \cdot e^{-\frac{q}{kT}} \cdot \frac{\Delta G}{kT}$$

$$\Rightarrow \quad J_{tot}^{L \to S} = \nu \cdot n \cdot e^{-\frac{q}{kT}} \cdot \frac{1}{kT} \cdot \Delta H \left(1 - \frac{T}{T_m} \right)$$

$$\boxed{H_L - H_S > 0}$$

$$\boxed{> 0 \ \text{ for } \ T < T_m \, ; \quad \propto \frac{\Delta T}{T_m}}$$



here, again, the temperature is too low to jump the main barrier

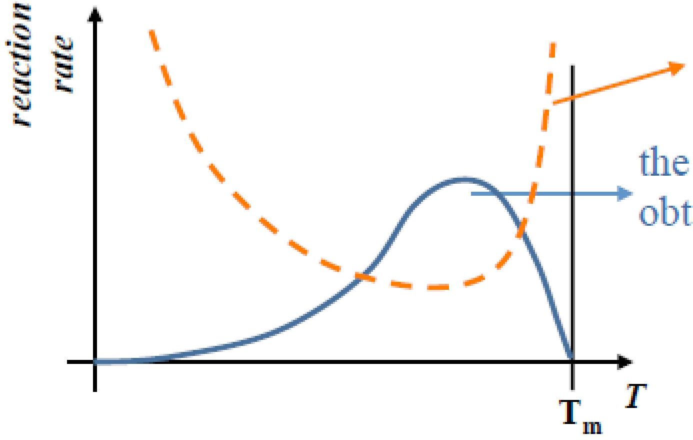
Here the rate goes to 0 for lack of driving force

This looks like the nucleation rate!!

REACTION PROGRESS RATE

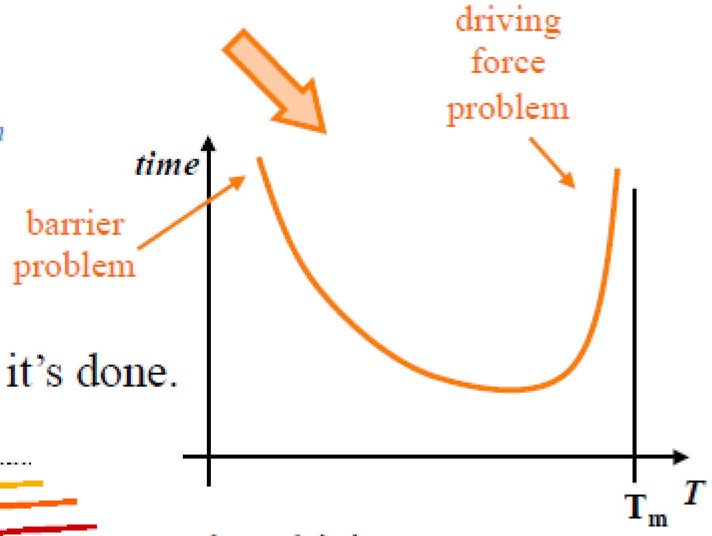
Now consider the overall reaction *speed* of any reaction, e.g., the nucleation f a solid phase into another one. This will involve both nucleation and growth at some $T=T_m$

Globally, the graph will display a behaviour similar to what we have seen

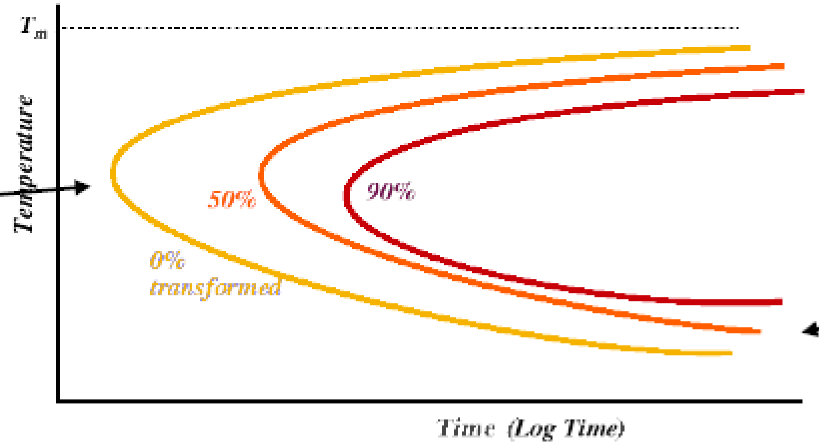


the maximum will be obtained for some $T<T_m$

Time is proportional to *1/(reaction rate)*



Normally, however, Temperature To Time (TTT) is the way it's done.



"Nose" or "Elbow" of the curve: it can be avoided by rapid cooling… thermal treatments will enable some control of the microstructure!

low driving force

T is to low to to jump barriers

TEMPERATURE TO TIME (TTT) CURVES

We saw already one for iron:

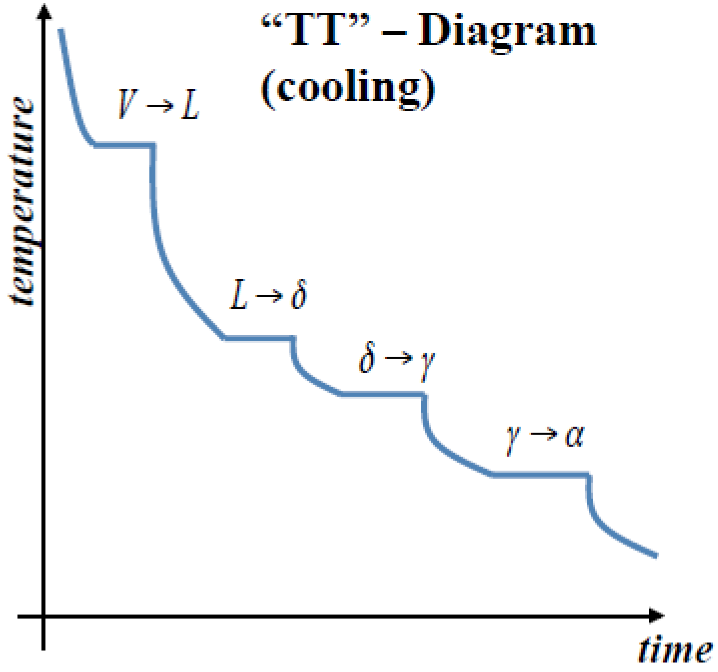
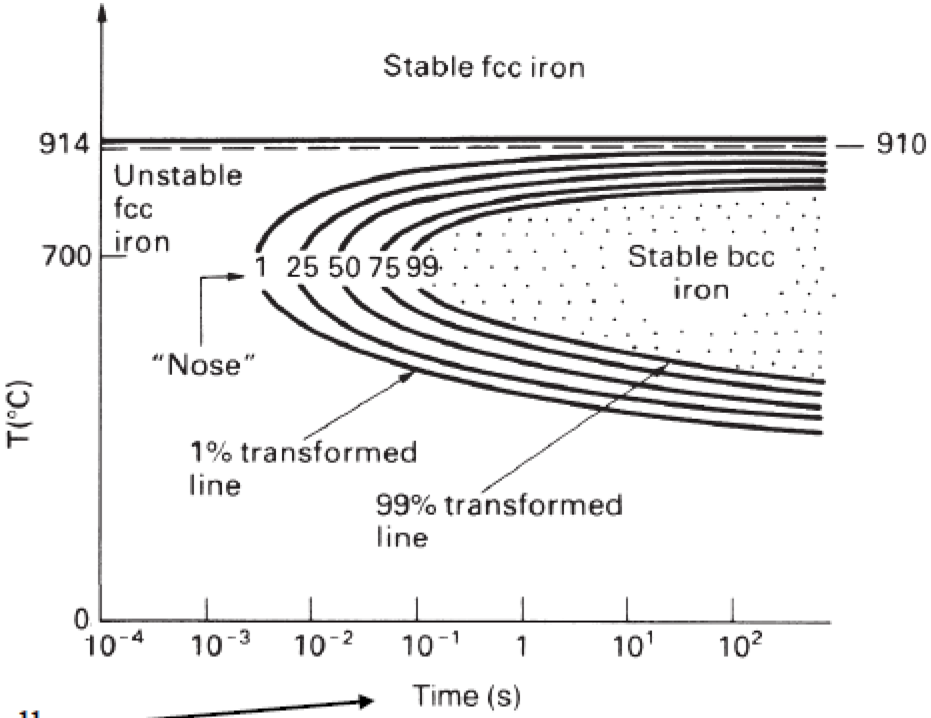


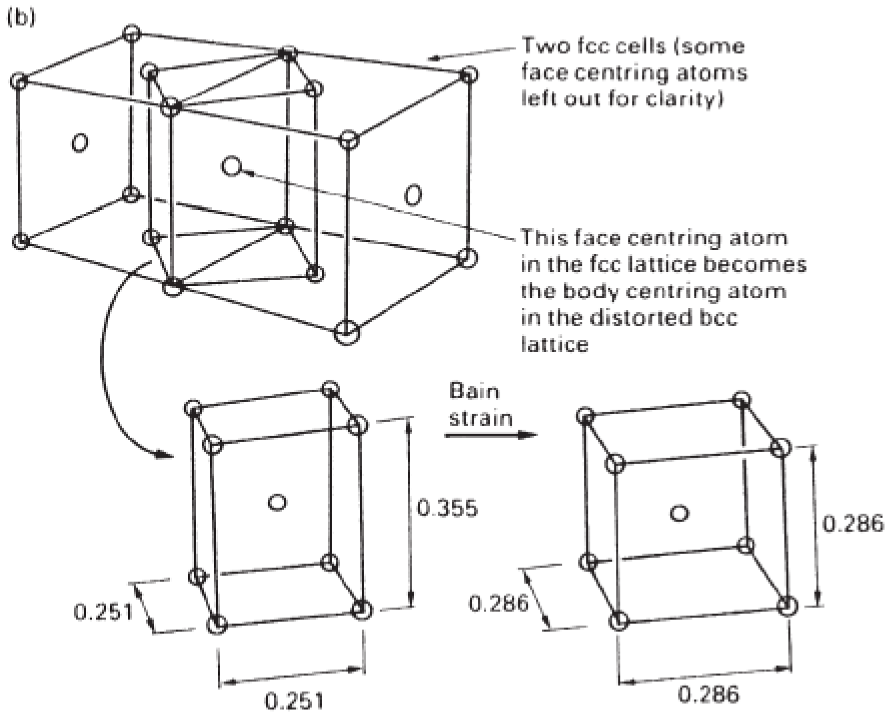
Fig. 8.5 of Ashby – Jones, shows the TTT curves for the diffusive $\gamma \to \alpha$ transition in iron



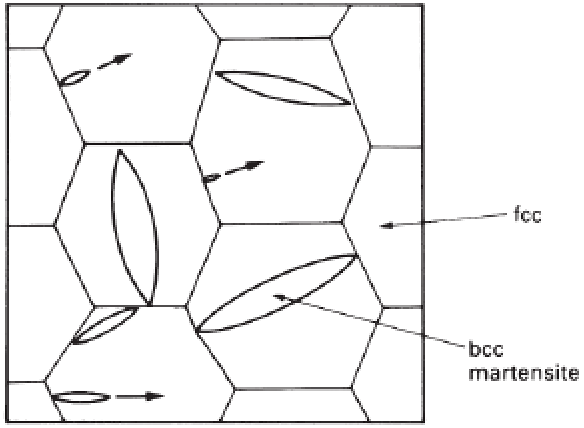
logarithmic usually

MARTENSITIC TRANSITIONS

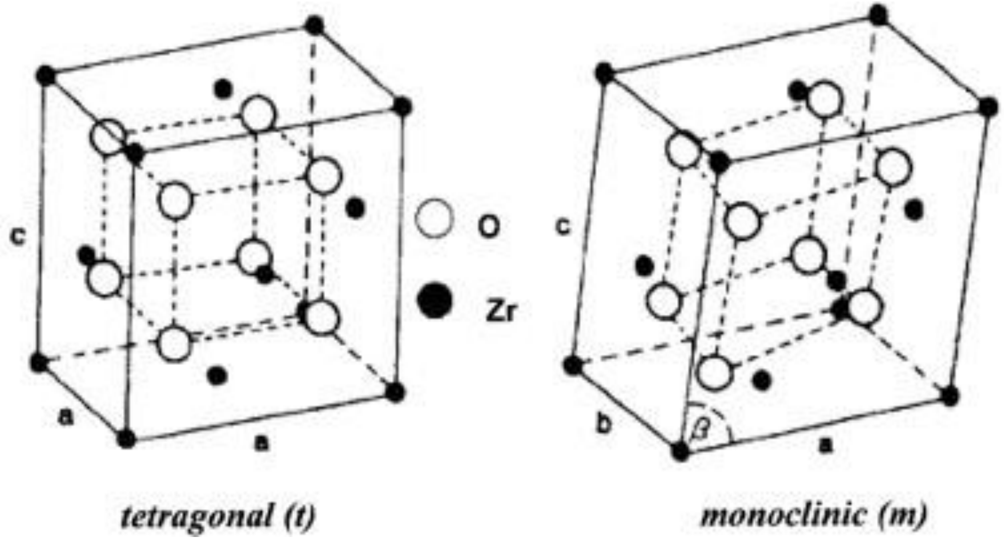
Not all phase transitions are diffusive: the “**martensitic**” transition (another name for displacive) $\gamma \rightarrow \alpha$ at 914°C is, generally, diffusive. But below 550°C it can happen “in place” as some sort of “rotation” and compression

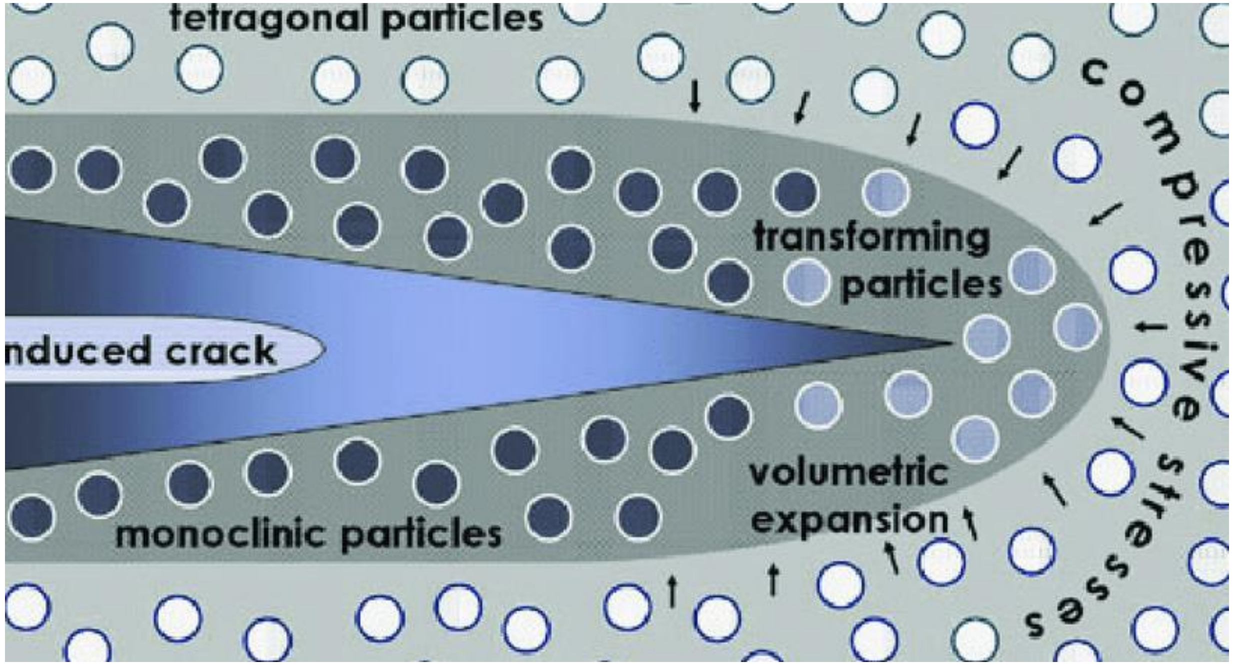


However now the ***bcc*** lattice is orthorhombic, not cubic, with height/ width ratio $\sqrt{2}$, which then decreases. Quenching the crystal is the following move. This creates “lenses” that grow until they hit a grain boundary.

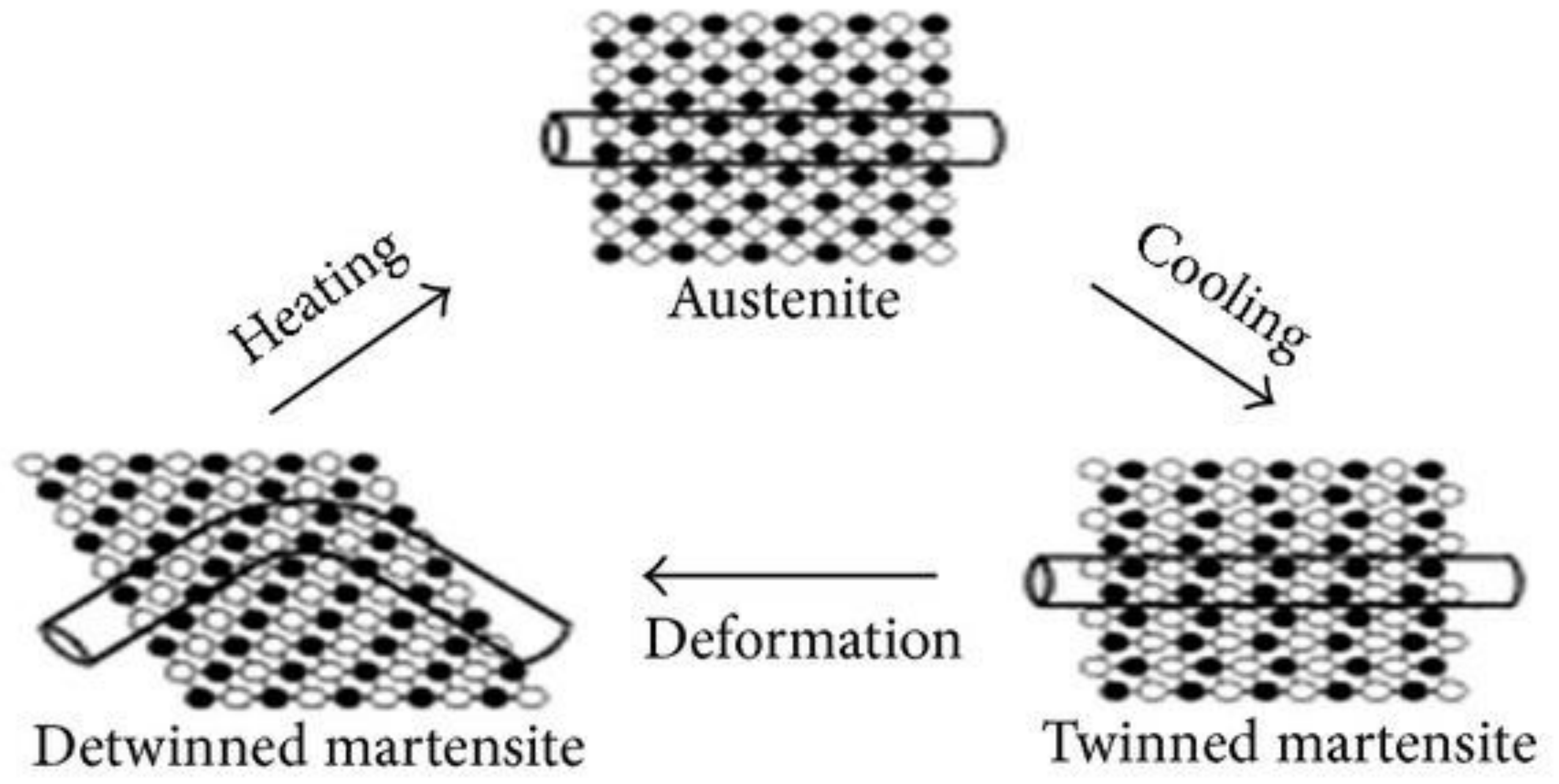


Martensitic transformation in transformation toughenining of zirconia-based materials



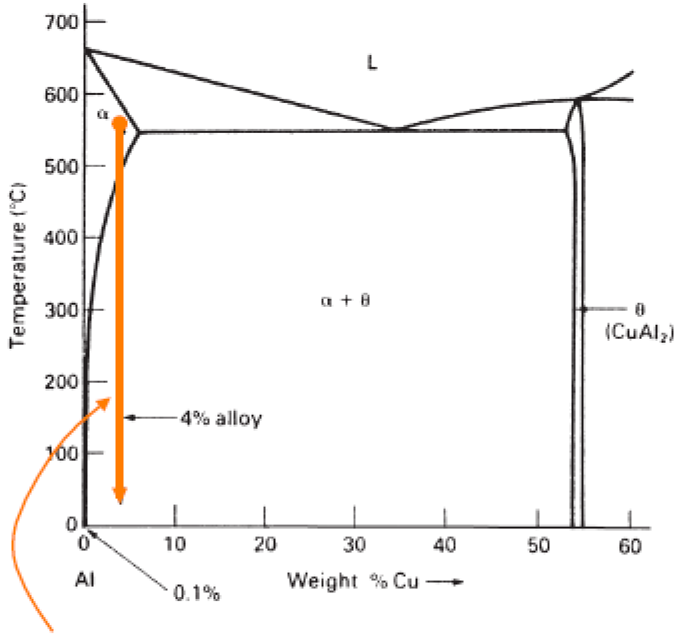


Martensitic transformation in shape-memory alloys



THERMAL TREATMENTS

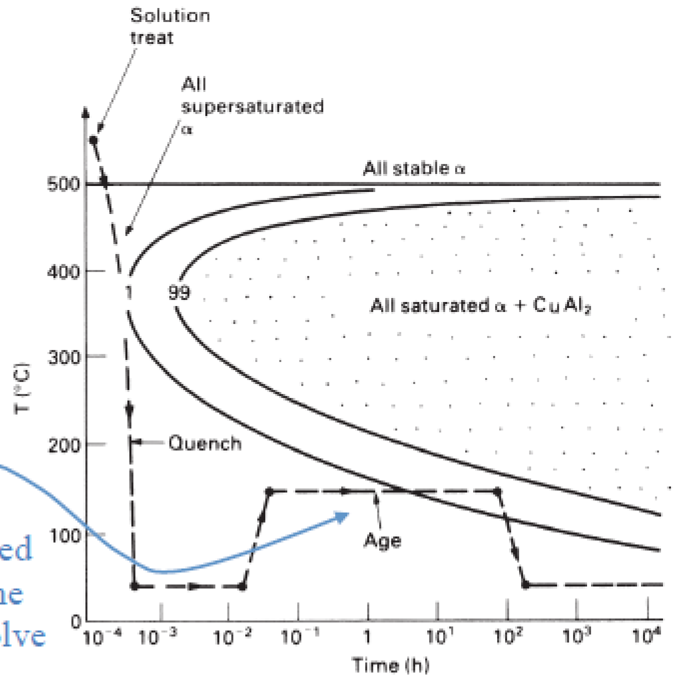
Next example: Al/Cu alloy



rapid quenching will create Al with supersaturated Cu in it, with no chance for CuAl$_2$ to nucleate.

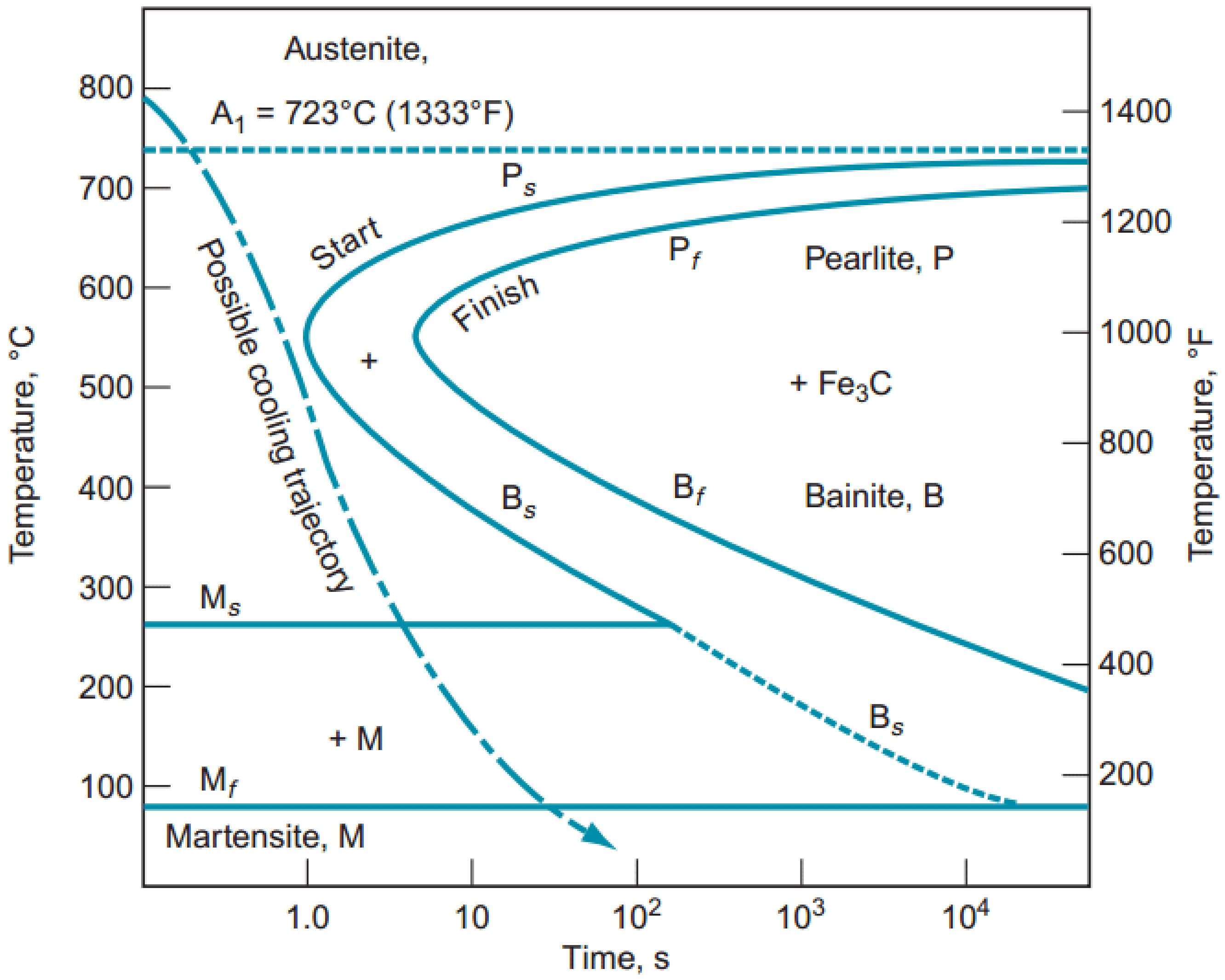
Ageing diagram

below 512°C we have segregation between Al with Cu and CuAl$_2$ (above there is a liquid mixture + Cu@Al).



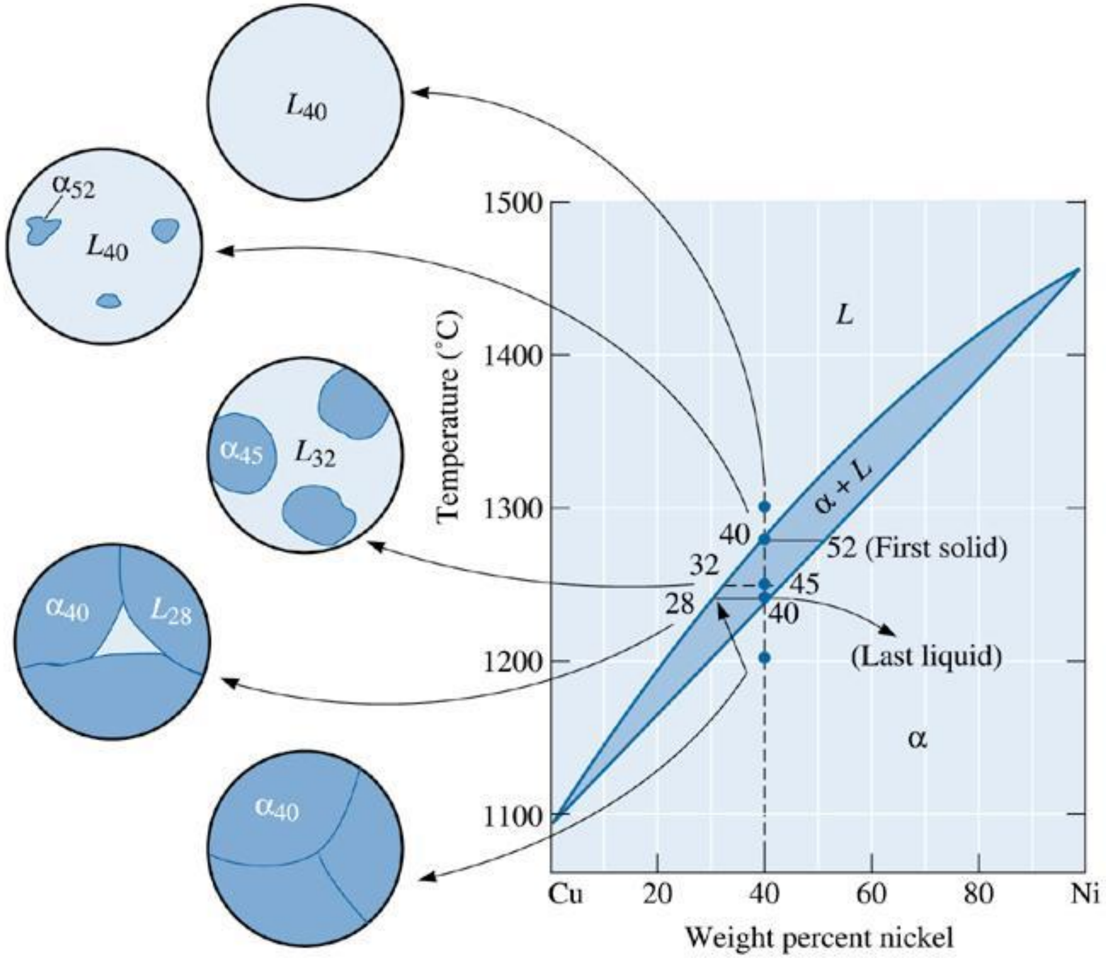
Here, the controlled reaction makes the microstructure evolve

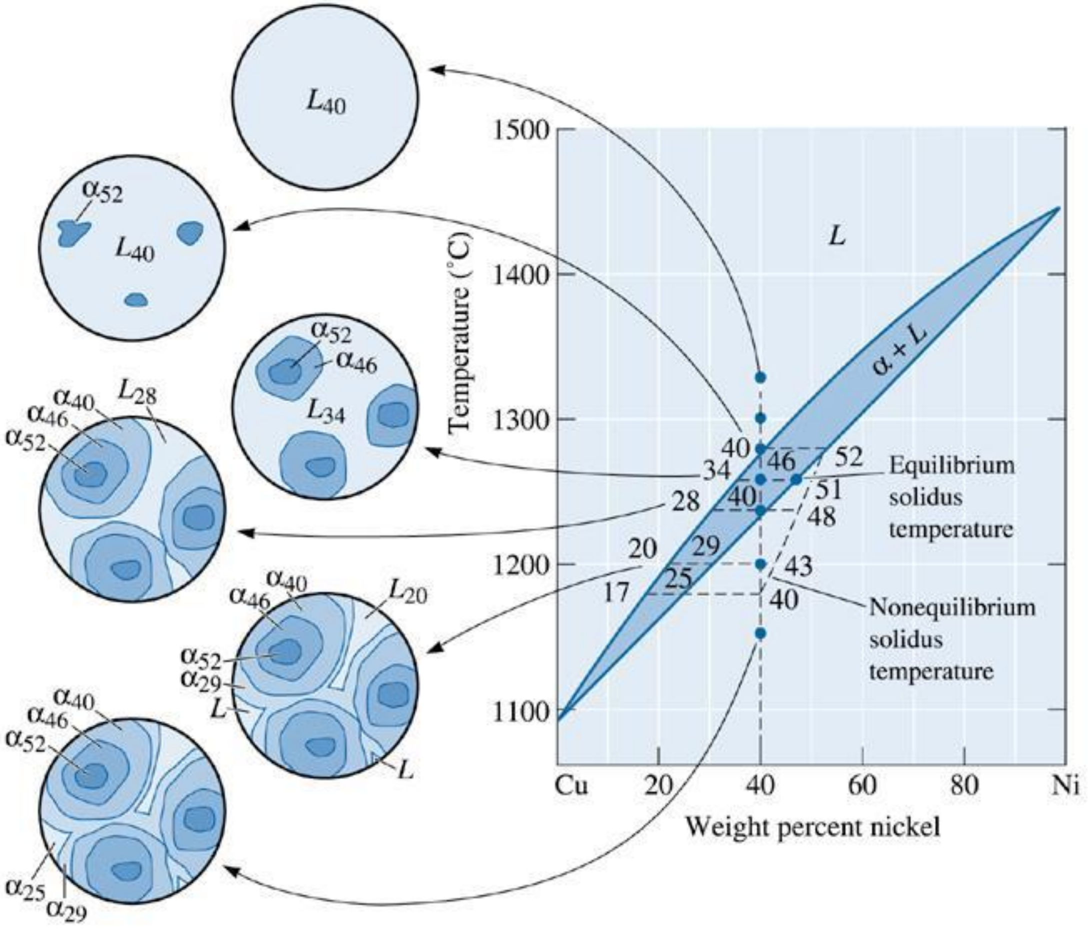
Naure of Transformations



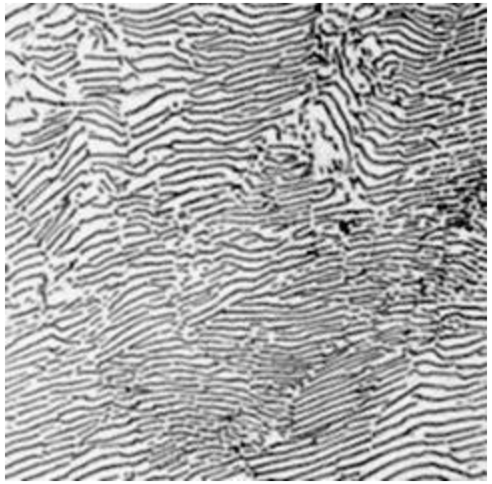
Diffusion-limited
vs
Martensitic

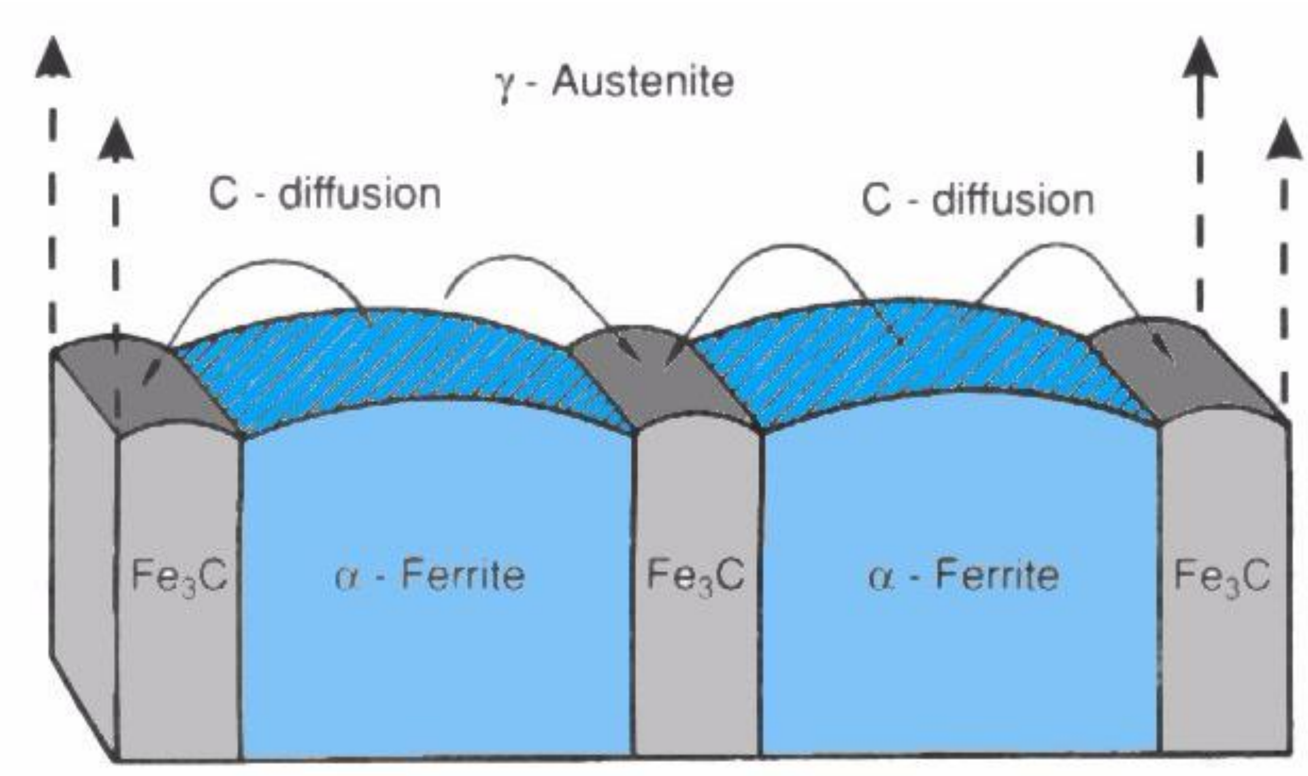
Example of Diffusion limited transformation





Example of Diffusion limited transformation



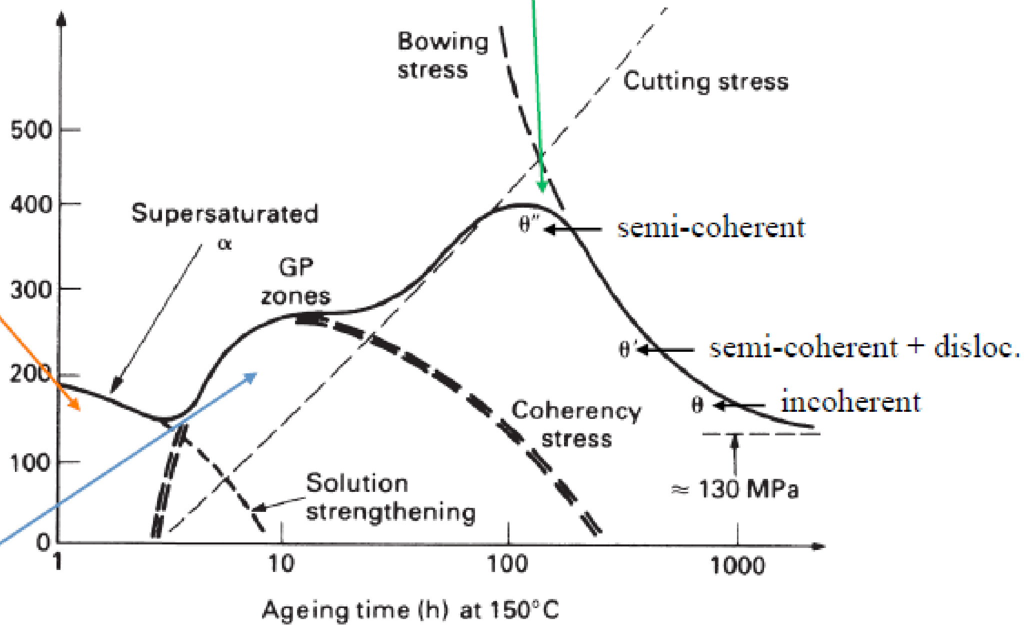


THERMAL TREATMENTS

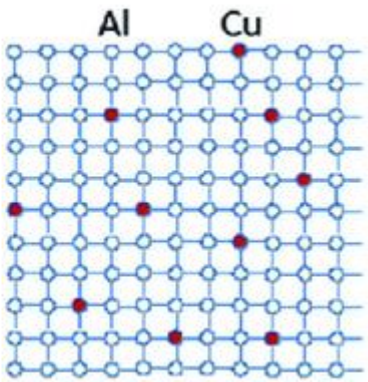
yield strength vs. aging time

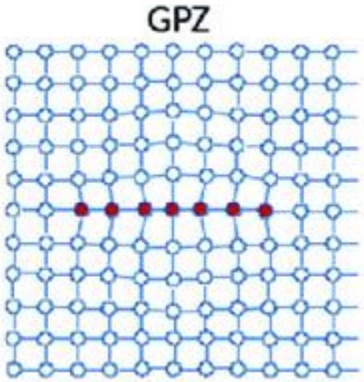
here there is the equilibrium between the increasing cost of cutting the zones with dislocations and bowing of dislocations between the increasingly separated zones

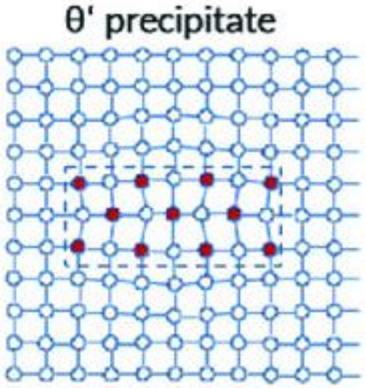
first, the supersaturated solid solution starts aggregating Cu, yielding solution strngthening

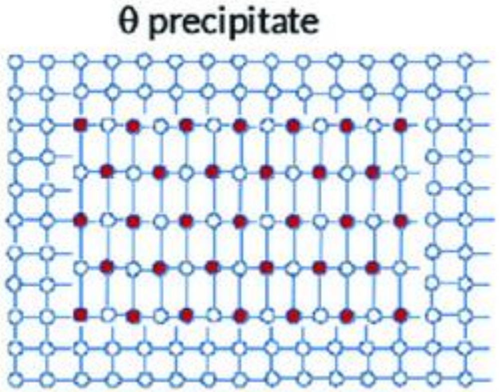


Here, coherent precipitates load up elastic fields, then becomes **bigger** and less coherent (and also **fewer**)



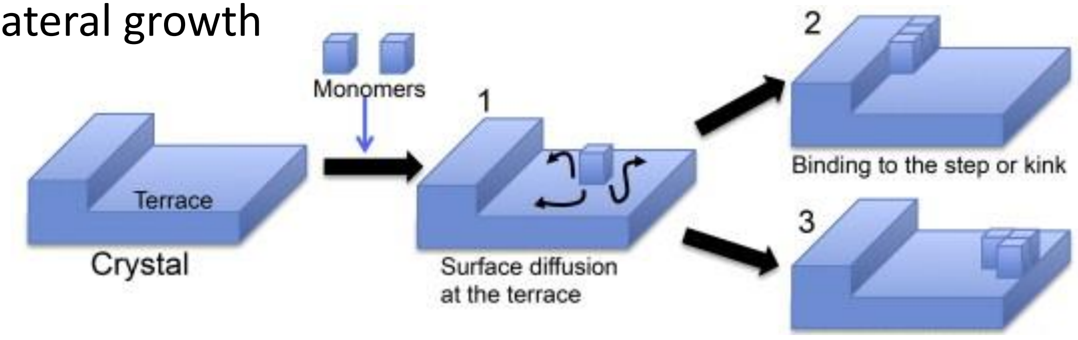




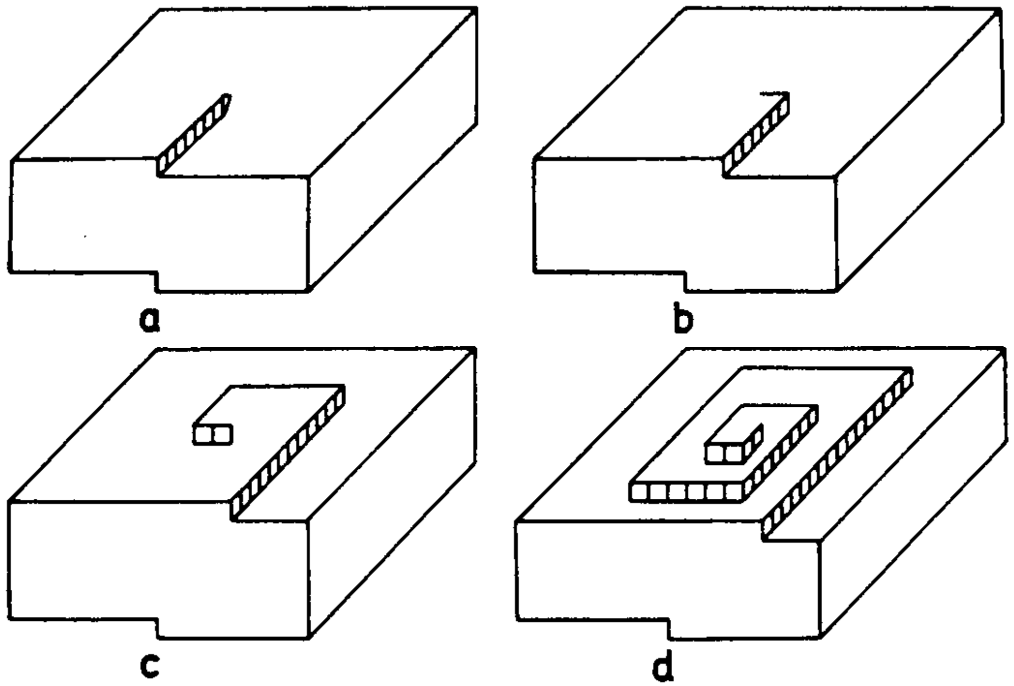


Growth

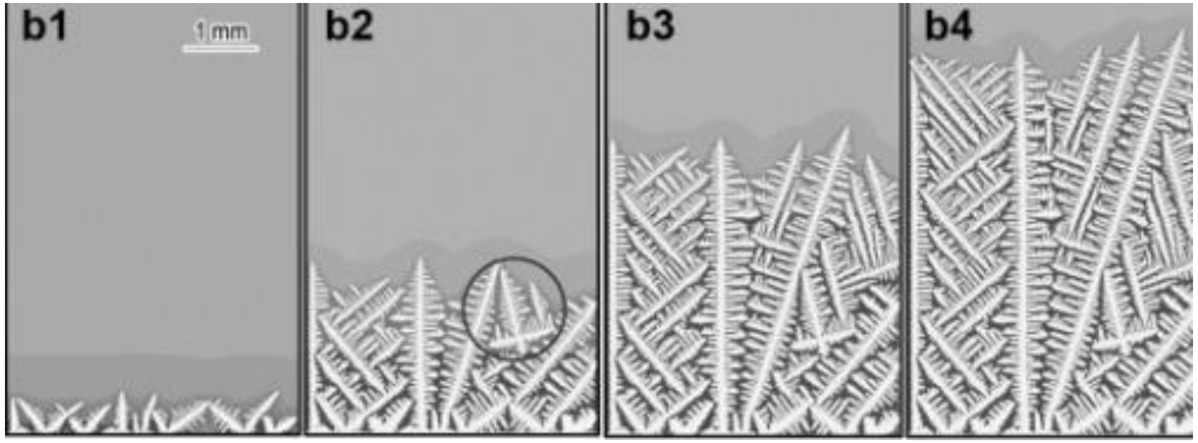
Lateral growth



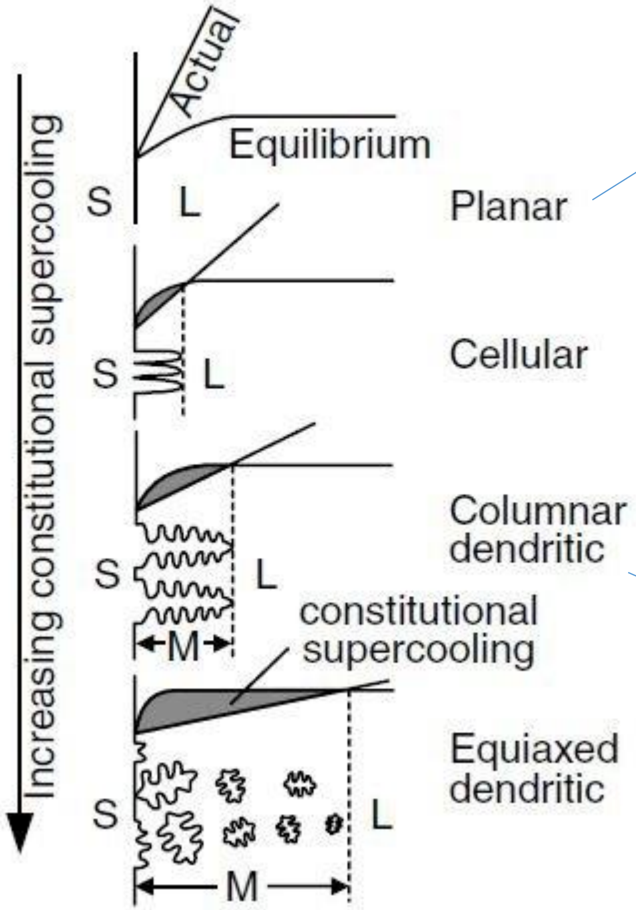
Spiral growth

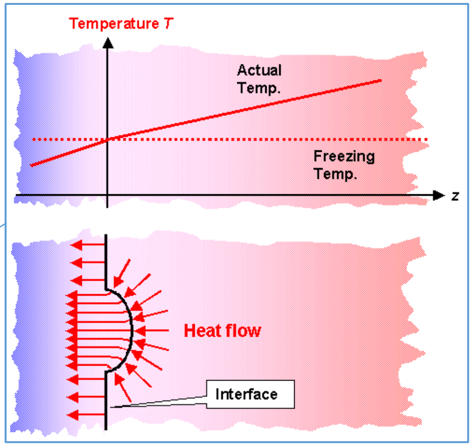


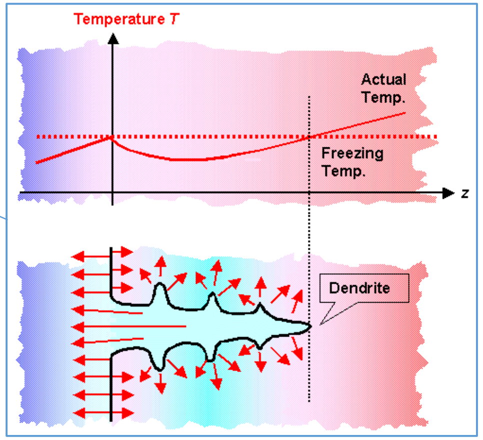
Dendrites formation

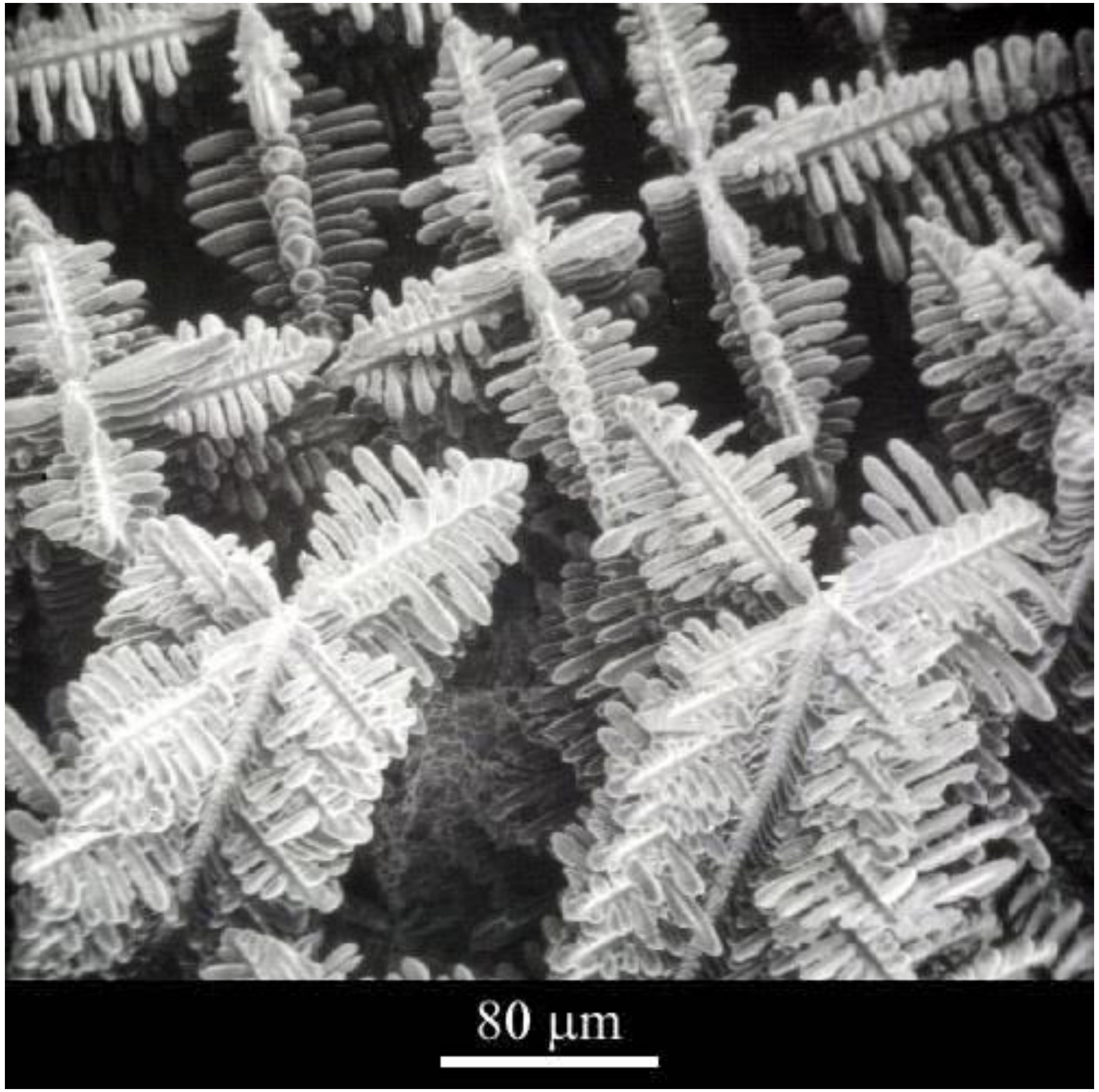


Dendrites


Increasing constitutional supercooling
Actual
Equilibrium
S
L
Planar
S
L
Cellular
S
L
Columnar dendritic
M
constitutional supercooling
S
L
Equiaxed dendritic
M


Temperature T
Actual Temp.
Freezing Temp.
z
Heat flow
Interface


Temperature T
Actual Temp.
Freezing Temp.
z
Dendrite


80 µm

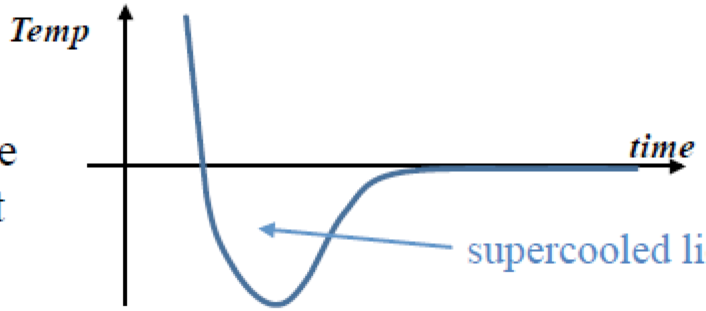
SUPERCOOLING AND OVERHEATING

Coming back to phase transitions, there are two nice further concepts: **undercooling** (or **supercooling**) and **overheating**. They are associated with the difficulty of nucleating new phases homogeneously in specific temperature directions

Supercooling

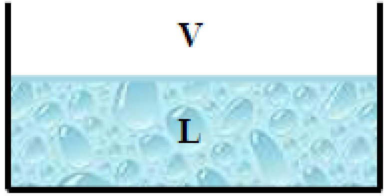
Liquid → Solid; Typical of water.

Typical if the L-V interface is less expensive than the S-V (the molecules adjust poorly at solid surfaces). Therefore $\gamma_{SV} > \gamma_{SL} + \gamma_{LV}$

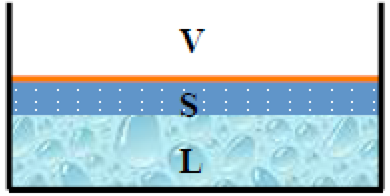


supercooled liquid

So we have a slightly supercooled liquid:

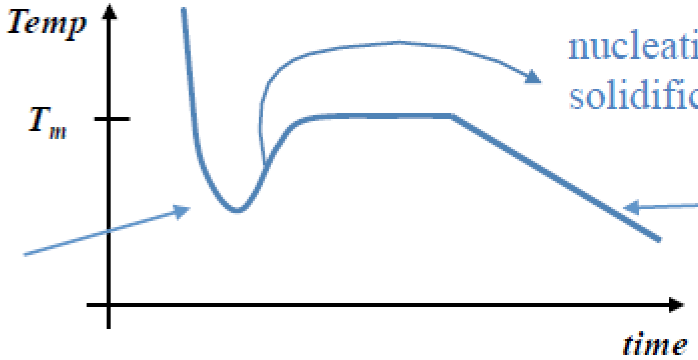


It does **not** create a **solid surface**



due to the **extra cost** of the **V-S interface**.

And, in general, the cooling curve is:



nucleation and growth releases the ΔH of solidification which heats back the system

Finally all L is solidified and the solid is cooling down.

Undercooling before the nucleation happens somewhere.

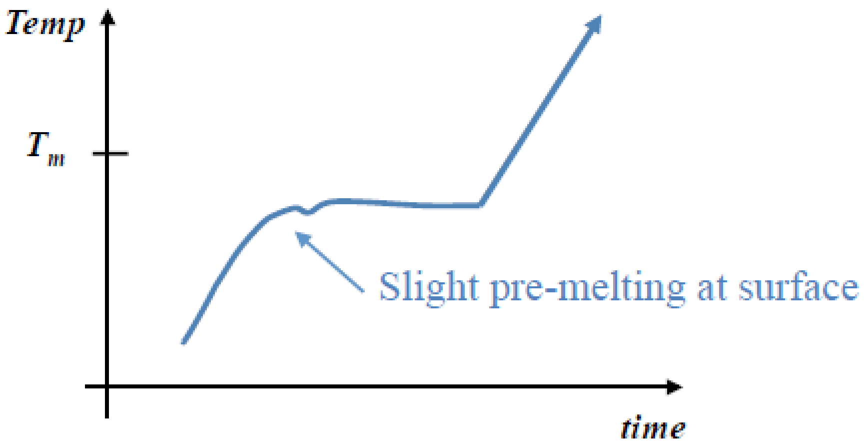
Q: why is ice slippery?

SUPERCOOLING AND OVERHEATING

But melting does *not* imply overheated solids! Indeed

In fact, the surface **might melt** at a slightly lower T than the bulk since it gains the

$$\Delta E = \underbrace{\gamma_{LV} + \gamma_{LS}}_{\boxed{\text{small}}} - \underset{\boxed{\text{big}}}{\gamma_{SV}} < 0$$



but this is only a very thin film below the melting point, and is hardly noticed in macroscopic samples close to *T*m. Things are different at the nanoscale…