Phase Diagrams and Phase Separation

Books

MF Ashby and DA Jones, Engineering Materials Vol 2, Pergamon

P Haasen, Physical Metallurgy,

G Strobl, The Physics of Polymers, Springer

Introduction

Mixing two (or more) components together can lead to new properties:
Metal alloys e.g. steel, bronze, brass….
Polymers e.g. rubber toughened systems.

Can either get complete mixing on the atomic/molecular level, or phase separation.

Phase Diagrams allow us to map out what happens under different conditions (specifically of concentration and temperature).

Free Energy of Mixing

Entropy of Mixing

n_A atoms of A
n_B atoms of B

Total atoms N = $n_A + n_B$

Then S_{mix} = k ln W

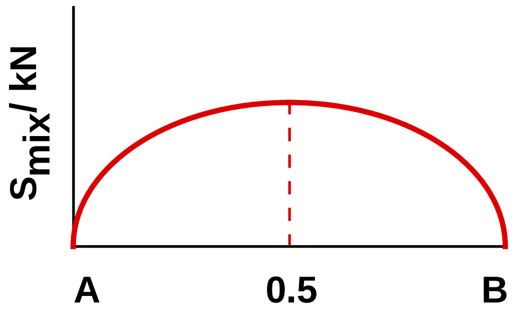
$$= k \ln \frac{N!}{n_A! n_{b!}}$$

This can be rewritten in terms of concentrations of the two types of atoms:

$n_A/N = c_A$ $\qquad$ $n_B/N = c_B$

and using Stirling's approximation

$$S_{mix} = -Nk\,(c_A \ln c_A + c_B \ln c_B)$$



This is a parabolic curve.

There is always a positive entropy gain on mixing (note the logarithms are negative) – so that entropic considerations alone will lead to a homogeneous mixture.

The infinite slope at c_A=0 and 1 means that it is very hard to remove final few impurities from a mixture.

This is the situation if no molecular interactions to lead to enthalpic contribution to the free energy (this corresponds to the athermal or ideal mixing case).

Enthalpic Contribution

Assume a coordination number Z.

Within a mean field approximation there are

n_{AA} **bonds of A-A type** $= 1/2\ Nc_AZc_A = 1/2\ NZc_A^2$

n_{BB} **bonds of B-B type** $= 1/2\ Nc_BZc_B = 1/2\ NZ(1-c_A)^2$

and n_{AB} **bonds of A-B type** $= NZc_A(1-c_A)$

where the factor 1/2 comes in to avoid double counting and $c_B = (1-c_A)$**.**

If the bond energies are E_{AA}, E_{BB} **and** E_{AB} **respectively, then the energy of interaction is (writing** c_A **as simply c)**

$$1/2\ NZ\ [cE_{AA} + (1-c)E_{BB} + c(1-c)\ (2E_{AB} - E_{AA} - E_{BB})]$$

energy of 2 separate starting materials

$$\therefore\ U_{mix} = 1/2\ NZ\ c(1-c)\ (2E_{AB} - E_{AA} - E_{BB})$$

The term ($2E_{AB} - E_{AA} - E_{BB}$) determines whether mixing or demixing occurs.

Define $\chi kT = Z/2\ (2E_{AB} - E_{AA} - E_{BB})$

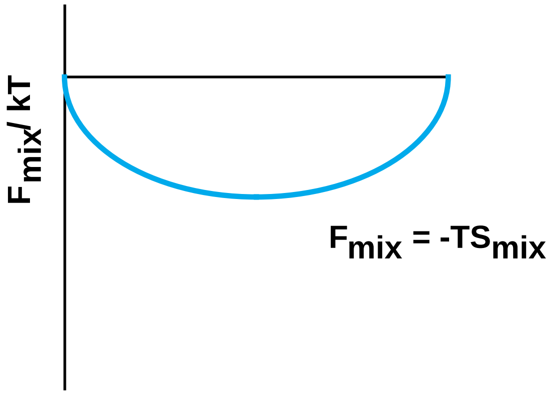
where χ is known as the interaction parameter, and is dimensionless.

(The definition of χ in this way, including the kT term, is for historical reasons).

$$F_{mix}/\ kT = c \ln c + (1-c) \ln (1-c) + \chi\ kT\ c(1-c)$$

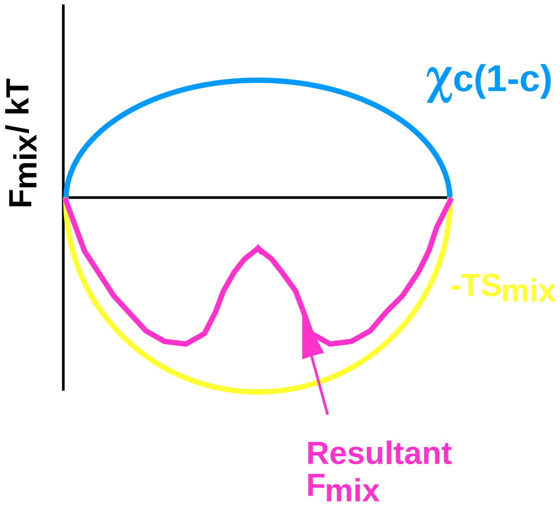
Three cases to consider

⇒ $\chi=0$ athermal or ideal solution case.



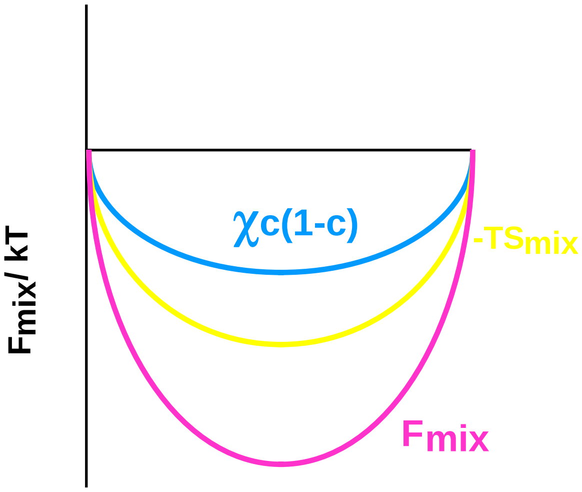
F_{mix} is always negative.

⇒ $\chi>0$ i.e. $2E_{AB} > E_{AA} + E_{BB}$



2 local minima result

⇒ $\chi < 0$



One deep minimum

These curves correspond to the case for one particular T.

In order to plot out a phase diagram, we need to be able to see how temperature affects these curves.

And we need to know whether or not these curves imply phase separation.

Finally we need to know, if phase separation occurs, how much of each phase is present.

Lever Rule for Determining Proportions of Phases

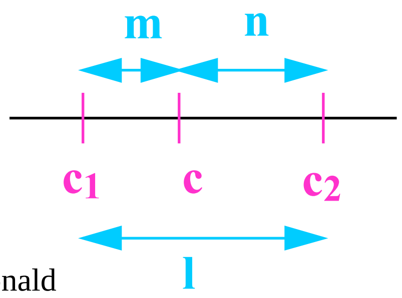
Imagine we have a system with 2 phases present (labelled 1 and 2), and two types of atoms A and B.

In phase 1 concentration of A = c_1
In phase 2 concentration of A = c_2

and that there is x of phase 1 present
and (1-x) of phase 2 present.

Total of N atoms, overall concentration of A = c

$$\therefore \text{ no of A atoms is } Nc = Nxc_1 + N(1-x)\,c_2$$



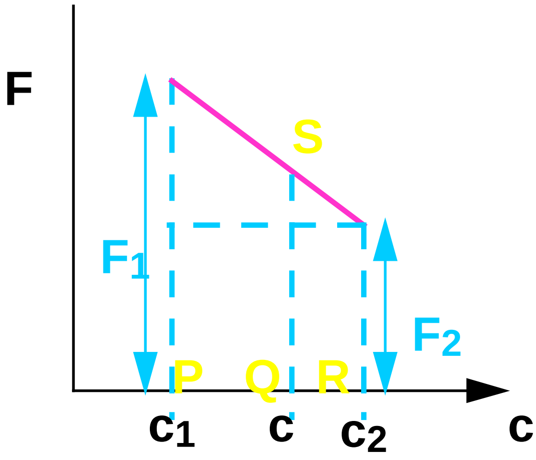
$$\Rightarrow \quad \boxed{x = \left|\frac{c-c_2}{c_1-c_2}\right| = \frac{n}{l}}$$

$\Rightarrow$ **Lever Rule**

Similarly 1-x= $\left|\dfrac{c-c_1}{c_1-c_2}\right| = \dfrac{m}{l}$ **and** $\dfrac{x}{1-x} = \left|\dfrac{c-c_2}{c-c_1}\right| = \dfrac{n}{m}$

Thus, when one wants to find the average of some quantity such as F, it is usually sufficient (neglecting surface effects) to take a weighted average.

Consider the free energy F as F(c)



$F(c) = F_2 + (F_1 - F_2)$ QR/PR

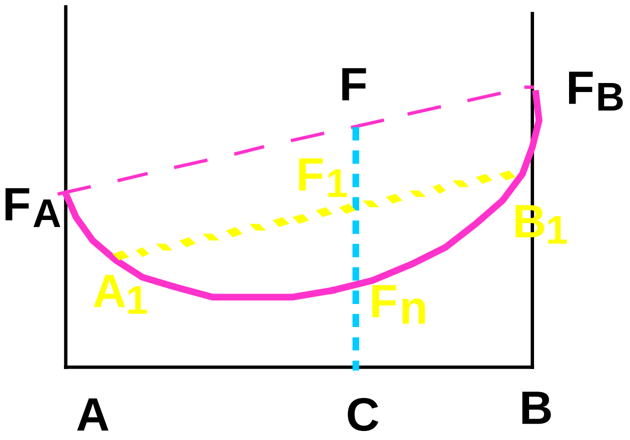
By similar triangles, ⇒ F(c) = SQ in the diagram.

Therefore one can find free energy of any intermediate composition by drawing straight line between the free energies of the two constituent phases.

Can now use this to interpret free energy curves.

Consider cases of χ=0 or negative; free energy curve had a single minimum.

As pure components (A and B) F(c) = F



This can be lowered by going to compositions A_1,B_1 to give free energy F_1 etc

And as A and B continue to dissolve more and more of each other, free energy continues to drop.

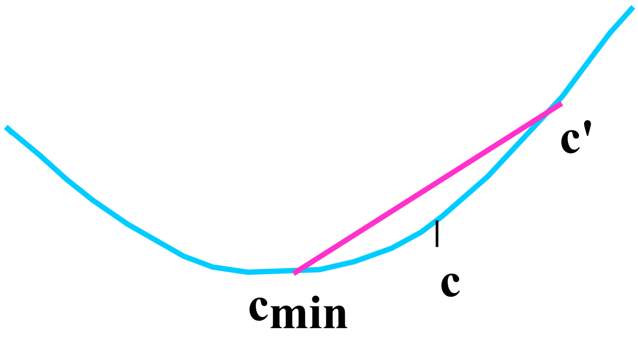
Minimum energy for homogeneous single phase, energy F_n

i.e no phase separation occurs in this case.

Composition overall determines the state of the mixture.

Minimum free energy will not be given (in general) by the minimum in the free energy curve.

e.g. starting with composition c, if this were to result in composition corresponding to the minimum on the curve $c_{min,}$ would necessarily also have phase with composition c' present.

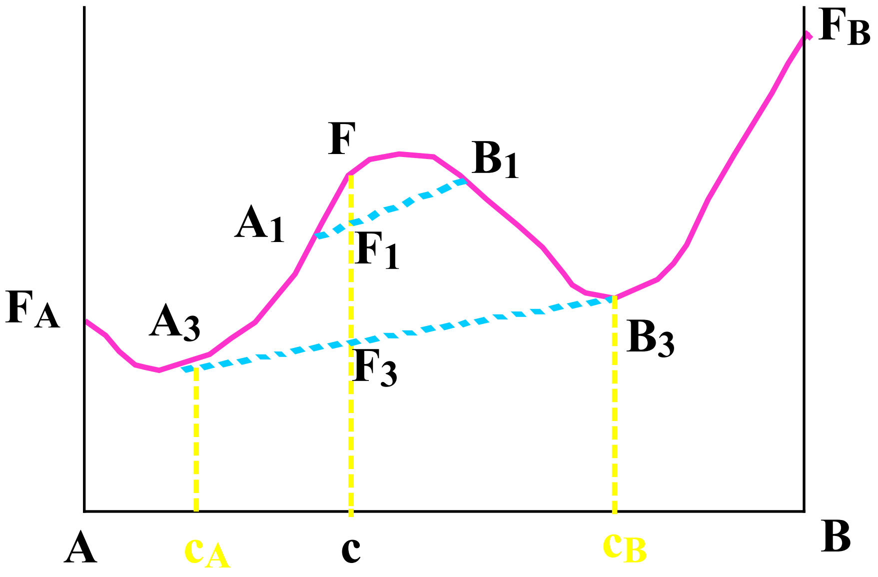


Necessary condition for homogeneous mixing to occur is for

$$\boxed{\frac{d^2 f}{dc^2} \geq 0 \text{ everywhere}}$$

However when χ is positive, this inequality does not hold, and the behaviour is very different.

Start with homogeneous free energy F, for concentration c.



This can split into A_1 and B_1; energy drops to F_1.

Minimum in energy occurs at F_3 when the representative points on the free energy curve are joined by the lowest straight line: common tangent construction.

In this case, have phase separation into compositions c_A and c_B, with phases α and β.

For compositions **$c < c_A$ have α phase**
$c_A < c < c_B$ have α + β
$c_B < c$ have just β.

Proportions of α and β given by Lever rule.

For $c<c_A$ A dissolves B
For $c_B<c$ B dissolves A

c_A and c_B define solubility limits.

This common tangent construction can be extended to quite complicated situations, with several minima, which then give rise to quite complicated free energy curves and hence phase diagrams.

For plotting a phase diagram we need to know how solubility limits (as determined by the common tangent construction) vary with temperature.

Have seen that if d^2F/dc^2 everywhere ≥0 have a homogeneous solution.

Phase separation occurs when free energy curve has regions of negative curvature.

This permits us to evaluate the limits of solubility in terms of χ.

For the symmetric case (i.e $F_A = F_B$ i.e terms involving E_{AA} and E_{BB} are assumed equal)

$F_{mix}/ kT = c \ln c + (1-c) \ln (1-c) + \chi c (1-c)$ per site

$$\therefore \frac{d^2F}{dc^2} = kT\left(\frac{1}{c} + \frac{1}{1-c} - 2\chi\right)$$

Critical value when $d^2F/dc^2 = 0$

$$\boxed{\Rightarrow c = \frac{1}{2} \pm \frac{1}{2}\sqrt{1 - \frac{2}{\chi}}}$$

For a regular solution $\chi \propto 1/T = A/T$

Then limits of solubility vary with temperature according to

$$c = \frac{1}{2} \pm \frac{1}{2}\sqrt{1 - \frac{2T}{A}}$$

i.e. as T raised the two compositions of phases α and β converge, until at $T_{crit} = A/2$ there is no further separation and a homogeneous mixture results.

In general, critical value of $\chi = 2$.

There is no solution for c for $\chi < 2$ so there is no phase separation.

Also, for the symmetrical case, the common tangent construction reduces to the condition

df/dc = 0 (i.e. horizontal tangent)

This equation defines the binodal or coexistence curve.

$$\chi_{binodal} = \frac{1}{2c-1}\ln\left(\frac{c}{1-c}\right)$$

For the regular solution case, with $\chi \propto 1/T$ this allows us to plot out how the binodal behaves.

Some comments on this Approach

This approach of a 'symmetrical' AB mixture is very similar to the Ising model, where the 2 states correspond to opposite spins (although of course A cannot transform to B as spins can).

The approach used has been a mean field theory. This will fail:

- **⇒ near a critical point: will give the wrong critical point and the wrong critical exponents. In practice most of the phase diagram will be well away from this point, so this is not too severe.**
- **⇒ for strongly negative χ. In this case there are strong attractions between unlike atoms and the idea of random distributions breaks down. This can lead to order-disorder transitions.**

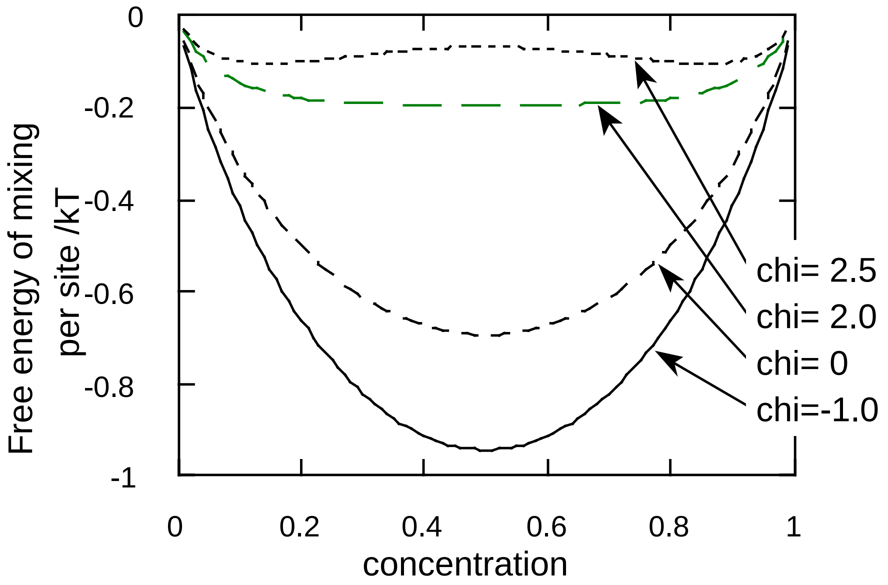
In general it is difficult to calculate χ from 1st principles.

Picture described here works best for liquid-liquid phase separation. Melting may complicate matters.

For solid-solid transitions have additional problems, leading to very complicated phase diagrams, due to
Strain energy
Other intermediate compounds eg AB_2.

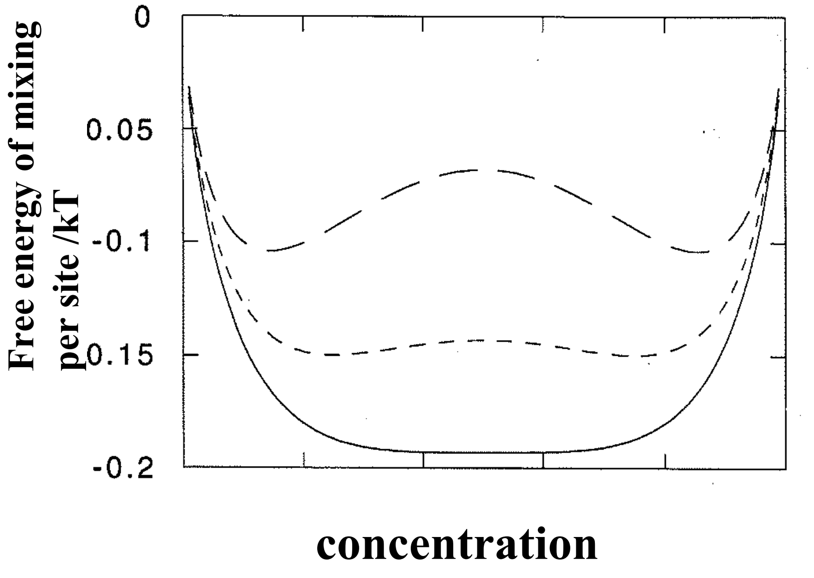
However for the regular solution model we now can construct a phase diagram – which contains all the essential physics.

$\chi<2$, only a single minimum ⇒ homogeneous mixture



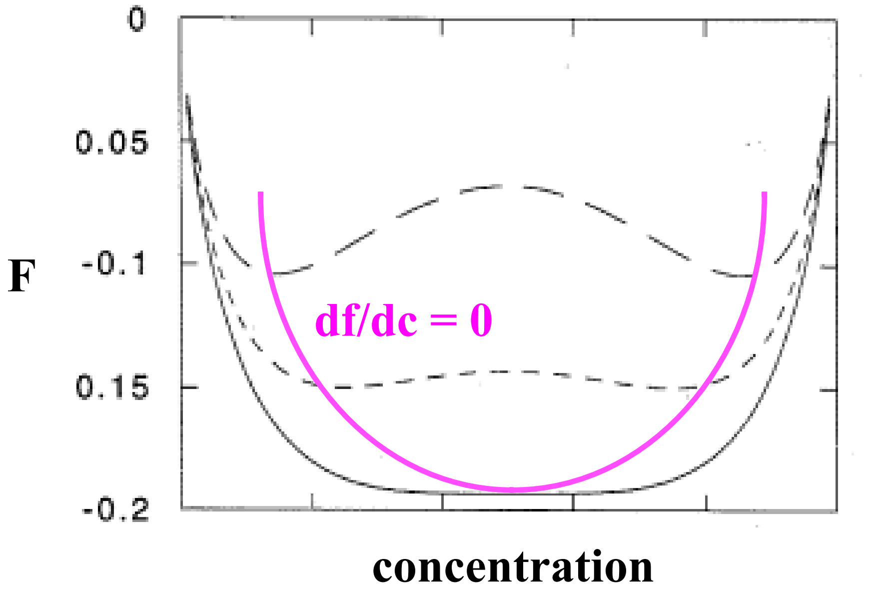
T decreasing

$\chi>2$, two minima develop ⇒ phase separation

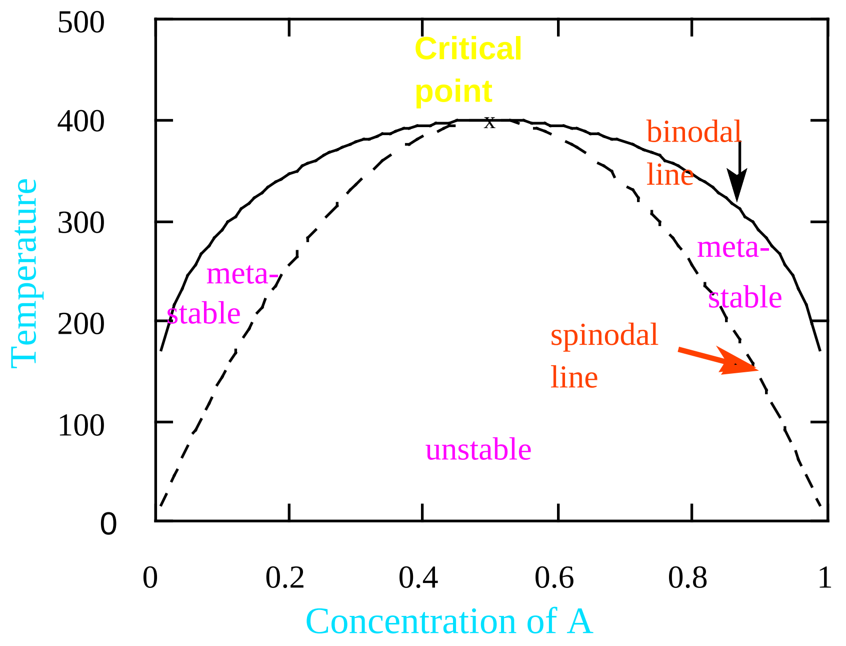


T decreasing

Knowing the form of the free energy curves as a function of T means that we can map out the limits of solubility etc.



Plotting out the locus of the binodal enables us to see the shape of the phase diagram.



The binodal or coexistence curve describes the limits of solid solubility.

Have seen condition for homogeneous mixing everywhere is $d^2f/dc^2 \geq 0$ everywhere.

The locus $d^2f/dc^2 = 0$ is called the spinodal curve.

We need to distinguish how phase separation occurs inside this curve from between binodal and spinodal.

Spinodal Curve and Spinodal Decomposition

In the two phase region, two kinds of decomposition can occur.

1. **Nucleation and Growth – which we have already talked about, and is the most familiar.**

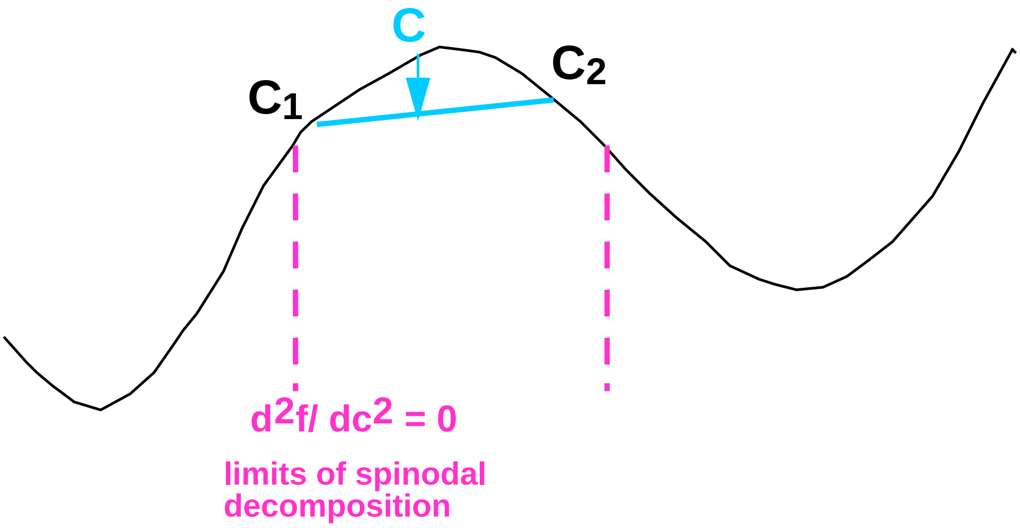
2. **Spinodal Decomposition**

In the nucleation and growth regime we know that a nucleus of a critical size has to form before it is energetically favourable for it to grow.

Nucleation and growth corresponds to a metastable region of the phase diagram.

Spinodal decomposition occurs when any composition fluctuation is unstable – the unstable region of the phase diagram.

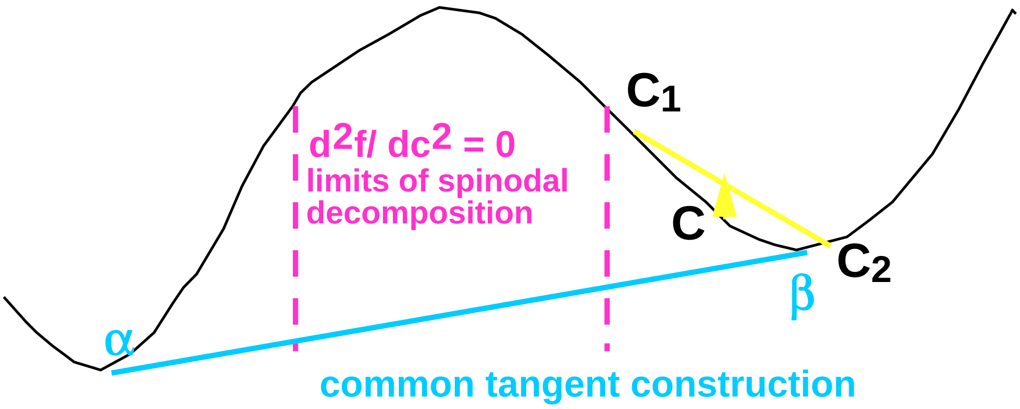
Section of free energy curve:



Start at composition c, split into 2 slightly different compositions c_1 and c_2 to give net lowering of energy.

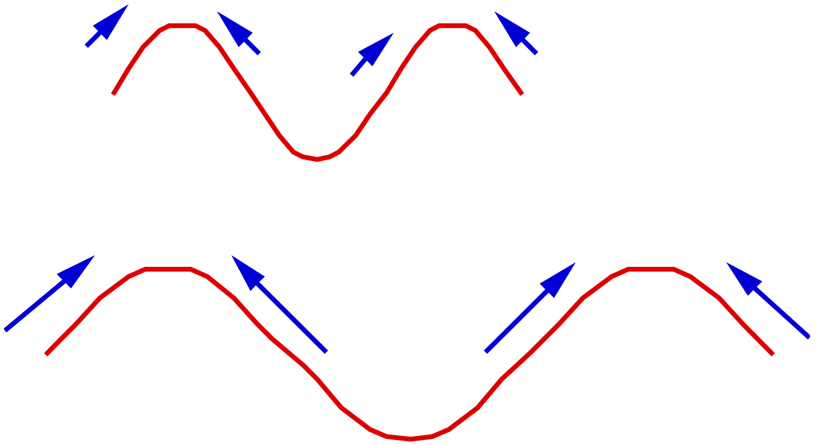
Where the curvature is negative, any composition fluctuation leads to a drop in F, and is therefore unstable.

This contrasts with region between spinodal and binodal:



Net increase in F as compositions diverge – hence nucleation barrier, even though ultimately end up with overall lowering of energy when split into phases α and β.

Since any composition fluctuation is stable in the spinodal region, which wavelength dominates?



Large fluctuations grow comparatively slowly because atoms have to diffuse over large distances.

Small fluctuations are suppressed, because they involve a lot of diffuse interfaces.

However the fact that interfaces aren't sharp means that we have to think carefully about how to account for the interfacial energy.

Local free energy density depends on the composition at that point and in the vicinity, since this will determine the sharpness of the interface.

Local free energy therefore can be written (1D case)

$$F = A\int f(c, \frac{dc}{dx}, \frac{d^2c}{dx^2}, \ldots.)dx$$

where A is a constant

Expand as Taylor series

$$f(c, \frac{\partial c}{\partial x}, \frac{\partial^2 c}{\partial x^2} \ldots) = f_o(c) + k_{11}\frac{\partial c}{\partial x} + k_{12}\left(\frac{\partial c}{\partial x}\right)^2 + k_{21}\frac{\partial^2 c}{\partial x^2} + \ldots$$

Discarding higher order terms, and noting that *k*$_{11}$ must be zero by symmetry

$$F = A\int\left[f_o(c) + k_{12}(\frac{\partial c}{dx})^2 + k_{21}\frac{\partial^2 c}{\partial x^2}\right]dx$$

Which can be shown to lead to

$$\boxed{F = A\int[f_o(c) + K\left(\frac{\partial c}{\partial x}\right)^2]dx}$$

Where *K* is the gradient energy coefficient

$$K = k_{12} - \frac{\partial k_{21}}{\partial c}$$

This theory is due to Cahn and Hilliard for metal alloys. An equivalent theory for magnetic domains is due to Landau and Ginsburg.

System will try to equilibrate by having a uniform chemical potential.

General transport equation, flux of A, J_A

$$-J_A = M\frac{\partial}{\partial x}(\mu_A - \mu_B)$$ **Onsager relation**

M is an Onsager coefficient
μ_A and μ_B are the chemical potentials of A and B respectively.

(μ_A - μ_B) is the free energy to remove 1 atom of A and replace it by B atom

$$\mu_A - \mu_B = \frac{\partial}{dc}\left(f_o(c) + K(\frac{\partial c}{\partial x})^2 \right)$$

$$= \frac{\partial f_o}{\partial c} + 2K\frac{\partial^2 c}{\partial x^2}$$

$$-J_A = M\frac{\partial^2 f_o}{\partial c^2}\frac{\partial c}{\partial x} + 2MK\frac{\partial^3 x}{\partial x^3}$$

For early times, c will not differ greatly from overall concentration c_o. Can then make assumptions M, $\partial^2 f_o/\partial c^2$ and K are independent of c, i.e. linearise – linear Cahn-Hilliard theory.

Now, continuity equation is

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}$$

$$= M\frac{\partial^2 f_o}{\partial c^2}\frac{\partial^2 c}{\partial x^2} + 2MK\frac{\partial^4 c}{\partial x^4} \qquad \textbf{[1]}$$

And if the term involving K, the gradient energy term, can be neglected, this equation is equivalent to a standard diffusion equation with an effective diffusion coefficient D_{eff} given by

$$\boxed{D_{eff} = M\frac{\partial^2 f_o}{\partial c^2}}$$

Note that this diffusion coefficient now contains thermodynamics, and is not simply a transport coefficient.

M contains transport information and is always positive.

But we know that within the spinodal regime $\partial^2 f_o/\partial c^2$ is always negative, by definition.

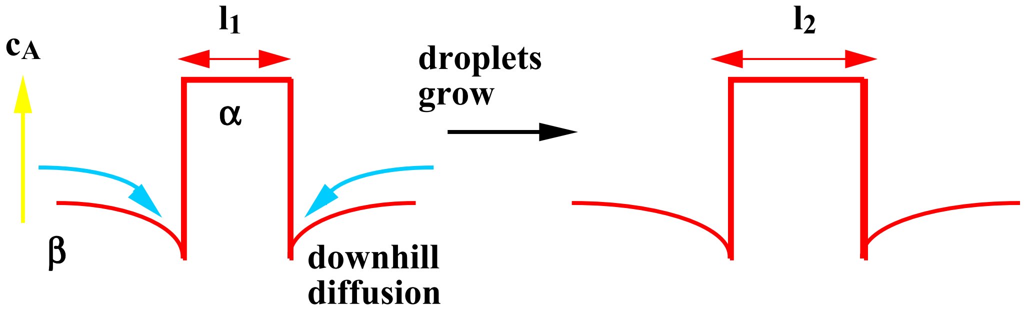
Thus D_{eff} is negative – 'uphill diffusion'.

All fluctuations tend to encourage concentration fluctuations to increase, so that neighbouring regions get more and more different.

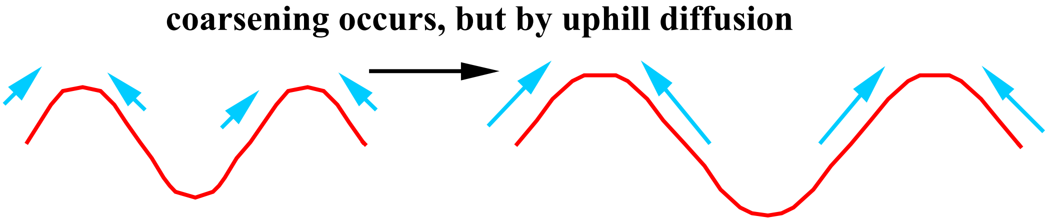
This is in contrast to most diffusion.

The contrast between Spinodal Decomposition and Nucleation and Growth.

Nucleation and Growth



Spinodal Decomposition



Now return to the full equation involving the gradient energy term.

General solution to the diffusion equation is

$$c(x,t) = \cos(qx) \exp -(Dq^2 t) + c_o$$

For equation [1] this becomes

$$c(x,t) = c_o + \cos(qx)\exp[-(D_{eff}q^2t(1+\frac{2Kq^2}{f_o''})]$$

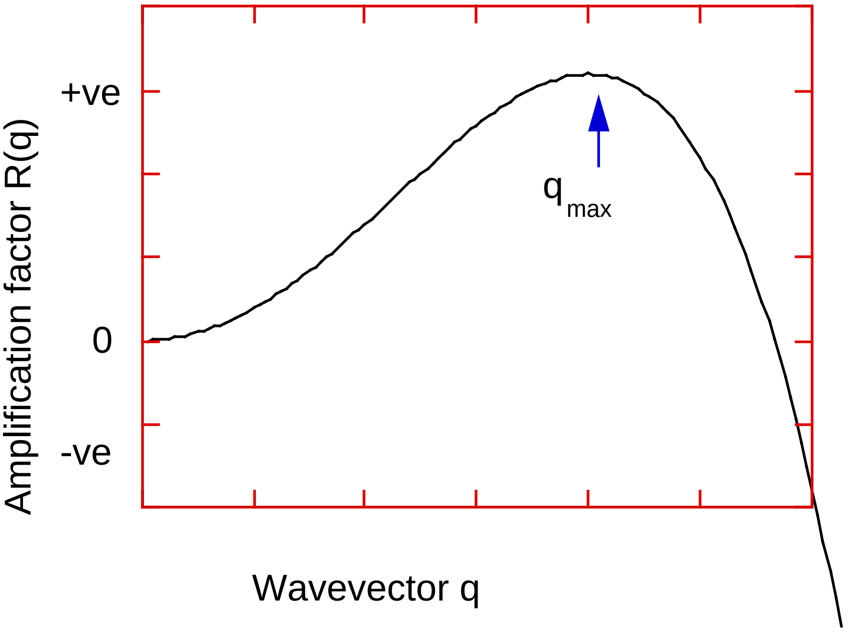
if the intitial composition is c$_o$, where f$_o$'' is the second derivative of f$_o$ wrt composition.

This form of the equation enables us to see which wavelengths grow and which shrink.

The amplitude of the composition fluctuation of wavevector q changes with an amplification factor

$$\boxed{R(q) = -D_{eff}(1+\frac{2Kq^2}{f_o''})q^2}$$

Recall f$_o$'' is always negative



The fastest growing wavelength is given by

$$q_{\max} = \frac{1}{2}\sqrt{\frac{f_o''}{K}}$$

What does this Morphology look like?

For nucleation and growth we are used to seeing droplets of one phase nucleating in the other.

For spinodal decomposition typically see (e.g. in an optical microscope) a random, interconnected structure, with a characteristic lengthscale related to q_{max}.

From such images, difficult to get a good measure of the average lengthscale.

Easier to do this using scattering methods from which q_{max} can be directly obtained.

Scattering shows a broad Bragg-like peak, from which q_{max} can be read off.

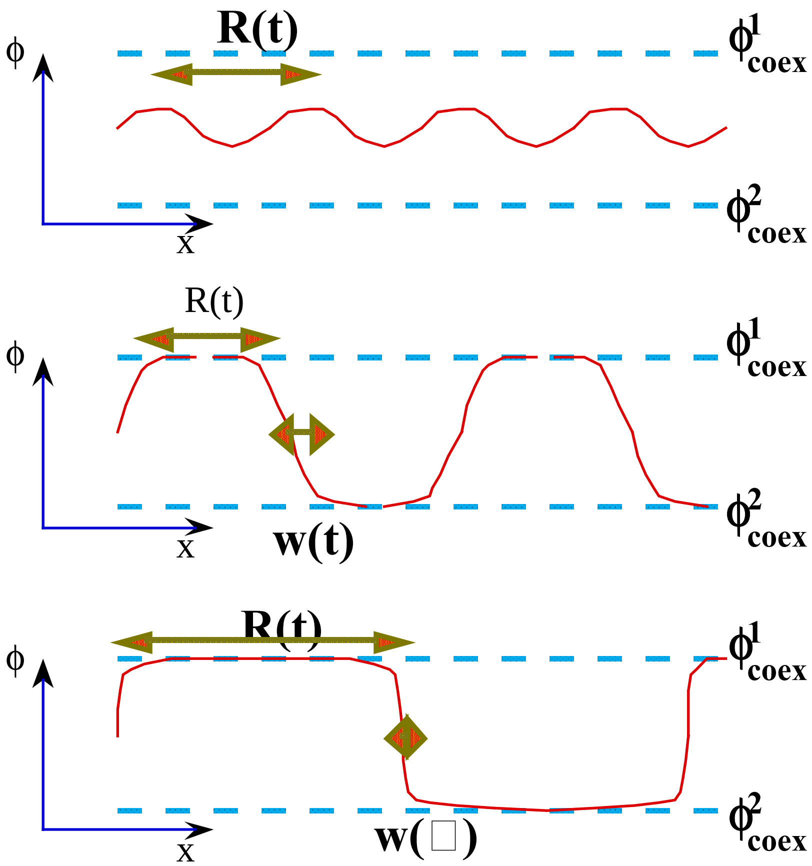
The scattering radiation can be light, X-rays… depending on actual lengthscale.

Light scattering works well for polymers, because lengthscales are large, but for atomic species X-rays need to be used as much finer structures.

This simple linearised theory will only work for early times, during which time q_{max} will be constant.

As time increases non-linear terms come into play, and the analysis gets more complicated.

Domain size R(t); Interface width w(t)



Early
R(t)~w(t)
Both increase

Intermediate
R(t)≠w(t)
R(t) increases
w(t) decreases

Late stage
w(t) = w(∞)
constant

At early times, linear theory OK; one lengthscale (corresponding to q_{max})

Intermediate times – analysis very complicated. Two lengthscales important

Size of domains
Width of interface

Late times – simple theory again with only one lengthscale (interfaces are sharp). Compositions have now reached those of coexisting phases; coarsening continues to occur.

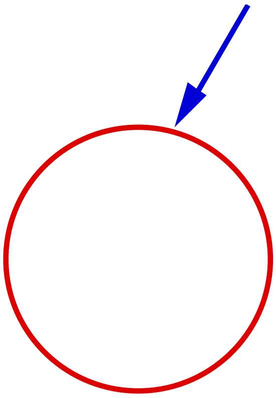
During late stage growth, large droplets grow at the expense of small ones.

Morphology may cease to be interconnected, and starts to resemble that of nucleation and growth regime.

This phenomenon of coarsening also occurs in the nucleation and growth regime, and is known as Ostwald ripening.

Why do Small Droplets Shrink and Large Ones Grow?

Imagine adding one atom from an ideal solution to a precipitate particle, which thereby grows by Δr.



(Same basic argument applies in both metastable and unstable regimes.)

$$\Delta F = \underset{\text{surface energy change}}{\underset{\uparrow}{8\pi r\gamma\Delta r}} \quad + \quad \underset{\text{bulk free energy change}}{\underset{\uparrow}{\Delta F_v 4\pi r^2\Delta r}} \quad - \quad \underset{\text{entropy change}}{\underset{\uparrow}{kT \ln c}}$$

At equilibrium, $\Delta F = 0$.

Put $\Omega = 4\pi r^2\Delta r$

Then $$0 = \frac{2\gamma\Omega}{r} + \Delta F_v\Omega - kT\ln c$$

$$\therefore c = \exp(\frac{\Delta F_v\Omega}{kT})\exp\frac{2\gamma\Omega}{rkT}$$

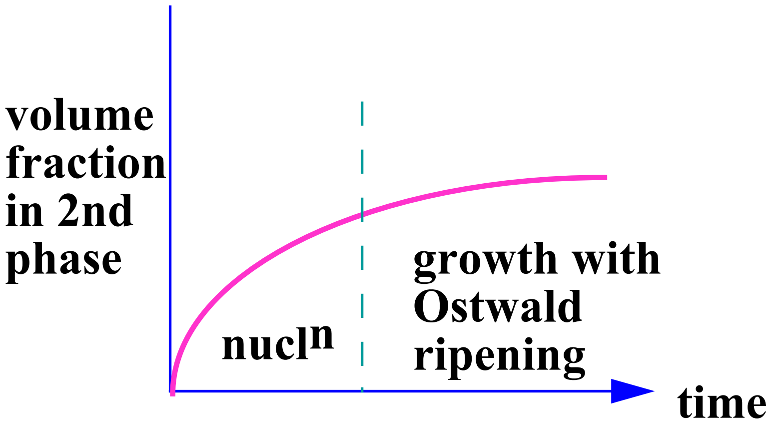
Now $c_\infty = \exp\frac{\Delta F_v\Omega}{kT}$ is the concentration in equilibrium with a flat surface

$$\boxed{c_r = c_\infty \exp(\frac{2\gamma\Omega}{rkT})}$$

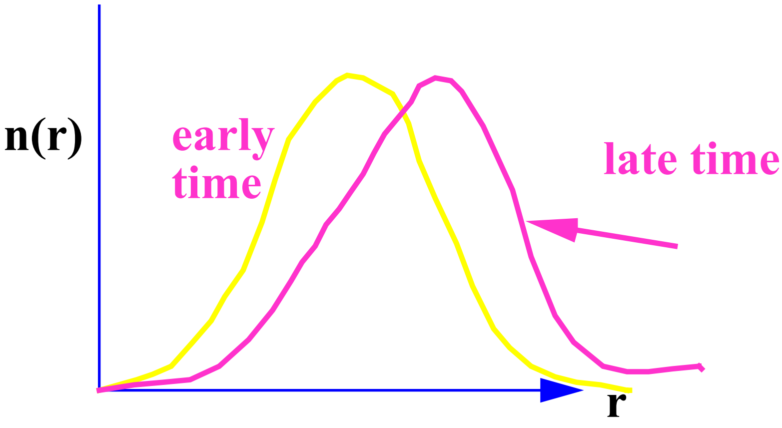
The local concentration depends on particle size.

Concentration highest just outside small particles, and the atoms will diffuse away to try to recover c_∞.

Hence small particles shrink, whilst overall volume fraction remains essentially constant (otherwise c_∞ would be changing).



n(r) = no/unit volume with radius r



n(r) = no/unit volume with radius r

Can work out how particle size scales with time by a heuristic argument.

Flux $\propto$ chemical potential gradient across interface

$$\propto \frac{dc}{dr} \qquad\qquad c_r = c_\infty \exp(\frac{2\gamma\Omega}{rkT})$$

$$\therefore \frac{dc}{dr} = -\frac{1}{r^2} c_r$$

Flux also determines how radius grows or shrinks

$$\therefore \text{flux} \propto -\frac{dr}{dt}$$

$$\therefore \frac{dr}{dt} \propto \frac{1}{r^2} c_r$$

$\Rightarrow r^3 \propto t$ or

$r \propto t^{1/3}$ **Lifshitz-Slyozov law**

This is found to give good agreement with experiment when diffusion, rather than hydrodynamics, is dominating.

Utilising Phase Diagrams

Phase diagrams are inherently for equilibrium.

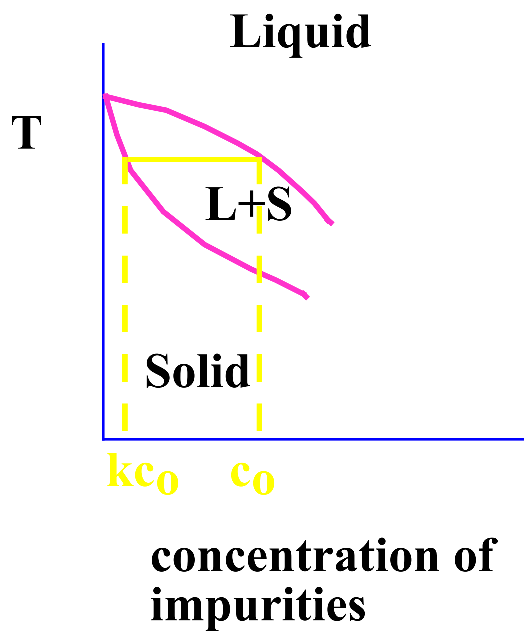
In practice equilibrium may not always pertain, and one can end up with structures which are far from equilibrium but are 'frozen in' because there is insufficient thermal energy to allow further transformation to occur.

Thus must always bear in mind kinetics as well as thermodynamics.

Case Study I – Zone-refining Silicon

Silicon chips are only possible because native silicon, which naturally contains sufficient impurities to mess up any device, can be purified by a method known as zone-refining.

Starting with c_o, when this is melted will be in equilibrium with a solid with concentration kc_o ($k<1$) level of impurities present.



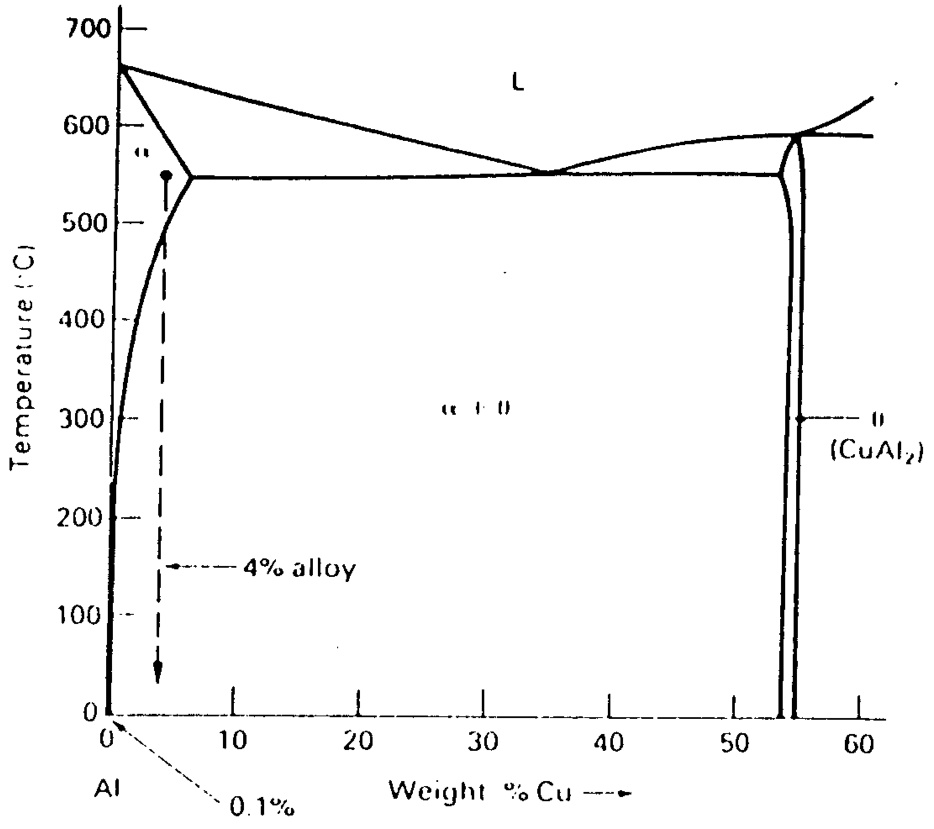
Thus the process of melting and solidification leads to rejection of impurities into remaining liquid, whose impurity concentration goes up.

By passing a heater over a solid bar, can effectively push impurities along.

By doing this several times, end up with very pure Si (at one end).

Case Study II – Hardening of aluminium by copper

In this case exactly what happens, depends on thermal history – e.g. cooling rate, ageing etc.



At the so-called eutectic point T_e, 3 phases are in equilibrium: L, α and θ.

No degrees of freedom.

Corresponds to the composition with the lowest melting point.

At T_e, upon cooling, all remaining liquid solidifies isothermally.

~4% Cu in AL corresponds to Duralumins, designed with Cu present to harden Al, which is typically a fairly soft material.

Above 500°C 4% alloy is single phase α.

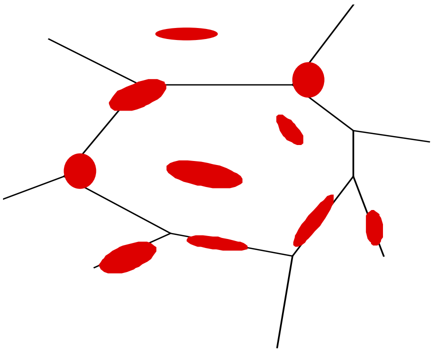
Below 500˚C θ ($CuAl_2$) phase starts to form.

Proportion dependent on T and given by Lever Rule.

However how the microstructure develops depends on rate of cooling.

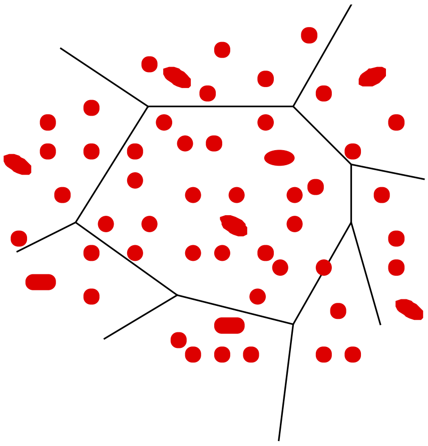
Cool slowly – low driving force for nucleating $CuAl_2$ precipitates.

Few nuclei, but these then grow quite large.



Large, well-separated precipitates, typically at grain boundaries, which do not provide much barrier to dislocation motion

Cool fast – large driving force for nucleation, and therefore many nuclei form which then do not grow much.



Much finer structure - more obstacles to dislocation motion

Material which has been fast cooled is much harder.

However if you cool too fast, can kinetically frustrate this process, and Cu remains in supersaturated α solid solution.

Harden now by 'age-hardening' i.e. hold at low T (typically around 150°C) for long time (~100 hours).

Fine precipitates will now form during this heat treatment, by a series of steps.

1. **Solid solution – Cu randomly distributed on lattice.**

2. **Small 'Guinier-Preston' zones form – small discs of Cu form on 001 Al lattice planes.**

3. **These zones coarsen and form θ'' phase, which has coherent lattice wrt Al lattice. This gives rise to 'coherency strain' which strain field impedes dislocation motion. In this case size of lattice mismatch and distances involved mean that lattice planes can still bend to accommodate this mismatch.**

4. **Further coarsening and formation of θ', which is incoherent (on edges) with Al lattice.**

5. **Final θ phase forms, mainly nucleating at grain boundaries i.e. heterogeneous nucleation. Because completely incoherent, shape now not determined by lattice.**

Alloy hardest when θ'' phase present, since particles have to cut through precipitates.

Later stages is overaged, and the large θ precipitates provide little obstacle, as dislocations can bow round the large precipitate particles.