## 2. Phase transitions

2.1 Phase transitions in soft matter

Soft matter often has a very rich and complicated morphology-

rather than having a simple structure its components are often arranged in a complicated way, with features often at length scales intermediate between atomic length scales and macroscopic length scales.

Examples:

- block copolymer morphologies

- soap morphologies

- emulsions
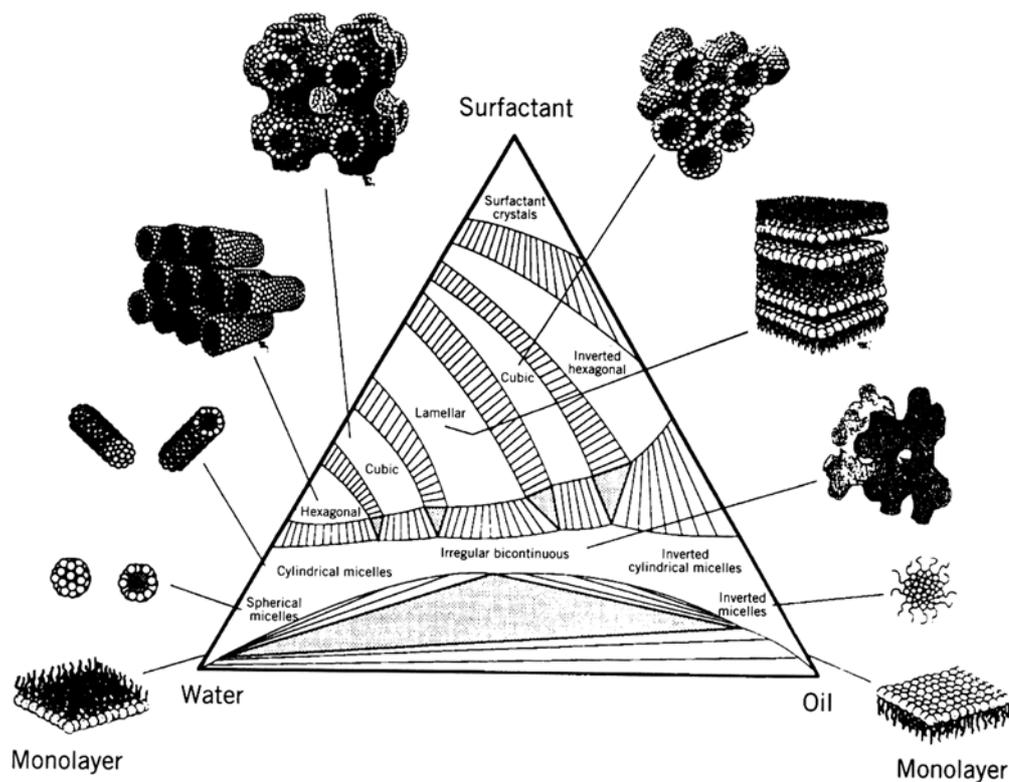
Schematic phase diagram of a surfactant/water/oil ternary solution

How do these structures arise?

the remarkable thing is that these structures put themselves together in very complicated arrangements without outside assistance - they *self-assemble*. Understanding self-assembly involves understanding *phase transitions* and there kinetics. This is important for soft condensed matter, but much of what we need to know applies also to simpler kinds of matter too, and our discussion and examples will not be restricted to soft matter.

To understand self-assembly we've got to understand three things:

- Equilibrium

If the system is left to evolve for a long time it finally settles down to an equilibrium - the situation of minimum free energy. While in normal solids and liquids the equilibrium situation is usually rather boring - a perfect crystal, a mixture of two liquids macroscopically separated into two layers - soft matter systems can often exhibit complex and interesting equilibrium phases. Block copolymers and surfactant solutions offer good examples.

- Phase transitions

If we change some external parameter (e.g. temperature) a different structure may turn out to be the one with the lowest free energy. The system will make a qualitative change of structure in response to a quantitative change in a control parameter.

Phase transitions almost always involve a change from a *more ordered* state to a *less ordered* state. For example, a liquid is less ordered than a solid. Phase transitions reflect a change with temperature of the relative importance of *entropy* and *energy:*

Free energy F = U- TS

where U is internal energy and S is entropy. In general at high temperature disordered phases are more stable.

For a phase transition one can define an *order parameter*, which typically takes a zero value in the disordered phase, and a finite value in the ordered phase. The way the order parameter varies with temperature tells one about the nature of the transition. A fundamental distinction is between first order phase transitions, where the order parameter changes discontinuously at the phase transition (e.g. melting of a crystal) and second order transitions, where the order parameter is continuous. The classic example of a second order transition is the change from a liquid to a gas at a critical point.
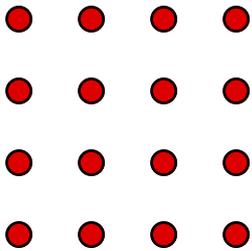
- Kinetics of phase transitions

Just because at equilibrium a system will take up a certain minimum free energy structure doesn't mean that when one goes through a phase transition the system will instantly adopt its new structure. Atoms and molecules will have to rearrange themselves, and this motion takes time. This time can be very long, so that systems can be caught in states in which they have not yet reached equilibrium. In many cases interesting structures are formed in the process, and although these structures are not at equilibrium they may be effectively frozen in, for example by cooling liquids through a glass transition. We need to understand the mechanisms by which phase transitions take place, and the nature of the non-equilibrium structures that the system must go through on its way to reach equilibrium.

We will discuss two examples of phase transitions - the unmixing of two immiscible liquids, and melting and crystallisation. A third phase transition - between an isotropic liquid and a nematic liquid crystal - will be discussed when we talk about liquid crystals.

2.2 Order parameters

Phase transitions take you from a low temperature ordered state to a high temperature disordered state. Below are some examples, both from soft matter systems and elsewhere, to illustrate the generality of the concept.
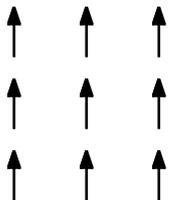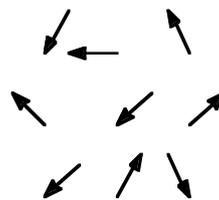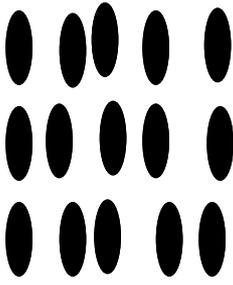
Solid - crystal
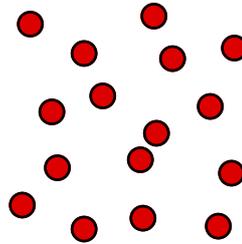
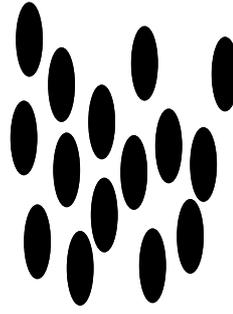Liquid

Separated liquids

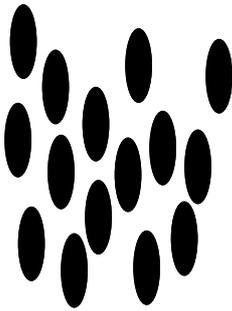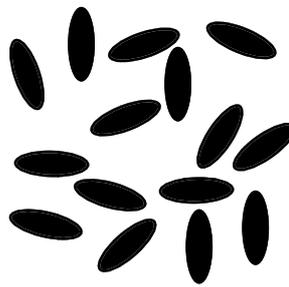Mixed liquids

Ferromagnetic

Paramagnetic

Smectic liquid crystal

Nematic liquid crystal

Nematic liquid crystal

Isotropic liquid

For any phase transition, the first task is to find a parameter which characterises the state of order of the system - an *order parameter*.

2.3 Liquid/liquid unmixing - phase diagrams

The free energy of mixing
We now consider in more detail the phase transition involved in the unmixing of two initially miscible liquids. We introduce a statistical mechanical model which is reasonably realistic, though relatively easy to handle. Using this model we can calculate the equilibrium state of the system as a function of temperature and composition - *the phase diagram* - and also, in the next sections, we can use it to deduce something about the mechanism by which phase separation takes place.

A very simple model for consideration of unmixing phase transitions is the regular solution model. This is a mean field theory with strong family resemblances to the Bragg-Williams theory for order-disorder transitions in alloys and the Curie-Weiss theory for the paramagnetic-ferromagnetic phase transition.

Imagine we have two liquids, a and b. For the sake of argument, imagine that the atoms of the two liquids are arranged on a lattice, where each lattice site has z nearest neighbours. (Of course being liquids the lattice is not a regular crystalline one). If the concentration of a atoms is ϕ_a, and the concentration of b atoms is ϕ_b, we don't know for certain whether a given site is occupied by a atoms or b atoms. In fact there are just two possibilities; either it is occupied by an a atom or it is occupied by a b atom, with probabilities ϕ_a and ϕ_b respectively. We can now use the Boltzmann formula to write down the entropy per site associated with this uncertainty:

$$S_{mix} = k \sum_i p_i \ln(p_i)$$

where k is Boltzmann's constant and the sum is over all possible states. Here the possible states are simply that it is occupied either by an A atom or a B atom, so we have

$$S_{mix} = k(\phi_A \ln \phi_A + \phi_B \ln \phi_B)$$

(Q. What assumption have we made here?
A. Neighbouring sites are independent of each other - no correlations)

Note this is zero if either ϕ_A or ϕ_B is unity - that is if we have a pure liquid.

If we mix the two liquids the energy changes; assuming the interactions between the components are nearest neighbour, pairwise additive, with an energy of ε_{aa} between two a atoms, ε_{bb} between two b atoms, and ε_{ab}

between an a atom and a b atom, we find we can write the change in energy on mixing pure a and pure b as

$$U_{mix} = \chi \, \phi_a \phi_b$$

where the parameter χ (the Flory-Huggins interaction parameter) is defined in terms of the energy of interaction between an a molecule and a b molecule ε_{ab}, between two a molecules ε_{aa}, and between two b molecules ε_{bb}, and the number of neighbours z:

$$\chi = \frac{z}{2kT} \left(2\varepsilon_{ab} - \varepsilon_{aa} - \varepsilon_{bb} \right) .$$

(Q. What assumptions are made here?
A. the number of neighbours of each type of molecule at a given site is simply given by the overall concentration - no concentration fluctuations. This is the mean field assumption).

Using the formula for free energy F = U- TS, we find for the free energy of mixing:

$$\frac{F_{mix}}{kT} = \phi_a \ln \phi_a + \phi_b \ln \phi_b + \chi \, \phi_a \phi_b$$

per lattice site, with χ a dimensionless parameter expressing the strength of the interaction between the two components.

As χ is varied, the shape of the free energy curve changes:
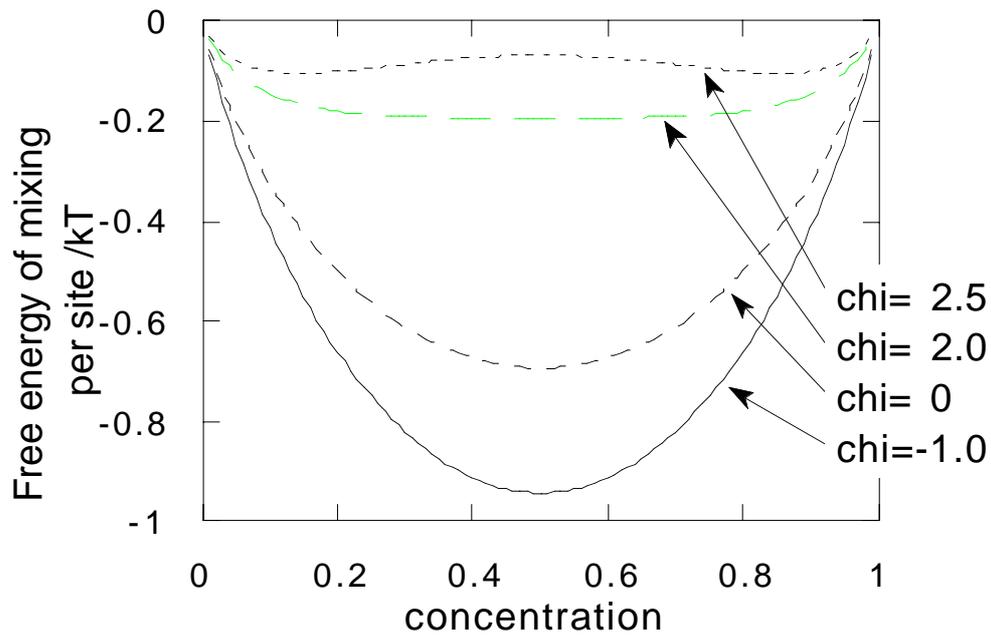
For $\chi > 2$, there exist compositions for which the system can lower its total free energy by phase separating into the two coexisting compositions defined by a common tangent construction. If the curvature of the free energy curve, $\frac{d^2F}{dc^2}$, is negative, the system is unstable to small composition fluctuations; this defines the spinodal.

The coexistence curve

To illustrate this in more detail, the left hand diagram shows the free energy as a function of composition at a temperature where the mixture is stable over all compositions. Any phase separation raises the total free energy of the mixture. On the right, in contrast if the system starts out at any composition between ϕ_1 and ϕ_2 the total free energy is lowered if it splits into two phases with these compositions. The compositions defined by the common tangent construction are called the *coexisting compositions,* and the locus of these compositions as the concentration is changed is known as the *coexistence curve.*
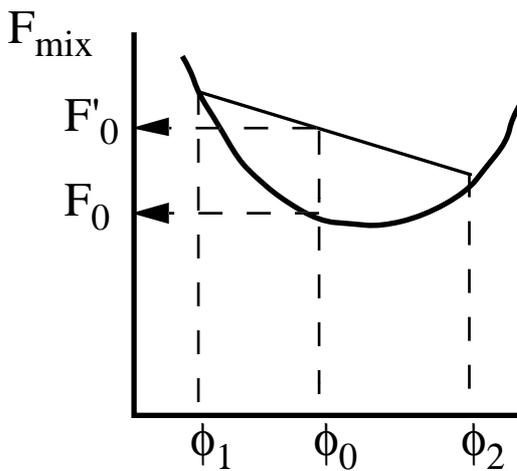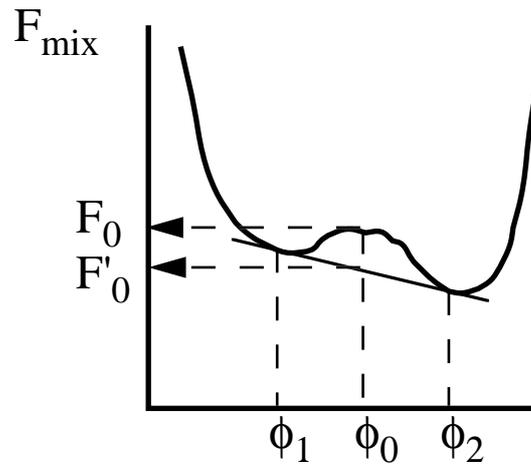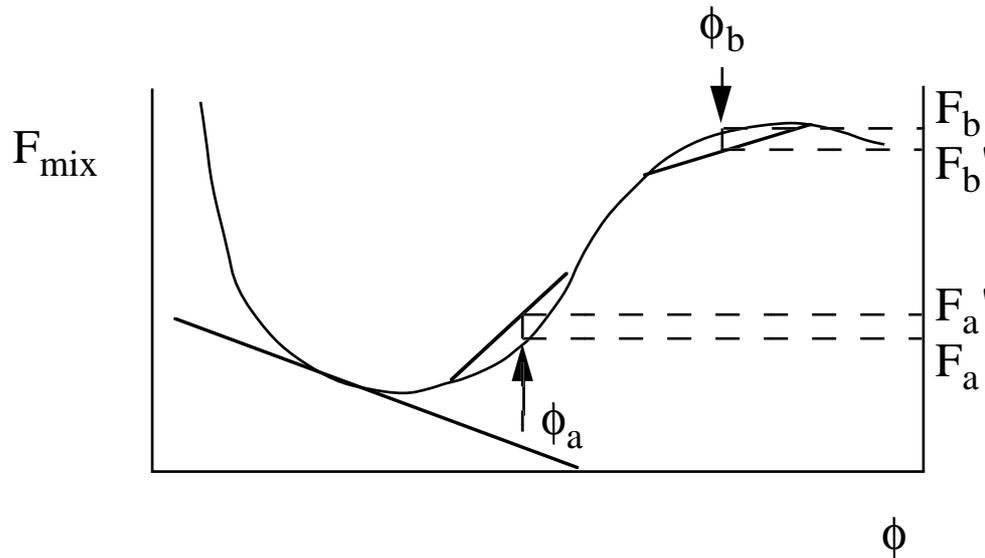

(a)   (b)

Metastability and instability

If we look in more detail at the free energy curve for compositions that fall within the the coexistence curve, we find another important distinction: the curvature of the free energy function $\left(\dfrac{d^2F}{d\phi^2}\right)$ may be either positive or negative. At a composition ϕ_b phase separation to two compositions close to ϕ_b results in a lowering of free energy from F_b to F_b'. At this composition the system is unstable with respect to small fluctuations in composition, and will immediately begin to phase separate. This composition is *unstable.*

However at composition ϕ_a a similar small change in composition leads to an increase in free energy from F_a to F_a'; the system is locally stable with respect to such small composition fluctuations, even though it is still globally unstable with respect to separation into the two coexisting phases. There is an energy barrier which needs to be surmounted in order to achieve the global energy minimum associated with phase separation, and as a result this composition is *metastable.*

Clearly the limit of local stability is defined by the condition that the curvature $\left(\dfrac{d^2F}{d\phi^2}\right) = 0$; the locus of these points is known as the *spinodal.*

Finally we note that a *critical temperature* T_c separates the two types of situation for which mixtures are always stable, and situations for which there are compositions which will phase separate. In the former, the curvature of the free energy function $\left(\dfrac{d^2F}{d\phi^2}\right)$ is always positive, while in the latter $\left(\dfrac{d^2F}{d\phi^2}\right)$ is negative within a certain range of ϕ. The critical point is thus defined by the condition $\left(\dfrac{d^3F}{d\phi^3}\right)\bigg|_{\phi_c} = 0$, and it is the point at which the coexistence curve and spinodal line meet. The diagram shows the shape of the free energy curve at the critical point:
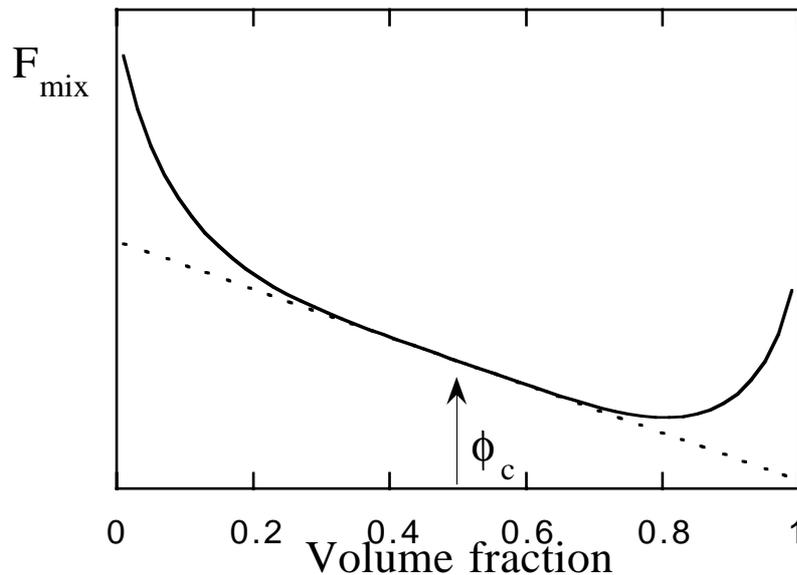
The phase diagram

Collecting together our definitions in terms of the free energy function of the critical point, the spinodal line, and the coexistence curve, it is possible to calculate for any free energy the phase diagram. For the regular solution model if we known the way the interaction parameter χ varies with temperature we can calculate the phase diagram; an example is shown below.
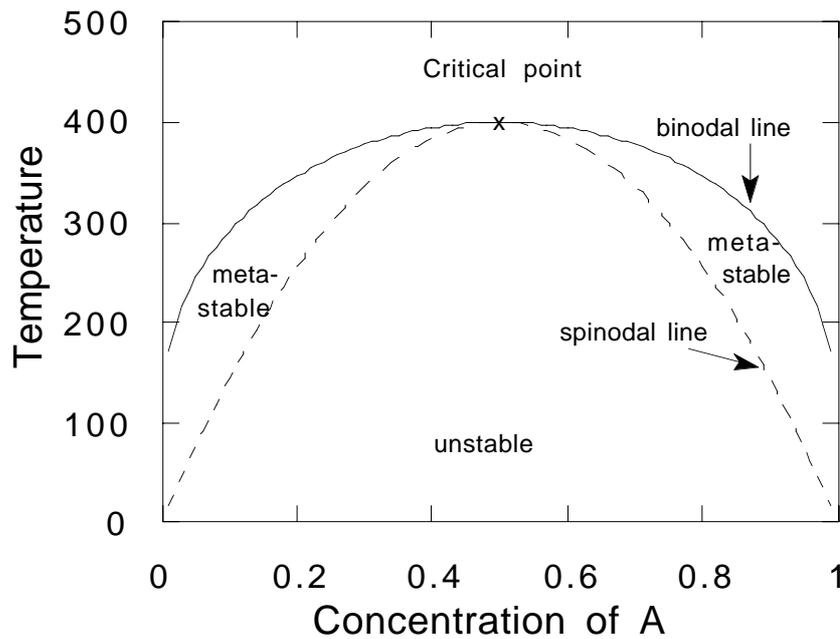
2.4 Kinetics of unmixing - spinodal decomposition

The mechanism of phase separation depends on where we are in the phase diagram. If we are within the spinodal line, any small local change in composition lowers the free energy; the system is unstable, and any small fluctuation in composition is amplified. This process is known as *spinodal decomposition.*

In spinodal decomposition, material flows from regions of low concentration to regions of high concentration. This is a reversal of the normal situation, in which we expect material to diffuse from regions of high concentration to regions of low concentration. This process is sometimes known as *uphill diffusion.*

Why, in spinodal decomposition, do we get this reversal in the direction of diffusion? We are used to the idea that diffusion acts to make the concentration uniform. This is usually true, but in general the fundamental quantity that must be uniform at equilibrium is not the concentration, but the *chemical potential.* Material will diffuse down the gradient of chemical potential, from regions of high chemical potential to regions of low chemical potential. The chemical potential is related to the first derivative of the free energy with respect to concentration; this means that if the second derivative of free energy with respect to concentration is positive then regions of high concentration have high chemical potential and diffusion is in the normal, downhill direction. But inside the spinodal region the second derivative of free energy with respect to concentration is *negative,* the chemical potential gradient has the opposite sign to the concentration gradient and material flows from regions of low concentration to regions of high concentration - *uphill diffusion.*

Thus any fluctuation in composition will grow, ultimately leading to a phase separated domain at the coexisting composition. However, not all concentration fluctuations grow at the same rate. The growth of long wavelength fluctuations involves the diffusion of molecules over long distances, which is relatively slow; on the other hand if very short wavelength fluctuations were to grow they would create a large amount of interface, which itself would cost too much energy. There is thus an optimal size of concentration fluctuation which grows the fastest. Patterns created by spinodal decomposition are random, but have a characteristic length scale.

φ

Z

(a)

φ

Z

(b)

φ

Z
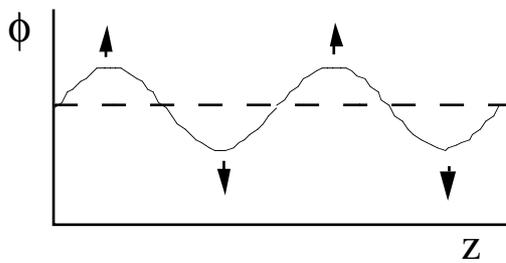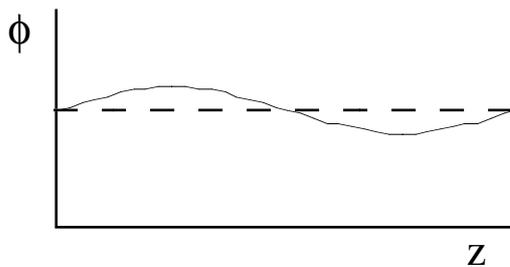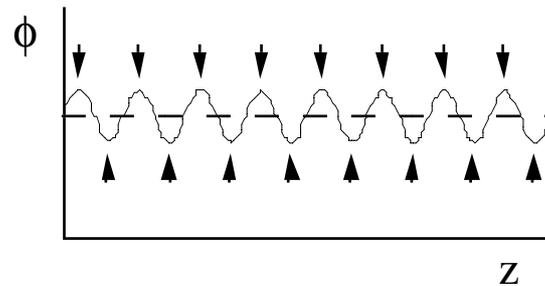
(c)

Spinodal decomposition. (a) In the unstable part of the phase diagram, random concentration fluctuations are unstable and grow in amplitude. Long wavelength fluctuations (b) grow slowly because of the large distances through which material needs to be transported, while short fluctuations (c) are suppressed, because of the high free energy penalty associated with sharp concentration gradients. Thus fluctuations on an intermediate length scale (a) grow the fastest and dominate the resulting morphology.

We can use an extension of our regular solution model to make a theory of spinodal decomposition, expressing this insight mathematically.

In the presence of composition gradients, the local free energy density depends both on the local composition, and the size of composition gradients. For small composition gradients, and for composition changes in one dimension, the total free energy may be written as

$$F = A \int \left(f_0(\phi) + k \left(\frac{\partial \phi}{\partial x} \right)^2 \right) dx$$

where $f_0(c)$ is the free energy per site of the uniform mixture as given by the regular solution theory, and κ is the <u>gradient energy coefficient</u>. It has the dimensions of a length squared; the length is set by the range of interatomic interactions.

This free energy leads to a modified diffusion equation; this has a solution

$$\phi(x,t) = A \cos(qx) \exp\left(-D_{eff}q^2\left(1 + \frac{2kq^2}{f_0{}''}\right)t\right).$$

(Where $f_0{}'' = \dfrac{d^2 f_0}{d\phi^2}$)

Thus a composition fluctuation with wavevector grows exponentially (as D_{eff} is negative) with an <u>amplification factor</u>

$$R(q) = -D_{eff}\left(1 + \frac{2\,\kappa\,q^2}{f_0{}''}\right)q^2.$$

Inside the spinodal region $f_0{}''$ is negative, so $R(q)$ has a maximum value. This defines a fastest growing wavevector q_{max}, which sets the length scale on which spinodal decomposition occurs.
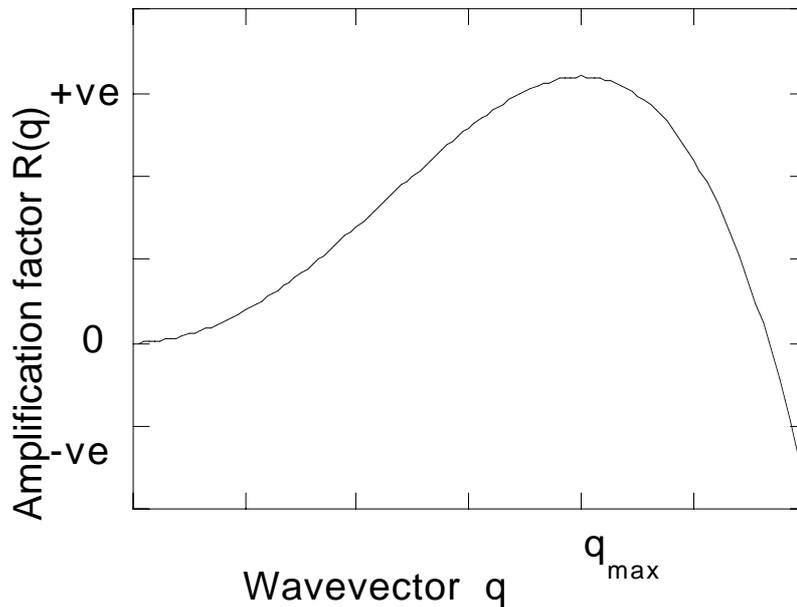

Amplification factor for spinodal decomposition.

How do we recognise spinodal decomposition experimentally? If we look at a sample undergoing spinodal decomposition with a microscope we would expect to see a random pattern (because the pattern of domains results from the amplification of random fluctuations in composition), but with a characteristic length corresponding to the wavelength of the fastest growing fluctuation $2\pi/q_{max}$. An example of such a pattern, obtained from a computer simulation, is given below.
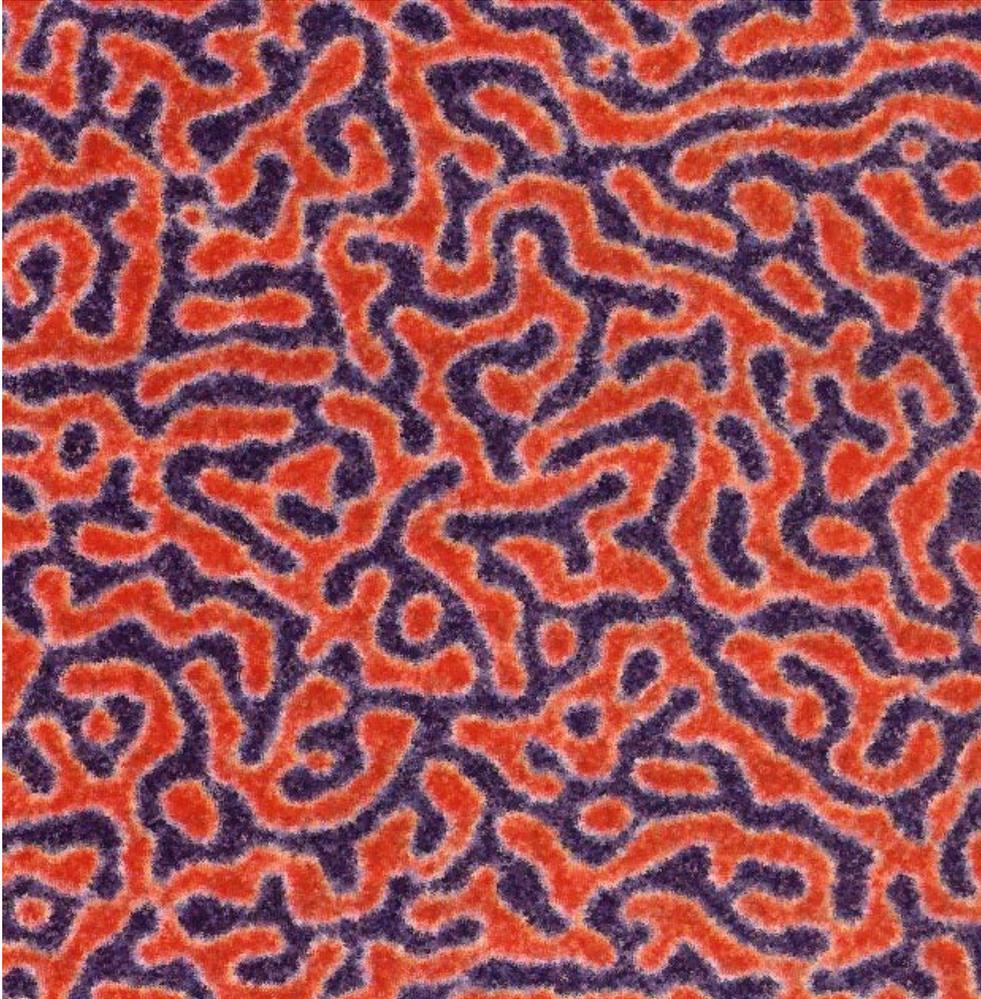

Simulation of pattern formed by spinodal decomposition in real space.
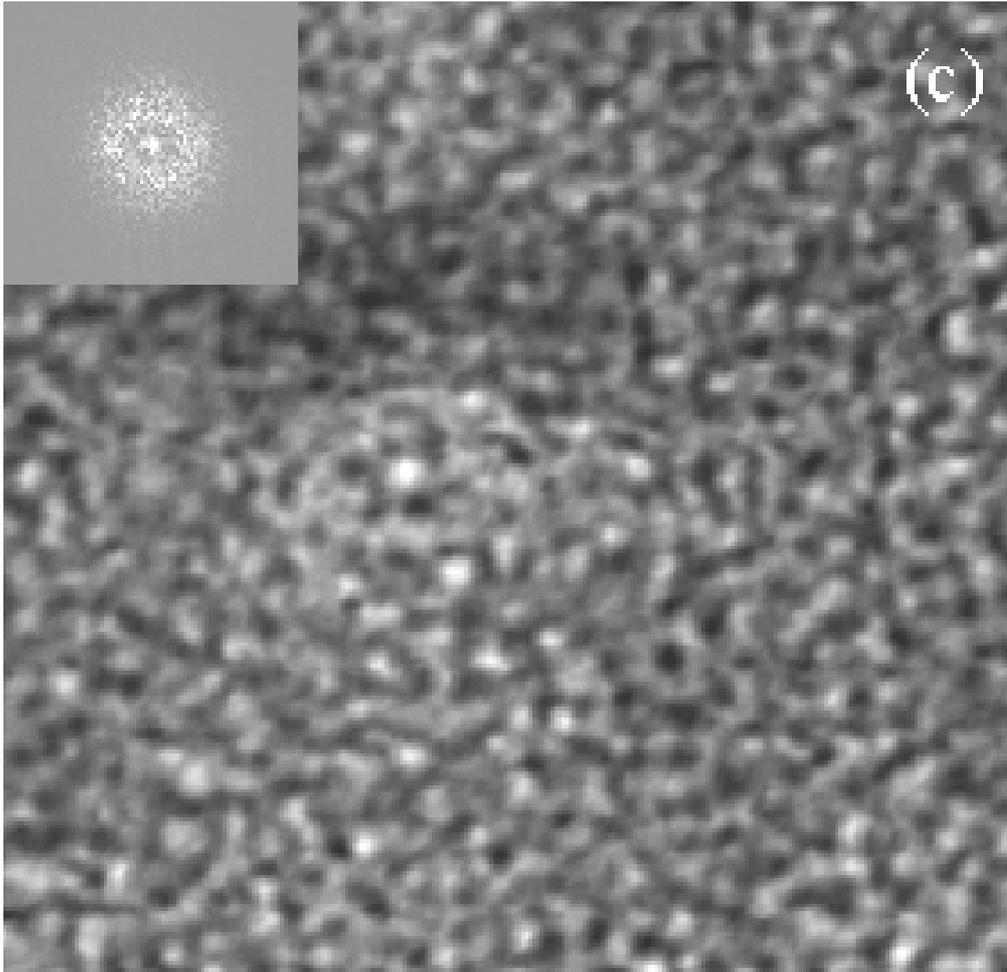
Pattern formed by spinodal decomposition of a mixture of two polymers in a common solvent. Confocal micrograph of a mixture of polystyrene, polybutadiene and toluene after 82 seconds quenching. Data from Boom Jung's PhD thesis (University of Cambridge 1999).

One gets more information about spinodal decomposition by doing a scattering experiment - looking at either light, x-rays or neutrons scattered from the concentration fluctuations. Just as a perfectly regular, periodic, array of obstacles results in sharp diffraction spots, if one scatters radiation from obstacles which are irregular and diffuse - but still with some characteristic wavelength - one sees a maximum in the scattering pattern at a wavevector corresponding to the fastest growing wavevector of the spinodal pattern.
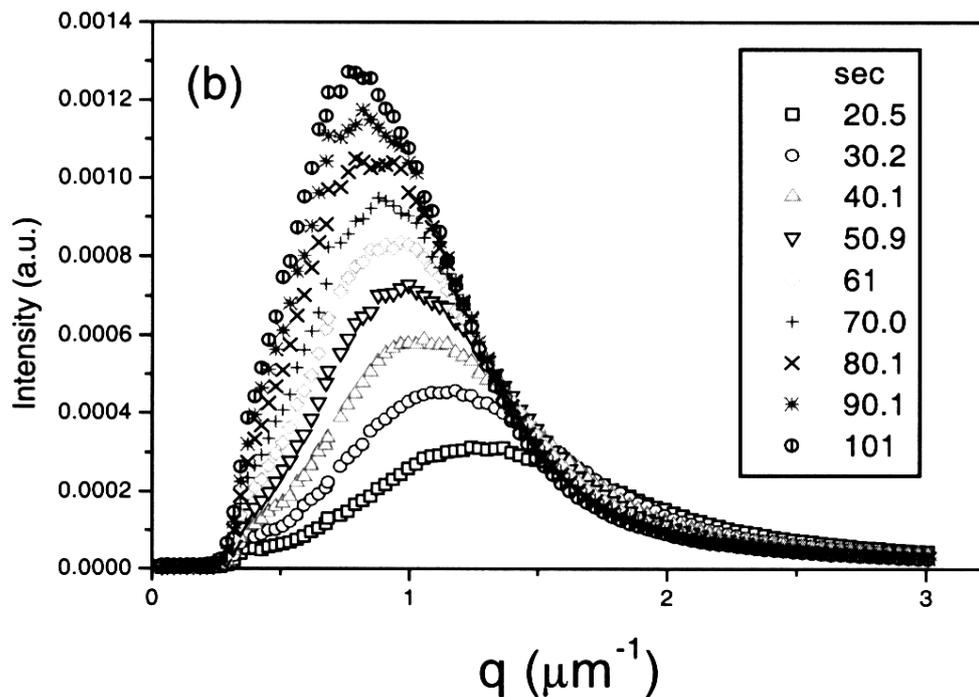
Light scattering curves from a polymer mixture quenched into the unstable region of the phase diagram, showing the maximum in intensity at q_{max} characteristic of spinodal decomposition. q_{max} moves to smaller values at loner annealing times, due to non-linear coarsening effects. Data from Boom Jung's PhD thesis (University of Cambridge 1999).

2.5 Kinetics of unmixing - nucleation and growth

If a particle of size r is nucleated, the system's change in free energy is

$$\Delta F(r) = 4/3 \; \pi \; r^3 \; \Delta F_V + 4 \; \pi \; r^2 \; \gamma$$

where ΔF_V is the bulk change in free energy per unit volume when the metastable phase breaks up into coexisting compositions (and is negative), and γ is the interfacial energy. Thus droplets below a critical size r* are unstable, and for nucleation to occur an energy barrier ΔF^* must be overcome.
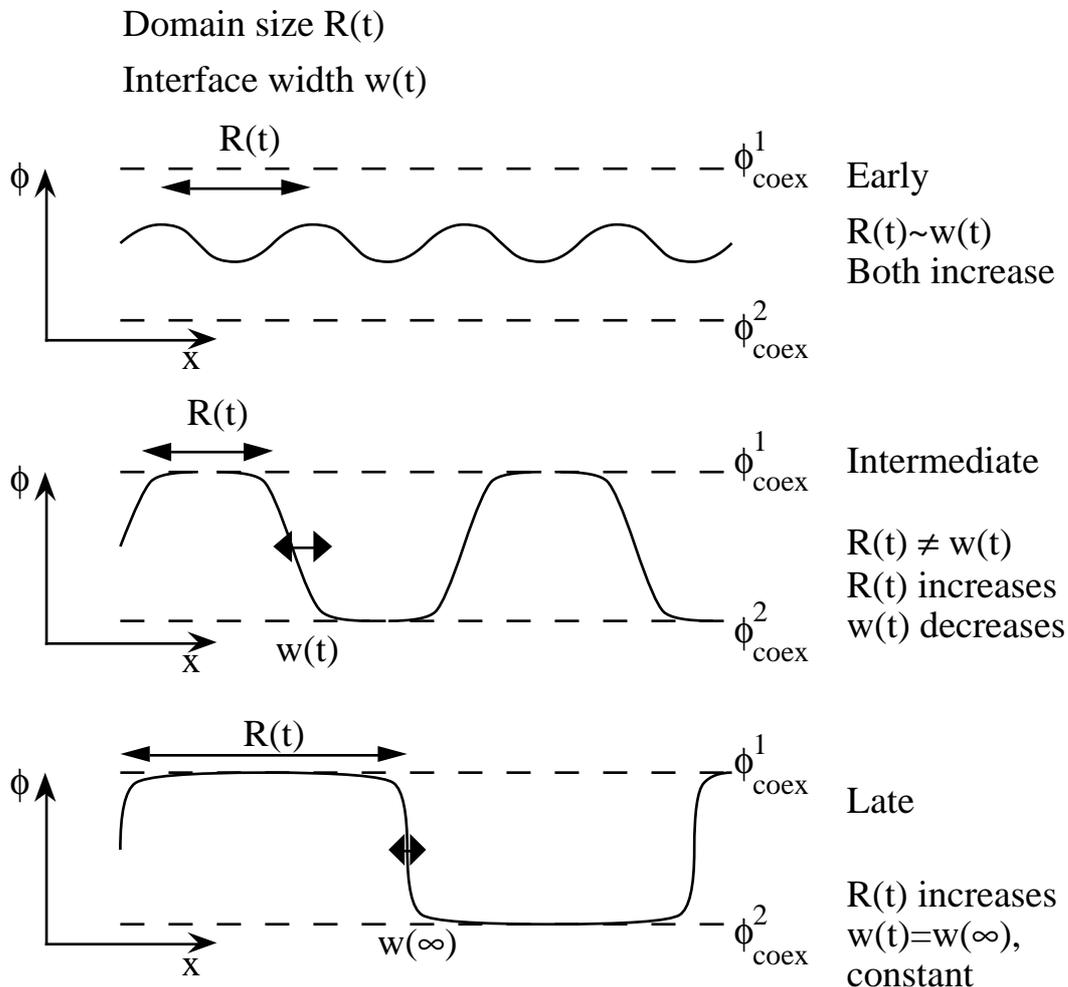
$$r^* = -\frac{2\gamma}{\Delta F_v} \quad \text{and} \quad \Delta F^* = \frac{16\pi\gamma^3}{3\Delta F_v^2} \; ;$$

thus nucleation is an activated process with a rate ~ exp(-ΔF^*/kT).

The diffusion coefficent is positive, so subsequent growth of particles occurs by conventional, downhill diffusion.

Kinetics of unmixing - growth in the late stages

The different stages of spinodal decomposition are defined by the way the length scales characterising the domain size and the interface width behave:

Domain size R(t)

Interface width w(t)

Early
$R(t) \sim w(t)$
Both increase

Intermediate
$R(t) \neq w(t)$
R(t) increases
w(t) decreases

Late
R(t) increases
$w(t) = w(\infty)$,
constant

In the late stage of phase separation, there is only one important length scale, the characteristic size of the domains L(t). This leads to the idea of dynamical scaling.
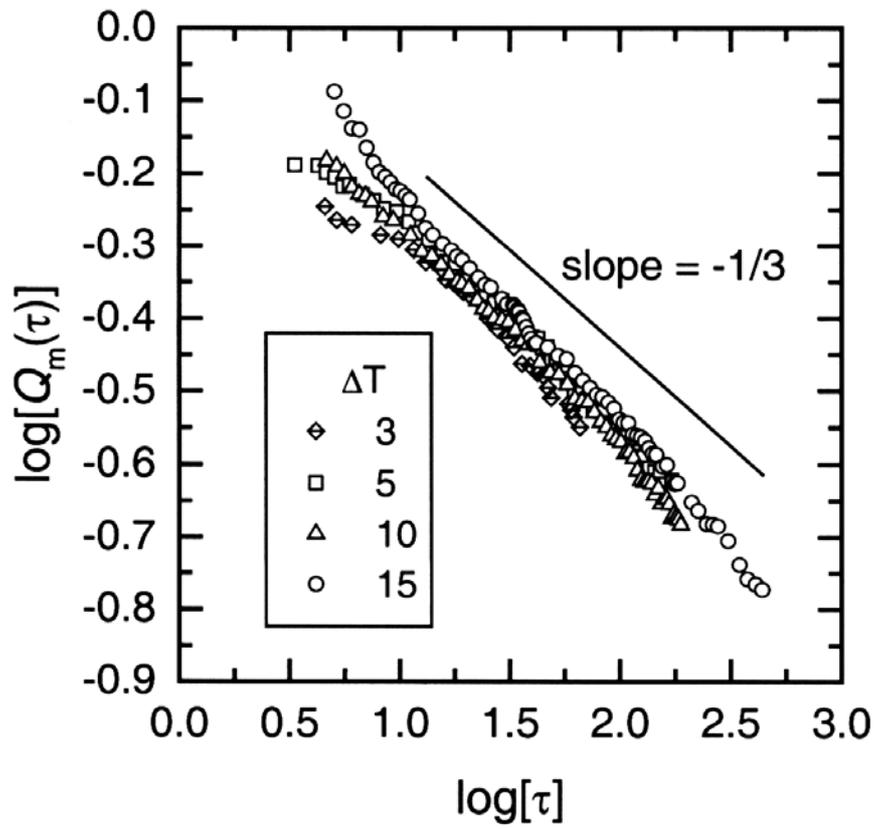
The pair correlation function G(r,t) can be written G'(x) where x=r/L(t).

The structure function S(q,t) can be written $L(t)^3 S'(y)$ where y=qL(t).

The growth of the domains is driven by the reduction of interfacial energy, with the transport of material being controlled by diffusion.
This leads to a scaling form for L(t):

$L(t) \sim (D\gamma t)^{1/3}$: the Lifshitz-Slyozov law.

Experimental evidence for the Lifschitz-Slyozov law. Time dependence of the maximum wavevector in a polymer/polymer/solvent system. Data from Boom Jung's PhD thesis (University of Cambridge 1999).

2.6 Solidification - homogenous nucleation

The liquid solid transition is a first order transition - the state of order of the material changes discontinuously at the transition.
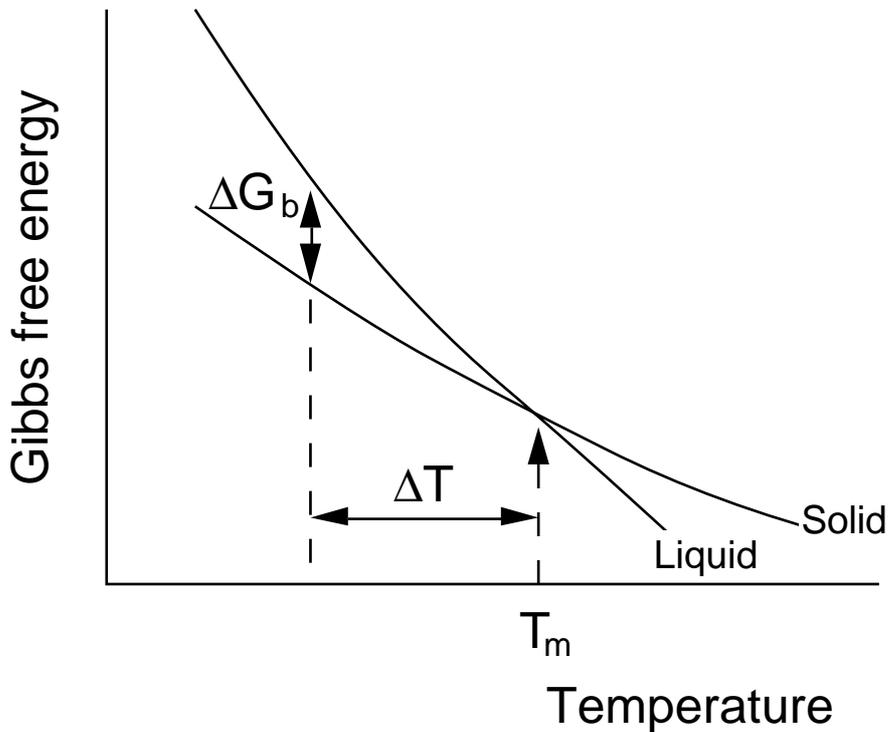
On freezing, the entropy changes:

$$\Delta S_m = \left(\frac{\partial G_S}{\partial T}\right)_P - \left(\frac{\partial G_L}{\partial T}\right)_P = \frac{\Delta H_m}{T_m}$$

where ΔH_m is the latent heat of fusion. Thus the free energy change when a melt undercooled by ΔT freezes is approximately

$$\Delta G_b = - \frac{\Delta H_m}{T_m} \Delta T$$

The overall free energy change when a droplet of size r freezes must include a term associated with the interfacial energy of the droplet; thus the total free energy change is

$$\Delta G = -\frac{4}{3} \pi r^3 \frac{\Delta H_m}{T_m} \Delta T + 4 \pi r^2 \gamma_{sl}$$

where γ_{sl} is the solid-liquid interfacial energy.
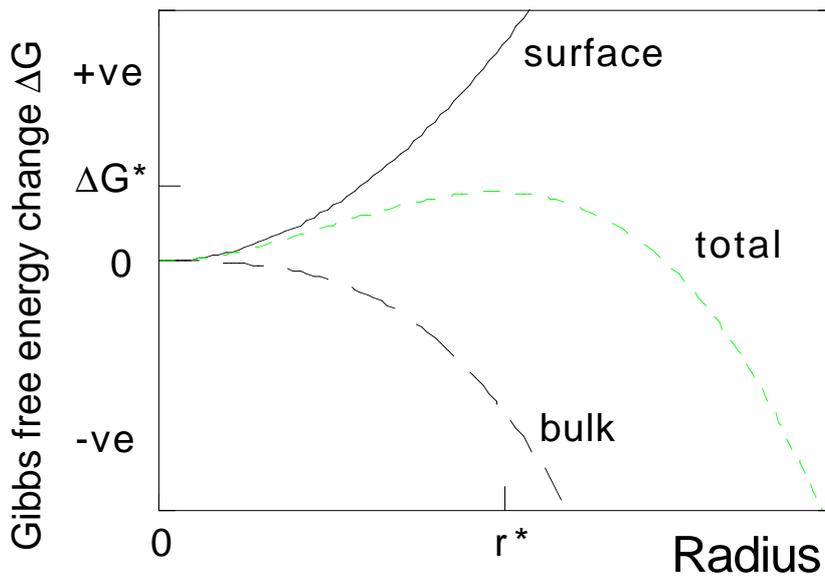
Thus the critical radius is

$$r^* = \frac{2 \gamma_{sl} T_m}{\Delta H_m \Delta T}$$

and the corresponding free energy barrier is

$$\Delta G^* = \frac{16\pi}{3} \gamma_{sl}^3 \left(\frac{T_m}{\Delta H_m}\right)^2 \frac{1}{\Delta T^2} \quad .$$

The number of nuclei of critical size is proportional to $\exp\left(-\frac{\Delta G^*}{kT}\right)$, which is a very strong function of temperature. This function dominates the temperature dependence of the rate of nucleation.

Example: Tin -
Melting point   505.7 K
Interfacial energy 54.5×10^{-3} J m^{-2}
Latent heat 4.4×10^{8} J m^{-3}

Nucleation Rate for Tin
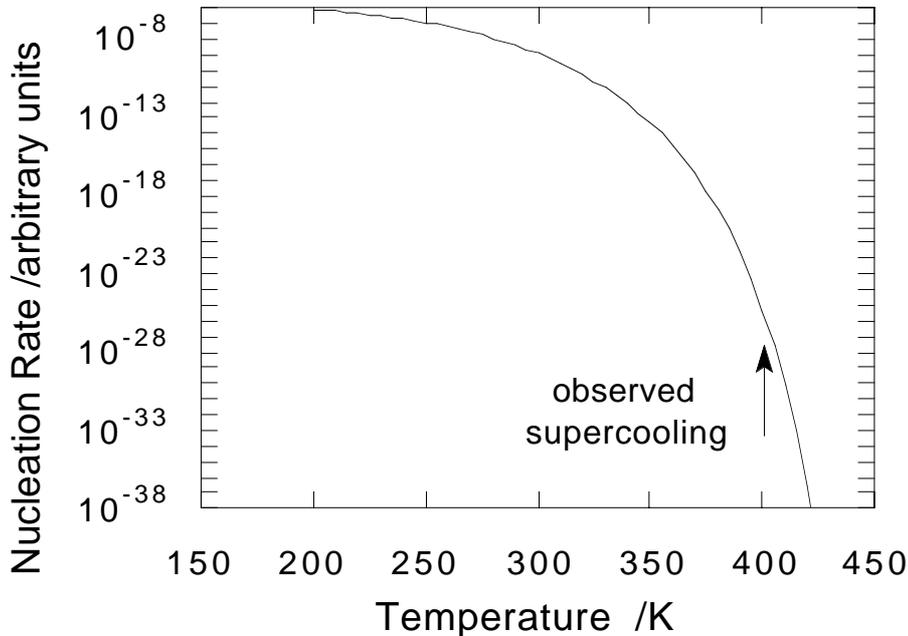
Exercises

1. Show that the Flory-Huggins interaction parameter χ is the energy change, in units of kT, when a molecule of a is taken from an environment of pure a and put in an environment of pure b.

2. Calculate the phase diagram for a certain liquid mixture, assuming that the interaction parameter is given by $\chi = 600/T$, where T is the temperature in Kelvin.
Calculate the following quantities:
a) The temperature at the critical point
     b)   The coexisting compositions at 273 K
     c)   The compositions on the spinodal line at 273 K

3. Droplets of molten silver, with radius 100 μm, are observed under a microscope as the temperature is lowered below the melting point. A large number of droplets all solidify 227 K below the melting point.

a) Assuming that these droplets are solidifying by homogenous nucleation, calculate the solid/liquid interfacial energy of silver. You may assume that a droplet solidifies when it contains, on average, one nucleus of the critical size.

b) Recent computer simulations suggest that the interface between a crystal and its melt, rather than being atomically sharp, is between 5 and 10 atomic spacings broad. What are the implications of this result for classical nucleation theory?
Illustrate your answer by calculating the classical critical nucleus size in part (a).

[Data required: Silver: relative atomic mass = 108, density = 10.49 g cm-3, Melting point 1234 K, Latent heat of fusion = 1.1 x 109 Jm-3].