Lecture 4: Thermodynamics of Diffusion: Spinodals

Fick's first law is empirical in that it assumes that the diffusion flux is proportional to a concentration gradient. It would be more reasonable to assume that diffusion occurs in order to minimise the free energy so that the flux should be driven by a gradient of free energy:

$$J_A = -C_A M_A \frac{\partial \mu_A}{\partial x} \qquad \text{so that} \qquad D_A = C_A M_A \frac{\partial \mu_A}{\partial C_A}$$

where the (positive) proportionality constant M_A is known as the mobility of A. In this equation, the diffusion coefficient is related to the mobility by comparison with Fick's first law.

If $\partial \mu_A / \partial C_A > 0$ then the diffusion coefficient is positive and the chemical potential gradient is along the same direction as the concentration gradient. However, if $\partial \mu_A / \partial C_A < 0$ then the diffusion will occur against a concentration gradient. The diffusion coefficient will be zero when $\partial \mu_A / \partial C_A = 0$.

Fig. 1 illustrates the miscibility gap defined by curve ad which is obtained by applying the common–tangent construction. Any homogeneous solution cooled into the miscibility gap will tend to decompose into A–rich and B–rich regions with a net reduction in the free energy. The chemical spinodal bc is defined by the locus of the points of inflexion $(\partial \mu_A / \partial C_A = 0)$ on the free energy diagram as a function of temperature. Homogeneous solutions which are cooled within the chemical spinodal

can in principle become unstable to infinitesimal perturbations in the chemical composition, leading to the development of A–rich and B–rich regions. Note that if a homogeneous solution is cooled into the region between the chemical spinodal and the miscibility gap, then large composition fluctuations are needed before phase separation can occur; this happens by a process known as nucleation and growth.
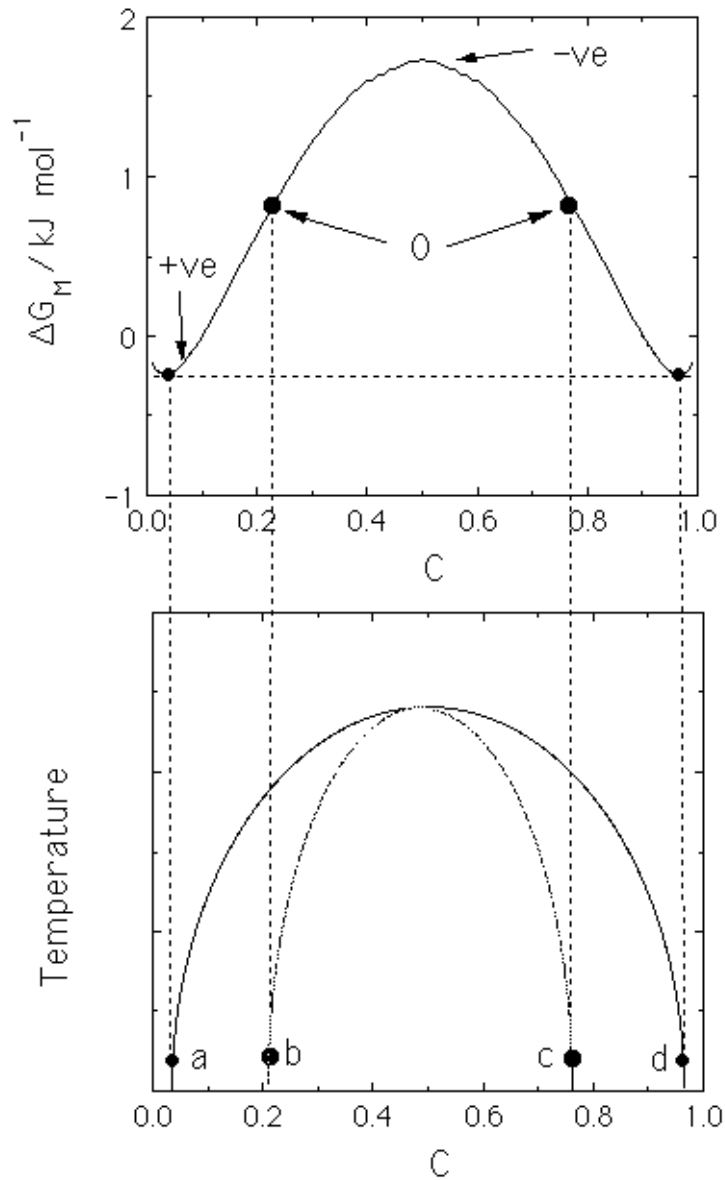

Fig. 1: The miscibility gap and the chemical spinodal.

Comparison with Nucleation and Growth

An initially homogeneous solution develops fluctuations of chemical composition when supercooled into the spinodal region. These fluctuations are at first small in amplitude but grow with time until there are identifiable precipitates of equilibrium composition (Fig. 2). During nucleation and growth, there is a sharp interface between the parent and product crystals; furthermore, the precipitate at all stages of its existence has the required equilibrium composition (Fig. 2). Spinodal decomposition involves *uphill diffusion* whereas diffusion is always down a concentration gradient for nucleation and growth of the type illustrated in Fig. 2.
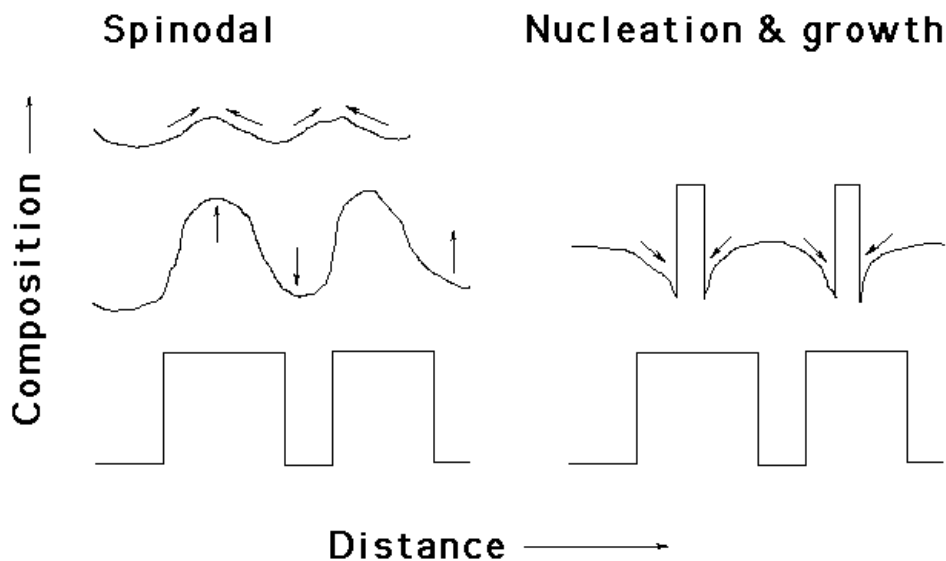

Fig. 2: Evolution of phase separation in spinodal decomposition and during nucleation and growth. The arrows indicate the direction of diffusion.

Factors Opposing Spinodal Decomposition

Solute concentration affects the lattice parameter. Chemical composition gradients are therefore associated with lattice parameter gradients which in turn lead to a coherency strain energy:

$$\text{coherency energy} \propto \eta^2 E$$

where η is the strain due to a unit composition difference and E is the elastic modulus. Large gradients are consequently not favoured and the undercooling has to be greater than that indicated by the chemical spinodal in order to achieve spinodal decomposition. Indeed, spinodal decomposition does not occur in practice unless the undercooling brings the homogeneous solution within the coherent spinodal (Fig. 3).

It is always the case in crystalline materials that the elastic modulus is anisotropic. The spinodal then takes advantage of the directions along which the modulus is smallest, giving rise to anisotropic microstructures. The coherent spinodal is also not symmetric since alloying can affect the modulus in a complex manner.

The second factor opposing the development of composition waves with small wavelength comes about because an inhomogeneous solution does not have the same free energy as a homogeneous solution with the same average composition. Fig. 4 shows that the average environment that a region (**a**) feels is different (**b**) from its own chemical composition because of the curvature in the concentration gradient. This gives rise to a gradient term which is an additional free energy in a heterogeneous system, to be regarded as an interfacial energy describing a "soft interface".
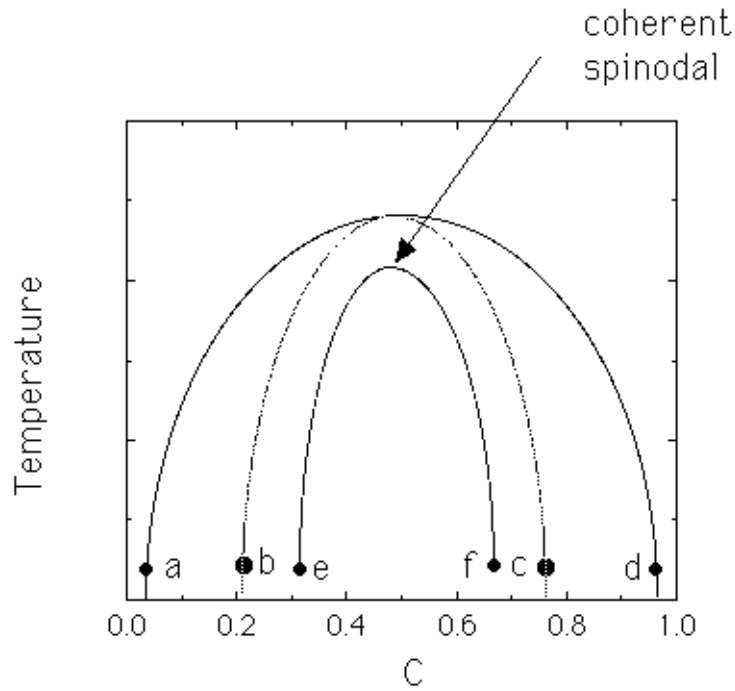
Fig. 3: The coherent spinodal *ef* illustrated in the context of the miscibility gap and the chemical spinodal.
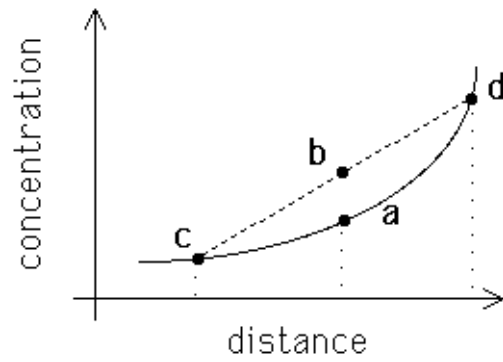

Fig. 4: Gradient of chemical composition. Point a represents a small region of the solution, point b the average composition of the environment around point a, *i.e.* the average of points c and d.