Last time

Elastic Energy Contribution to Coherent Nucleation

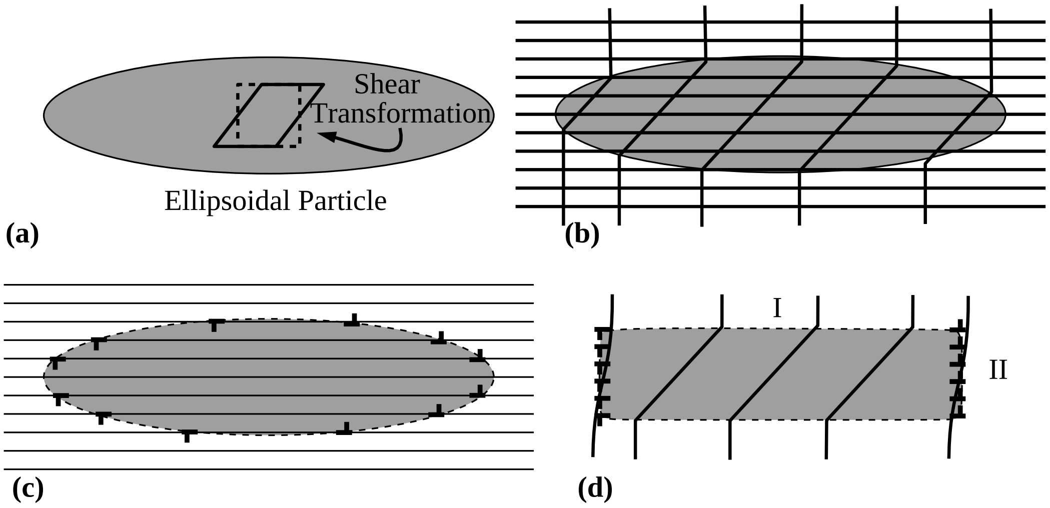

Figure 32-1: Illustration of role of misfit dislocations in transition from coherent to semi-coherent interfaces

Eshelby Cycle

Shape and Elastic Heterogeneity

Homogeneous Nucleation

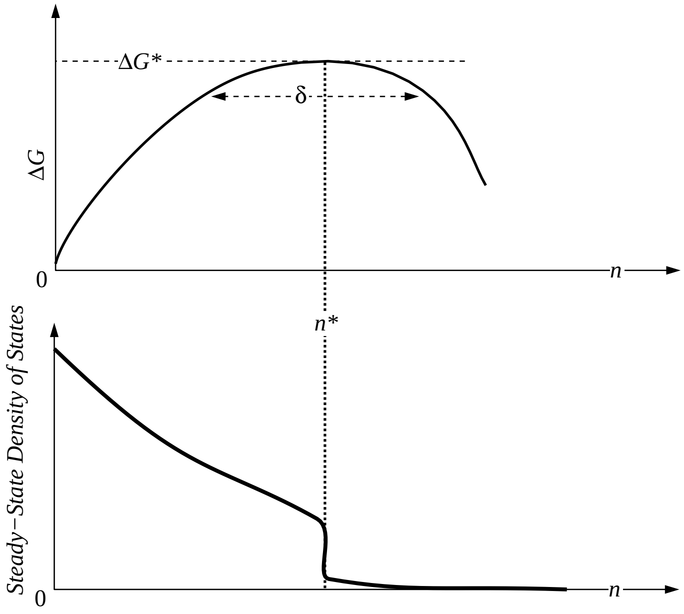

Figure 32-2: Schematic illustration of the steady-state probability distribution of subcritical nuclei.

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Heterogeneous Nucleation

Heterogeneous nucleation can occur on imperfections when the nucleating particle effectively "replaces" some energetic feature of the original configuration. For instance, nucleation on a grain boundary removes grain boundary area and replaces it with interphase boundary area that would have been created anyway by formation of the new phase. Thus, preexisting imperfections effectively "catalyze" the nucleation process.

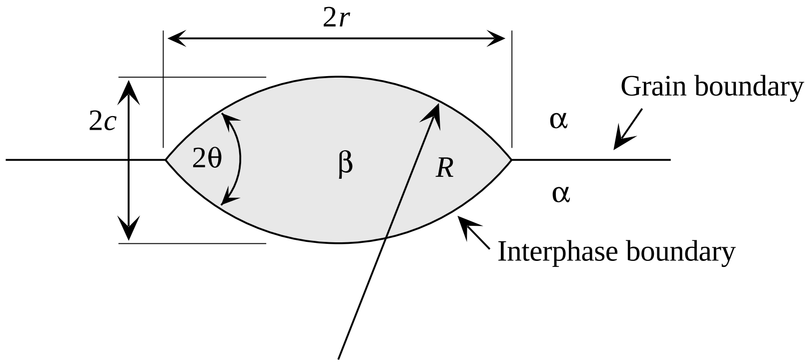

Figure 32-3: Geometrical parameters defining size and shape of a lenticular β particle situated on a grain boundary in phase α for the case of isotropic surface energy. Students should be able to derive and expression for the critical volume for this case. In this case, the mathematics will show that the radius of the heterogeneous particle is the same as that of the homogeneous (spherical) particle.

Heterogeneous nucleation is a commonly observed phenomenon.
Question: How do you explain the following phenomena?

1. If you gently open a carbonated beverage without shaking it, how does it approach equilibrium?

2. If you open a carbonated beverage soon after vigorously shaking it, how does it approach equilibrium?

3. If you leave a (previously shaken) carbonated beverage undisturbed for a long time and then gently open it, how does it approach equilibrium? What sets the time scale for the time it must be left undisturbed?

Heterogeneous nucleation can be understood by considerations of the geometry of the nucleus. The steps can be illustrated by a simple example of a cubic crystal with {100}-facets nucleating in a (100)-direction.

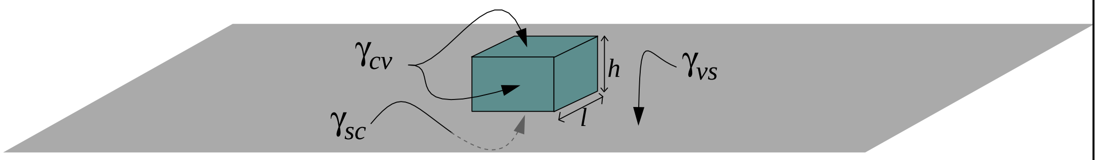

Figure 32-4: Illustration of a completely faceted cubic particle nucleating on a flat substrate with interfacial energies $\gamma_{\{100\}} = \gamma_{cv}$, vapor-substrate γ_{vs}, and substrate-crystal γ_{sc}.

For this case, the ΔG for homogeneous nucleation is given by the maximum of

$$\Delta G_{homog} = \Delta g w^3 + 6\gamma_{cv} w^2 \tag{32-1}$$

Therefore,

$$\begin{aligned} w^* &= -\frac{4\gamma_{cv}}{\Delta g} \\ \Delta G^*_{homog} &= \frac{32\gamma_{cv}^3}{\Delta g^2} \end{aligned} \tag{32-2}$$

For heterogeneous nucleation,

$$\Delta G_{heter} = \Delta g l^2 h \gamma_{cv}(l^2 + 4lh) + (\gamma_{sc} - \gamma_{vs})l^2 \tag{32-3}$$

Therefore,

$$
\begin{aligned}
l^* &= \frac{-4\gamma_{cv}}{\Delta g} \\
h^* &= \frac{-2(\gamma_{cv} + \gamma_{sc} - \gamma_{vs})}{\Delta g} \\
\Delta G^*_{heter} &= \frac{16\gamma_{cv}^2(\gamma_{cv} + \gamma_{sc} - \gamma_{vs})}{\Delta g^2}
\end{aligned}
\tag{32-4}
$$

The shape of the particle is determined by the differences in surface tensions and the geometrical factors associated with the shape of the particle determine the nucleation barrier for heterogeneous diffusion.

Spinodal Decomposition and Order-Disorder Transformation Kinetics

Background

The nucleation conditions for phase transformations have been discussed. The rest of this lecture will review another type of initiation mechanism that does not involve nucleation. These mechanisms can either be accompanied by mass flux as in the case of *spinodal decomposition* or without large-range mass flux as in the case of *order-disorder* transitions.

These nucleation-free transitions occur when a small local change in the system is never accompanied by an increase in free energy, but always a decrease in free energy.

Spinodal decomposition arises from free energy diagrams and phase diagrams like those illustrated below:

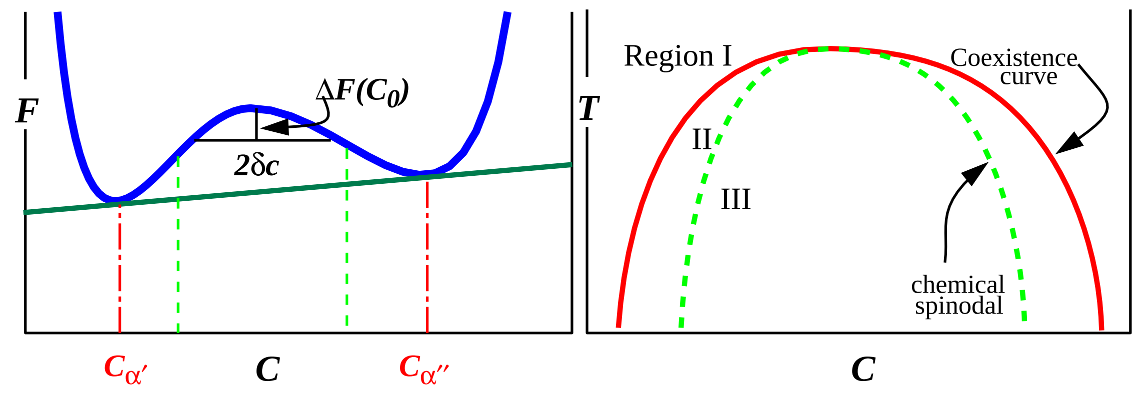

Figure 32-5: Illustration of the types of free energy curves and the regions on a phase diagram that are associated with spinodal decomposition.

In order-disorder transitions such as a ferromagnetic transition or a lattice-ordering, there are no conserved quantities which would give rise to a common tangent in the above diagram.

The two different kinds of processes can be illustrated schematically:

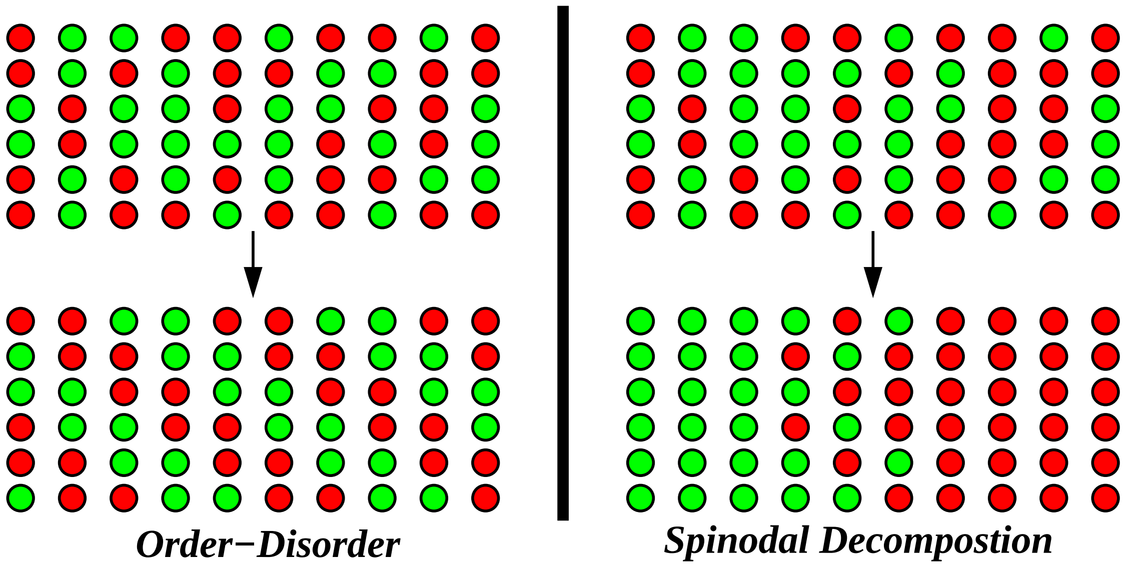

Figure 32-6: Illustration of two atomic rearrangement processes.

The ordering reaction does not require long-range diffusion, but the decomposition reaction must move mass over long distances.

In the appendix to these notes, it is demonstrated how the changes in free energy depend on whether flux is required or not. The important results can be summarized as follows:

- **Non-conserved quantities**: If η is a non-conserved quantity, like spin, or crystalline order, then for small changes in η given by $\delta\eta$:

  $$\Delta G = \delta\eta \frac{dG}{d\eta}\bigg|_{\eta=\eta_0} \tag{32-5}$$

  Therefore, an order parameter can always decrease the free energy by picking a variation $\delta\eta$ with a sign that makes the product in Eq. 32-24 negative. An non-conserved order parameter has no barrier against reaching a value which makes the free energy a local minimum.

- **Conserved quantities**: If c is a non-conserved quantity, like concentration, then for small changes in c given by δc:

  $$\Delta G = \frac{1}{2}(\delta c)^2 \frac{d^2G}{dc^2}\bigg|_{c=c_0} \tag{32-6}$$

Therefore, a barrier to the growth of small variations exists whenever the second derivative in Eq. 32-23 is positive. Thus, nucleation is required for a transformation outside of the spinodal curves.

In fact, it can be shown that the sign of the diffusivity, D, for concentration flux is given by the second derivative $\partial^2 G/\partial c^2$. This has the effect of causing "up-hill" diffusion.

Macroscopic Theories for Decomposition Kinetics

If transformations occur without nucleation, then the thermodynamics must account for continuous variations of thermodynamic state variables. These continuous variations are called "diffuse interfaces" and they are addressed in this section. The important result is that the local free energy density has a contribution due to gradients of thermodynamic state variables.

The theory for the free energy of inhomogeneous systems was developed by Cahn and Hilliard in 1958. The theory was originally developed to account for contributions to the free energy from gradients in the composition—or any other conserved field. The diffuse interface method was extended to non-conserved order parameters by Allen and Cahn (1979) in their study of the kinetics of the order-disorder transition. The theories for both can be developed in parallel since their construction follows from the same principles. $c(\vec{x})$ describes any conserved field quantity (like the concentration field in a closed system) and $\eta(\vec{x})$ represents any non-conserved order parameter field.

A two-phase system with a miscibility gap at equilibrium with a planar interface will have an equilibrium composition profile $c(x)$ through the interfacial region. The form of the equilibrium composition distribution is determined by the $c(x)$ which minimizes F, the total free energy of the system. Similarly, a system that tends to form long-range ordered domains will have a distribution of order, $\eta(x)$, across a planar interface between two identical domains having different local minima in their order parameters.

Example profiles, $c(x)$ and $\eta(x)$, through diffuse interfaces in these two types of systems are shown schematically below:

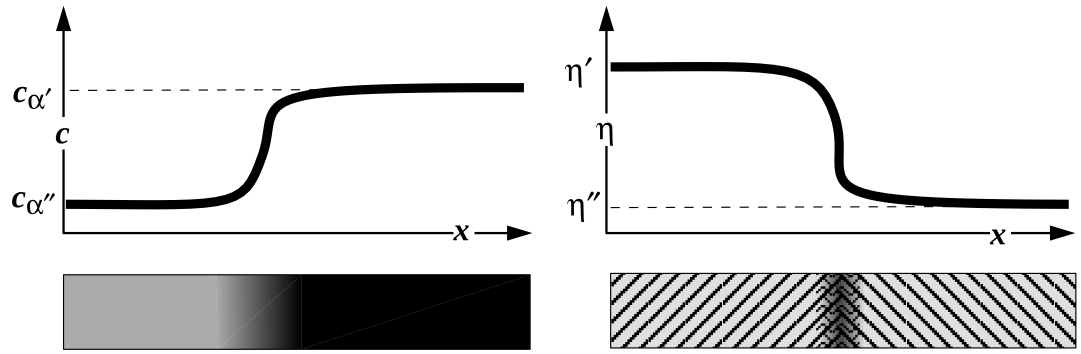

Figure 32-7: Illustration of order parameter fields in the diffuse interface theories.

The profiles $c(x)$ and $\eta(x)$ are continuous and the compositions $c_{\alpha'}$ and $c_{\alpha''}$ are the equilibrium compositions of the bulk phases. The values of order parameter η' and η'' correspond to local minima in the free energy.

Let $y(x)$ stand for either $c(x)$ or $\eta(x)$. Also, let $f(y, \nabla y)$ be the free energy of a small volume dV which has average composition y and a gradient ∇y across it. If the free energy density is expanded about its homogeneous value $f(y) = f(y, 0)$ (presumably a known function) then then

$$f(y, \nabla y) = f(y, 0) + \vec{L} \cdot \nabla y + \frac{1}{2} \nabla y \underline{K} \nabla y + \dots \tag{32-7}$$

where

$$\vec{L} = \frac{\partial f}{\partial(\partial y / \partial x_i)} \tag{32-8}$$

is a vector evaluated at zero gradient and

$$\underline{K} = \frac{\partial^2 f}{\partial(\partial y / \partial x_i) \partial(\partial y / \partial x_j)} \tag{32-9}$$

is a matrix of second derivatives.

If homogeneous material has a center of symmetry, the free energy cannot depend on the direction of the gradient and thus $\vec{L} = 0$ and $\underline{K}$ will be a symmetric matrix. Furthermore, if the homogeneous material is isotropic (or cubic), then $\underline{K}$ will be a diagonal matrix (with components K along the diagonal), then free energy density is, to second order:

$$f(y, \nabla y) = f(y, 0) + \frac{K}{2} \nabla y \cdot \nabla y = f(y, 0) + \frac{K}{2} |\nabla y|^2 \tag{32-10}$$

Only the second term contributes to the free energy only in the region near the interface (where the gradient is non-zero). The gradient-energy coefficient K is a parameter which contributes to the interfacial area. However, it is not the only term which contributes: as the composition profile traverses the interface region, compositions from the non-equilibrium parts of the free energy curve are contributing to the excess free energy associated with the interface as well.

It is possible to calculate equilibrium profiles in terms of the parameters in Eq. 32-10. However, our purpose is describe the kinetics of how an arbitrary distribution $y(\vec{x})$ evolves towards equilibrium.

We will take a variational calculus approach. The treatment below assumes no prior knowledge of the calculus of variations and will serve as an introduction to the subject.

The total free energy of the entire system (occupying the domain Ω) is:

$$F[y(x)] = \int_{\Omega} (f(y) + \frac{K}{2} \nabla y \cdot \nabla y) dV \tag{32-11}$$

which defines F as a functional with the argument $y(\vec{x})$[34]. The function $y(\vec{x})$ will also have specified boundary conditions on $\partial\Omega$ (the boundary of Ω); for instance, $y(\partial\Omega)$ will have fixed values or fixed derivatives.

If the field $y(\vec{x})$ is changing with velocity $v(\vec{x})$, the is the rate of change of F is

$$F(y + vt) = \int_{\Omega} [f(y + vt) + + \frac{K}{2} (\nabla y \cdot \nabla y + 2t \nabla y \cdot \nabla v + t^2 \nabla v \cdot \nabla v] dV \tag{32-12}$$

so that

$$\left. \frac{\partial F}{\partial t} \right|_{t=0} = \int_{\Omega} [f'(y) v + K \nabla y \cdot \nabla v] dV \tag{32-13}$$

using

$$\nabla \cdot (v \nabla y) = \nabla v \cdot \nabla y + v \nabla^2 y \tag{32-14}$$

and using the divergence theorem,

$$\left. \frac{\partial F}{\partial t} \right|_{t=0} = \int_{\Omega} (f'(y) - K \nabla^2 y) v dV + \int_{\partial\Omega} v \nabla y \cdot d\vec{A} \tag{32-15}$$

The boundary integral vanishes if $v(\partial\Omega) = 0$, which would be the case if $y(\partial\Omega)$ had fixed boundary values[35]; or, if the projections of the gradients onto the boundary vanish. If these two cases are not satisfied, then when the volume to surface ratio is greater than the inherent diffusion length, the system may be considered to be large enough so that the contributions due to boundary can be neglected.

The change in total energy in Eq. 32-15 is the sum of local variations: $(f'(y) - K\nabla^2 y)v$. Therefore, the *largest possible increase* of F is when the *flow*, $v(\vec{x})$, is proportional to

$$f'(y) - K \nabla^2 y \tag{32-16}$$

Therefore, Equation 32-16 is the functional gradient of $F(y)$.[36] Sometimes Eq. 32-16 is called the variational derivative of F.[37] When the variational derivative vanishes, $y(x)$ is an *extremal*

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[34] A functional is a *function of a function*; in this case, it takes a function and maps it to a scalar which is numerically equal to the total free energy of the system

[35] If y represents a conserved quantity like c, then the variation vt must not contribute to the total content of the system ($\int vtdV = 0$), but we will satisfy this requirement automatically below.

[36] This is one particular choice for the functional gradient, for which there are an infinite number of choices. This particular choice (the gradient in the $L2$-norm of functions) describes the physics of the problem.

[37] For the general functional, $P[y] = \int Q[y(\vec{x}), \nabla y] dV$, the variational derivative of P is

$$\frac{\partial Q}{\partial y} - \nabla \cdot \frac{\partial Q}{\partial \nabla y}$$

function and a candidate for a local maximum or minimum. For the case of the gradient energy, if Eq. 32-16 vanishes, then y is an equilibrium profile.

The functional gradient is the starting point for the kinetic equations for conserved and non-conserved parameter fields.

Appendix: Free Energy Changes and Geometric Constructions

The free energy versus composition curve, illustrated in the above for a constant temperature, is a familiar example of a free energy which gives rise to a miscibility gap. The region between the spinodal lines delimits those compositions for which there is no barrier to decomposition. Inside the miscibility gaps, but outside of the spinodal region, decomposition is favored but a thermodynamic barrier requires large fluctuations in composition (i.e., nucleation) for decomposition. The position of spinodal lines is determined by the sign of the free energy change for a small fluctuation in composition. The following derivation is from Hilliard which derives the variation of the molar free energy, $\overline{F}(c)$, but this derivation applies to any extensive molar quantity.[38].

We can write $\overline{F}(c)$ in terms of its *partial* molar quantities, $\overline{F}_A(c)$ and $\overline{F}_B(c)$:

$$\begin{aligned} \overline{F}(c) &= \tfrac{N_A}{N_A+N_B}\overline{F}_A(c) + \tfrac{N_B}{N_A+N_B}\overline{F}_B(c) \\ &= c\overline{F}_A(c) + (1-c)\overline{F}_B(c) = c\mu_A(c) + (1-c)\mu_B(c) \end{aligned} \tag{32-17}$$

which plots as a straight line when the arguments of the partial molar quantities are evaluated at a particular point c_0 on the curve $\overline{F}(c)$: $c\mu_A(c_0) + (1-c)\mu_B(c_0)$. Consider a large system at composition c_0 which transforms 1 mole to a new composition c'. If the system is open and the composition is free to change, then the change in $\overline{F}$ is simply the difference $\Delta\overline{F} = \overline{F}(c') - \overline{F}(c_0)$. Similarly, for any non-conserved parameter η, the change in molar free energy is:

$$\Delta\overline{F} = \overline{F}(\eta') - \overline{F}(\eta) \tag{32-18}$$

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[38] An extensive quantity is one which depend on the total size of a system, like the volume, enthalpy, or free energy. A molar extensive quantity is scaled by diving by the total number of moles in the system: $\overline{V}(c) = V(c)/(N_A+N_B) = \overline{V}(N_A/(N_A+N_B)) = \overline{V}(\overline{N}_A)$. A *molal* extensive quantity is scaled by dividing by the number of moles of a particular species.

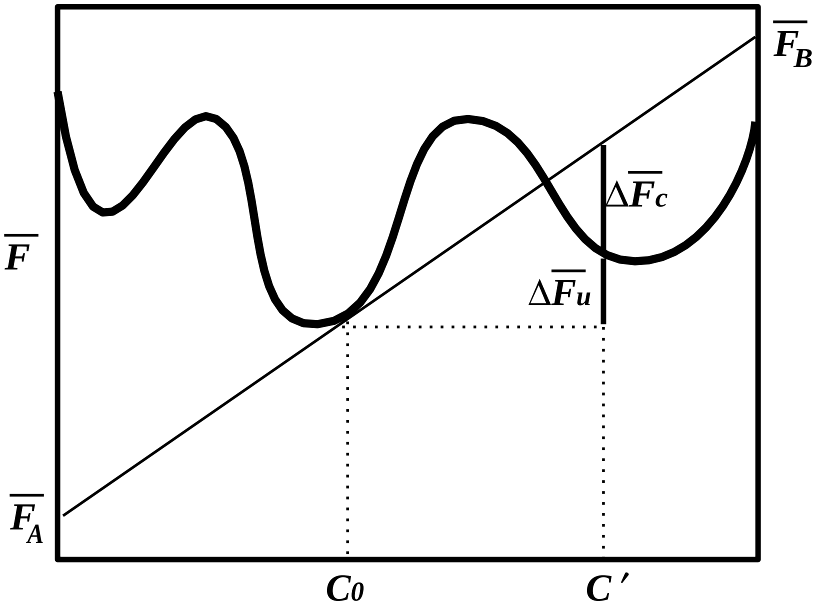

Figure 32-8: Illustration of the change in molar free energy from a composition c_0. If the system is closed so the composition is fixed, then the change in the molar free energy is $\Delta\overline{F}_c$ for every mole which forms at composition c'. If the system is open and the composition is free to change its value, then $\Delta\overline{F}_u$ is the change per mole transformed.

However, if the system is closed (which is the case for a localized fluctuation in composition), then it is necessary to account for the exchange of material necessary to satisfy the constraint of fixed composition. For each mole transformed, the change in $\overline{F}$ for the c' moles of the B component is $[\overline{F}_B(c') - \overline{F}_B(c_0)]c'$, with a similar term for the A component:

$$\Delta\overline{F} = [\overline{F}_B(c') - \overline{F}_B(c_0)]c' + [\overline{F}_A(c') - \overline{F}_A(c_0)](1-c') \tag{32-19}$$

which can be rewritten as

$$\begin{aligned}\Delta\overline{F} = \; & c'\overline{F}_B(c') + (1-c')\overline{F}_A(c') - c_0\overline{F}_B(c_0) - (1-c_0)\overline{F}_A(c_0) + \\ & (c_0 - c')[\overline{F}_B(c_0) - \overline{F}_A(c_0)]\end{aligned} \tag{32-20}$$

or

$$\Delta\overline{F} = \overline{F}(c') - \overline{F}(c_0) - (c'-c_0)\frac{d\overline{F}}{dc}\bigg|_{c=c_0} \tag{32-21}$$

which is numerically equal to the distance indicated in the figure by the distance $\Delta\overline{F}_c$. $\Delta\overline{F}_c$ is negative if the curve for $\overline{F}(c)$ lies below the tangent at $c = c'$. Equation 32-21 holds for any concentration c' when the composition c_0 is fixed.

Consider the special case of a small composition fluctuation, $\delta c = c' - c_0$. Expanding $\overline{F}(c)$ in δc:

$$\overline{F}(c') = \overline{F}(c_0) + \delta c\frac{d\overline{F}}{dc}\bigg|_{c=c_0} + \frac{1}{2}(\delta c)^2\frac{d^2\overline{F}}{dc^2}\bigg|_{c=c_0} + \ldots \tag{32-22}$$

Substituting Eq. 32-21 into Eq. 32-22 results in the **change in the molar free energy for a variation of a conserved parameter** c:

$$\Delta\overline{F} = \frac{1}{2}(\delta c)^2 \frac{d^2\overline{F}}{dc^2}\bigg|_{c=c_0} \tag{32-23}$$

Similarly, the lowest order term for the **change in the molar free energy for a variation of a non-conserved order parameter** η is

$$\Delta\overline{F} = \delta\eta \frac{d\overline{F}}{d\eta}\bigg|_{\eta=\eta_0} \tag{32-24}$$

Therefore, an order parameter can always decrease the free energy by picking a variation $\delta\eta$ with a sign that makes the product in Eq. 32-24 negative. An non-conserved order parameter has no barrier against reaching a value which makes the free energy a local minimum.

On the other hand, for a conserved quantity like c, the variation in molar free energy is proportional to $(\delta c)^2$. Therefore, a barrier to the growth of small variations exists whenever the second derivative in Eq. 32-23 is positive. Thus, nucleation is required for a transformation outside of the spinodal curves.

The sign of Eq. 32-23 determines the sign of the interdiffusion coefficient.