Lecture 32

Unstable Solutions

Last Time

Other Types of Phase Diagrams

Models for Solutions

Limiting Behavior for Dilute and nearly Pure Solutions

Non-Ideal Solution Behavior

In this section, a simple model for the enthalpy of mixing will be derived. It will be shown that a positive enthalpy of mixing tends to make a system separate and have a miscibility gap at low temperature. A negative enthalpy of mixing tends to favor stable homogeneous solutions.

Consider two neighbors in a solution. The probability that one of the neighbors is an A-type or a B-type is simply:

$$\pi_A = \frac{N_A}{N_A + N_B} = X_A \quad \text{and} \quad \pi_B = \frac{N_B}{N_A + N_B} = X_B \tag{32-1}$$

Therefore the probability that a given "bond" is an A–B type is:

$$\pi_{(AB)} = \pi_{AB} + \pi_{BA} = \frac{2N_A N_B}{(N_A + N_B)^2} = 2X_A X_B \tag{32-2}$$

If each atom has z nearest neighbors, the number of bonds, total, is

$$B^{\text{total}} = \frac{z}{2}(N_A + N_B) \quad \Longrightarrow \quad \overline{B^{\text{total}}} = \frac{z}{2} \tag{32-3}$$

The bond density of A–B type is therefore:

$$\overline{B_{(AB)}} = zX_AX_B \tag{32-4}$$

If the energy per $A - B$ bond is ω_{AB}[31] then the enthalpy density (due to the A–B bonds) is:

$$\overline{H^{\mathcal{RS}}_{(AB)}} = z\omega_{AB}X_AX_B \tag{32-5}$$

Similarly, the bond density of A-types is $\overline{B}_{AA} = \frac{z}{2}X_AX_A$ so that $\overline{H_{AA}} = \frac{z}{2}X_A^2\omega_{AA}$. Similarly $\overline{H_{BB}} = \frac{z}{2}X_B^2\omega_{BB}$.

Putting this all together

$$\overline{H^{\text{total}^{\mathcal{RS}}}} = z(\omega_{AB}X_AX_B + \frac{\omega_{AA}}{2}X_A^2 + \frac{\omega_{BB}}{2}X_B^2) \tag{32-6}$$

$$\overline{H^{\text{total}^{\mathcal{UM}}}} = \frac{z\omega_{AA}}{2}X_A + \frac{z\omega_{BB}}{2}X_B \tag{32-7}$$

Therefore since, $\Delta\overline{H_{mixing}} = \overline{H^{sol}} - \overline{H^{pure\ mix}}$:

$$\begin{aligned}\overline{\Delta H^{\mathcal{RS}}} &= \frac{z}{2}X_AX_B(2\omega_{AB} - \omega_{AA} - \omega_{BB})\\ &\equiv \frac{z}{2}X_AX_B\omega^{\mathcal{RS}}\end{aligned} \tag{32-8}$$

$$\begin{aligned}\overline{\Delta G^{\mathcal{RS}}} &= \overline{\Delta H^{\mathcal{RS}}} - T\overline{\Delta S^{\mathcal{IS}}}\\ &= \frac{z}{2}X_AX_B\omega^{\mathcal{RS}} - T[(-R)(X_A\log X_A + X_B\log X_B)]\end{aligned} \tag{32-9}$$

This is the *Regular Solution Model*

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[31] relative to no bond having zero energy, i.e., $\omega_{AB} < 0$ is more stable.

Behavior of the Regular Solution Model

Above, a "first-order" correction to the ideal solution model based on an atomic averaging for the enthalpy of mixing.

This is called the regular solution model.

$$\overline{\Delta G^{\mathcal{RS}}} = \overline{\Delta H^{\mathcal{RS}}} - T\overline{\Delta S^{\mathcal{IS}}} \tag{32-10}$$

where

$$\overline{\Delta H^{\mathcal{RS}}} = \frac{z}{2}X_A X_B(2\omega_{AB} - \omega_{AA} - \omega_{BB}) = \frac{z}{2}X_A X_B \omega^{\mathcal{RS}} \tag{32-11}$$

and

$$\overline{\Delta S^{\mathcal{IS}}} = -R(X_A \log X_A + X_B \log X_B) \tag{32-12}$$

Consider both terms:

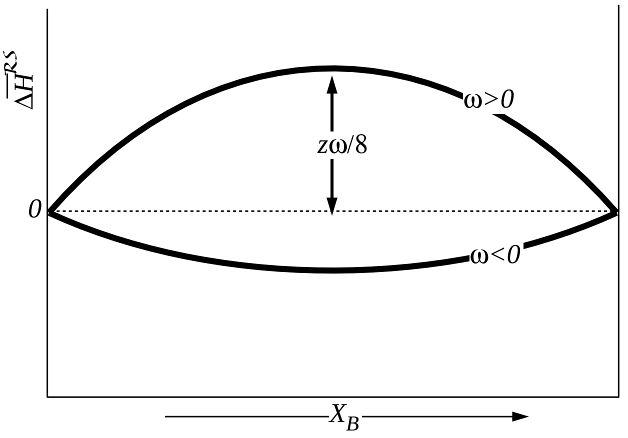

Figure 32-1: The behavior of enthalpy in the regular solution model.

Note that $\omega < 0$ favors mixing, and makes sense because ω_{AB} is more negative than $\langle \omega_{AA} + \omega_{BB} \rangle$.

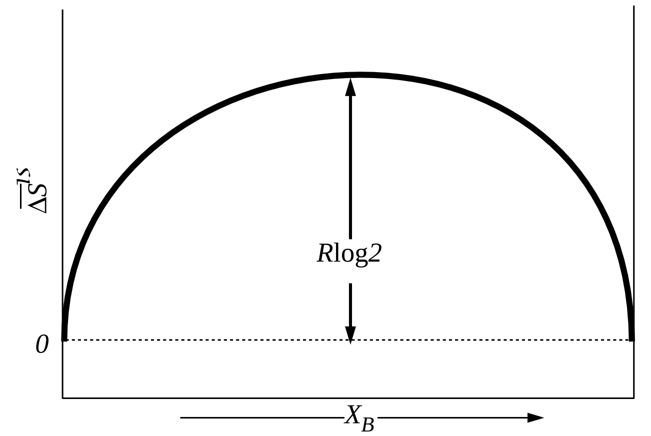

Figure 32-2: The behavior of the ideal entropy of mixing: $\Delta\overline{S}^{\mathcal{IS}} = -R(X_A \log X_A + X_B \log X_B)$

So that, taken together: $\Delta\overline{G^{mix}} = \Delta\overline{H^{mix}} - T\Delta\overline{S^{mix}}$:

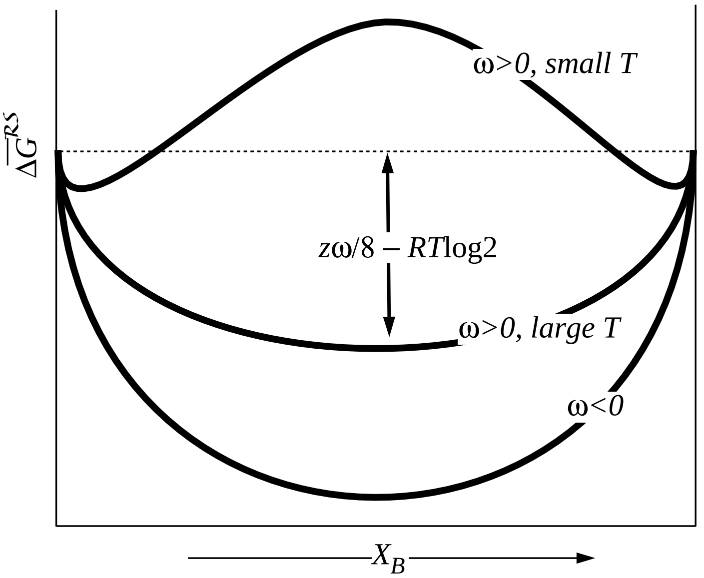

Figure 32-3: The behavior of the molar Gibbs free energy of mixing for the regular solution.

Note that the limiting behavior for pure or extremely dilute solutions is dictated by:

$$\lim_{x \to 0} \frac{\partial \Delta G^{\text{mixing}}}{\partial x} = -\infty \tag{32-13}$$

A solution can *always* lower its free energy by dissolving at least a small amount component. There is *thermodynamically always some finite solubility* (but it can be, and often is, very, very small). This implies that the width of a single-phase region must always be finite.

Consider the case where $\omega > 0$, so the system will tend to "unmix" at low temperatures.

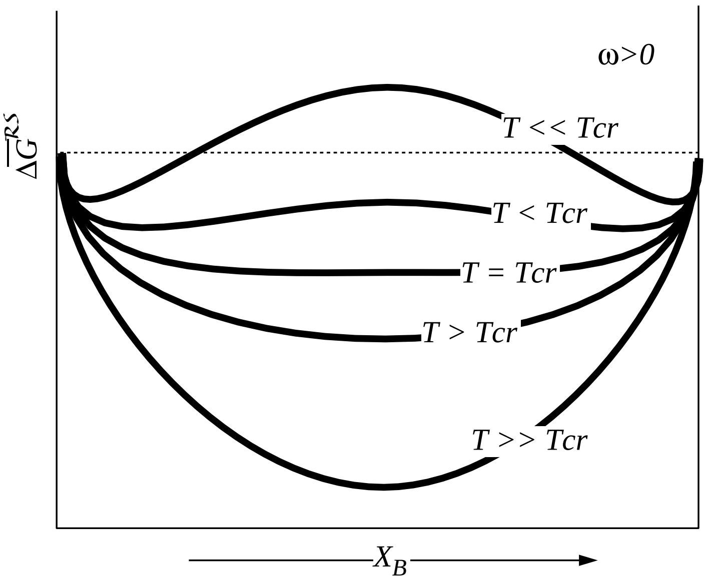

Figure 32-4: The dependence of the regular solution model on temperature for $\omega > 0$. At low temperatures, the curve develops a "self-common-tangent" and is thus unstable at compositions within the tangent points with respect a decomposition into a composition-rich and a composition-poor phase.

For the case of a regular solution, the curve is symmetric around $X = 1/2$, and in this case we can calculate the positions of the common tangents:[32]

$$\frac{\partial \Delta\overline{G}^{\mathcal{RS}}}{\partial x} = \frac{z\omega}{2} - z\omega X_B + RT[(1 + \log X_B) + (-1 - \log(1 - X_B))] = 0 \qquad (32\text{-}14)$$

However, this is hard to solve (see Equation 32-15).

The critical temperate can be determined analytically by noting that as the common tangents form that the curvature changes sign at $X_B = 1/2$.

$$\begin{aligned} \Delta\overline{G}^{\mathcal{RS}} &= \frac{z}{2}\omega X_B(1 - X_B) + RT\left(X_B \log X_B + (1 - X_B)\log(1 - X_B)\right) \\ \frac{\partial \Delta\overline{G}^{\mathcal{RS}}}{\partial X_B} &= z\omega(\frac{1}{2} - X_B) + RT\left(\log X_B - \log(1 - X_B)\right) \\ \frac{\partial^2 \Delta\overline{G}^{\mathcal{RS}}}{\partial {X_B}^2} &= -z\omega + RT(\frac{1}{X_B} + \frac{1}{1 - X_B}) = 0 \end{aligned} \qquad (32\text{-}15)$$

At $X_B = 1/2$, the zero first appears at

$$T_{\text{crit}}^{\mathcal{RS}} = \frac{z\omega}{4R} \qquad (32\text{-}16)$$

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[32] Because the curve is symmetric around $X = 1/2$ the common tangents, in this special case, will coincide with the minima of the molar free energy of solution.

Spinodal Decomposition

For those cases in which the molar free energy of mixing has regions of negative curvature (as in the example of the regular solution model), the mechanism by which the system decomposes into its equilibrium phases is different than the mechanism when the curvature is positive. This distinction between mechanisms when the curvature is negative (called the spinodal decomposition mechanism) when the curvature is positive (called the nucleation and growth mechanism) is important for kinetics. It will be useful to discuss the spinodal mechanism in the context of free energy curves.

Consider a part of the free energy curve where the curvature is negative:

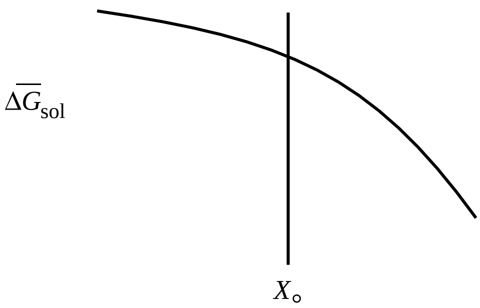

Figure 32-5: $\frac{\partial^2 \overline{G^{mix}}}{\partial X_B^2} < 0$

Suppose that a material is manufactured with a composition $X_\circ$ that is a function of some spatial coordinate z:

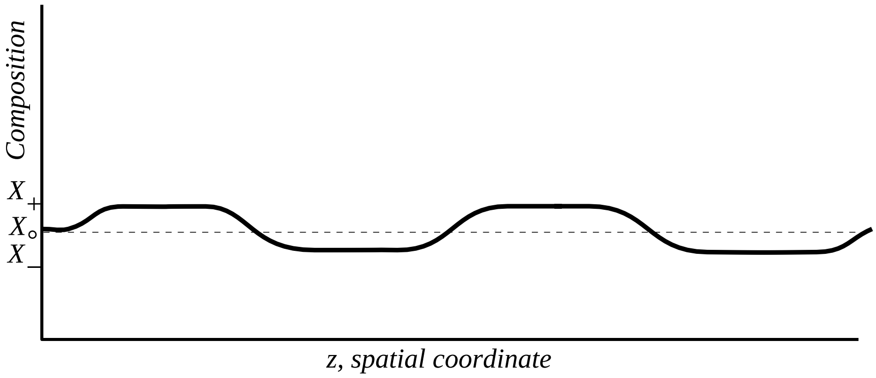

Figure 32-6: Composition as a function of a spatial coordinate with a small fluctuation about a fixed value of composition.

Suppose that a very small fluctuation occurs and consider what happens to the free energy for the small fluctuation:

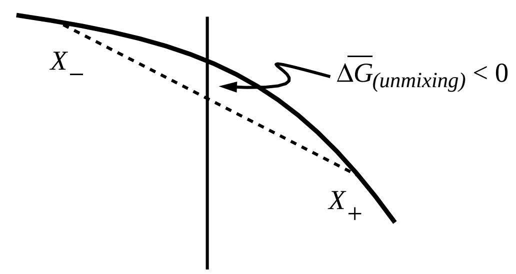

Figure 32-7: The Gibbs free energy construction for a small decomposition fluctuation.

Apparently, the free-energy charge is negative for an arbitrarily small fluctuation in composition such that one part of the system gets more concentrated at the expense of another. The system is inherently unstable and and phase separation will proceed as illustrated:

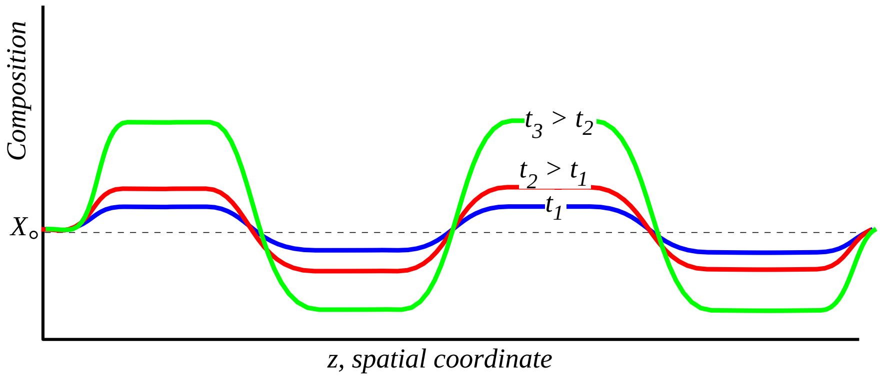

Figure 32-8: Composition profiles drawn at different times during decomposition.

This process is called spinodal decomposition and it occurs spontaneously when

$$\frac{\partial^2 \Delta\overline{G^{\text{mixing}}}}{\partial {X_B}^2} < 0 \quad \text{(condition for spinodal decomposition)} \tag{32-17}$$

Consider the part of the curve where the curvature is positive but inside the miscibility gap (miscibility gap is another way of saying the two-phase region):

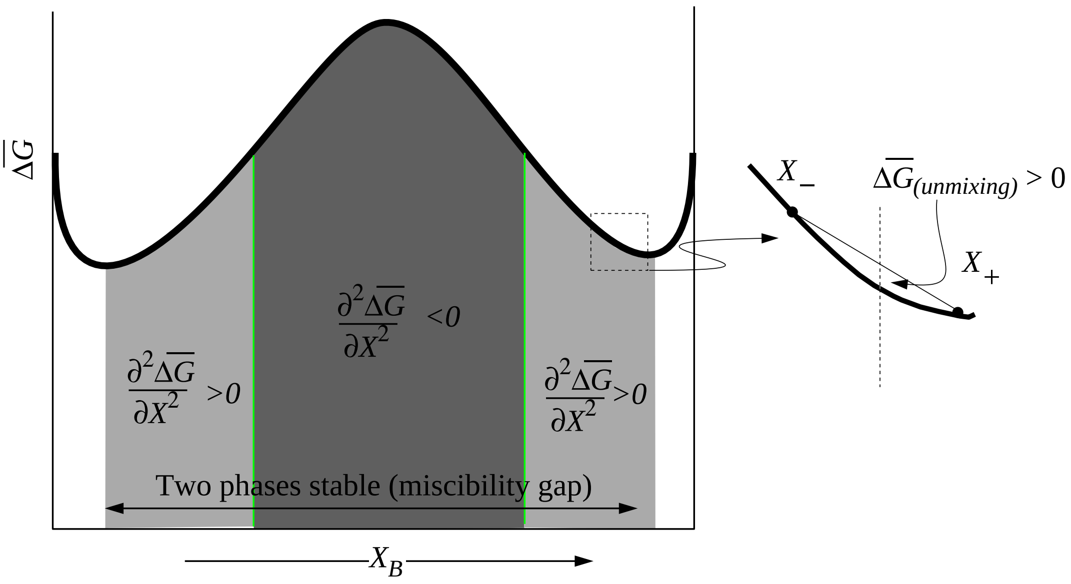

Figure 32-9: The molar free energy change for the case $(\partial^2 \overline{G^{mix}})/(\partial X_B^2) > 0$.

Apparently, the free energy increases. Therefore, the system is "stable" with respect to small fluctuations. In other words, it is metastable with respect to infinitesimal composition fluctuations.

Such a system is clearly unstable to the separation into the limiting compositions given by the common tangent construction. How does the system phase separate?

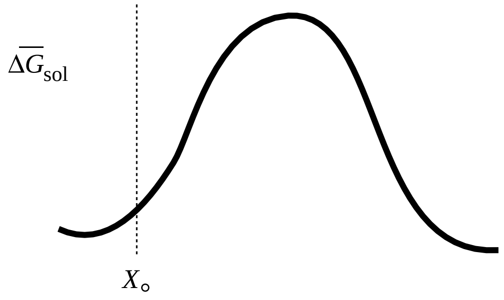

Figure 32-10: Illustrating that a large composition difference is required to nucleate a the stable phases.

Apparently an average composition within the two phase region, but outside of the spinodal curves requires large composition fluctuations to decrease the energy. Therefore, the system phase separates as illustrated in the following cartoon:

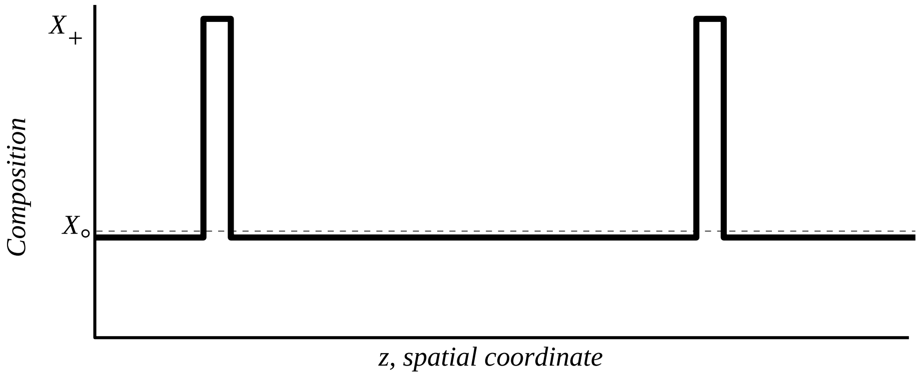

Figure 32-11: Illustration of the nucleation of an unstable phase. For nucleation—by contrast to phase separation by spinodal decomposition—the new phase must initiate with a composition that is *not* near that of the parent phase. Nucleation is a phase transition that is large in degree (composition change) but small in extent (size); whereas spinodal decomposition is small in degree but large in extent.

A process requiring a large composition fluctuation is called "nucleation." After the nucleus forms, the new phase grows. Together, the process is called *nucleation and growth.*

This kinetic information can be graphically codified into the phase diagram:

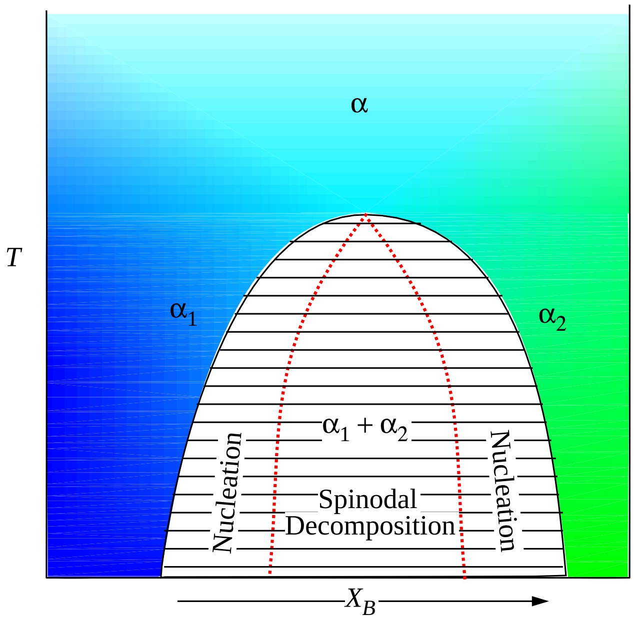

Figure 32-12: A phase diagram with a spinodal miscibility gap.

Nucleation and Growth

Nucleation of a new phase occurs when a phase in an alloy of composition $X_\circ$ is unstable with respect a composition that is *not near* $X_\circ$.

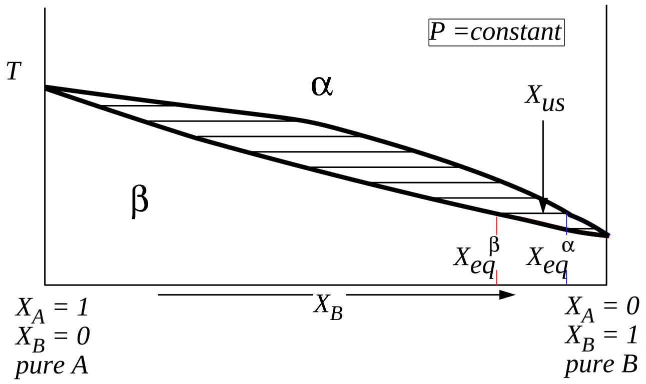

Figure 32-13: Example of a phase diagram that might require nucleation and growth for a phase transformation to occur. Suppose that an β-phase at composition $X_\circ$ is quickly cooled into the two-phase (α-β) region and then the transformation to the equilibrium phases and compositions is allowed to occur.

The transformation will require nucleation of an α-phase at a composition that, when combined with the molar free energy of the resultant α-phase, gives a mixture with a molar Gibbs free energy that is less than the value of $\overline{G^{\beta}}(X_\circ)$

In other words, $\partial^2\overline{G}/\partial X^2 > 0$ at $X = X_\circ$, but there is some X^{nuc} for which $\overline{G^{\text{mixture}}}(\langle X_\circ\rangle) - \overline{G}(X_\circ) = \Delta\overline{G}^{\text{nuc}} < 0$. The negative $\Delta\overline{G}^{\text{nuc}}$ is the driving force for the creation of a new phase.

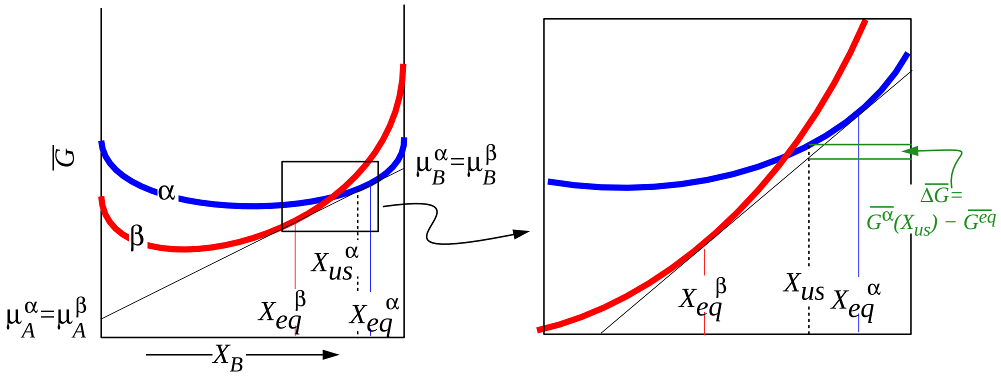

Figure 32-14: Illustration of the driving force for nucleation derived from the molar Gibbs free energies of solution for the case where the nucleated α-phase appears at its equilibrium composition X_{eq}^α at the expense of enriching the B-composition of the β-phase to its equilibrium concentration X_{eq}^β. $\Delta\overline{G^{\text{nuc}}}$ is the (negative) distance between the β-phase solution free energy curve and the common tangent. $\Delta\mu_A$ is the difference of the two tangents, evaluated at the pure A axis. Similarly, $\Delta\mu_B$ is the difference extrapolated to the pure B axis. Because $\Delta\mu_A = \mu_A^\alpha - \mu_A^{\text{unstable}}(X_\circ)$ is negative, there is a driving force for the A-component to diffuse towards a nucleating α phase from the parent unstable phase.

Notice that the driving force for the phase transformation goes away as the unstable composition $X_\circ$ approaches the limiting compositions on the tie-line.

The driving force for nucleation is important because it has to be utilized to overcome the additional energy associated with the interface between the α and the β phase. This is the interfacial energy.

The surface (or interfacial) tension is the amount of energy that is required to produce interface per unit area interface. Let the interfacial tension between the α and the β phase be $\gamma^{\alpha\beta}$ and suppose that when the α-phase nucleates, that it forms a little sphere of radius R:

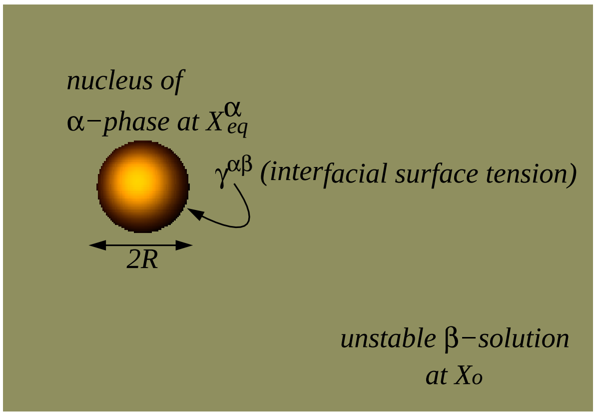

Figure 32-15: Illustration of the nucleation process.

The *total (extensive)* extra energy required for the phase transformation is:

$$\Delta G^{surface} = \gamma^{\alpha\beta}\text{surface area of nucleus} = 4\pi\gamma^{\alpha\beta}R^2 \tag{32-18}$$

Therefore the total free energy required to create a nucleus is given by

$$\Delta G^{nucleus} = 4\pi\gamma^{\alpha\beta}R^2 - \frac{4\pi}{3}|\Delta\overline{G^{nuc}}|\overline{V^{\alpha}}R^3 \tag{32-19}$$

where $|\Delta\overline{G^{nuc}}|$ is the (magnitude) of the molar driving force to create the nucleating α-phase and $\overline{V^{\alpha}}$ is its molar volume.

Therefore the total energy has contributions from two parts:

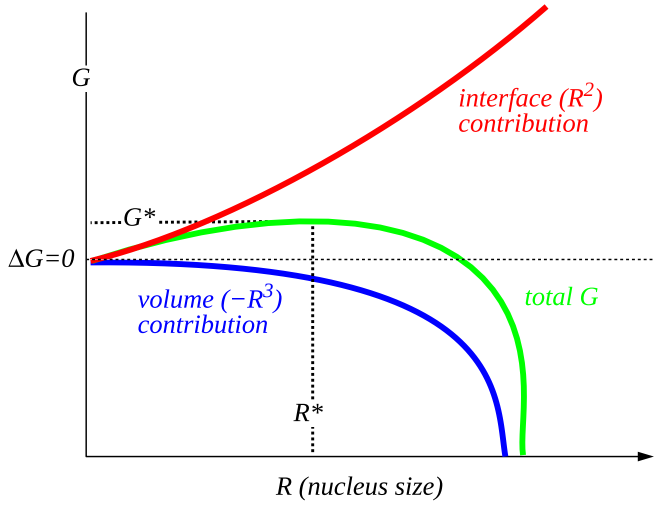

Figure 32-16: Total (spherical) nucleation energy as a function of nucleus size. The interfacial contribution opposes nucleation while the volumetric driving force propels nucleation. A small sizes, the interfacial term dominates and nucleation is prevented. At larger sizes, the volumetric term dominates.

If a nucleus can attain a size that exceeds the maximum, G^* of the curve in Fig. 32-16, then it can increase its size while continuously decreasing its free energy—-therefore any nucleus with size R^* or larger will grow continously.

To calculate this critical size, take the derivative of Eq. 32-19 and set it equal to zero and solve for R:

$$R^* = \frac{2\gamma^{\alpha\beta}}{|\Delta\overline{G^{nuc}}|} \tag{32-20}$$

and substituting this radius into the expression for the nucleation energy gives the nucleation barrier energy:

$$G^* = \frac{16\pi(\gamma^{\alpha\beta})^3}{3(\Delta\overline{G^{nuc}})^2} \tag{32-21}$$

This expression illustrates that nucleation must occur at a critical size and that the energy barrier to nucleation can be reduced by a decrease in the interfacial tension or by an increase in the volumetric driving force.[33] The time required for the phase transition to occur is related to the time required for a critical composition fluctuation to occur that will produce a critical nucleus of size R^*—-and that time increases exponentially with the barrier G^*.

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[33] By contrast, spinodal decomposition occurs without a nucleation barrier—it is a "barrierless" phase transformation.