Phase Transformations: Nucleation Theory

Today's topics:

- **Phase transformations: general context**
- **Continuous vs. discontinuous *transformations***
- **Nucleation**

  •**Interplay between surface and volumetric energy terms**

  •**Effect of coherency strain energy on nucleation in solids**

  •**Heterogeneous nucleation at surfaces and grain boundaries**

Transformations: General Aspects

■ **Transformations occur in systems that are not in equilibrium, e.g., precipitation can result from cooling a single phase to a temperature where it is supersaturated.**

$1 \longrightarrow 2:$

$1 \longrightarrow 3:$
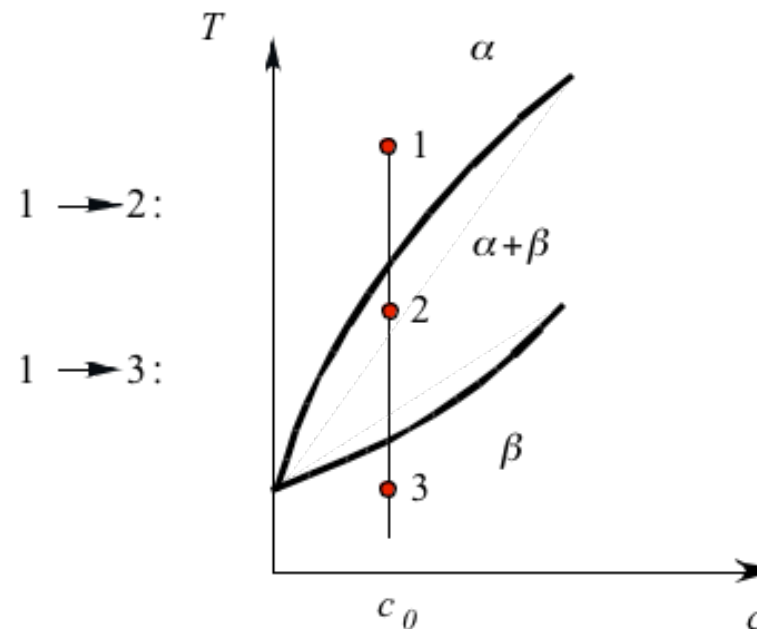
Transformations: General Aspects, cont'd

- **Systems away from equilibrium behave in fundamentally different ways, depending on whether they are in a *unstable* or in an *metastable* state.**

  Consider binary solution, initially homogeneous, that undergoes an infinitesimal composition variation such that half the solution increases *X* by ΔX and half decreases by ΔX

  **At *X*, the homogeneous solution is *metastable*;
  At Y, the homogeneous solution is *unstable***
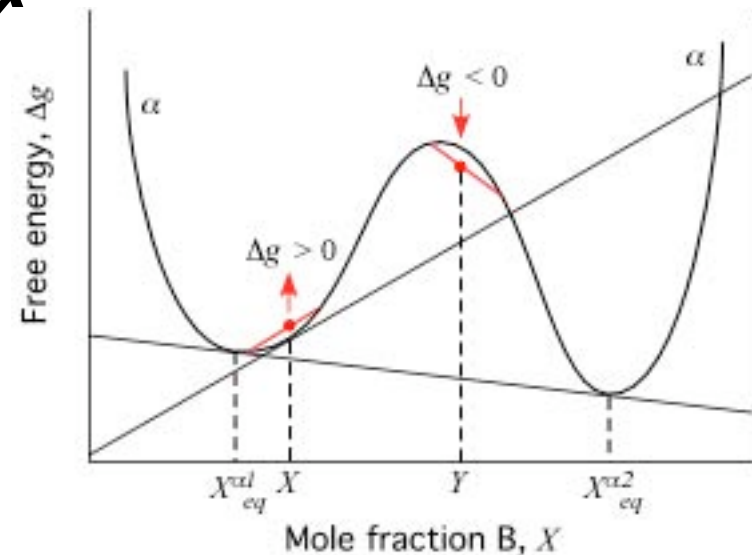
Transformations: General Aspects, cont'd

- **Nucleation occurs in metastable systems and it involves the energetics and kinetics of the formation of a stable cluster that, once formed, can grow continuously to macroscopic size.**

- **The construction shown gives the *driving force* for nucleation of β phase from a super-saturated solution at X^α ("tangent-to-curve" con-struction.)**
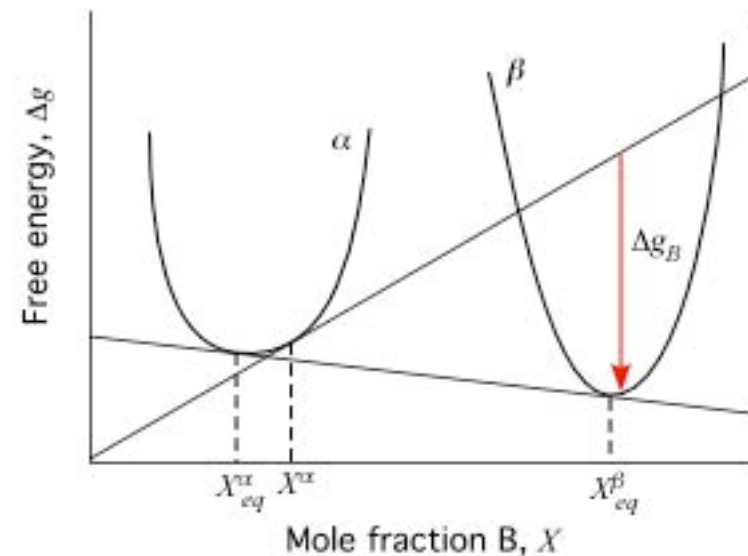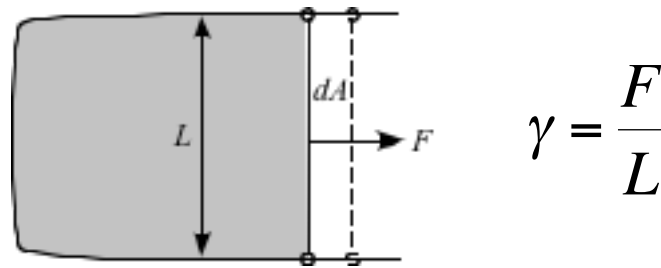
Transformations: General Aspects, cont'd

- **The extra free energy associated with the nucleus/matrix interface serves as a *barrier* to nucleation.**

- **The *excess free energy per unit area*, γ, is defined as the work to create a unit area of interface:**
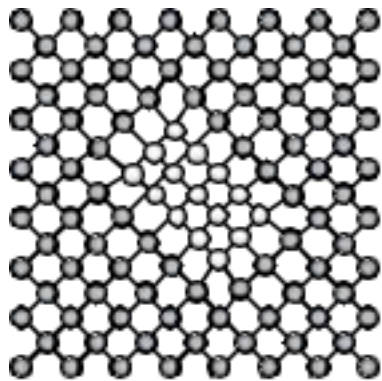
$$\left(\frac{\partial E}{\partial A}\right)_{S,V,N_i} = \gamma$$

- **In fluid systems, γ is numerically equal to the force per unit length acting along the perimeter of the interface, in the plane of the interface**
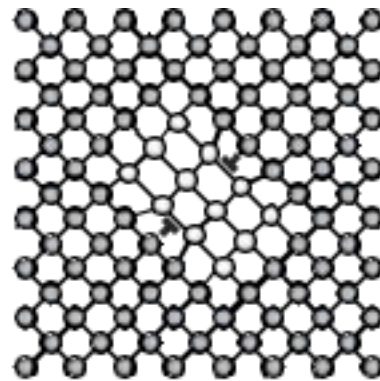

$$\gamma = \frac{F}{L}$$

Transformations: General Aspects, cont'd

- **In crystalline solids, structure of the nucleus/matrix interface plays a role in determining its energy.**
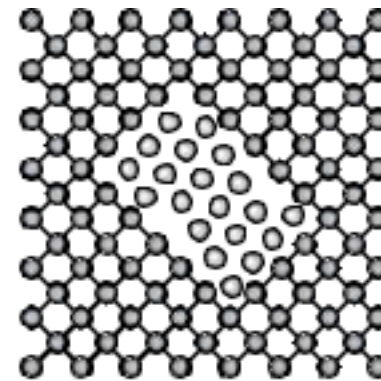
Coherent

~50 mJ/m^2

Semicoherent

~250 mJ/m^2

Incoherent

~500 mJ/m^2

Because of the low value of γ, new phases often start out as coherent at the nucleation stage.

Transformations: General Aspects, cont'd

- **In crystalline solids, the molar volumes of the nucleus and matrix phases can differ, and this may arise in *elastic strain energy* that also acts to impede nucleation.**

- **The elastic strain energy is hard to model. It depends on the transformation strain (shape change), the nucleus shape, elastic constants of the nucleus and matrix, etc.**
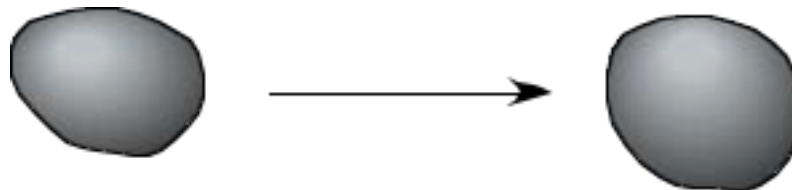
Nucleation: critical size and free energy

- **The free energy change of forming a nucleus of volume *V* and surface area *A* is**

$$\Delta G = \left(\Delta g_B + \Delta g_\varepsilon\right)V + \gamma A$$
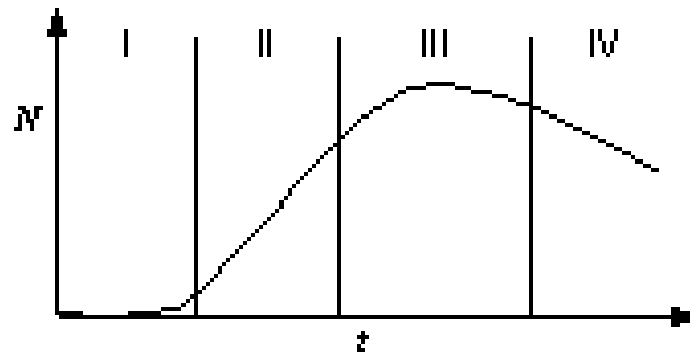
- **For a spherical nucleus in the absence of strain energy**

$$\Delta G = \left(\Delta g_B\right)\frac{4}{3}\pi r^3 + \gamma 4\pi r^2$$

$$\frac{\partial \Delta G}{\partial r} = 0 \implies r_c = -\frac{2\gamma}{\Delta g_B} \quad \text{and} \quad \Delta G_c = \frac{16\pi\gamma^3}{3\left(\Delta g_B\right)^2}$$

Nucleation: kinetics

- **Number of particles vs. time for a precipitation process typically looks like**

Region I is called the *transient nucleation* regime
Region II is the *steady-state nucleation* regime
Region III shows decreased nucleation at lower Δf_B
Revion IV is the *coarsening* regime

Nucleation: kinetics

- **In the *steady-state nucleation* regime, the steady-state nucleation rate J is the number of nuclei forming per unit volume per second**

$$J = Z\beta_c N \exp\left(-\frac{\Delta G_c}{kT}\right)$$

Z **is the Zeldovich non-equilibrium factor, ~ 0.1**
β_c **is a transport coeff. to bring atoms to nucleus**
N **is the number of sites available for nucleation**

- ΔG_c **plays a critical role in determining the nucleation rate**

Nucleation: kinetics

■ ΔG_c **plays a critical role in determining the nucleation rate**

$$J = Z\beta_c N \exp\left(-\frac{\Delta G_c}{kT}\right)$$

Taking reasonable values for the parameters in this relation, and making an educated guess about what the minimum detectable nucleation rate would be, gives a useful criterion for when nucleation by a particular mechanism is _possible:_
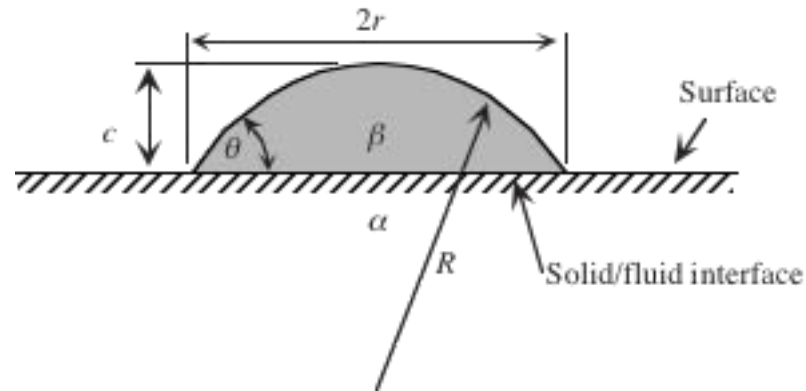
$$\Delta G_c \leq \sim 76kT$$

If this condition is not met, nucleation will take so long as to be effectively unobservable.

Homogeneous vs. heterogeneous nucleation

- **Homogeneous nucleation can occur anywhere in a system; if there are N atoms or molecules, the number of sites available is N.**

- **Special sites in the material such as surfaces, internal interfaces, dislocations, etc. can act to "catalyze" nucleation by effectively lowering ΔG_c.**

- **Although ΔG_c is smaller for heterogeneous nucleation, the number of heterogeneous sites available it is small compared to the total number of sites in the material that could be sites for homogeneous nucleation. Thus, homogeneous and heterogeneous nucleation compete with each other.**
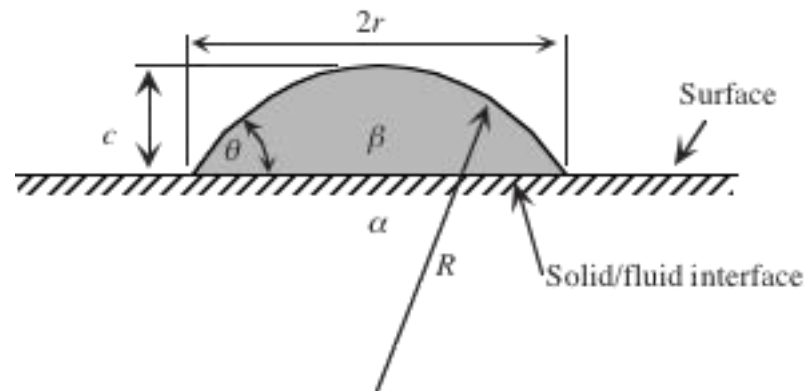
Heterogeneous nucleation at surfaces

$$V = \frac{\pi R^3}{3}\left(2 - 3\cos\theta + \cos^3\theta\right)$$

$$A = 2\pi R^2\left(1 - \cos\theta\right)$$

$$\Delta G^B = \left(\frac{4\pi R^3}{3}\Delta g_B + 4\pi R^2\gamma\right)\frac{2 - 3\cos\theta + \cos^3\theta}{4}$$

Heterogeneous nucleation at surfaces, cont'd

$$\Delta G_c = \left(\frac{16\pi\gamma^3}{3\Delta g_B{}^2}\right)\frac{2-3\cos\theta+\cos^3\theta}{4} = \Delta G_c{}^{\text{homog}}\left(\frac{2-3\cos\theta+\cos^3\theta}{4}\right)$$

- **Effects of contact angle θ; limiting values of 0 and π**