

# Nucleation and Growth

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- **Goal**  
Understand the basic thermodynamics behind the nucleation and growth processes
- **References**  
Handout  
Ch. 8, Intro. to Ceramics by Kingery, Bowen and Uhlmann  
Most books on glasses and glass-ceramics
- **Homework**  
None

# Phase Transformations

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- **Considered as a transformation of a homogeneous solution to a mixture of two phases**
- **For a stable solution,  $\Delta G_{\text{mix}}$  is less than zero. In other words, the solution is more stable than the individual components**
- **$\Delta G_{\text{mix}}$  is composed of entropic ( $-T\Delta S_{\text{mix}}$ ) and enthalpic ( $\Delta H_{\text{mix}}$ ) parts**
- **Consider**
  1.  **$\Delta H_{\text{mix}}$  less than zero: stable solution**
  2.  **$\Delta H_{\text{mix}} = \text{zero}$  (ideal solution), stable solution due to entropic**
  3.  **$\Delta H_{\text{mix}}$  slightly greater than zero: stable solution entropy dominates**
  4.  **$\Delta H_{\text{mix}} \gg 0$ : enthalpy dominates, phase separation occurs**
- **Note: in all cases as T increases, entropy becomes more important, so at very high temperatures, solutions are usually favored**

# Phase separation

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- If  $\Delta H_{\text{mix}}$  is greater than zero, the overall  $\Delta G_{\text{mix}}$  can be greater than zero meaning that phase separation is favored
- As T increases, homogeneous solution is favored
- $T_c$ , the consolute temperature is the point above which solution is favored
- Behavior described by a series of G vs. composition curves at different temperatures  
    Inflection points and minima plotted on T vs. comp. Diagram
- Spinodals from inflection points

# Spinodal Decomposition

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- **A continuous phase transformation**  
Initially, small composition changes that are wide-ranging  
Give interpenetrating microstructure (2 continuous phases)
- **No thermodynamic barrier to phase separation**  
One phase separates into two  
Infinitesimal composition changes lower the system free energy
- **Very important in glass and liquids**  
Vycor  
Liquid-liquid phase separation

# Nucleation and Growth

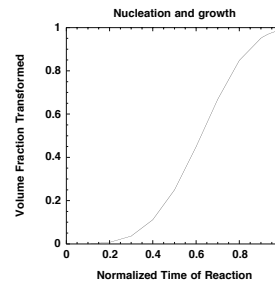
- Important for:  
Phase transitions, precipitation, crystallization of glasses  
Many other phenomena

- Nucleation has thermodynamic barrier

$$\frac{V^\beta}{V} = \frac{\pi}{3} I_v u^3 t^4$$

- Initially, large compositional change  
Small in size

- Volume transformations  
 $\alpha$  to  $\beta$  phase transformation  
Avrami equation  
 $V^\beta$  is the volume of second phase  
 $V$  is system volume  
 $I_v$  is the nucleation rate  
 $u$  is the growth rate  
 $t$  is time  
Sigmoidal transformation curves



- Infinitesimal changes raise system free energy

# Volume Energy

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- $\Delta G_v$  is  $\Delta G_{\text{rxn}}$  (energy/volume) times the new phase volume
- Spherical clusters have the minimum surface area/volume ratio
- So: the volume term can be:

$$\text{(volume)}\Delta G_v \text{ or}$$
$$\frac{4}{3}\pi r^3\Delta G_v$$

# Surface Energy

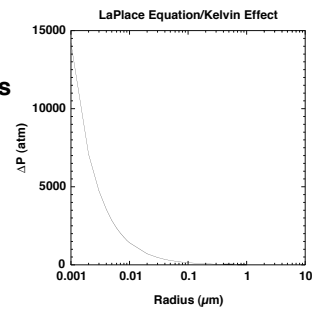
- The LaPlace equation shows the importance of surface energy

$$\Delta P = \frac{2\gamma}{r}$$

Where:  $\Delta P$  is the pressure drop across a curved surface  
 $\gamma$  is the surface energy  
 $r$  is particle radius

- Surface energy is important for small particles
- Nuclei are on the order of 100 molecules
- More generally, surface energy is given by:

$$\gamma = \left( \frac{\partial G}{\partial A} \right)_{T,P,\text{composition}}$$



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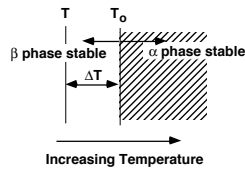
Where:  $A$  is the surface area of the particle, bubble, etc.

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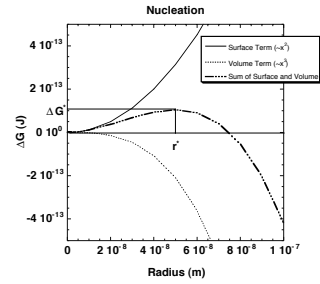
# Nucleation

- Consider the nucleation of a new phase at a temperature  $T$   
The transition temperature ( $T$ ) is below that predicted by thermodynamics when surface or volume are not considered
- We can estimate the free energy change as a function of the radius of the nuclei from the volume and surface terms
- When  $r$  is small, surface dominates
- When  $r$  is large, volume dominates
- $r^*$  is the inflection point

$$\Delta T = T_0 - T$$



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# Nucleation

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- $r^*$  is the critical size nucleus and inflection point on the curve

$$\text{At } r^*: \quad \frac{\partial(\Delta G_r)}{\partial r} = 0$$

- We can use this to calculate  $r^*$  and  $\Delta G_r^*$

$$r^* = -\frac{2\gamma}{\Delta G_v} \quad \Delta G_r^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$$

# Critical Nuclei

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- The number of molecules in the critical nucleus,  $n^*$ , can be calculated by equating the volume of the critical nucleus,  $\frac{4}{3}\pi(r^*)^3$ , with the volume of each molecule,  $V$ , times the number of molecules per nucleus

$$\frac{4}{3}\pi(r^*)^3 = n^* V$$

- Substituting the previous equations and solving gives

$$n^* = -\frac{32\pi\gamma^3}{3V(\Delta G_v)^3}$$

# Nucleus Formation

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- The number of nuclei can be calculated using statistical entropy

$$\Delta G_n = N_r \Delta G_r + kT \left[ \left( \frac{N_r}{N + N_r} \right) \ln \left( \frac{N_r}{N + N_r} \right) + \left( \frac{N}{N + N_r} \right) \ln \left( \frac{N}{N + N_r} \right) \right]$$

**Where:**  $\Delta G_n$  is the free energy for cluster formation  
 $N_r$  is the number of clusters of radius  $r$  per unit volume  
 $N$  is the number of molecules per unit volume

- At equilibrium,  $N_r \ll N$  so the previous equation simplifies to:

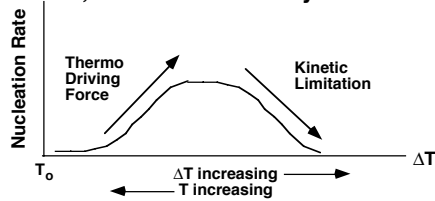
$$N_{r^*} = N \exp \left( - \frac{\Delta G^*}{kT} \right)$$

# Nucleation Rate

- The nucleation rate,  $I$ , is then the product of a thermodynamic barrier described by  $N_s$  and a kinetic barrier given by the rate of atomic attachment

$$I = N \exp\left(-\frac{\Delta G^*}{kT}\right) N_s \frac{kT}{h} \exp\left(-\frac{\Delta G_m}{kT}\right)$$

- As the degree of undercooling increases, the thermodynamic driving force increases, but atomic mobility decreases



$$I = N_s \frac{kT}{h} \exp\left(-\frac{\Delta G_m}{kT}\right) N \exp\left(-\frac{16\pi\gamma^3 T_0^2}{3(\Delta T)^2 (\Delta H_{rxn})^2 kT}\right)$$

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# Heterogeneous Nucleation

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- In many cases (some argue all cases), nucleation occurs at a surface, interface, impurity, or other heterogeneities in the system
- The energy required for nucleation is reduced by a factor related to the contact angle of the nucleus on the foreign surface

$$\Delta G_{\text{het}}^* = \Delta G_{\text{hom o}}^* f(\theta)$$
$$f(\theta) = \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4}$$

# Growth

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- Compared to nucleation, growth is relatively simple  
Assume that stable nuclei exist prior to growth  
Add molecules to a stable cluster  
Driven by free energy decrease of phase change  
Kinetically limited

$$u = va_0 \left[ 1 - \exp\left(-\frac{\Delta G_m}{kT}\right) \right]$$

Where:  $u$  = growth rate per unit area of interface

$a_0$  = distance across the  $\alpha$ - $\beta$  interface ( $\sim 1$  atomic dia.)

$\Delta G_m$  = activation energy for mobility or diffusion

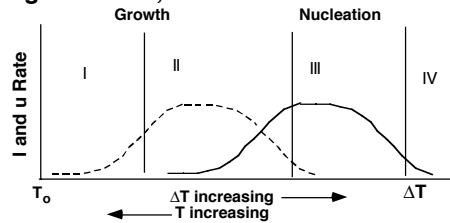
$v$  = frequency factor

$$v = \frac{kT}{3\pi a_0^3 \eta}$$

Where:  $\eta$  is atomic mobility of viscosity

# Summary

- The thermodynamic driving force for both nucleation and growth increases as undercooling increases, but both become limited by atomic mobility



- As we cool from the reaction temperature  $T_0$  we find 4 regions:
  - Region I,  $\alpha$  is metastable, no  $\beta$  grows since no nuclei have formed
  - Region II, mixed nucleation and growth
  - Region III, nucleation only
  - Region IV, no nucleation or growth due to atomic mobility
- Implications for tailoring microstructure