

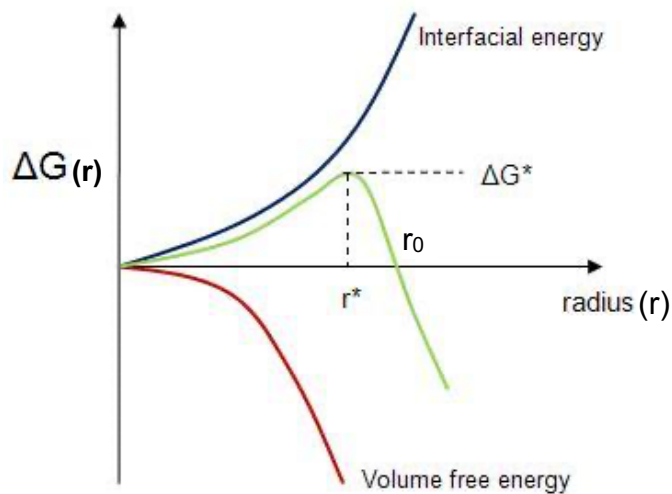
## Lecture 11: Homogeneous Nucleation: solid-solid phase transformation

### Today's topics

- Homogeneous nucleation for solid-solid phase transformation, and the major difference compared to the liquid-solid phase transformation: the role played by the strain energy due to the deformation caused by the phase transformation.
- Strain energy --- the factor determining the hysteresis in phase transformation, i.e., supercooling (under) or superheating (above) the equilibrium temperature.

### **Briefly in last Lecture 10:**

*For a particle formation, the free energy change  $\Delta G(r)$  is balanced by the two 'competitive' factors, the volume free energy and interfacial energy due to formation of solid phase, just as depicted in the diagram below.*



The nucleation barrier,

$$\Delta G^* = \Delta G(r^*) = \frac{16\pi\gamma^3}{3\Delta G_V^2}; \quad r^* = -\frac{2\gamma}{\Delta G_V}$$

### Today's lecture:

$\Delta G_V$  can be expressed as :

$$\Delta G_V = \frac{1}{V_M}(\mu_s^0 - \mu_l^0) = \frac{1}{V_M}(G_s^0 - G_l^0) = \frac{1}{V_M}[H_s^0 - TS_s^0 - H_l^0 + TS_l^0]$$

$$= \frac{1}{V_M} [T(S_l^0 - S_s^0) - (H_l^0 - H_s^0)]$$

At  $T=T_M$ ,  $\mu_l^0(T_M) = \mu_s^0(T_M)$ , or  $G_l^0(T_M) = G_s^0(T_M)$  due to the solid-liquid equilibrium, then

$H_l^0 - T_M S_l^0 = H_s^0 - T_M S_s^0 \rightarrow H_l^0 - H_s^0 = T_M (S_l^0 - S_s^0)$ , replace this into the Eq of  $\Delta G_V$ , we have

$$\begin{aligned} \Delta G_V &= \frac{1}{V_M} [T(S_l^0 - S_s^0) - T_M (S_l^0 - S_s^0)] \\ &= \frac{1}{V_M} (S_l^0 - S_s^0)(T - T_M) \end{aligned}$$

Lets define  $\Delta S_V = \frac{S_s^0 - S_l^0}{V_M}$ , then,  $\Delta G_V = -\Delta S_V \Delta T$

Since  $S_l^0 > S_s^0$ , thus  $\Delta S_V < 0$ , and since  $\Delta T = T - T_M < 0$ , we have  $\Delta G_V = -\Delta S_V \Delta T < 0$

Also by replacing  $\Delta G_V$  into the equation of  $\Delta G^*$ , we have

$$\Delta G^* = 16\pi\gamma^3/3(\Delta S_V)^2(\Delta T)^2$$

As  $T \rightarrow T_M$ ,  $\Delta T \rightarrow 0$ , then  $\Delta G^* \rightarrow \infty$ , **barrier for nucleation is infinite at  $T_M$ .**

*This implies that supercooling is needed for Homogeneous nucleation.* For example, a liquid nickel can be supercooled by 250K below  $T_M$  (1453 °C) without solidification, or pure water can be supercooled to as low as -42 °C without being frozen into ice.

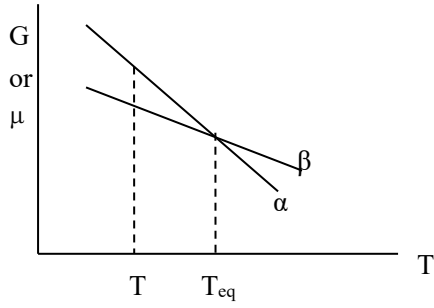
### **A special case: Homogeneous nucleation in a solid-solid phase transformation**

In a solid-solid transformation, a small change in specific volume that occurs must be accommodated elastically, leading to **strain energy effect**. Such a strain energy change must be included, together with the **volume free energy and interfacial energy** changes (as described for the liquid-to-solid transformation), into the free energy change of a solid-solid transformation,

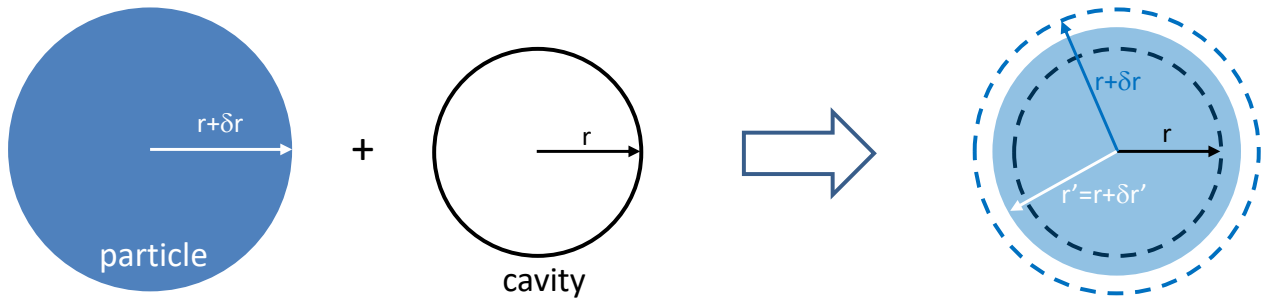
$$\Delta G(r) = \frac{4\pi}{3} r^3 \Delta G_V + 4\pi r^2 \gamma + \text{strain energy}$$

Now lets derive the strain energy

Consider  $\alpha \rightarrow \beta$  solid-solid transformation as depicted below



Assuming  $V_M^\beta > V_M^\alpha$ , when a  $\beta$  particle of radius  $r$  forms in  $\alpha$  matrix, both particle and matrix must deform elastically to accommodate the phase transformation. The formation of such coherent interface raises the free energy of the system on accounted of the elastic strain fields that arise. Somehow, we can consider such a misfit as fitting a  $\beta$  particle of radius  $r + \delta r$  into a cavity of radius  $r$  in  $\alpha$ , as depicted below,



With the mutual deformation of the two phases, the net radial strain:  $E = \frac{\delta r}{r'} \cong \frac{\delta r}{r}$

The strain energy per volume as defined as  $C'E^2 > 0$ , where  $C'$  is the elastic constant of  $\alpha$  and  $\beta$  (a coherent parameter of both the two phases) for nucleation of  $\beta$  in  $\alpha$  (i.e., transformation  $\alpha \rightarrow \beta$ ).

Then we have the net change of Gibbs free energy as expressed as:

$$\Delta G(r) = \frac{4\pi}{3} r^3 \Delta G_V + 4\pi r^2 \gamma + \frac{4\pi}{3} r^3 C' E^2$$

$$\text{At } r^*, \left. \frac{d\Delta G(r)}{dr} \right|_{r^*} = 0, \quad r^* = -\frac{2\gamma}{(\Delta G_V + C'E^2)} = -\frac{2\gamma}{(-\Delta S_V \Delta T + C'E^2)}$$

Note, for  $T < T_{eq}$ ,  $\Delta G_V$  or  $-\Delta S_V \Delta T < 0$ , but  $C'E^2 > 0$ .

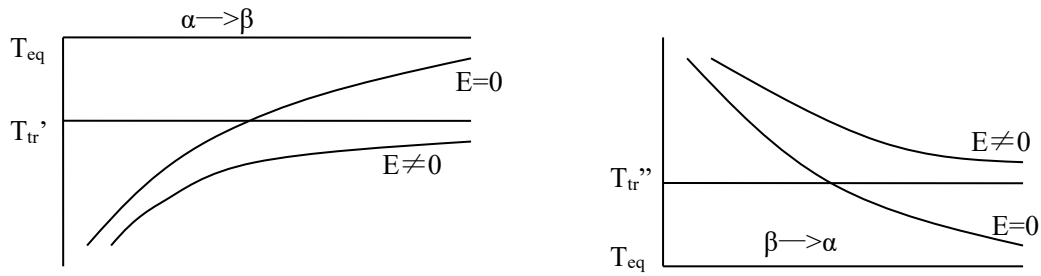
So, at a  $T$  just below  $T_{eq}$  ( $\Delta T$  too small) it is possible  $-\Delta S_V \Delta T + C'E^2 > 0$ , and then  $r^* < 0$  (**unphysical meaning!**), implying that nucleation can't occur. In other words, only when  $T \ll T_{eq}$ , i.e., sufficiently undercooled, so that

$$-\Delta S_V \Delta T + C'E^2 \leq 0; \text{ or}$$

$$-\frac{(S_\beta - S_\alpha)}{V} (T - T_{eq}) + C'E^2 \leq 0; \quad -\Delta S_V (T - T_{eq}) + C'E^2 \leq 0$$

$$T - T_{eq} \leq \frac{C'E^2}{\Delta S_V}; \quad T \leq T_{eq} + \frac{C'E^2}{\Delta S_V} \quad (\text{note: } \Delta S_V < 0)$$

Or temperature of phase transformation defined as  $T'_{tr} = T_{eq} - \frac{C'E^2}{|\Delta S_V|}$



Consider the reverse process,  $\beta \rightarrow \alpha$

The sample was cooled below  $T'_{tr}$  and is now fully transformed back into  $\alpha$ . Upon heating above  $T_{eq}$ ,  $\alpha$  nucleate in  $\beta$ -matrix.

Now  $\Delta G_V = - \frac{(S_\alpha - S_\beta)}{V} (T - T_{eq}) < 0$ , as  $T_{eq} < T$ ,  $S_\alpha - S_\beta > 0$ .

The elastic energy  $\beta \rightarrow \alpha$  transformation is  $C''E^2$ , and  $\Delta S_V = \frac{S_\alpha - S_\beta}{V} > 0$

Similarly as discussed above for  $\alpha \rightarrow \beta$  transformation, for  $\beta \rightarrow \alpha$  transformation to occur, the system must be *superheated*, i.e.,  $T \gg T_{eq}$ , so that

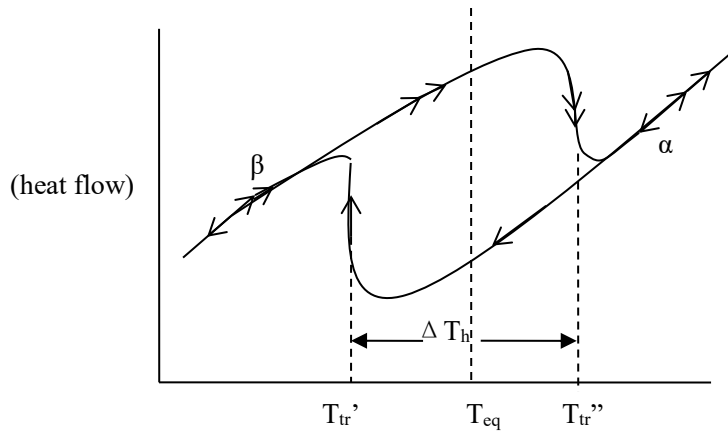
$-\Delta S_V \Delta T + C''E^2 \leq 0$ ; or  $-\Delta S_V (T - T_{eq}) + C''E^2 \leq 0$ , where  $C''$  is the elastic constant of  $\alpha$  and  $\beta$  (a coherent parameter of both the two phases) for nucleation of  $\alpha$  in  $\beta$  (i.e., transformation  $\beta \rightarrow \alpha$ ). For many cases,  $C'' \approx C'$

$$T - T_{eq} \geq \frac{C''E^2}{\Delta S_V}; \quad T \geq T_{eq} + \frac{C''E^2}{\Delta S_V} \quad (\text{note: } \Delta S_V > 0)$$

Or temperature of phase transformation defined as  $T_{tr}'' = T_{eq} + \frac{C''E^2}{\Delta S_V}$ ,  $T_{tr}'' = T_{eq} + \frac{C''E^2}{|\Delta S_V|} > T_{eq}$

This leads to a hysteresis in transformation cycle (diagram below):

$$\Delta T_h = \Delta T' + \Delta T'' = (T_{eq} - T'_{tr}) + (T_{tr}'' - T_{eq}) = T_{tr}'' - T'_{tr} = \frac{E^2}{|\Delta S_V|} (C' + C'')$$



### Summary of homogeneous nucleation in solid:

1. When the nucleation phase has a different volume or shape than the matrix it replaces, elastic energy ( $\Delta G_S$ ) must be considered as part of the volumetric contribution to nucleation, as described in the equation, 
$$\Delta G(r) = \frac{4\pi}{3} r^3 \Delta G_V + 4\pi r^2 \gamma + \frac{4\pi}{3} r^3 C' E^2 = \frac{4\pi}{3} r^3 (\Delta G_V + \Delta G_S) + 4\pi r^2 \gamma.$$
2. The interfacial contribution ( $4\pi r^2 \gamma$ ) to the nucleation barrier dominates at small nucleus sizes, and volumetric contributions ( $\frac{4\pi}{3} r^3 (\Delta G_V + \Delta G_S)$ ) dominate at large nucleus sizes. The competition between these two contributions can produce a complicated sequence of states for a developing phase, i.e., at small "r" the system may select a state that minimizes surface energy at the expense of elastic contribution, while at large "r", the interfacial structure can change with concomitant increases in interfacial energy whenever such a change leads to overall decrease in the free energy ( $\Delta G(r)$ ) through a decrease of the volumetric contribution. The sequence of states may include changes in interfacial structure that relax elastic energy or even phase changes in the nuclei if less stable phases have similar interfacial energies.
3. Typically for solid state nucleation, elastic energy contribution dominates at small particles sizes and the interfacial energy can be reduced significantly by adopting a *coherent* structure. As the particle grows, elastic energy can be reduced by the introduction of misfit dislocations into the interface. Such interfacial dislocations transform a coherent interface into a semi-coherent interface at the expense of increased interfacial energy.
4. In supersaturated crystalline solutions (matrix), the particles of the new phase initially formed are generally *coherent* with the matrix, due to their lowest interfacial energy compared to the semi-coherent or incoherent interfaces. Coherent inclusions have an associated *elastic strain energy that resists nucleation*. This elastic strain energy is not easy to express with simple algebraic expressions, except for ideal spherical particles (as we treated above in this lecture).

--- ref. Prof. Craig Carter and his book, Kinetics of Materials, 1<sup>st</sup> Ed., Wiley-Interscience, 2005.