

# Lecture 10: Homogeneous Nucleation

## Today's topics

- What is nucleation? What implied in real practice of materials processing, particularly phase transformation?
- General comparison between homogeneous and heterogeneous nucleation.
- Critical particle (or nucleus) size ( $r^*$ ) for a homogeneous nucleation from liquid (e.g., solidification of metals).
- How to derive and understand the critical size in terms of both thermodynamics and kinetics of nucleation.

## About Nucleation

- **Nucleation:** localized formation of a distinct [thermodynamic](#) phase.
- Nucleation can occur in a gas, liquid or solid phase. Some examples of phases that may form via nucleation include: 1) in gas: Creation of liquid [droplets](#) in saturated [vapor](#); 2) in liquid: formation of gaseous [bubbles](#), [crystals](#) (e.g., ice formation from water), or [glassy](#) regions; 3) in solid: Nucleation of crystalline, amorphous, and even vacancy clusters in solid materials. Such solid state nucleation is important, for example, to the semiconductor industry.
- Most nucleation processes are physical, rather than chemical.
- Nucleation normally occurs at *nucleation sites* on surfaces contacting the liquid or vapor. Suspended particles or minute bubbles also provide nucleation sites. This is called **heterogeneous nucleation (Lecture 12)**.
- Nucleation without preferential nucleation sites is **homogeneous nucleation (Lecture 10-11)**. Homogeneous nucleation occurs spontaneously and randomly, but it requires [superheating](#) or [supercooling](#) of the medium.
- Compared to the heterogeneous nucleation (which starts at *nucleation sites* on surfaces), **Homogeneous nucleation** occurs with much more difficulty in the interior of a uniform substance. The creation of a nucleus implies the formation of an interface at the boundaries of a new phase.
- Liquids cooled below the maximum heterogeneous nucleation temperature ([melting](#) temperature), but which are above the homogeneous nucleation temperature (pure substance [freezing](#) temperature) are called [supercooled](#).
- An example of supercooling: Pure [water freezes](#) at  $-42^\circ\text{C}$  rather than at its freezing temperature of  $0^\circ\text{C}$ . So, if cooled slowly below the freezing point, pure water may remain liquid (supercooled) as you see in this movie: <http://www.eng.utah.edu/~ljang/images/supercooled-water.avi>. The crystallization into ice may be facilitated by adding some nucleation "seeds": small ice particles, or simply by shaking --- enjoy the movie clip.

For a particle of radius  $r$  of a pure element (see Lecture 8, 9):

$$\Delta P = \frac{2\gamma}{r}, \quad \gamma \text{ — surface energy}$$

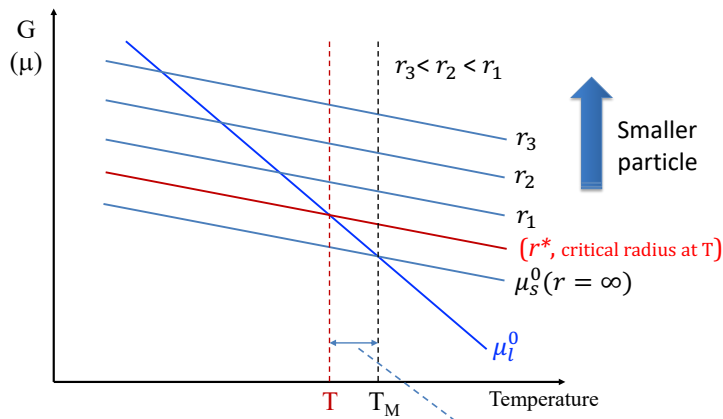
$$\mu(r) = \mu(\infty) + \frac{2\gamma V_M}{r} = \mu^0 + \frac{2\gamma V_M}{r}$$

Consider liquid metal cooled through its melting point,  $T_M$ , into the stability regime of solid phase. The process of solidification must occur by forming a small particle of solid phase,

$$\mu_s(r) = \mu_s(\infty) + \frac{2\gamma V_M}{r} = \mu_s^0 + \frac{2\gamma V_M}{r}$$

where  $\mu_s^0$  the chemical potential of the solid phase corresponding to a flat surface — bulk material. At  $T_M$ , solid (bulk) is in equilibrium with the liquid:  $\mu_s^0 = \mu_l^0$ , where  $\mu_l^0$  is the chemical potential of the liquid — molar Gibbs free energy.

For  $T < T_M$ ,  $\mu_s^0 < \mu_l^0$ , solidification should occur --- thermodynamically favorable for such bulk-phase solidification ( $r \rightarrow \infty$ ). However, for small particles (nucleus),  $\mu_s(r) > \mu_s^0$ ,  $\mu_s(r)$  may be no longer  $< \mu_l^0$ ; indeed, as shown in the diagram below, when  $r$  is very small, it is possible for  $\mu_s(r) > \mu_l^0$ . This implies that: even at a  $T < T_M$ , a very small particle of solid can still be thermodynamically unstable against the liquid phase --- *it might dissolve back to the liquid*.



Supercooling: for water, it is -42 °C below 0 °C; for nickel, it is about 250 °C below  $T_M$  1453 °C

As shown in the diagram, at a  $T < T_M$ , there is a critical size (radius,  $r^*$ ) for the nucleus (or particle): for particles larger than the  $r^*$ ,  $\mu_s(r) \leq \mu_l^0$ , continuous nucleation into larger particle and eventually transformed into a bulk phase of solid will becomes favorable; in comparison, for particles smaller than the  $r^*$ ,  $\mu_s(r) > \mu_l^0$ , continuous nucleation becomes unfavorable, and dissolving back to liquid becomes more favorable.

At  $T$ , particle of the critical size ( $r^*$ ) in equilibrium with the liquid,  $\mu_s(r^*) = \mu_l^0$ , then we have

$$\mu_s(r^*) = \mu_s^0 + \frac{2\gamma V_M}{r^*} = \mu_l^0$$

Once a critical size is achieved, if particle grows,  $\mu_s(r > r^*) < \mu_l^0$ , solidification can proceed (as pointed by the red arrow in the diagram).

then

$$r^* = -\frac{2\gamma V_M}{\mu_s^0 - \mu_l^0} = -\frac{2\gamma}{\left(\frac{\mu_s^0 - \mu_l^0}{V_M}\right)} = -\frac{2\gamma}{\Delta G_V}$$

$V_M$ : molar volume of the solid;

$\Delta G_V$  = Gibbs free energy change for solidification (per unit volume, neglecting the difference in molar volume of the solid and liquid) --- such assumption is based on the fact that at  $T_M$  liquid has a volume only 2-4% larger than the solid.

### An alternative way to derive $r^*$ :

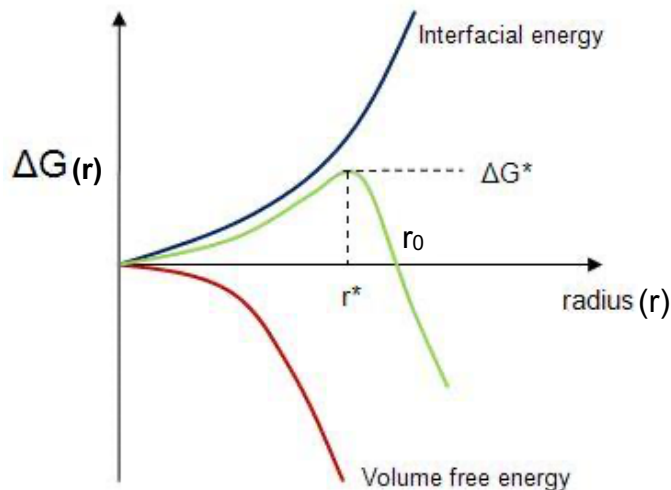
As a solid particle of radius  $r$  forms from the liquid, the change of Gibbs free energy is

$$\Delta G(r) = \frac{4\pi}{3} r^3 \left( \frac{\mu_s^0 - \mu_l^0}{V_M} \right) + 4\pi r^2 \gamma$$

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

--- 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, as depicted in the diagram below.

For  $T < T_M$ ,  $\mu_s^0 - \mu_l^0 < 0$ , hence  $\Delta G_V < 0$ . As  $r$  increases, initially for small  $r$ ,  $r^2 > r^3$ , so  $\Delta G(r) > 0$ ; for large  $r$ ,  $r^2 < r^3$ ,  $\Delta G(r) < 0$ . Thus,  $\Delta G(r)$  must go through a maximum as shown in the diagram below.



At the maximum,  $\left. \frac{d\Delta G(r)}{dr} \right|_{r^*} = 0 = 4\pi r^2 \Delta G_V + 8\pi r \gamma$

Then,  $r^* = -\frac{2\gamma}{\Delta G_V}$

Then,  $\Delta G^* = \Delta G(r^*) = \frac{4}{3} \pi r^{*3} \Delta G_V + 4\pi r^{*2} \gamma$

$$= \frac{4}{3} \pi \left( -\frac{8r^3}{\Delta G_V^3} \right) \Delta G_V + 4\pi \left( \frac{4\gamma^2}{\Delta G_V^2} \right) \gamma = \frac{16\pi\gamma^3}{3\Delta G_V^2}$$

$\Delta G^*$  is nucleation barrier for solidification. Beyond  $r^*$ ,  $\Delta G(r)$  decrease with increasing  $r$ , and at  $r_0$ ,  $\Delta G(r) = 0$

$$-\frac{4\pi}{3} r_0^3 \Delta G_V + 4\pi r_0^2 \gamma = 0$$

Then we have,  $r_0 = -\frac{3\gamma}{\Delta G_V}$

When a particle size grows to  $r_0$ , the nucleation barrier decreases to zero. However,  $\Delta G(r_0)$  is not a minimum, the nucleation is presumed to continue as the  $\Delta G(r)$  will become  $< 0$  (thermodynamically favorable) after passing  $r_0$ .

The nucleation depicted in the diagram above can be understood in 3 thermodynamic regimes depending on the size of particle ( $r$ ):

- 1) nucleation from the free molecules or atoms to form small particles (nucleus), e.g., several water molecules form clusters. As the particles grow,  $\Delta G(r)$  increases (mainly dominated by the rapid increase in surface energy), implying that the particle growth or the continuous nucleation in this regime is not thermodynamically favorable, i.e., most of the particles dissolve back to liquid phase. This is typically the case of homogeneous nucleation, like the supercooled water as you see in the online movie clip.
- 2) once some of the particles reach the size of  $r^*$  and pass the barrier of  $\Delta G(r^*)$ , further growth of particles will lead to decrease in  $\Delta G(r)$ , a tendency favorable for the continuous solidification, although  $\Delta G(r)$  in this regime before reaching the size of  $r_0$  is still  $> 0$  (not thermodynamically favorable). How many particles in this regime can pass over the barrier  $\Delta G(r^*)$  concerns the kinetics of nucleation, and will be addressed in the following lectures.
- 3) after passing  $r_0$ ,  $\Delta G(r)$  will become more negative, and the growth of particle will be highly favored and eventually lead to formation of bulk-phase solid ( $r \rightarrow \infty$ ).