

Lecture 12: Heterogeneous Nucleation: a surface catalyzed process

Today's topics

- What is heterogeneous nucleation? What implied in real practice of materials processing and phase transformation?
- Heterogeneous nucleation can be considered as a surface catalyzed or assisted nucleation process. The extent of how a surface can catalyze or facilitate the nucleation depends on the contact angle of the nucleus with respect to the substrate. The smaller the angle (or the stronger the wetting of the surface), the lower the free energy change, and the lower the nucleation barrier will be.
- Critical radius of the nucleus (r^*) for a heterogeneous nucleation is the same as that for a homogeneous nucleation, whereas the critical volume of the nucleus (like the droplet for liquid nucleated from gas/vapor phase) is usually smaller for heterogeneous nucleation than for homogeneous nucleation, due to the surface wetting (spreading).

About Heterogeneous Nucleation

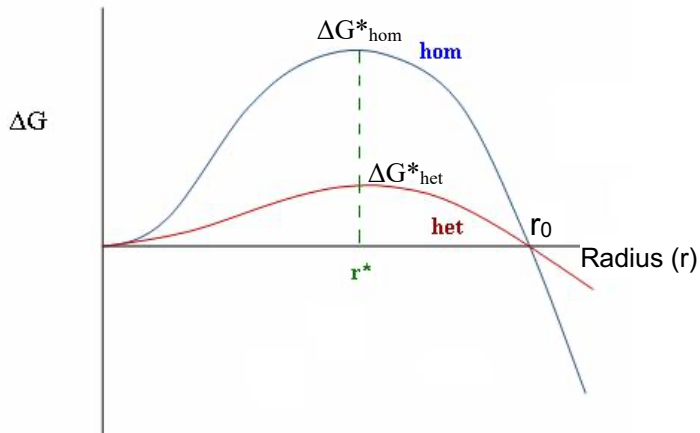
- **Heterogeneous nucleation** occurs much more often than homogeneous nucleation. Heterogeneous nucleation applies to the phase transformation between any two phases of gas, liquid, or solid, typically for example, condensation of gas/vapor, solidification from liquid, bubble formation from liquid, etc.
- Heterogeneous nucleation forms at preferential sites such as phase boundaries, surfaces (of container, bottles, etc.) or impurities like dust. At such preferential sites, the effective surface energy is lower, thus diminishes the free energy barrier and facilitating nucleation.
- Surfaces promote nucleation because of [wetting](#) – small contact angles (e.g., $< 90^\circ$) between phases facilitate particles to nucleate. The free energy needed for heterogeneous nucleation is equal to the product of homogeneous nucleation and a function of the contact angle (θ):

$$\Delta G_{heterogeneous} = \Delta G_{homogeneous} * f(\theta)$$

where

$$f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$

- The barrier energy needed for heterogeneous nucleation is reduced (see the plot below). The wetting angle determines the ease of nucleation by reducing the energy needed.



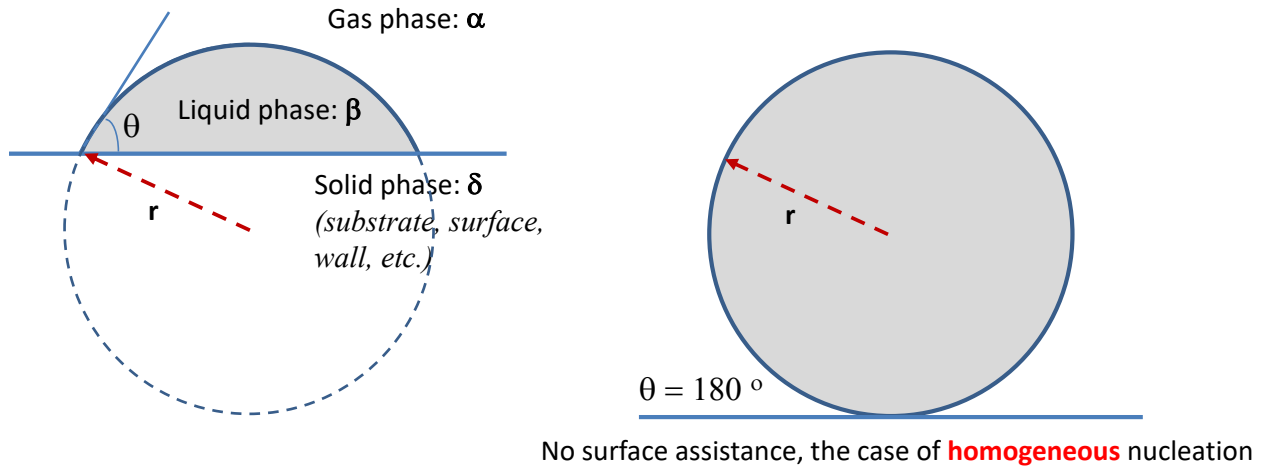
- Some examples of heterogeneous nucleation include: 1) Bubbles of carbon dioxide *nucleate* shortly on the inner surface of a container after it is gently opened (as the pressure is released). Since the surface is smooth and flat (specific surface area is small), bubble formation on such surface is usually slow as you often see in life. 2) putting a finger into the carbonated water usually facilitates the bubble formation as you see from the picture below, because finger surface (more rough compared to the glass or plastic substrate) provides much larger surface area. 3) putting a chalk (with even larger surface area due to the porous structure) leads to much faster formation (nucleation) of bubbles from the carbonated water just as you can see from the movie clip attached to this Lecture, <http://www.eng.utah.edu/~lzang/images/bubble.wmv> --- have fun!



Nucleation of carbon dioxide bubbles around a finger

A droplet of liquid on a flat solid surface takes the shape of a truncated sphere. The surface must be spherical since a liquid does not support a shear stress --- and γ is isotropic.

There are three different surface energies of interest:



$$\gamma_{\alpha\beta} = (\text{gas - liquid}), \quad \gamma_{\alpha\delta} = (\text{gas - solid}), \quad \gamma_{\beta\delta} = (\text{liquid - solid})$$

Consider a droplet of liquid on a flat surface with fixed volume (at equilibrium). The total surface energy of the system is a function of the shape of the droplet.

The diagram above shows two different shapes of the same size (radius), but of different surface area → leading to different Surface energy:

$$G_s = \gamma_{\alpha\beta} A_{\alpha\beta} + \gamma_{\alpha\delta} A_{\alpha\delta} + \gamma_{\beta\delta} A_{\beta\delta}$$

where $A_{\alpha\beta}$, $A_{\alpha\delta}$ and $A_{\beta\delta}$ are areas of $\alpha\beta$, $\alpha\delta$ and $\beta\delta$ interfaces, respectively.

Assume r be the radius of curvature of the droplet, then:

$$A_{\beta\delta} = \pi r^2 \sin^2\theta$$

$$A_{\alpha\delta} = A_0 - \pi r^2 \sin^2\theta; \quad A_0 \text{ is the area of } \alpha\delta \text{ interface without } \beta$$

$$A_{\alpha\beta} = \int_0^\theta (2\pi r \sin \varepsilon)(r d\varepsilon) = 2\pi r^2 (1 - \cos \theta)$$

$$\text{Thus, } G_s = G_s(r, \theta) = \gamma_{\alpha\beta} 2\pi r^2 (1 - \cos \theta) + \gamma_{\alpha\delta} (A_0 - \pi r^2 \sin^2\theta) + \gamma_{\beta\delta} \pi r^2 \sin^2\theta$$

At equilibrium,

$$dG_s = \left(\frac{\partial G_s}{\partial r}\right)_\theta dr + \left(\frac{\partial G_s}{\partial \theta}\right)_r d\theta = 0$$

then,

$$dG_s = \{4 \pi r \gamma_{\alpha\beta}(1-\cos\theta) + 2 \pi r (\gamma_{\beta\delta} - \gamma_{\alpha\delta}) \sin^2\theta\} dr + \{2 \pi r^2 \gamma_{\alpha\beta} \sin\theta + 2 \pi r^2 (\gamma_{\beta\delta} - \gamma_{\alpha\delta}) \sin\theta \cos\theta\} d\theta = 0 \quad (1)$$

Volume of β , V_β , can be obtained as,

$$V_\beta = \int_0^\theta (\pi r^2 \sin^2 \varepsilon)(rd\varepsilon \cdot \sin \varepsilon) = \pi r^3 \int_0^\theta \sin^3 \varepsilon d\varepsilon = \frac{\pi r^3}{3} [2 - 3 \cos \theta + \cos^3 \theta]$$

Since volume of β remains fixed at equilibrium,

$$dV_\beta = 0 = \left(\frac{\partial V_\beta}{\partial r}\right)_\theta dr + \left(\frac{\partial V_\beta}{\partial \theta}\right)_r d\theta$$

then, we have

$$dr = -\frac{r \sin \theta (1 + \cos \theta)}{(2 - \cos \theta - \cos^2 \theta)} d\theta \quad (2)$$

replacing (2) \rightarrow (1), then we have,

$$\cos\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}} \quad (3)$$

Now lets derive the heterogeneous nucleation energy and critical size:

Assume nucleus to be spherical with radius r , the free energy change for the nucleation is

$$\begin{aligned} \Delta G(r) &= V_\beta \Delta G_V + \gamma_{\alpha\beta} A_{\alpha\beta} + (\gamma_{\beta\delta} - \gamma_{\alpha\delta}) A_{\beta\delta} \quad (\text{two contributions: volumetric free energy + surface energy}) \\ &= \frac{\pi r^3}{3} [2 - 3 \cos \theta + \cos^3 \theta] \Delta G_V + \gamma_{\alpha\beta} 2\pi r^2 [1 - \cos \theta] + (\gamma_{\beta\delta} - \gamma_{\alpha\delta}) \pi r^2 \sin^2 \theta \end{aligned}$$

From Eq. (3), we have $(\gamma_{\beta\delta} - \gamma_{\alpha\delta}) = -\gamma_{\alpha\beta} \cos \theta$, replacing this into above equation, then we have

$$\begin{aligned} \Delta G(r) &= \frac{\pi r^3}{3} \Delta G_V [2 - 3 \cos \theta + \cos^3 \theta] + \gamma_{\alpha\beta} 2\pi r^2 [1 - \cos \theta] - \gamma_{\alpha\beta} \pi r^2 \cos \theta \sin^2 \theta \\ &= \left[\frac{4\pi}{3} r^3 \Delta G_V + 4\pi r^2 \gamma_{\alpha\beta} \right] \cdot \left[\frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \right] \quad (\text{note: } \sin^2 \theta = 1 - \cos^2 \theta) \end{aligned}$$

Note the first term in parenthesis is the $\Delta G(r)$ for homogenous nucleation.

Then we can re-write

$$\Delta G_{\text{het}}(r) = \Delta G_{\text{hom}}(r) \cdot f(\theta) \quad (4)$$

$$\text{where } f(\theta) = \frac{2 - 3 \cos \theta + \cos^3 \theta}{4}$$

$$0 \leq f(\theta) \leq 1.0$$

for $\theta=180^\circ$, $f(\theta) = 1 \rightarrow$ no wetting of the surface, and thus no catalysis by the surface --- falling into the case of homogeneous nucleation.

for $\theta=0^\circ$, $f(\theta) = 0 \rightarrow$ full wetting, fully catalyzed, no barrier for nucleation at surface.

The $\Delta G(r)$ must go through a maximum, where $\frac{d\Delta G(r)}{dr} = 0$, then,

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

Then we have the critical radius,

$$r^* = - \frac{2\gamma_{\alpha\beta}}{\Delta G_V}$$

It is important to note that the critical radius r^ remains unchanged for heterogeneous nucleation and homogeneous nucleation. However, the volume (V_β) can be significantly less for heterogeneous nucleation due to the wetting angle affecting the shape of the nucleus.*

$$V_\beta (\text{het}) = \frac{\pi r^3}{3} [2 - 3 \cos \theta + \cos^3 \theta] = \frac{4\pi r^3}{3} \left[\frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \right] = V_\beta (\text{hom}) \cdot f(\theta)$$

From Eq. (4), we also have

$$\begin{aligned} \Delta G_{\text{het}}^* &= \Delta G_{\text{het}}(r^*) = \Delta G_{\text{hom}}(r^*) \cdot f(\theta) = \Delta G_{\text{hom}}^* \cdot f(\theta) \\ &= \left[-\frac{4\pi}{3} r^{*3} \Delta G_V + 4\pi r^{*2} \gamma_{\alpha\beta} \right] \cdot f(\theta) = \frac{16\pi \gamma_{\alpha\beta}^3}{3\Delta G_V^2} \cdot f(\theta) \end{aligned}$$

--- nucleation barrier can be significantly lower for heterogeneous nucleation due to wetting angle affecting the shape of the nucleus.

Note: The above addressed nucleation is for gas-to-liquid nucleation. The similar theoretical treatment is also applied to the liquid-to-solid nucleation.