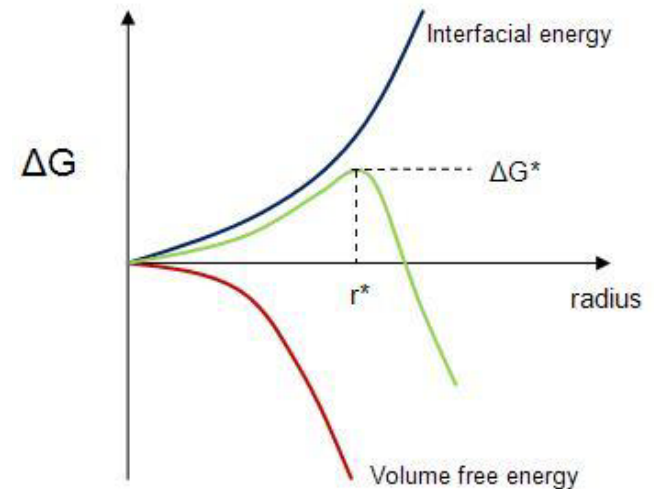


Nucleation

- **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.

Homogeneous Nucleation

- 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 said to be supercooled. This is useful for making amorphous solids and other metastable structures, but can delay the progress of industrial chemical processes or produce undesirable effects in the context of casting.
- Supercooling brings about supersaturation, the driving force for nucleation. Supersaturation occurs when the pressure in the newly formed solid is less than the vapor pressure, and brings about a change in free energy per unit volume, G_v , between the liquid and newly created solid phase. This change in free energy is balanced by the energy gain of creating a new volume, and the energy cost due to creation of a new interface. When the overall change in free energy, ΔG is negative, nucleation is favored. (see the plot on right)
- Some energy is consumed to form an interface, based on the surface energy of each phase. If a hypothetical nucleus is too small (known as an unstable nucleus), the energy that would be released by forming its volume is not enough to create its surface, and nucleation does not proceed. The critical nucleus size can be denoted by its radius, and it is when $r = r^*$ (or r critical) that the nucleation proceeds.
- An example of supercooling: Pure water freezes at -42°C rather than at its freezing temperature of 0°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 slip.



Heterogeneous Nucleation

- **Heterogeneous nucleation** occurs much more often than homogeneous nucleation.
- Heterogeneous nucleation forms at preferential sites such as phase boundaries or impurities like dust and requires less energy than homogeneous nucleation. At such preferential sites, the effective surface energy is lower, thus diminishes the free energy barrier and facilitating nucleation. (see the plot at right)
- Surfaces promote nucleation because of wetting – contact angles greater than zero 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 :

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

where

$$f(\theta) = \frac{1}{2} + \frac{3}{4}\cos\theta - \frac{1}{4}\cos^3\theta$$

- The barrier energy needed for heterogeneous nucleation is reduced (see the plot), and less supercooling is needed. The wetting angle determines the ease of nucleation by reducing the energy needed. It is important to note that the critical radius remains unchanged. *However, the volume can be significantly less for heterogeneous nucleation due to the wetting angle affecting the shape of the cluster.*

