*Phase transformation heat treatment

Nucleation & Growth

- All phase transformations can be described as ***nucleation & growth* processes.**
- The crucial point is to understand it as a balance between the free energy available from the driving force, and the energy consumed in forming new interface. Once the rate of change of free energy becomes negative, then an embryo can grow.

Driving Force

- solidification: as you cool a liquid below the liquid us, so the driving force for solidification increases. This driving force is often called ***undercooling or Supercooling***.

Superheating / supercooling

- Crossing phase boundary → new equilibrium state
- Takes time ⇒ transformation is delayed
- **During cooling, transformations occur at temperatures less than predicted by phase diagram: supercooling.**
- **During heating, transformations occur at temperatures greater than predicted by phase diagram: superheating.**
- **Degree of supercooling/superheating increases with rate of cooling/heating.**
- **Microstructure is strongly affected by the rate of cooling.**

Driving force for nucleation

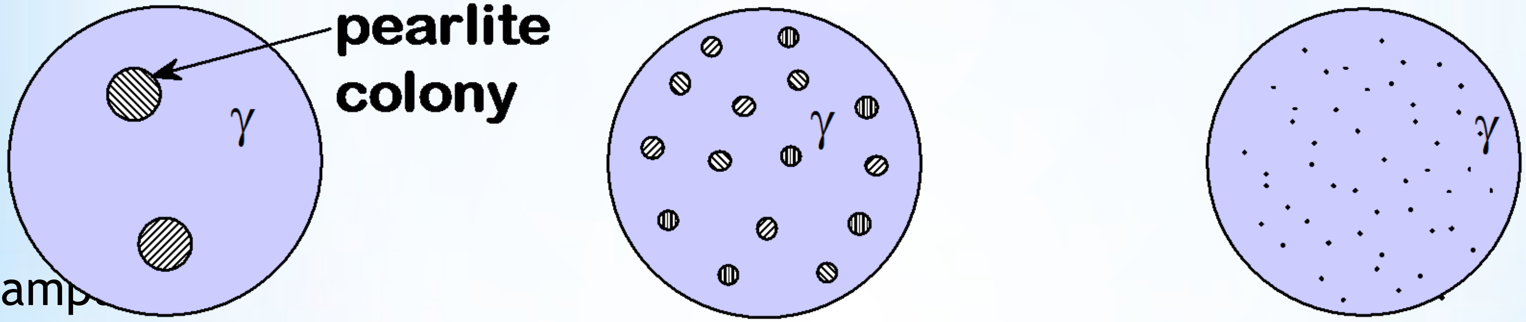
It is important to realize the difference between the driving force for the reaction as a whole, which is given by the change in free energy between the supersaturated solid solution and the two-phase mixture.

- Why a different free energy for nucleation?

Because the first nuclei of beta to appear do not significantly change the composition of the parent material. Thus the free energy change for nucleation is the rate of change of free energy for the new, product phase (beta).

*Nucleation and Growth

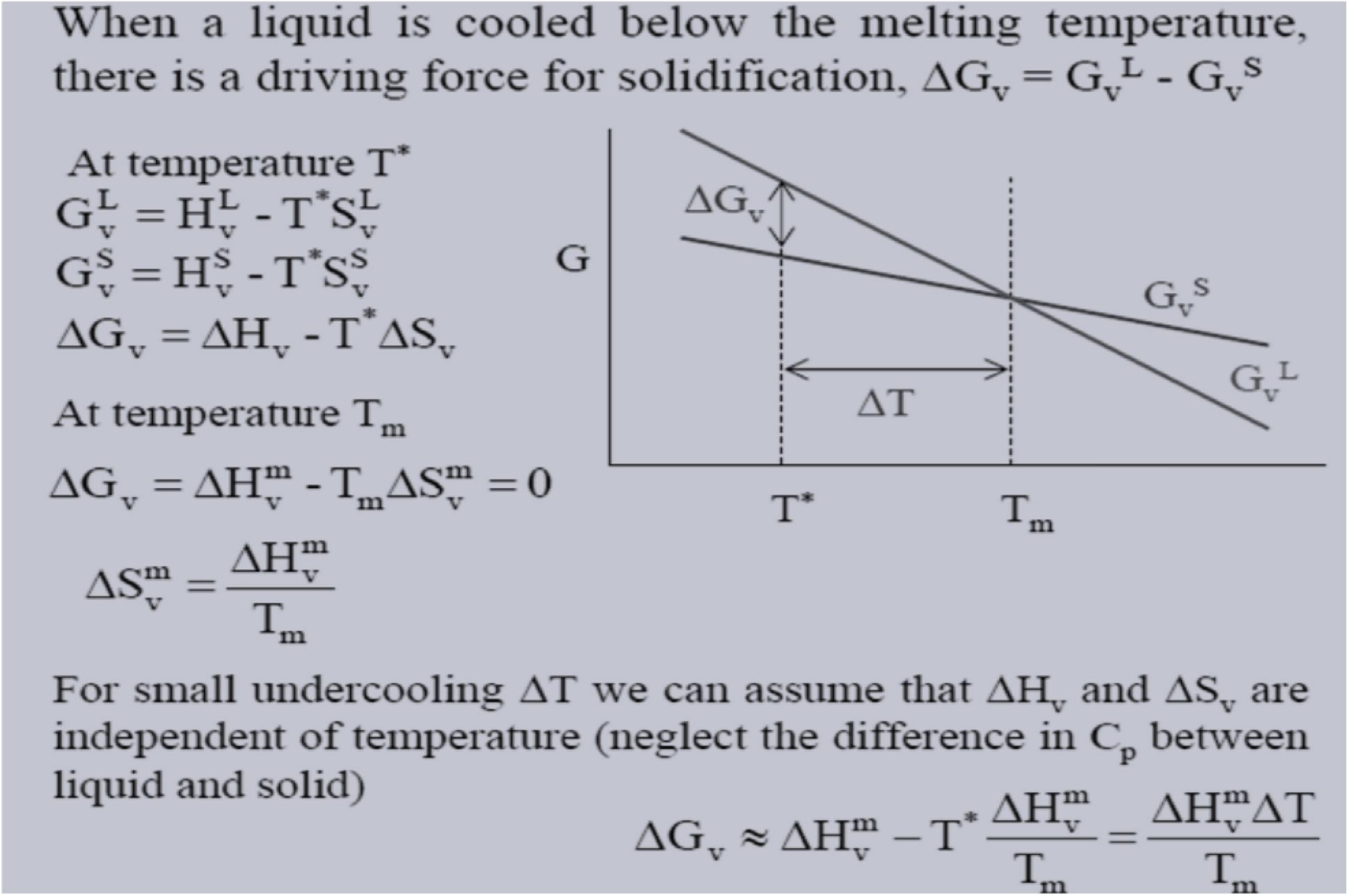
- Reaction rate is a result of nucleation and growth of crystals.



- Examp

T just below T_E	T moderately below T_E	T way below T_E
Nucleation rate low	Nucleation rate med .	Nucleation rate high
Growth rate high	Growth rate med.	Growth rate low

Driving force for solidification (ΔGv)



When a liquid is cooled below the melting temperature, there is a driving force for solidification, $\Delta G_v = G_v{}^L - G_v{}^S$

At temperature T^*

$$G_v^L = H_v^L - T^* S_v^L$$

$$G_v^S = H_v^S - T^* S_v^S$$

$$\Delta G_v = \Delta H_v - T^* \Delta S_v$$

At temperature T_m

$$\Delta G_v = \Delta H_v^m - T_m \Delta S_v^m = 0$$

$$\Delta S_v^m = \frac{\Delta H_v^m}{T_m}$$

For small undercooling ΔT we can assume that ΔH_v and ΔS_v are independent of temperature (neglect the difference in C_p between liquid and solid)

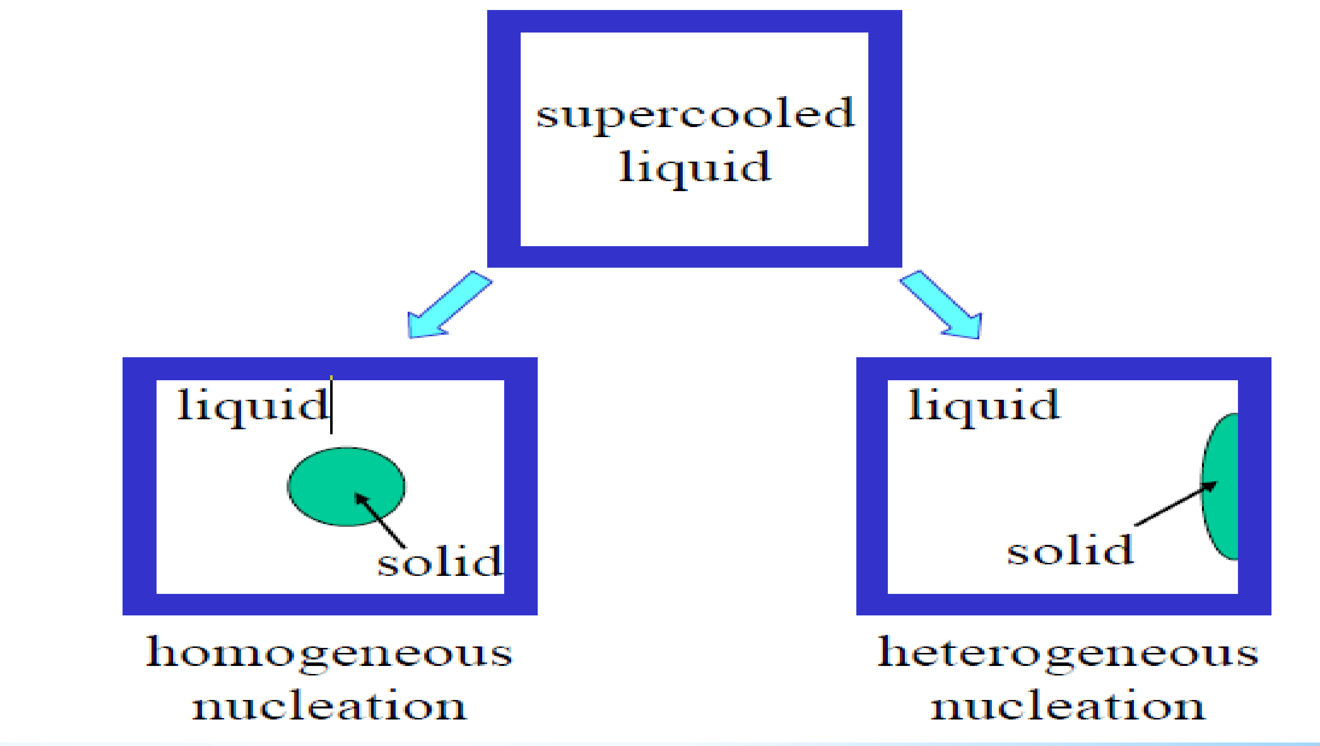
$$\Delta G_v \approx \Delta H_v^m - T^* \frac{\Delta H_v^m}{T_m} = \frac{\Delta H_v^m \Delta T}{T_m}$$

Nucleation can be:

Homogeneous – solid nuclei spontaneously appear within the undercooled phase (supercooling (typically 80-300°C max)) or precipitation occurs within a completely homogeneous medium.

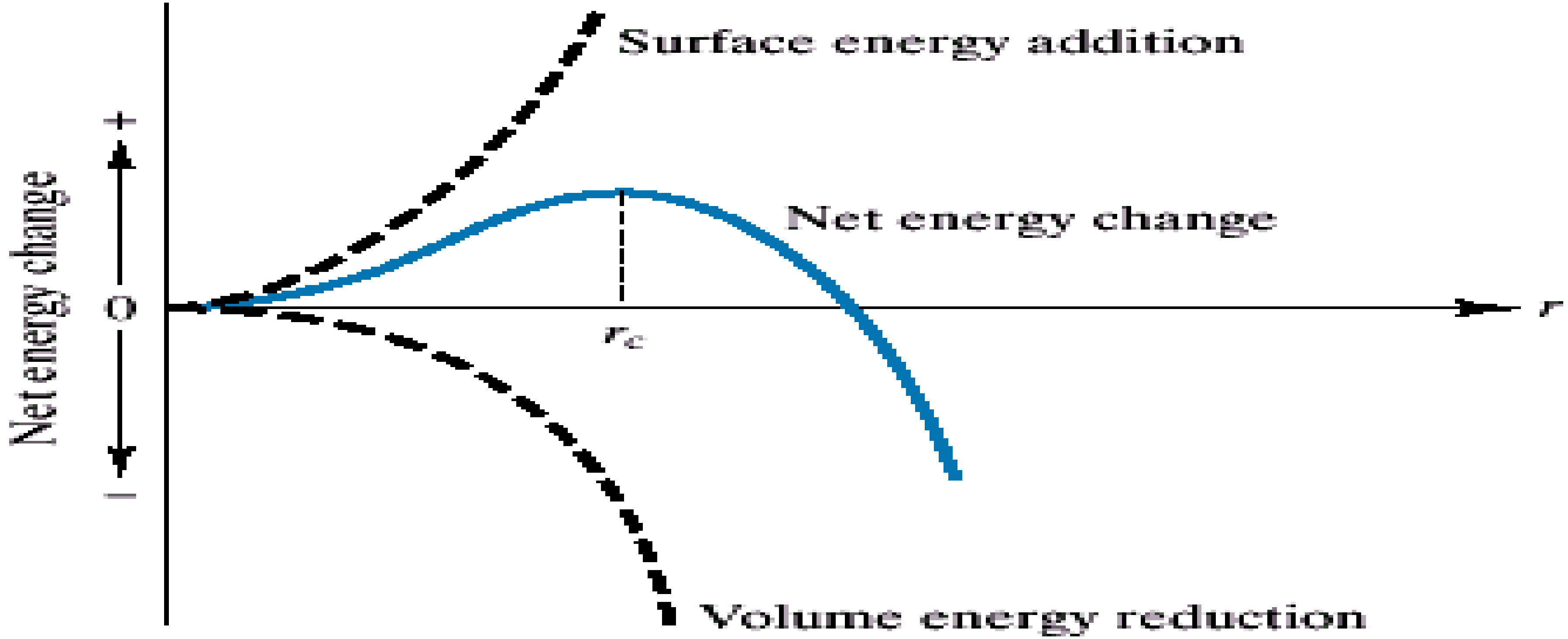
Heterogeneous – the new phase appears on the walls of the container, at impurity particles, etc. or precipitation may be occurs also on the surface which separate media. much easier since stable "nucleus" is already present and allows solidification with only 0.1-10ºC supercooling

Let's consider solidification of a liquid phase undercooled below the Tm as a simple example of a phase transformation



Nucleation

Energy =surface + volume



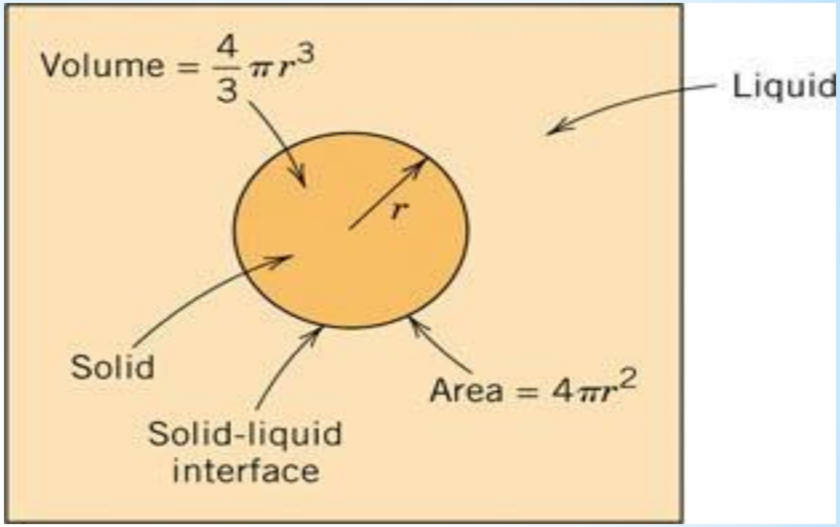
Nuclei are stable if growth reduces its energy. For r > r_c the nucleus is stable.

Homogeneous nucleation

Nuclei of the new phase form uniformly throughout the parent phase.

- Will occur spontaneously only when free energy change Δ G is negative.

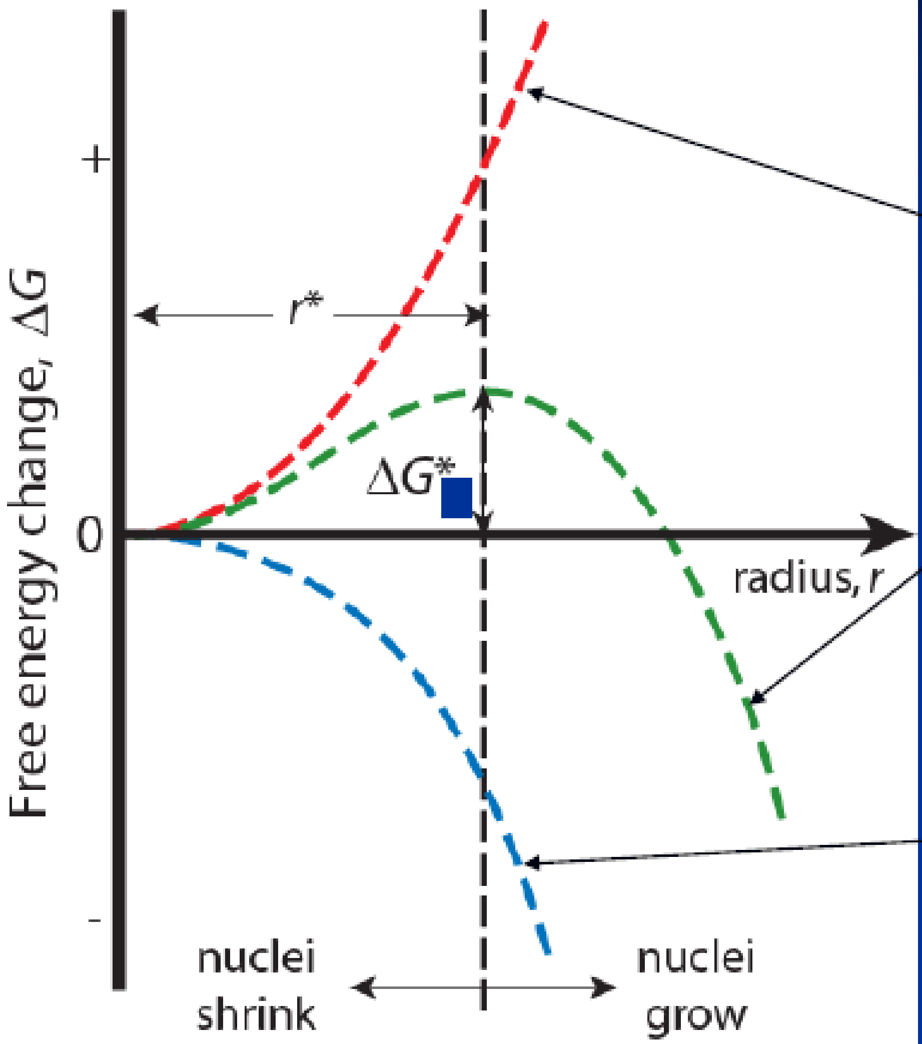
$$\Delta G = \frac{4}{3}\pi r^3 \cdot \Delta G_v + 4\pi r^2 \cdot \gamma$$



The are two contributions to the total free energy change that accompany a solidification transformation:

- Free energy difference between the solid and liquid phase: Volume free energy: $\Delta G_v < 0$
- Formation of the solid-liquid phase boundary: surface free energy: $\gamma > 0$

Homogeneous Nucleation & Energy Effects



Surface Free Energy- destabilizes the nuclei (it takes energy to make an interface)

$$\Delta G_S = 4\pi r^2\gamma$$

γ = surface tension

ΔG_T = Total Free Energy

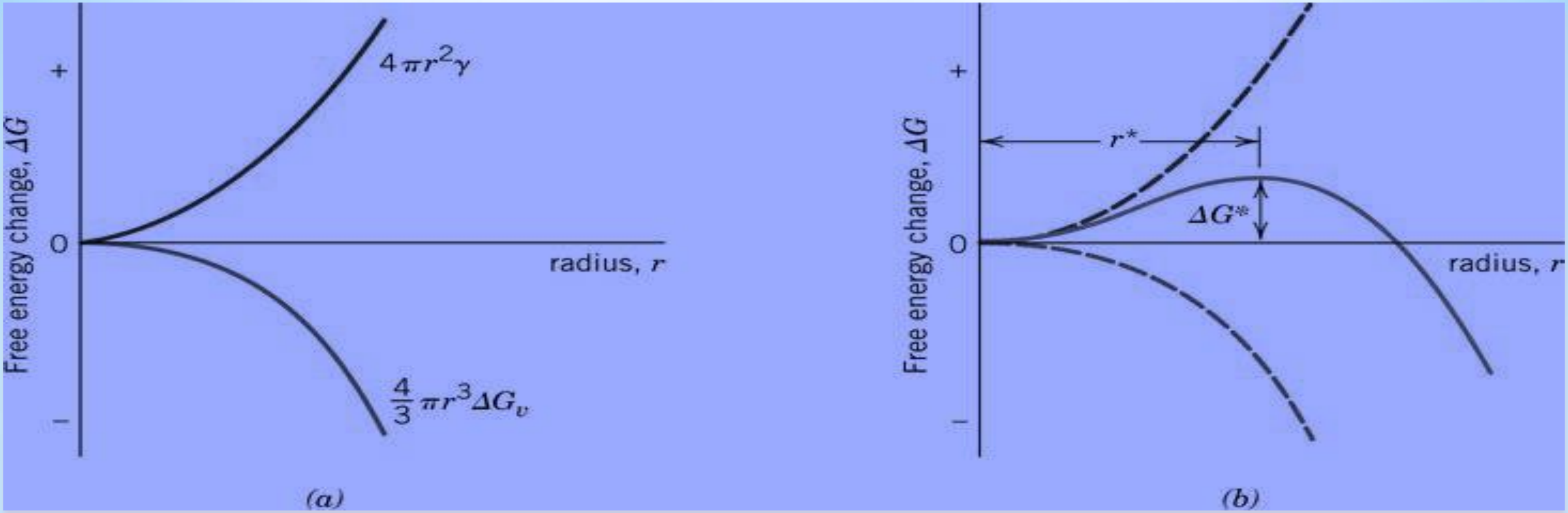
$= \Delta G_S + \Delta G_V$

Volume (Bulk) Free Energy – stabilizes the nuclei (releases energy)

$$\Delta G_V = \frac{4}{3}\pi r^3 \Delta G_\upsilon$$

$$\Delta G_\upsilon = \frac{\text{volume free energy}}{\text{unit volume}}$$

r^* = critical nucleus: nuclei < r^* shrink; nuclei>r^* grow (to reduce energy)



(a)

(b)

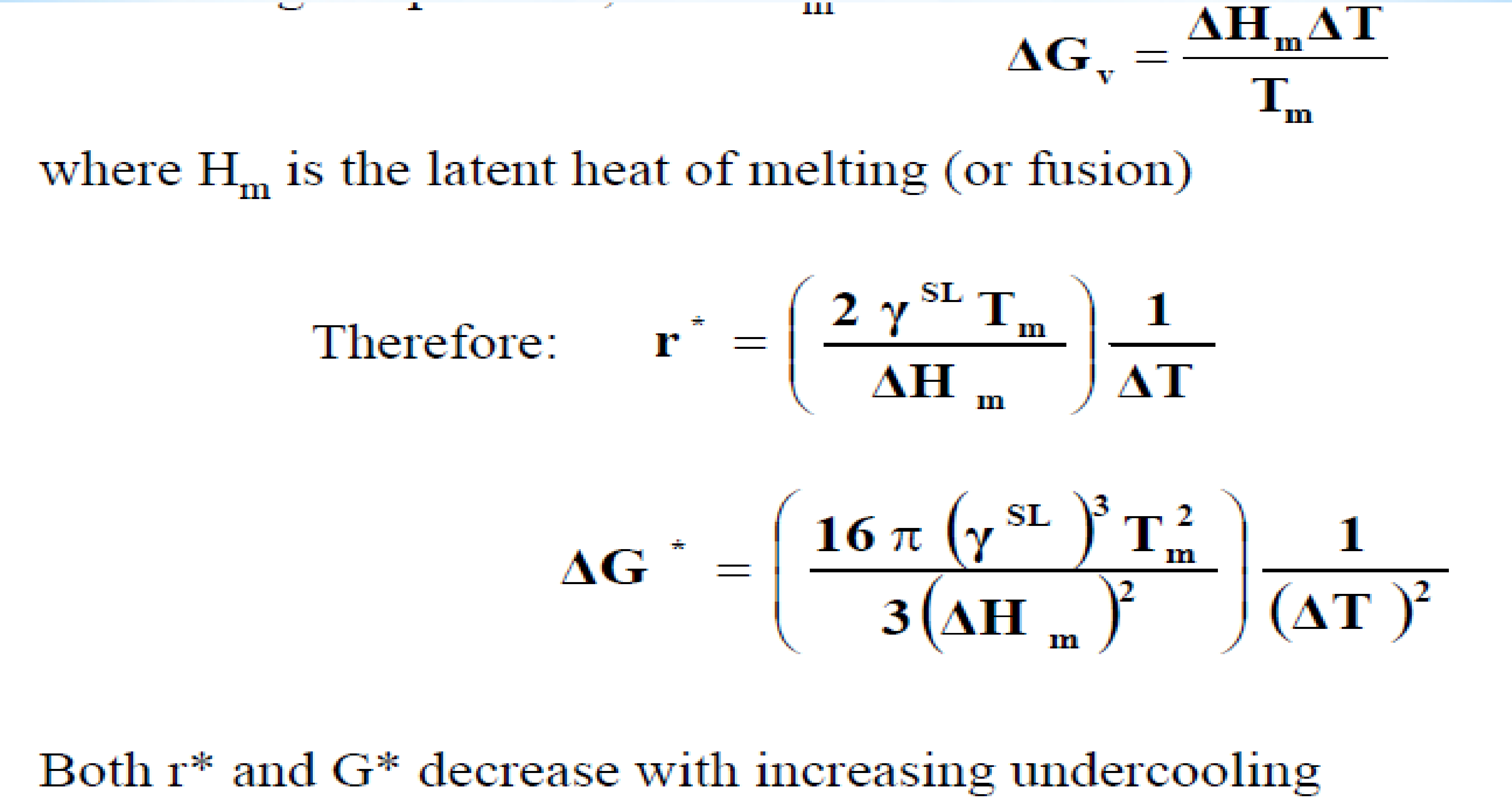
$$\boxed{r^* = -\frac{2\gamma}{\Delta G_v}} \longrightarrow \boxed{r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{T_m - T}\right)}$$

Critical radius

$$\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m}$$

$$\boxed{\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}} \longrightarrow \boxed{\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\frac{1}{(T_m - T)^2}}$$

The difference between the Gibbs free energy of liquid and solid (also called “driving force” for the phase transformation) is proportional to the undercooling below the melting temperature, ΔT = Tm – T:



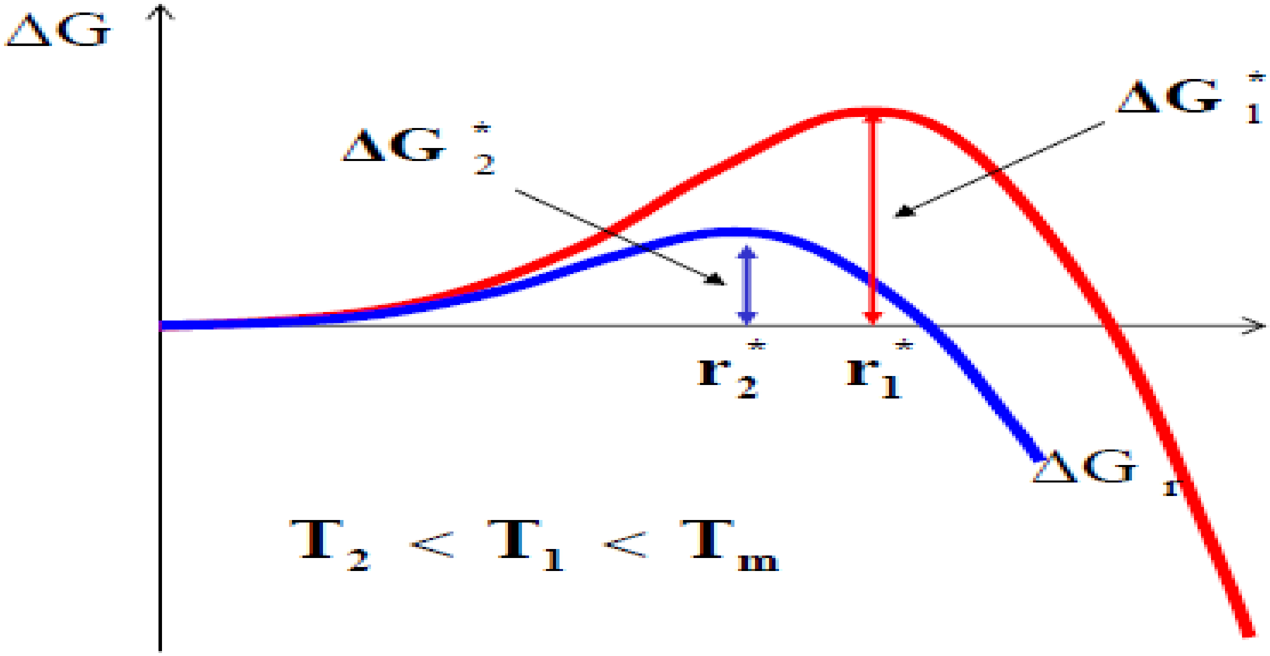
$$\Delta G_v = \frac{\Delta H_m \Delta T}{T_m}$$

where H_m is the latent heat of melting (or fusion)

Therefore:
$$r^* = \left(\frac{2\gamma^{SL} T_m}{\Delta H_m}\right)\frac{1}{\Delta T}$$

$$\Delta G^* = \left(\frac{16\pi\left(\gamma^{SL}\right)^3 T_m^2}{3\left(\Delta H_m\right)^2}\right)\frac{1}{(\Delta T)^2}$$

Both r* and G* decrease with increasing undercooling



$$r^* = \left(\frac{2\gamma^{SL} T_m}{\Delta H_m} \right) \frac{1}{\Delta T}$$

$$\Delta G^* = \left(\frac{16\pi \left(\gamma^{SL}\right)^3 T_m^2}{3\left(\Delta H_m\right)^2} \right) \frac{1}{(\Delta T)^2}$$

Both r* and G* decrease with increasing undercooling

Example Problem

- Computation of critical nucleus radius and activation free energy
- Computing the number of atoms in a critical nucleus.

Cluster and Nuclei

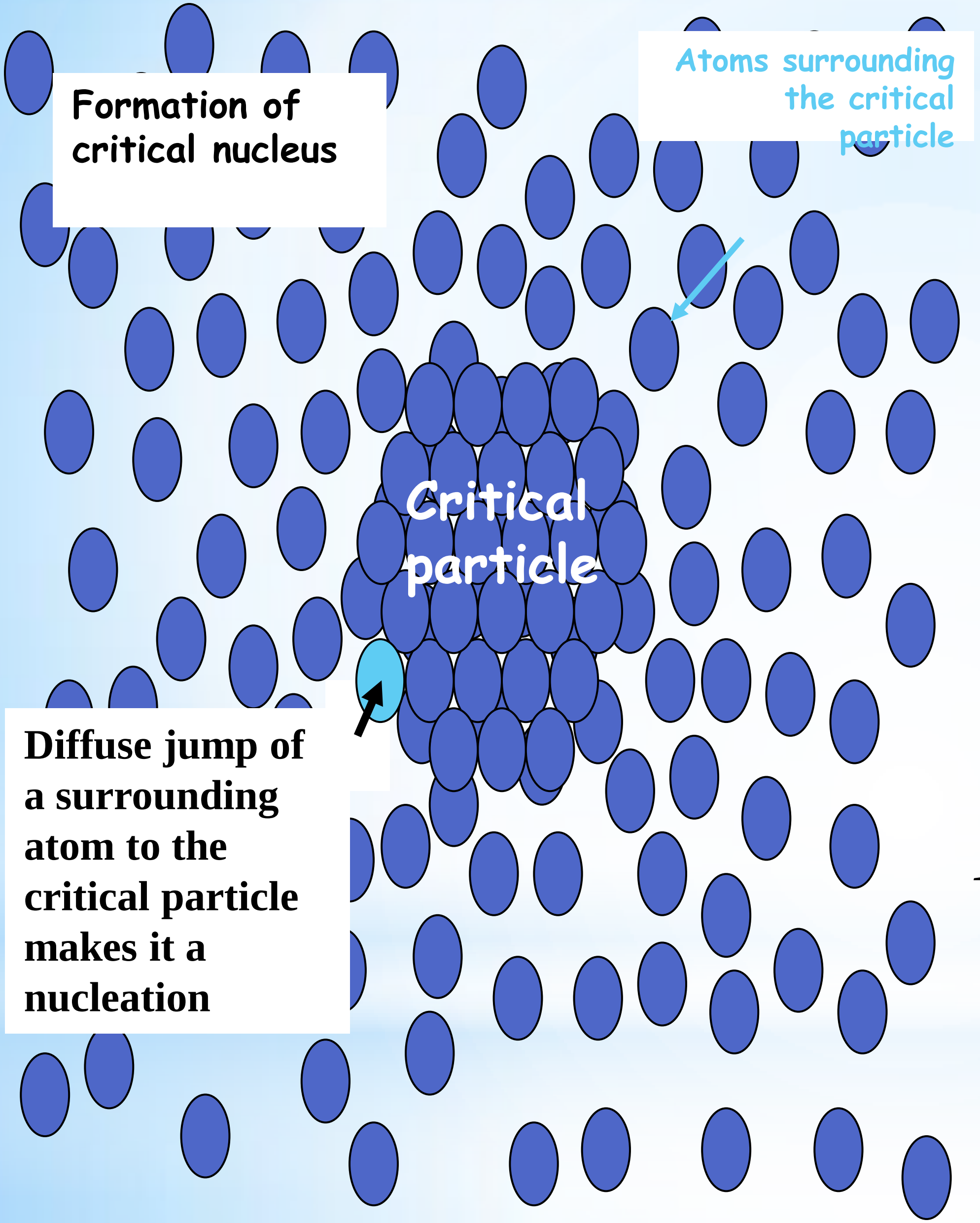
1- if $r<r^*$ the system can lower its free energy by dissolution of the solid Unstable solid particles with $r<r^*$ are known as clusters or embryos.

2- if $r>r^*$ the free energy of the system decreases if the solid grows Stable solid particles with $r>r^*$ are referred to as nuclei

3- Since $\Delta G = 0$ when $r = r^*$ the critical nuclei is effectively in (unstable) equilibrium with the surrounding liquid

For nucleus with a radius $r > r^*$, the Gibbs free energy will decrease if the nucleus grows. **r^* is the critical nucleus size, ΔG^* is the nucleation barrier.**

The Nucleation Rate



Formation of critical nucleus

Atoms surrounding the critical particle

Diffuse jump of a surrounding atom to the critical particle makes it a nucleation

N_t=total number of clusters of atoms per unit volume

N^* = number of clusters of critical size per unit volume

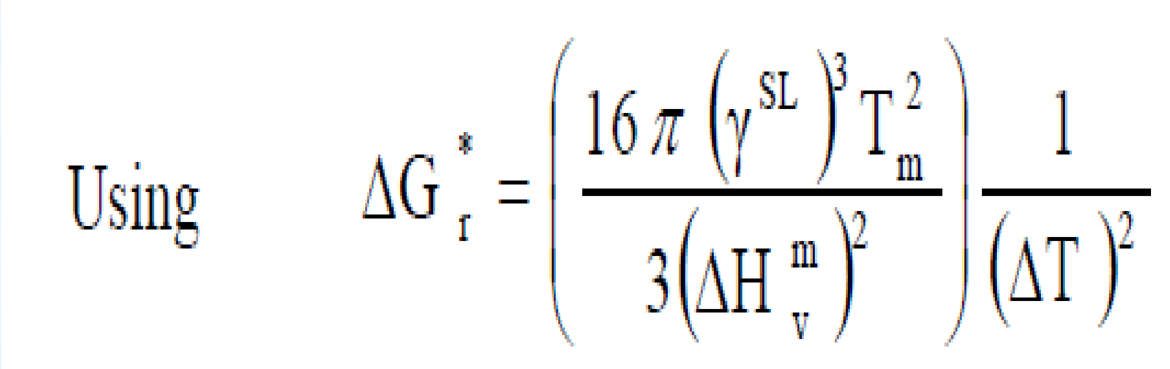
By Maxwell-Boltzmann statistics

$$N^* = N_t \exp\left(-\frac{\Delta G^*}{RT}\right)$$

- To estimate the nucleation rate we need to know the population density of embryos of the critical size and the rate at which such embryos are formed.
- The population (concentration) of critical embryos is given by:

$$N^* = N_t \exp\left(-\frac{\Delta G^*}{RT}\right)$$

k is the Boltzmann factor, Nt is the total number of atoms in the system ΔG_r is the excess of free energy associated with the cluster



Using $$\Delta G_r^* = \left(\frac{16\pi\left(\gamma^{SL}\right)^3 T_m^2}{3\left(\Delta H_v^m\right)^2}\right)\frac{1}{\left(\Delta T\right)^2}$$

$$\boxed{\dot{N} = I_0 \exp\left(-\frac{A}{(\Delta T)^2} \right)}$$

where A has a relatively weak dependence on temperature (as compared to ΔT^2)

very strong temperature dependence!

There is critical undercooling for homogeneous nucleation ΔT^{cr} ⇒ there are virtually no nuclei until ΔT^{cr} is reached, and there is an "explosive" nucleation at ΔT^{cr}.