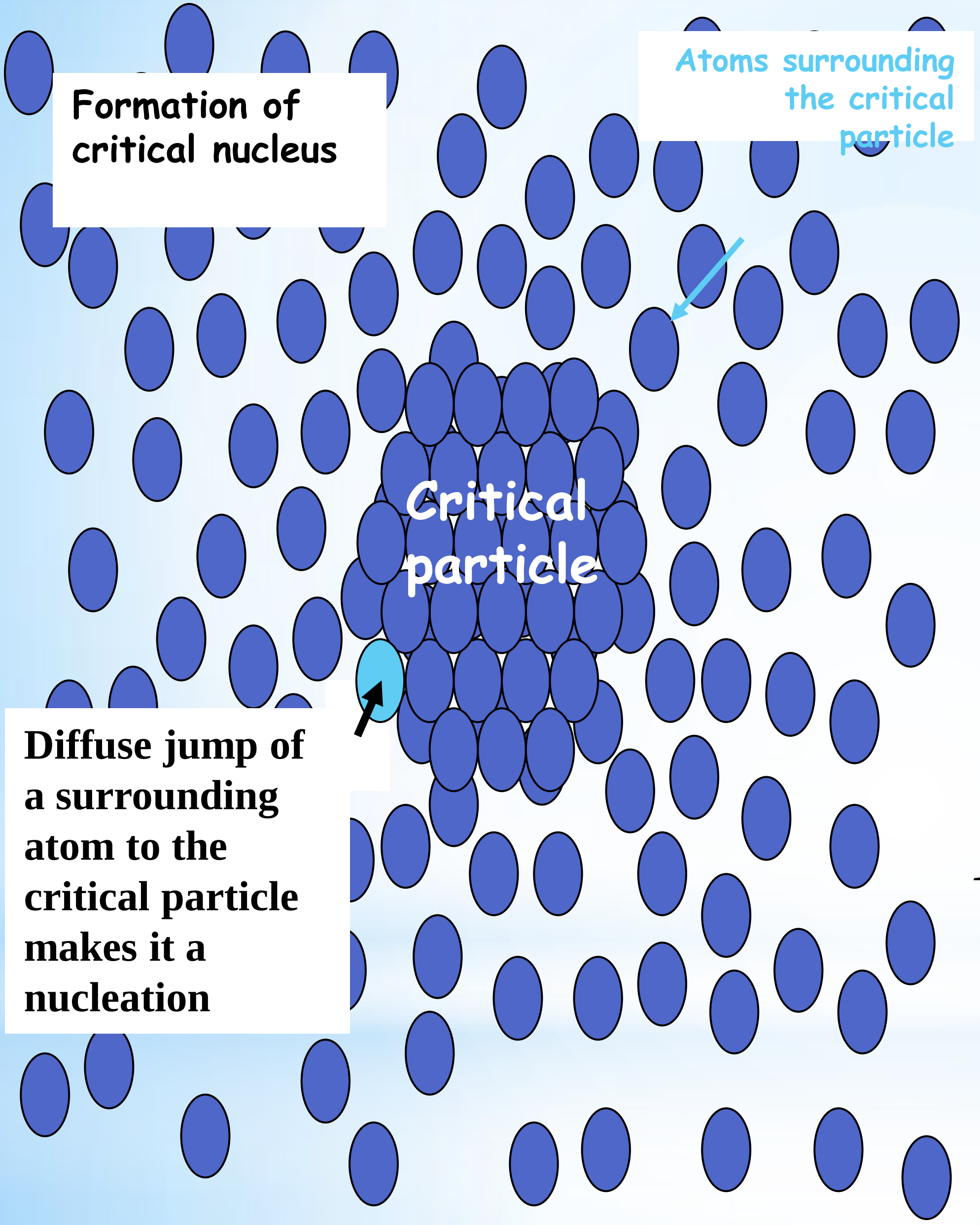
Kinetics&Thermodynamics and Phase transformation heat treatment

The Nucleation Rate



Formation of critical nucleus

Atoms surrounding the critical particle

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 ΔGr is the excess of free energy associated with the cluster

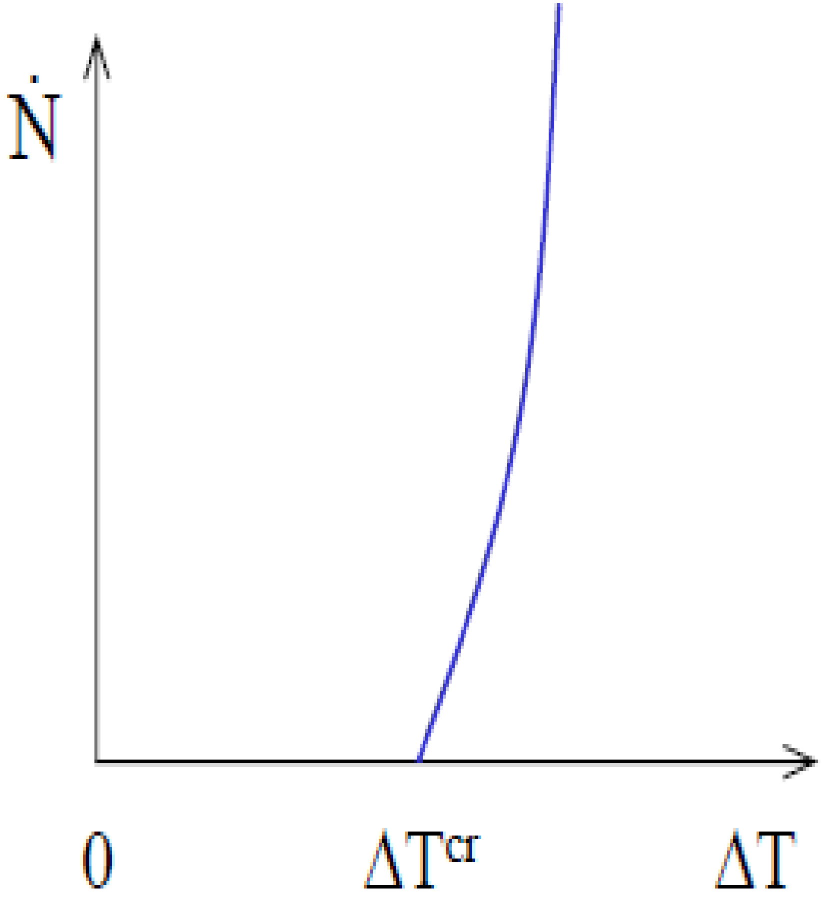
Using $$\Delta G_r^* = \left(\frac{16\pi\left(\gamma^{SL}\right)^3 T_m^2}{3\left(\Delta H_v^m\right)^2}\right)\frac{1}{\left(\Delta T\right)^2}$$

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

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

very strong temperature dependence!

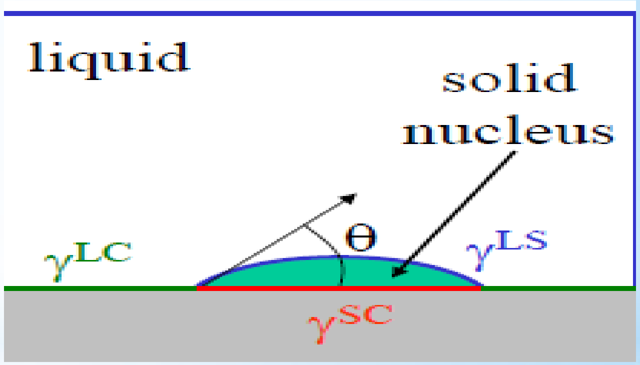
There is critical undercooling for homogeneous nucleation ΔT^{cr} $\Rightarrow$ there are virtually no nuclei until ΔT^{cr} is reached, and there is an "explosive" nucleation at ΔT^{cr}.



Heterogeneous Nucleation

- Here, the probability of nucleation is much higher at certain preferred sites such as mold wall, inclusions, grain boundaries, compared to rest of the parent phase.

- As we will see, the contribution of interfacial energy (γ_{SL}) results in a kinetic barrier for the phase transformation.



Origin of the interfacial energy (γSL)

Consider a solid-liquid interface. Depending on the type of material and crystallographic orientation of the interface, the interface can be atomically flat (smooth, faceted) or rough (diffuse).

*Heterogeneous nucleation

- Heterogeneous nucleation is typically much faster than homogeneous nucleation because the nucleation barrier ΔG* is much lower at a surface.
- This is because the nucleation barrier comes from the positive term in the free energy ΔG, which is the surface term.
- For homogeneous nucleation the nucleus is pproximated by a sphere and so has a free energy equal to the surface area of a sphere, $4\pi r^2$, times the surface tension σ.

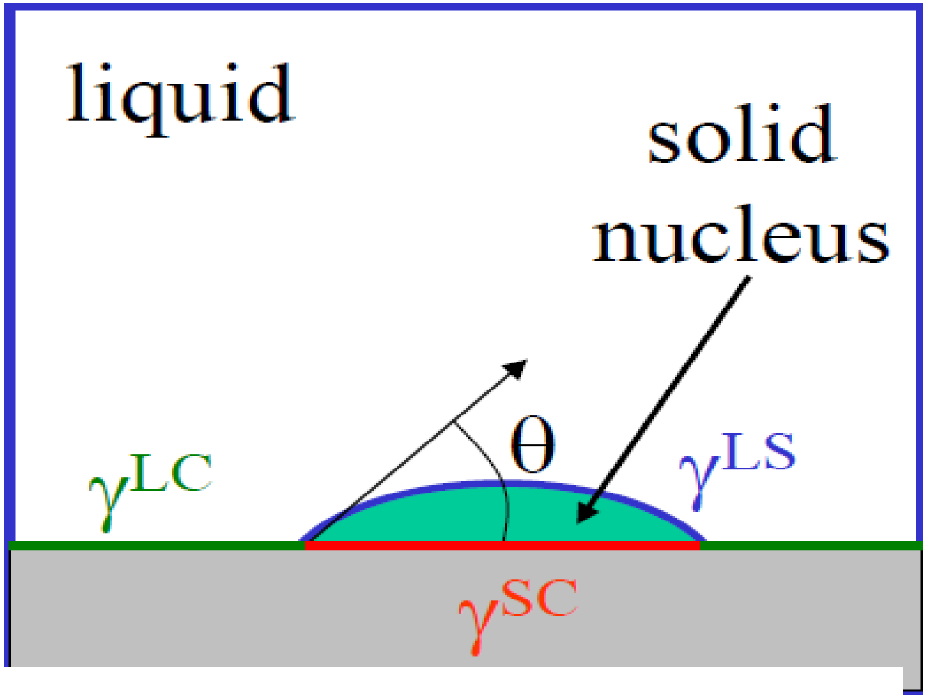
Heterogeneous Nucleation

Let’s consider a simple example of heterogeneous nucleation of a nucleus of the shape of a spherical cap on a wall of a container. Three interfacial energies:

γ_{LC} – liquid container interface,

γ_{LS} – liquid-solid interface,

γ_{SC} – solid-container interface.



Balancing the interfacial tensions in the plane of the container wall gives $\gamma^{LC} = \gamma^{SC} + \gamma^{LS}\cos(\theta)$ and the wetting angle θ is defined by $\cos(\theta) = (\gamma^{LC} - \gamma^{SC})/\gamma^{LS}$

Heterogeneous Nucleation

$$\Delta G_r^{het} = \left\{ -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma^{SL} \right\} S(\theta) = \Delta G_r^{hom} S(\theta)$$

where $S(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2 / 4 \le 1$

At $r = r^*$ $\quad \frac{d\Delta G_r}{dr} = \left(-4\pi r^2 \Delta G_v + 8\pi r \gamma^{SL}\right) S(\theta) = 0$

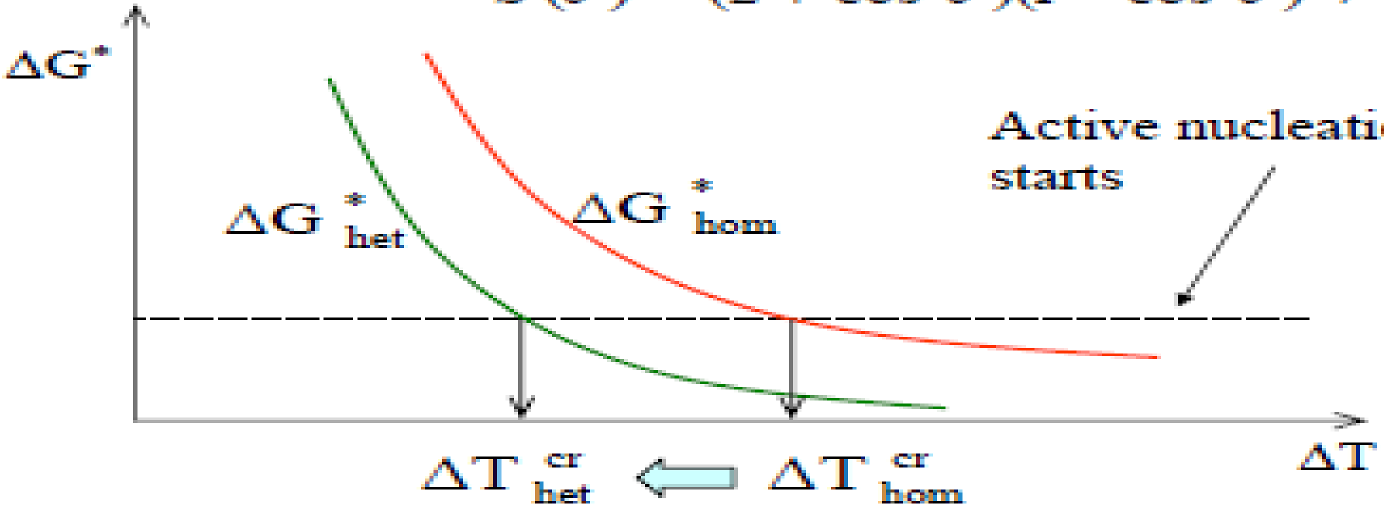
$$r^* = \frac{2\gamma^{SL}}{\Delta G_v}$$

- same as for homogeneous nucleation

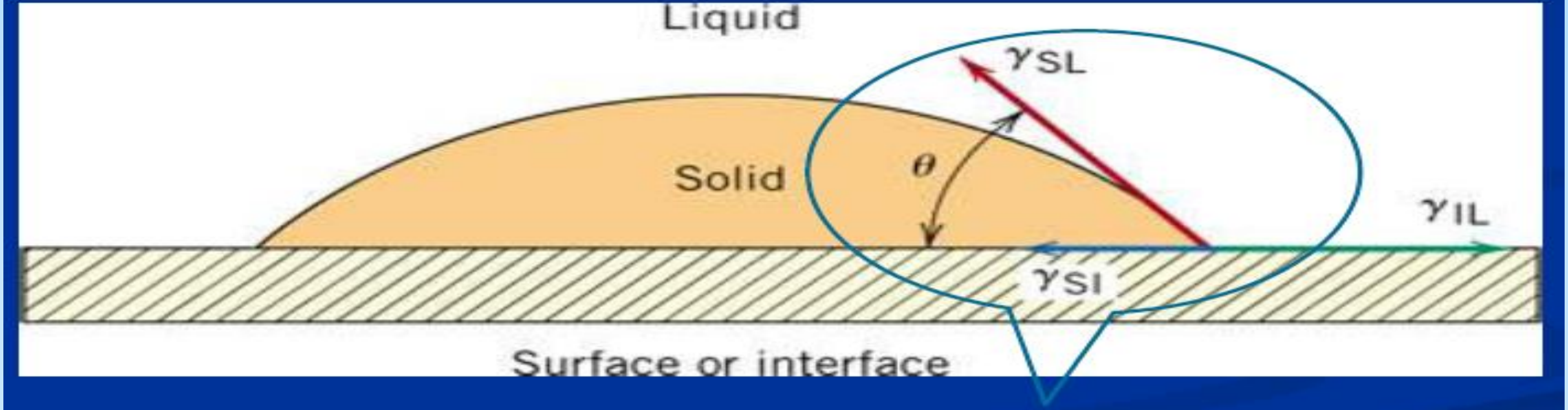
$$\Delta G_{het}^* = S(\theta)\frac{16\pi \left(\gamma^{SL}\right)^3}{3(\Delta G_v)^2} = S(\theta)\Delta G_{hom}^*$$

$S(\theta)$ can be small $\Rightarrow$ *if* $\theta = 10^\circ$

$$S(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2 / 4 \approx 10^{-4}$$



Heterogeneous Nucleation



$$\gamma_{IL} = \gamma_{SI} + \gamma_{SL}\cos\theta$$

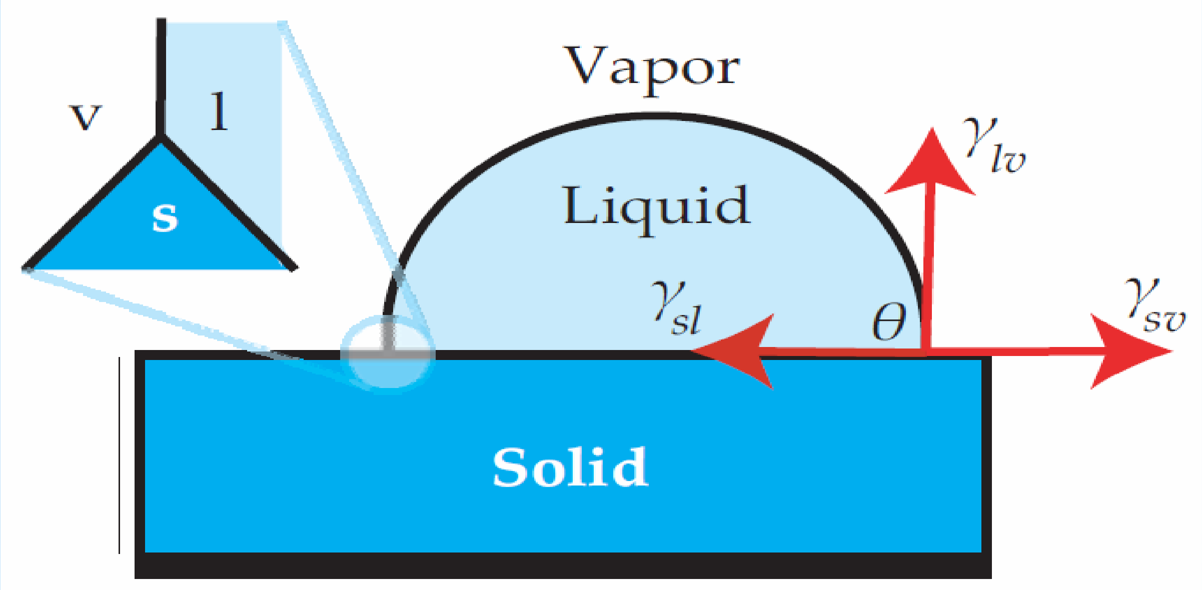
$$\boxed{r^* = -\frac{2\gamma_{SL}}{\Delta G_v}}$$

$$\boxed{\Delta G^*_{het} = \left(\frac{16\pi\gamma_{SL}^{3}}{3(\Delta G_v)^2}\right)\cdot S(\theta) = \Delta G^*_{\mathrm{hom}}\cdot S(\theta)}$$

θ=30-90°, $S(\theta)$=0.01~0.5

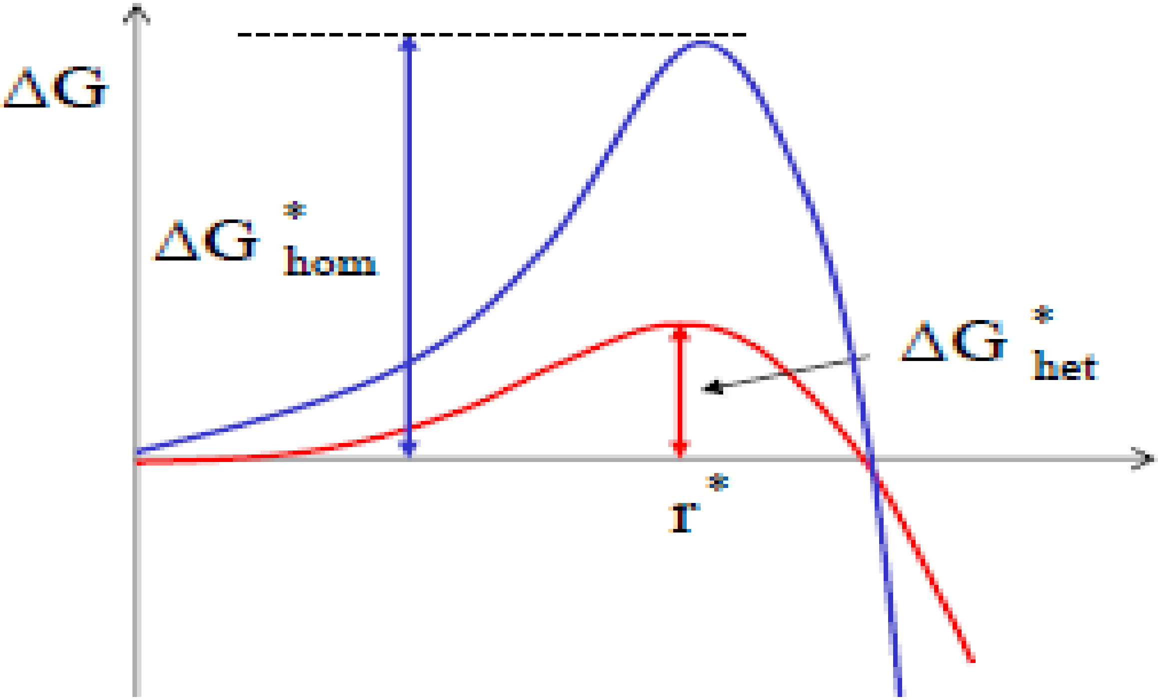
Hetergeneous Nucleation

How about the out-of-plane component of the liquid vapor surface tension?



Heterogeneous Nucleation

$$r^* = \frac{2\gamma^{SL}}{\Delta G_v} \qquad \Delta G^*_{het} = S(\theta)\Delta G^*_{hom}$$



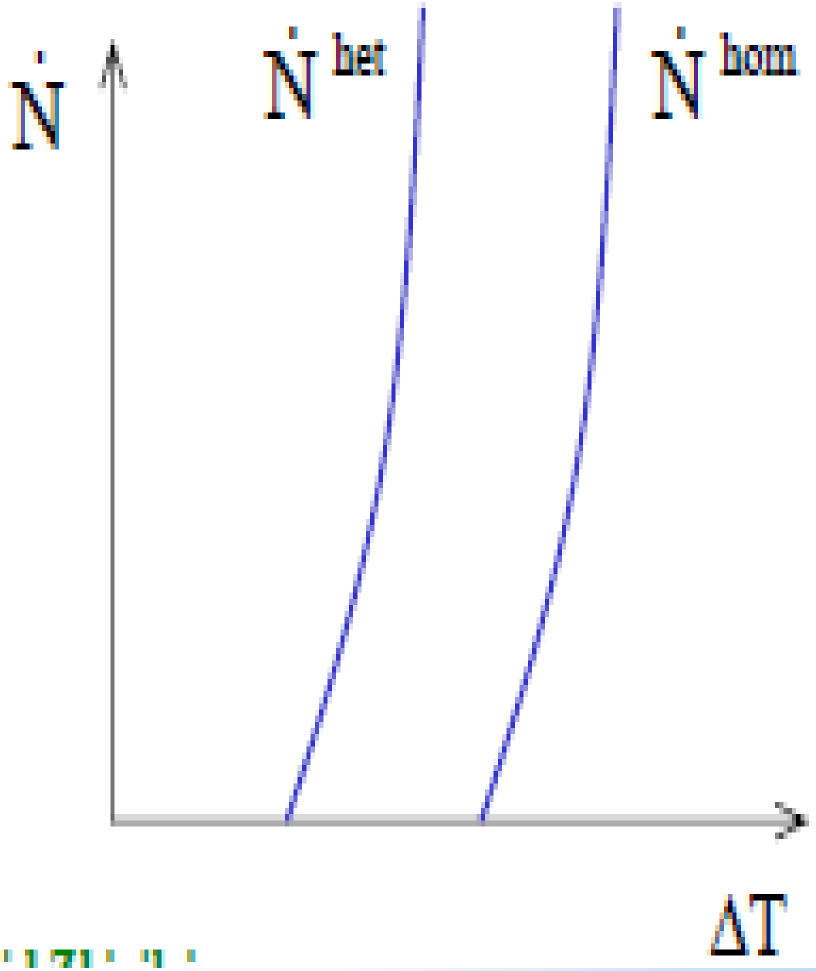
heterogeneous nucleation starts at a lower undercooling

Heterogeneous Nucleation

$$\dot{N}^{hom} \sim \exp\left(-\frac{\Delta G^{*}_{hom}}{kT}\right)$$

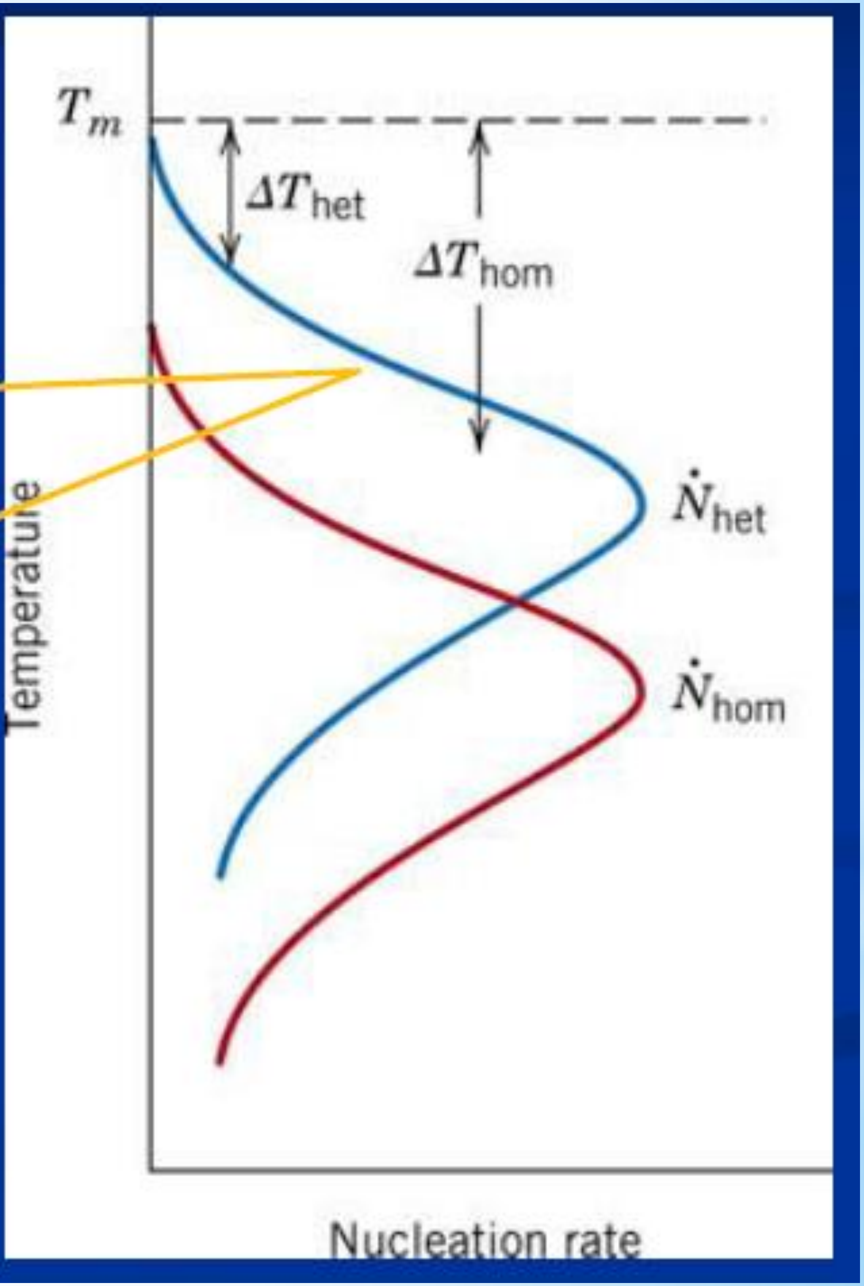
$$\dot{N}^{het} \sim \exp\left(-\frac{\Delta G^{*}_{het}}{kT}\right)$$

$$\dot{N}^{het} >> \dot{N}^{hom}$$



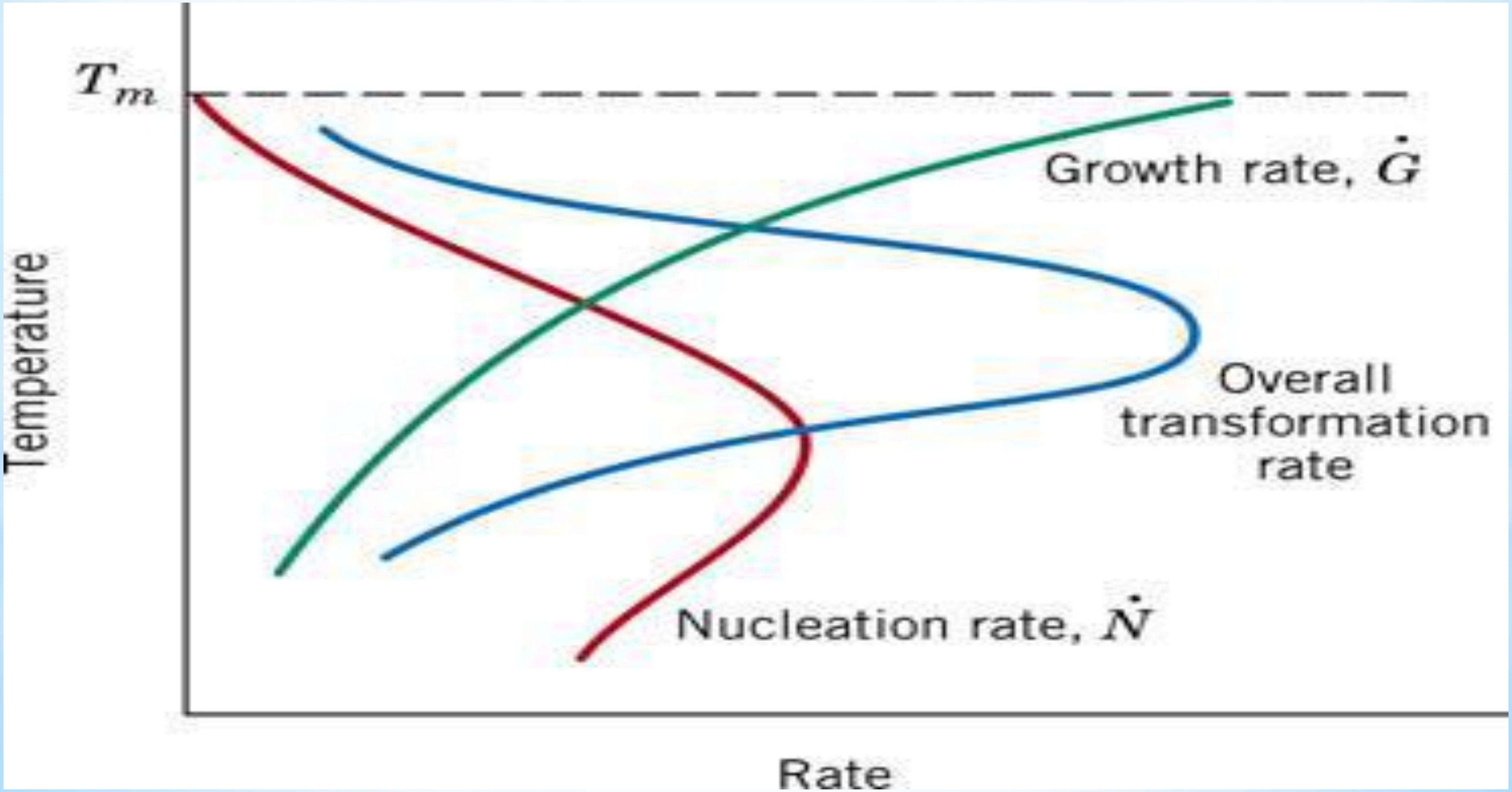
The Kinetics of Phase Transformation

The nucleation rate is shifted to higher temperature for heterogeneous.



The growth rate is determined by the rate of diffusion and its temperature dependence is the same.

$$\dot{G} = C \cdot \exp\left(-\frac{Q}{kT}\right)$$

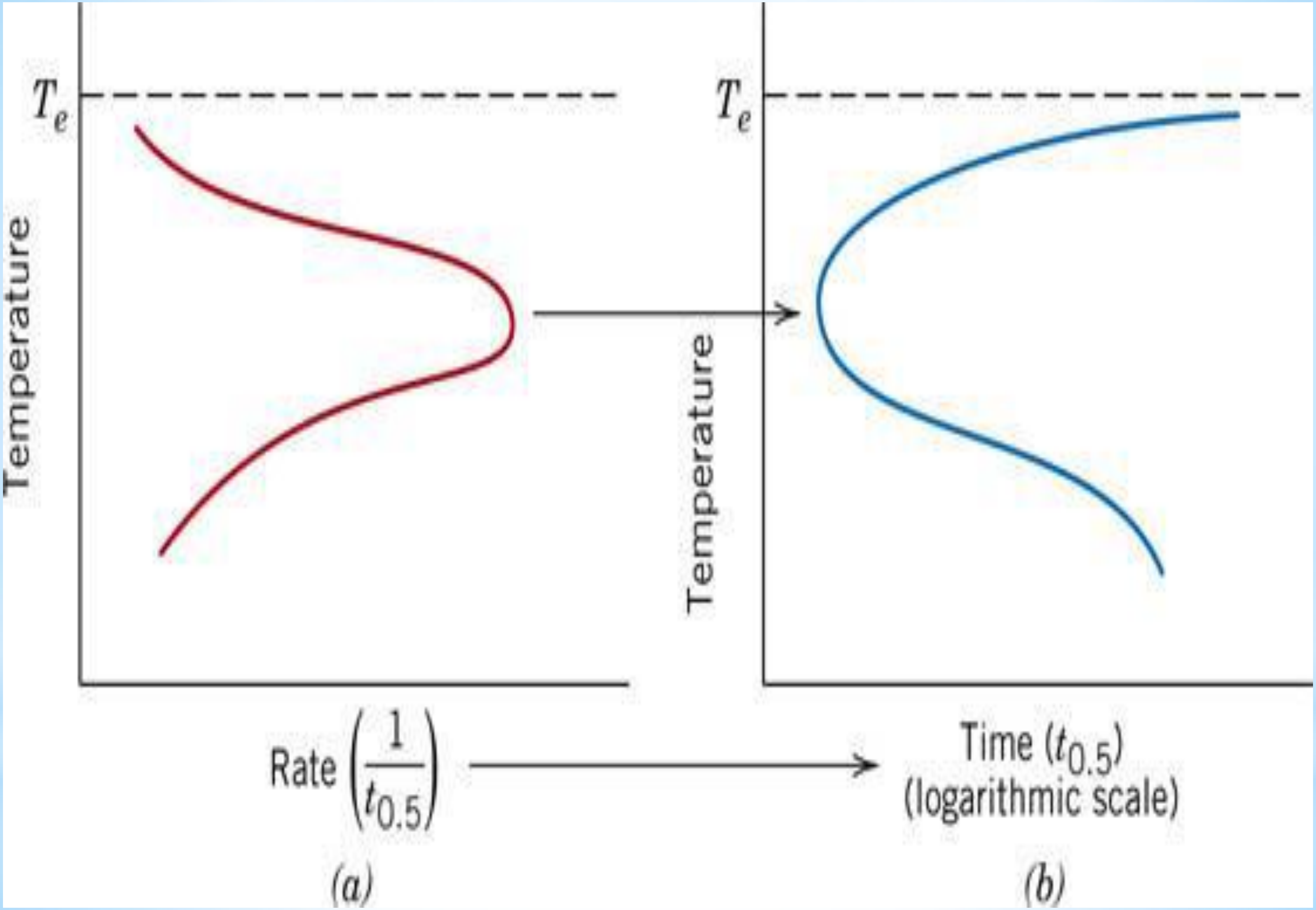


Kinetic considerations of solid-state transformation

$$r = A \cdot e^{(-\frac{Q}{RT})}$$

- Rate of transformation : r = 1/ t0.5 and Time-dependent process (kinetics)
- Temperature will affect the rate of transformation:

  Q = activation energy
- Phase transformation is a thermal activated process.
- Need composition redistribution or atomic rearrangement
- Energy increase for nucleation or new phase boundaries.


T_e
Temperature
Rate $\left(\frac{1}{t_{0.5}}\right)$
(a)
T_e
Temperature
Time ($t_{0.5}$)
(logarithmic scale)
(b)