



# **EMA5001 Lecture 13**

## **Solidification via**

### **Heterogeneous Nucleation,**

#### **Growth of Pure Solid from Liquid**



# Heterogeneous Nucleation (1)

Actual solidification often involves mold wall, insoluble oxides, etc., which become substrates for heterogeneous nucleation

Assuming

- $\gamma_{ML}$  is isotropic
- Mold wall flat

$$\gamma_{ML} = \gamma_{SM} + \gamma_{SL} \cos \theta$$

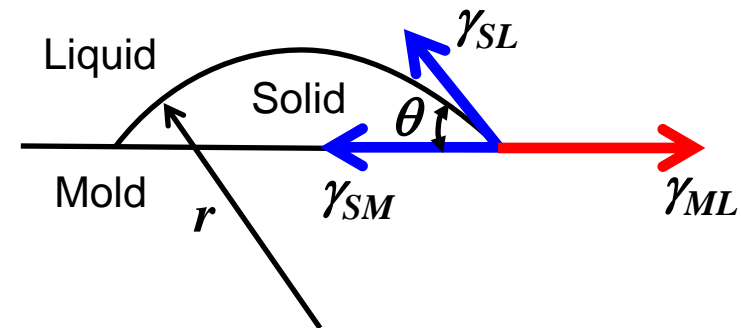
Free energy change in heterogeneous nucleation

$$\Delta G_{het} = -V_S \Delta G_v + A_{SL} \gamma_{SL} + A_{SM} \gamma_{SM} - A_{SM} \gamma_{ML}$$

Therefore,

$$\Delta G_{het} = \left[ -\frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma_{SL} \right] \cdot S(\theta)$$

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



Assuming sphere-cap geometry

$$V_S = \frac{4}{3} \pi r^3 \cdot \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4}$$

$$A_{SL} = 2 \pi r^2 (1 - \cos \theta)$$

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



# Heterogeneous Nucleation (2)

□ Continue from p.2

$$\Delta G_{het} = \left[ -\frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL} \right] \cdot S(\theta)$$

Remember for homogeneous nucleation

$$\Delta G_{hom} = -\frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}$$

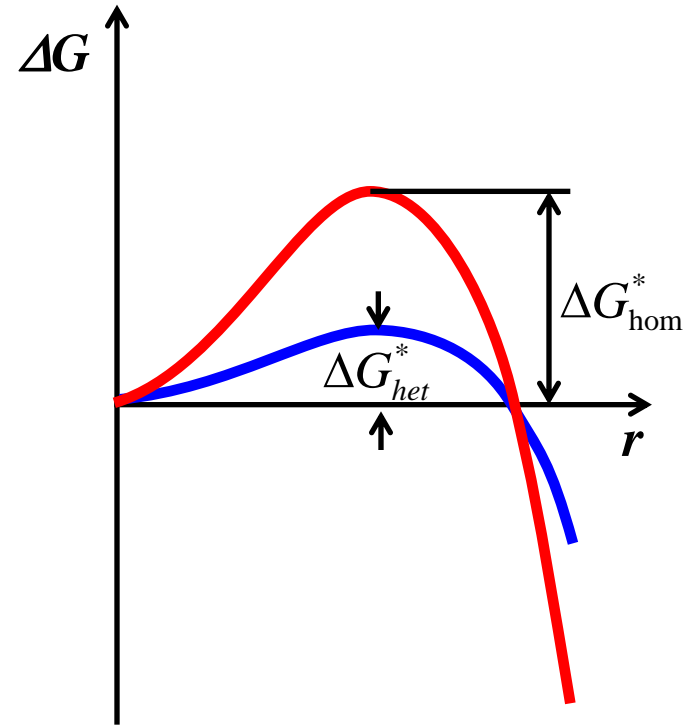
We have

$$\Delta G_{het} = \Delta G_{hom} \cdot S(\theta)$$

$$0 < S(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \leq 1$$

Critical nucleus size

$$r_{het}^* = r_{hom}^* = \frac{2\gamma_{SL}}{\Delta G_v}$$



**Heterogeneous nucleation has the same critical nucleus size as for homogeneous nucleation, but lower nucleation barrier (energy)**



# Heterogeneous Nucleation (3)

□ Continue from p.3

$$r_{het}^* = r_{hom}^* = \frac{2\gamma_{SL}}{\Delta G_v}$$

Critical nucleation energy

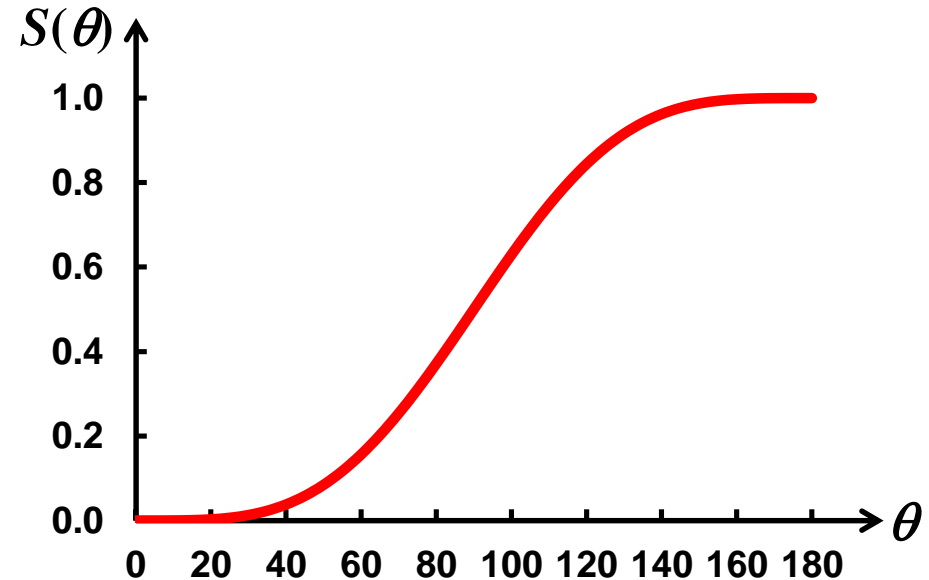
$$\Delta G_{het}^* = \Delta G_{hom}^* \cdot S(\theta)$$

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

Examples

- $\theta = 10^\circ$ ,  $S(\theta) = 0.00017$
- $\theta = 30^\circ$ ,  $S(\theta) = 0.013$
- $\theta = 60^\circ$ ,  $S(\theta) = 0.16$
- $\theta = 90^\circ$ ,  $S(\theta) = 0.50$

$$\gamma_{ML} - \gamma_{SM} = \gamma_{SL} \cos\theta$$



**Heterogeneous nucleation, especially on mold wall that is similar to solid (small  $\gamma_{SM}$ ), has much lower nucleation energy than homogeneous nucleation**



# Heterogeneous Nucleation Rate

## Define

$C_1$  Number of atoms contacting heterogeneous nucleation sites per unit liquid volume

$\Delta G_{het}^*$  Heterogeneous nucleation energy

$f_1$  Frequency of adding one atom to a heterogeneous nucleus with critical size

Heterogeneous nucleation rate ( $m^{-3}s^{-1}$ )

$$N_{het} = f_1 C_1 \exp\left(-\frac{\Delta G_{het}^*}{kT}\right)$$

Since

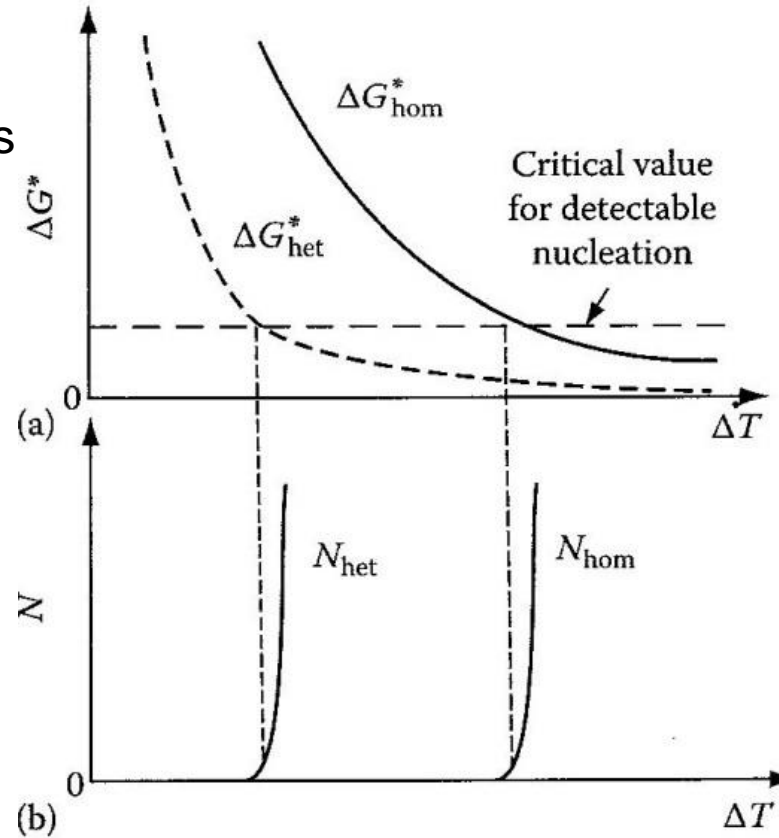
$$\Delta G_{het}^* = \Delta G_{hom}^* \cdot S(\theta)$$

$$\Delta G_{hom}^* = \frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2} \cdot \frac{1}{\Delta T^2}$$

We have

$$N_{het} = f_1 C_1 \exp\left(-\frac{A \cdot S(\theta)}{\Delta T^2}\right)$$

**Heterogeneous nucleation occurs at much smaller undercooling**



Phase Transformations in Metals & Alloys, Porter, 3<sup>rd</sup> Ed, 2008, p. 199



# Other Considerations on Heterogeneous Nucleation Rate

## □ Surface tension & contact angle

Small solid-mold (or impurity) interfacial energy  $\gamma_{SM}$   $\rightarrow$  small  $\theta$   $\rightarrow$  Faster nucleation

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

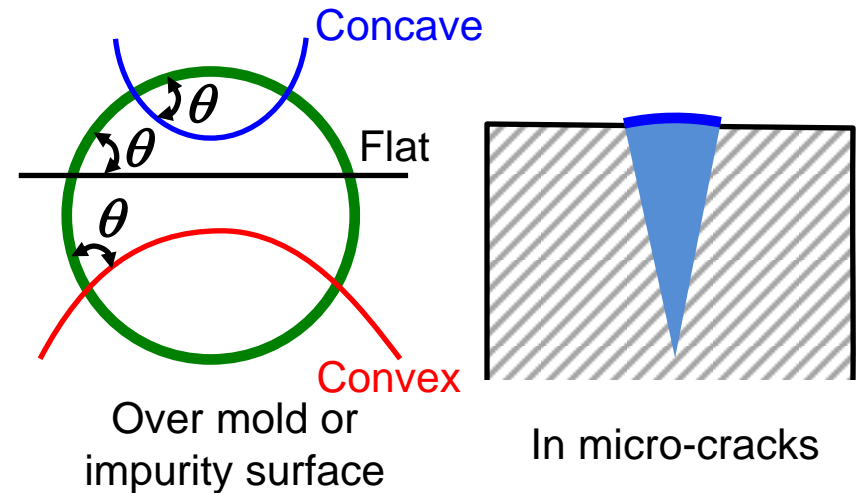
$$\cos\theta = \frac{\gamma_{ML} - \gamma_{SM}}{\gamma_{SL}}$$

## □ Mold surface microstructure

- In general, nucleation energy

$$\Delta G^* = \frac{1}{2} V^* \Delta G_v$$

- Concave mold (or impurity) surface and certain micro-cracks facilitate nucleation by decreasing  $V^*$  and nucleation energy



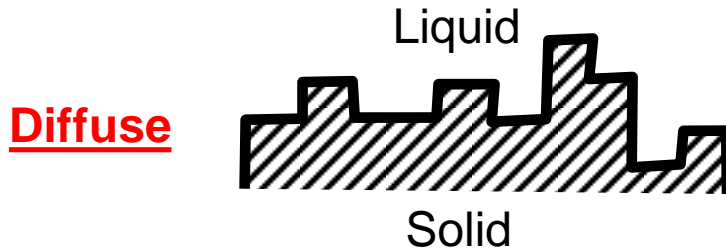
## □ Impurity density

- Added seeds or inoculants to increase nucleation rate to decrease grain size



# Growth of Pure Solid from Liquid

□ Growth of pure solid from liquid for different types of solid-liquid interfaces

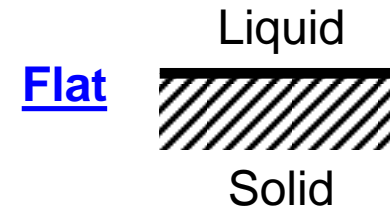


$$\frac{L_f}{T_m} \approx R \quad \Delta S \approx R$$

- **Microscopically diffuse**
- Macroscopically flat or branch-like
- Most metals:  
Ni:  $T_m = 1455 \text{ }^\circ\text{C}$   
 $L = 298 \text{ kJ/kg} = 17.4 \text{ kJ/mol} \rightarrow$   
Lower energy for broken bonds

## **Continuous growth**

- Microscopically, growth occurs by adding individual atoms



$$\frac{L_f}{T_m} \geq \sim 4R \quad \Delta S \geq \sim 4R$$

- **Microscopically flat**
- With stepped or zig-zagged Features
- Si, Ge, and nonmetals  
Si:  $T_m = 1414 \text{ }^\circ\text{C}$   
 $L = 1790 \text{ kJ/kg} = 50.26 \text{ kJ/mol} \rightarrow$   
Higher energy for broken bonds

## **Lateral growth**

- Microscopically, growth occurs along the solid-liquid interface



# Continuous Growth

## □ If broken bonds have lower energy

- High vacancy concentration at the solid-liquid interface
- Fast interface “reaction” or  $S \rightarrow L$  conversion
- Activation energy  $\Delta G_a \cong$  diffusion activation energy in liquid (very small)
- Driving force for solidification (solid growth)

$$\Delta G = \frac{L}{T_m} \cdot \Delta T_i$$

$L$  Latent heat of the melting

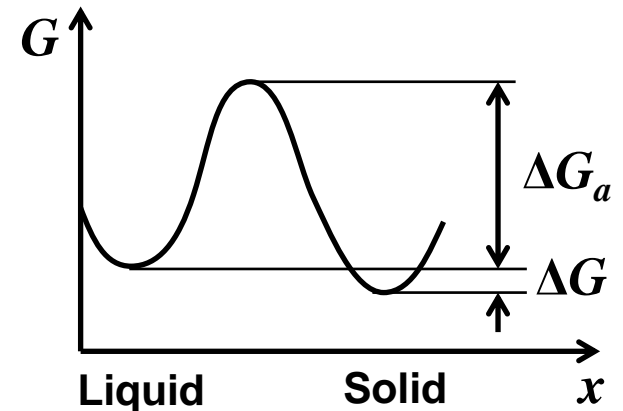
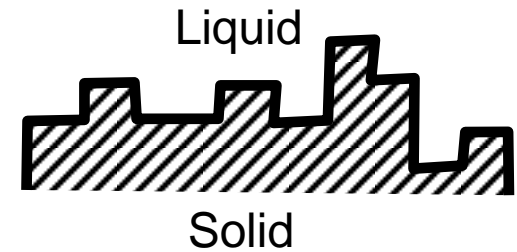
$\Delta T_i$  Undercooling at the solid-liquid interface

- Velocity of the solid-liquid interface (growth rate of solid)

$$v \propto \Delta G \propto \Delta T_i$$

- Mobility of diffuse solid-liquid interface is extremely high
- For normal rate of **metal** solidification,  $\Delta T_i < 1 \text{ }^\circ\text{C} \rightarrow$

**Solid-liquid “diffuse” interface at close to equilibrium  $T_m$  in solidification**





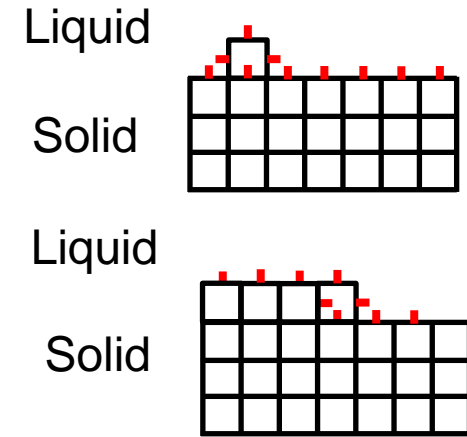


# Lateral Growth

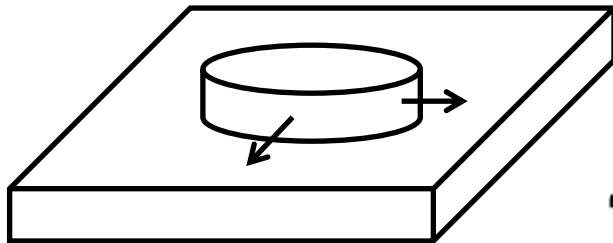
## ❑ If broken bonds have higher energy (e.g. for Si)

- A single atom attached to a flat surface creates multiple broken bonds and tend to dissolve back, leading to limited perpendicular growth
- Atoms prefer to attach to solid at existing ledge or jog positions, leading to lateral growth

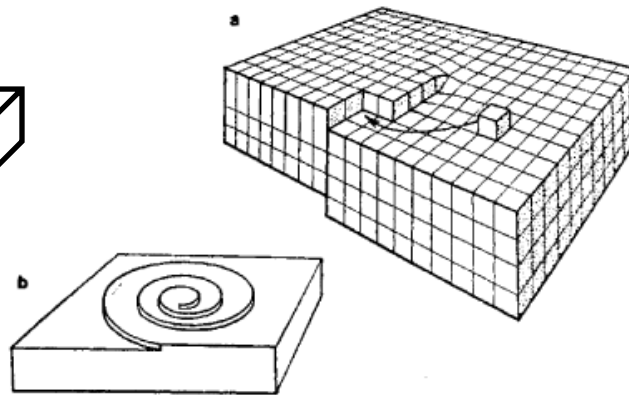
## ❑ Possible growth geometries



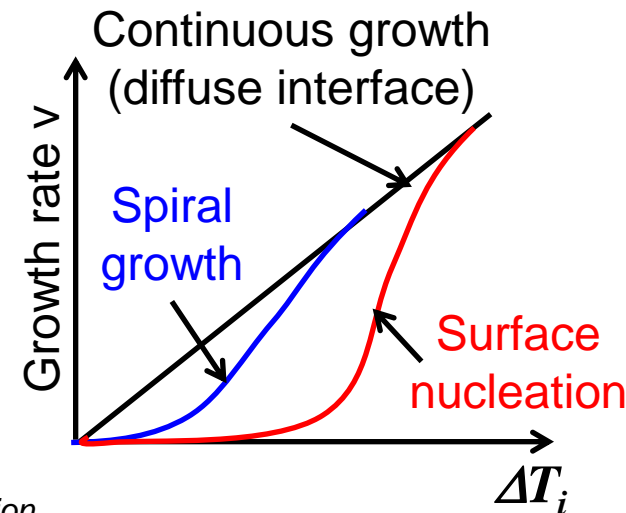
### Surface Nucleation



### Spiral Growth



<http://encyclopedia2.thefreedictionary.com/Crystallization>



- Lateral growth kinetically slower due to fewer geometric locations



# Temperature Profile & Growth of a Pure Solid (1)

❑ Rate of solidification of pure solid determined by heat conduction

❑ Solid grows into **superheated** liquid ( $T_S < T_L$ )

▪ Example

– Solidification of liquid in a mold and mold wall colder is than liquid

▪ Balance of heat flow

$\kappa_S$  Thermal conductivity of solid

$\kappa_L$  Thermal conductivity of liquid

$T_S'$  Temperature gradient in solid

$T_L'$  Temperature gradient in liquid

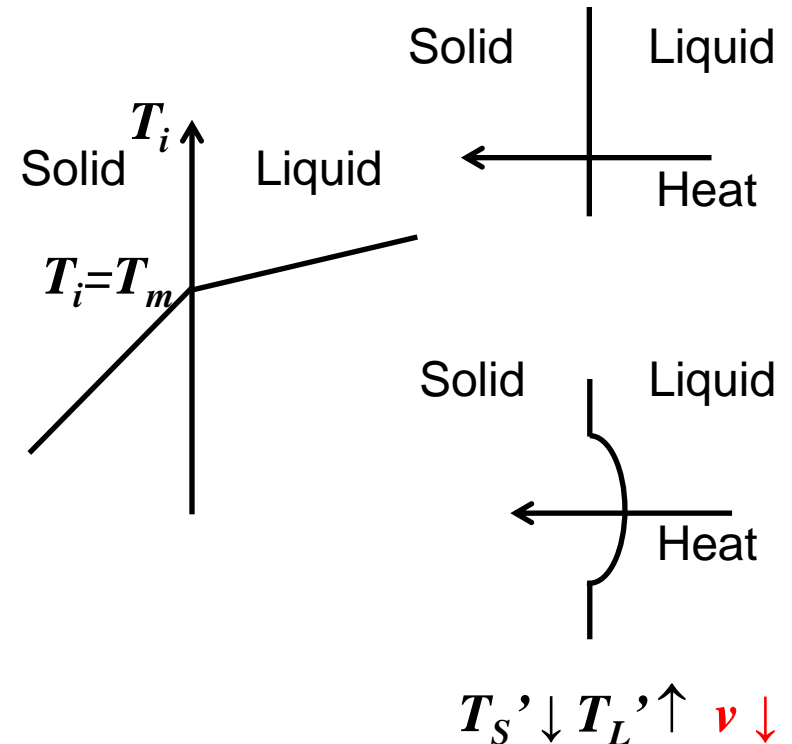
$L_v$  Latent heat of melting

$v$  Solid growth rate

$$\kappa_S T_S' = \kappa_L T_L' + v L_v$$

▪ Shape

– **Planar (macroscopically) solid-liquid interface is stable**





# Temperature Profile & Growth of a Pure Solid (2)

❑ Solid grows into supercooled liquid ( $T_S > T_L$ )

- Example
  - Beginning stage of solidification of supercooled liquid
- Balance of heat flow
$$\kappa_S T_S' + v L_v = \kappa_L T_L'$$
- Shape
  - Planar solid-liquid interface is unstable
  - Form dendrite (branch-like) structures

- (Tip) growth rate increases as tip radius decreases generally.  
Growth rate approaches zero as
  - $r$  decreases towards  $r^*$
  - $r$  increases towards  $\infty$

