

Phase Transformation of Materials

Nong-Moon Hwang

Nov. 13, 2008



$$N_{\text{hom}} \approx f_0 C_0 \exp\left\{-\frac{A}{(\Delta T)^2}\right\}$$

$$A = \frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2 kT} : \text{insensitive to Temp}$$

How do we define ΔT_N ?

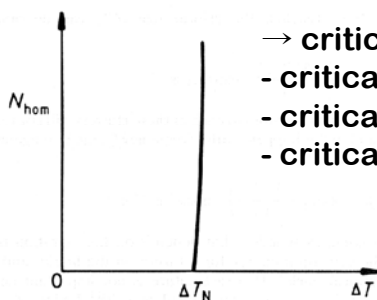
$$N_{\text{hom}} \approx 1 \text{ cm}^{-3} \text{ s}^{-1} \text{ when } \Delta G^* \sim 78 \text{ kT}$$

f_0 : frequency \propto

- The vibration frequency of the atoms,
- The activation energy for diffusion in the liquid,
- The surface area of the critical nuclei

$$f_0 \sim 10^{11}$$

$$C_0 \sim 10^{29} \text{ atoms/m}^3$$



- critical value for detectable nucleation
- critical supersaturation ratio
 - critical driving force
 - critical supercooling

Fig. 4.6 The homogeneous nucleation rate as a function of undercooling ΔT . ΔT_N is the **critical undercooling** for homogeneous nucleation.



Real Behavior of Nucleation

Under suitable conditions liquid nickel can be undercooled (or supercooled) to 250 K below T_m (1453°C) and held there indefinitely without any transformation occurring.

In the refrigerator, however, water freezes even ~ 1 K below zero.

In winter, we observe that water freezes ~ a few degrees below zero.

Why this happens? What is the underlying physics?

Which equation should we examine?

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

$$N_{\text{hom}} = f_0 C_0 \exp\left(-\frac{\Delta G_{\text{hom}}^*}{kT}\right)$$

Normally undercooling as large as 250 K are not observed.

The nucleation of solid at undercooling of only ~ 1 K is common.



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

Nucleation becomes easy if $\gamma_{SL} \downarrow$
by forming nucleus from mould wall

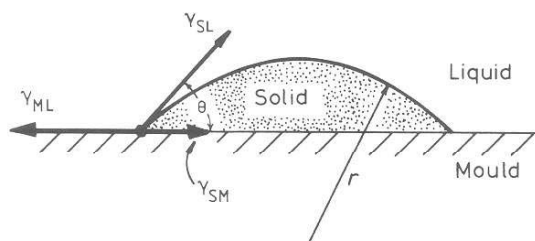


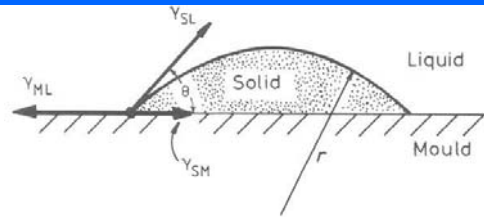
Fig. 4.7 Heterogeneous nucleation of spherical cap on a flat mould wall.



Nucleation on the wall

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

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



When nucleation takes place on the mould wall as shown in the figure, the free energy change for nucleation can be written as follows.

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

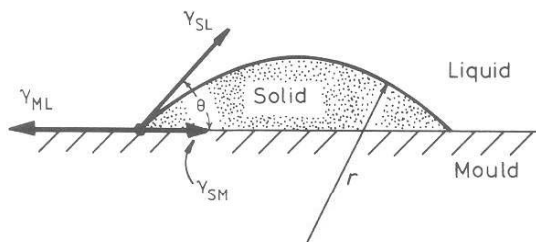
Here, V_s is the volume of the nucleus with a shape of a spherical cap and A_{SL} and A_{SM} are areas of solid-liquid and solid-mould interfaces, respectively.

Express V_s , A_{SL} and A_{SM} in terms of the wetting angle (θ) and the cap radius (r). And using these expressions, derive the new simplified expression of ΔG_{het} .



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

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



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

In terms of the wetting angle (θ) and the cap radius (r)

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

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



$S(\theta)$ has a numerical value ≤ 1 dependent only on θ (the shape of the nucleus)

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} \text{ and}$$

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot S(\theta)$$

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

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

- $\theta = 10 \rightarrow S(\theta) \sim 10^{-4}$
- $\theta = 30 \rightarrow S(\theta) \sim 0.02$
- $\theta = 90 \rightarrow S(\theta) \sim 0.5$

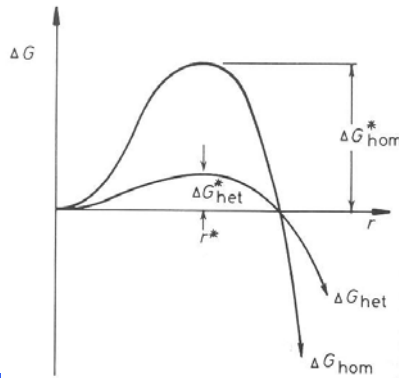
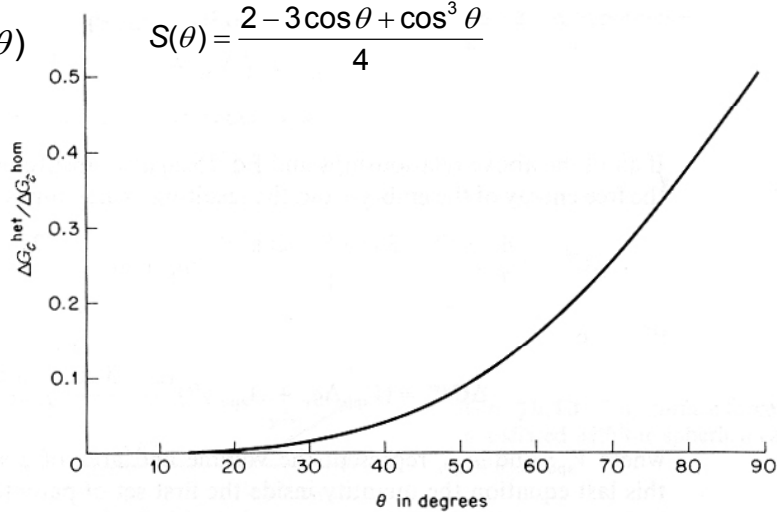


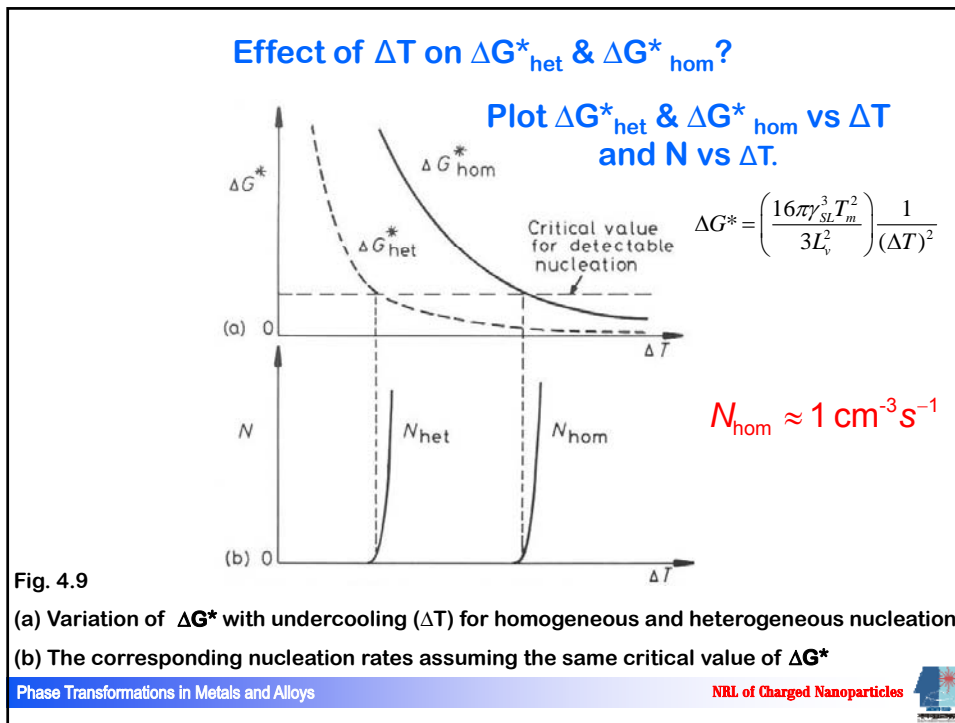
Fig. 4.8 The excess free energy of solid clusters for homogeneous and heterogeneous nucleation. Note r^* is independent of the nucleation site.



Heterogeneous Nucleation

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





Barrier of Heterogeneous Nucleation

$$\Delta G^*_{het} = \left(\frac{16\pi\gamma_{sl}^3}{3\Delta G_v^2} \right) \cdot \frac{(2 + \cos^3 \theta - 3\cos \theta)}{4}$$

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

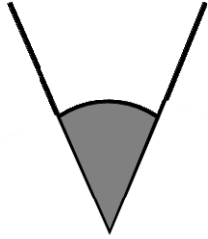
$\Delta G^*_{sub} = \Delta G^*_{homo} \left(\frac{2 - 3\cos \theta + \cos^3 \theta}{4} \right)$

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

How about the nucleation at the crevice or at the edge?

Phase Transformations in Metals and Alloys NRL of Charged Nanoparticles

Nucleation Barrier at the crevice



What would be the shape of nucleus and the nucleation barrier for the following conditions?

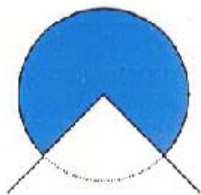
contact angle = 90
groove angle = 60

$$\frac{1}{6} \Delta G_{\text{homo}}^*$$

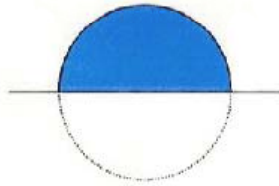
contact angle = 30
groove angle = 60



Effect of Substrate Geometry



$$\frac{3}{4} \Delta G_{\text{homo}}^*$$



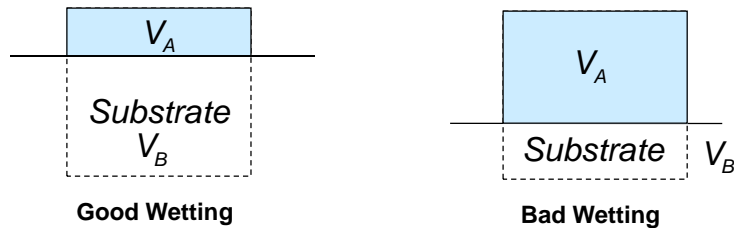
$$\frac{1}{2} \Delta G_{\text{homo}}^*$$



$$\frac{1}{4} \Delta G_{\text{homo}}^*$$



How do we treat the non-spherical shape?



$$\Delta G_{sub}^* = \Delta G_{homo}^* \left(\frac{V_A}{V_A + V_B} \right)$$

Effect of good and bad wetting on substrate



Nucleation of melting

Although nucleation during solidification usually requires some undercooling, melting invariably occurs at the equilibrium melting temperature even at relatively high rates of heating.

Why?

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

wetting angle = 0 → No superheating required!



Growth of a pure solid

Two types of solid-liquid interface

1. Continuous growth :
Atomically rough (or diffuse) interface
2. Lateral growth :
Atomically flat (of sharply defined) interface



Growth

We have learned nucleation.
Once nucleated, the nucleus will grow.
How does it grow?

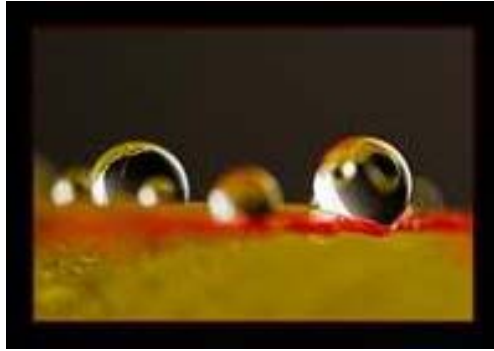
In order to see the details of growth,
we need to know the structure
of the surface on an atomic scale.

How does it look like?

Do liquid and solid nuclei differ
in growth mechanism?



Water Drops



Phase Transformations in Metals and Alloys

NRL of Charged Nanoparticles



Natural Minerals



Topaz



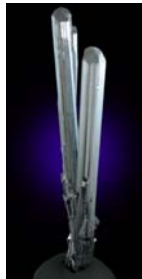
Elbaite Tourmaline



Azurite



Hematite + Quartz



Stibnite



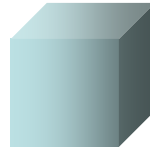
Fluorophyllite

Phase Transformations in Metals and Alloys

NRL of Charged Nanoparticles



Equilibrium Shape and Interface Structure on an Atomic Scale



How do you like to call them?

rough interface

singular (smooth) interface

What about the dependence of surface energy on crystal directions?

isotropic γ

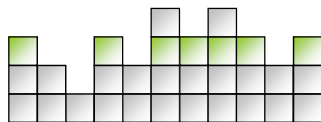
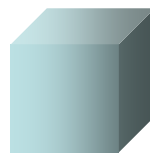
anisotropic γ

Compare the kinetic barrier for atomic attachment.

Which has a low growth barrier?



Equilibrium Shape and Interface Structure on an Atomic Scale



atomically-disordered

atomically-flat

Apply thermodynamics to this fact and derive more information.

Entropy-dominant

Enthalpy-dominant

stable at high T

stable at low T

