2023 Fall

“Phase Transformation *in* Materials”

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Contents for previous class

Solidification: Liquid → Solid

- **Nucleation in Pure Metals**
- **Homogeneous Nucleation**

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

r* & ΔG* ↓ as ΔT ↑

$$\boxed{N_{\text{hom}} \approx f_0 C_o \exp\{-\frac{A}{(\Delta T)^2}\} \sim \frac{1}{\Delta T^2}}$$

- **Heterogeneous Nucleation**

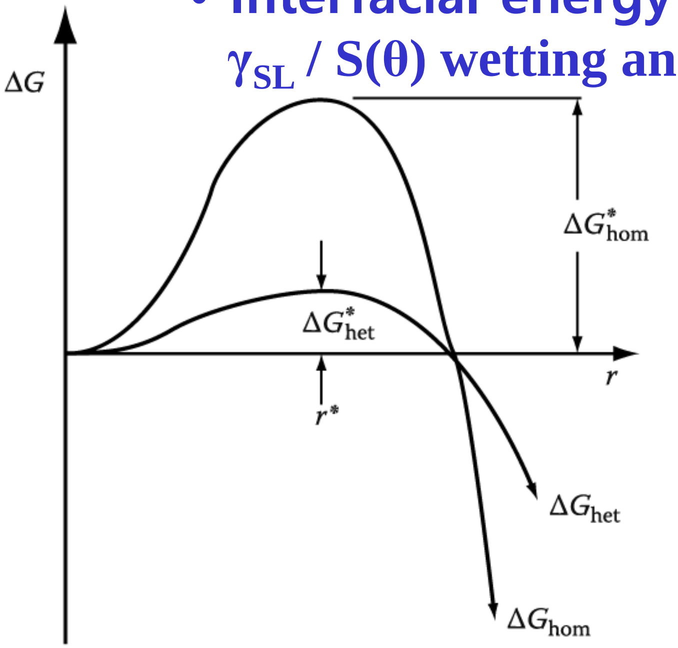
$$\boxed{\Delta G_{het}^* = S(\theta)\Delta G_{\text{hom}}^*}$$

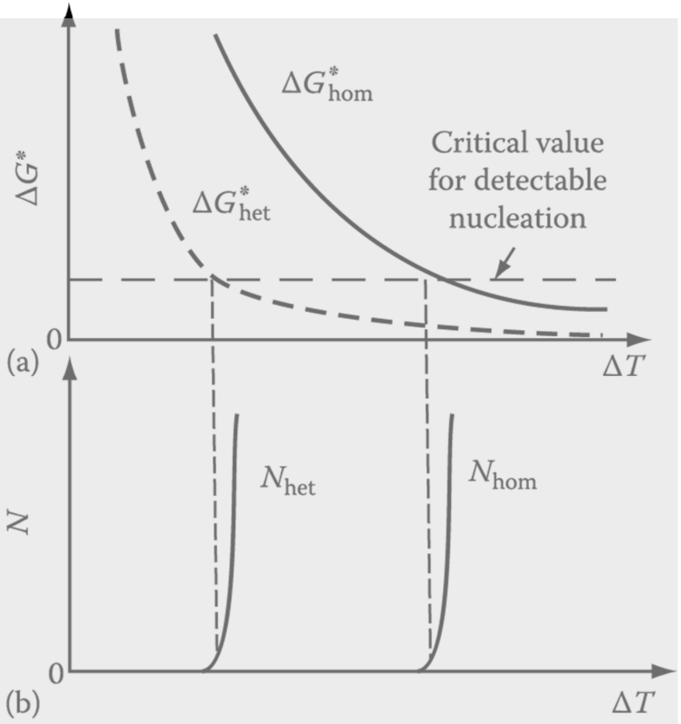
$$\boxed{\frac{V_A}{V_A + V_B} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = S(\theta)}$$

- **Nucleation of melting**

$$\boxed{\gamma_{SL} + \gamma_{LV} < \gamma_{SV}}$$ (commonly)

- **Undercooling ΔT**
- **Interfacial energy**
  γ_{SL} / S(θ) wetting angle





Contents for previous class

Solidification: Liquid $\longrightarrow$ Solid

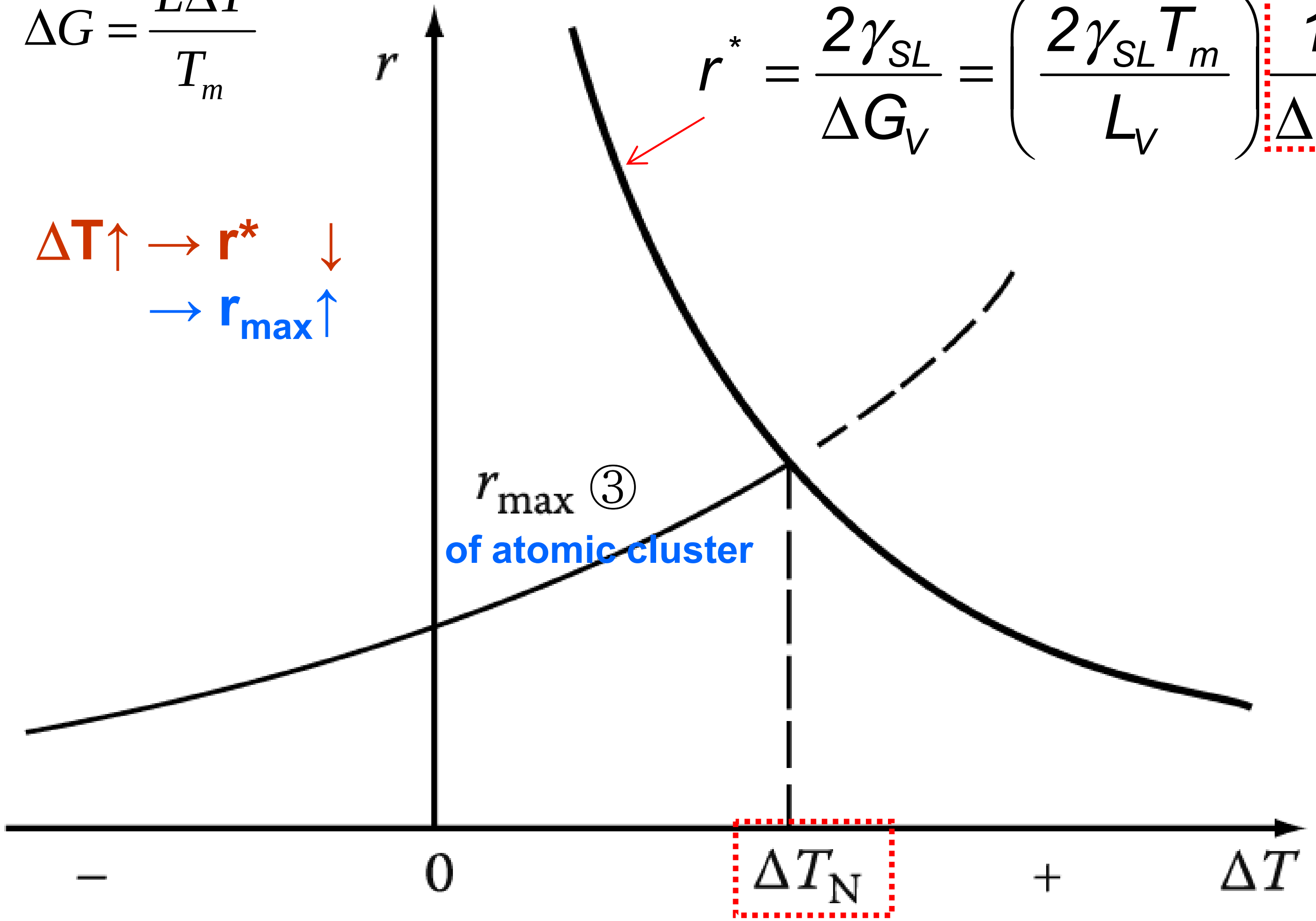
The creation of a critical nucleus ~ thermally activated process

$$\Delta G = \frac{L\Delta T}{T_m}$$

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \left(\frac{2\gamma_{SL}T_m}{L_V}\right)\boxed{\frac{1}{\Delta T}}$$

ΔT↑ → r* ↓

→ r_{max}↑



ΔT_N is the critical undercooling for homogeneous nucleation.

Fig. 4.5 The variation of r* and r_{max} with undercooling ΔT

The number of clusters with r^* at $\Delta T < \Delta T_N$ is negligible.

Real behavior of nucleation: metal $\Delta T_{bulk} < \Delta T_{small\ drop}$

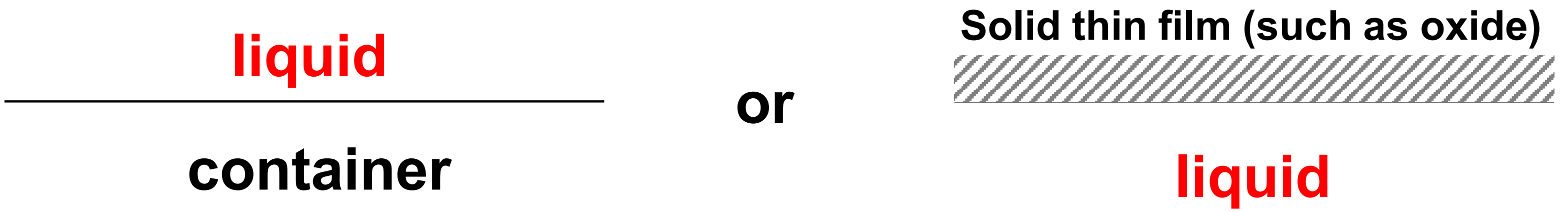
Under suitable conditions, liquid nickel can be undercooled (or supercooled) to 250 K below T_m (1453°C) and held there indefinitely without any transformation occurring.

Normally undercooling as large as 250 K are not observed.

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

The formation of a nucleus of critical size can be catalyzed by a suitable surface in contact with the liquid. → "Heterogeneous Nucleation"

Ex)



Why this happens? What is the underlying physics?

Which equation should we examine?

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

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

Q: Real behavior of nucleation: “Heterogeneous nucleation”

4.1.3. Heterogeneous nucleation

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

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

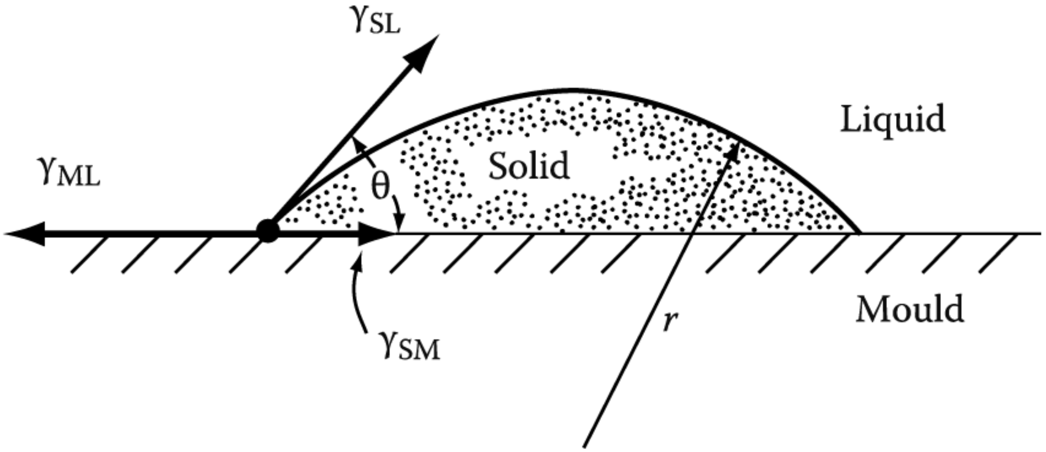


Fig. 4.7 Heterogeneous nucleation of spherical cap on a flat mould wall.

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

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

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

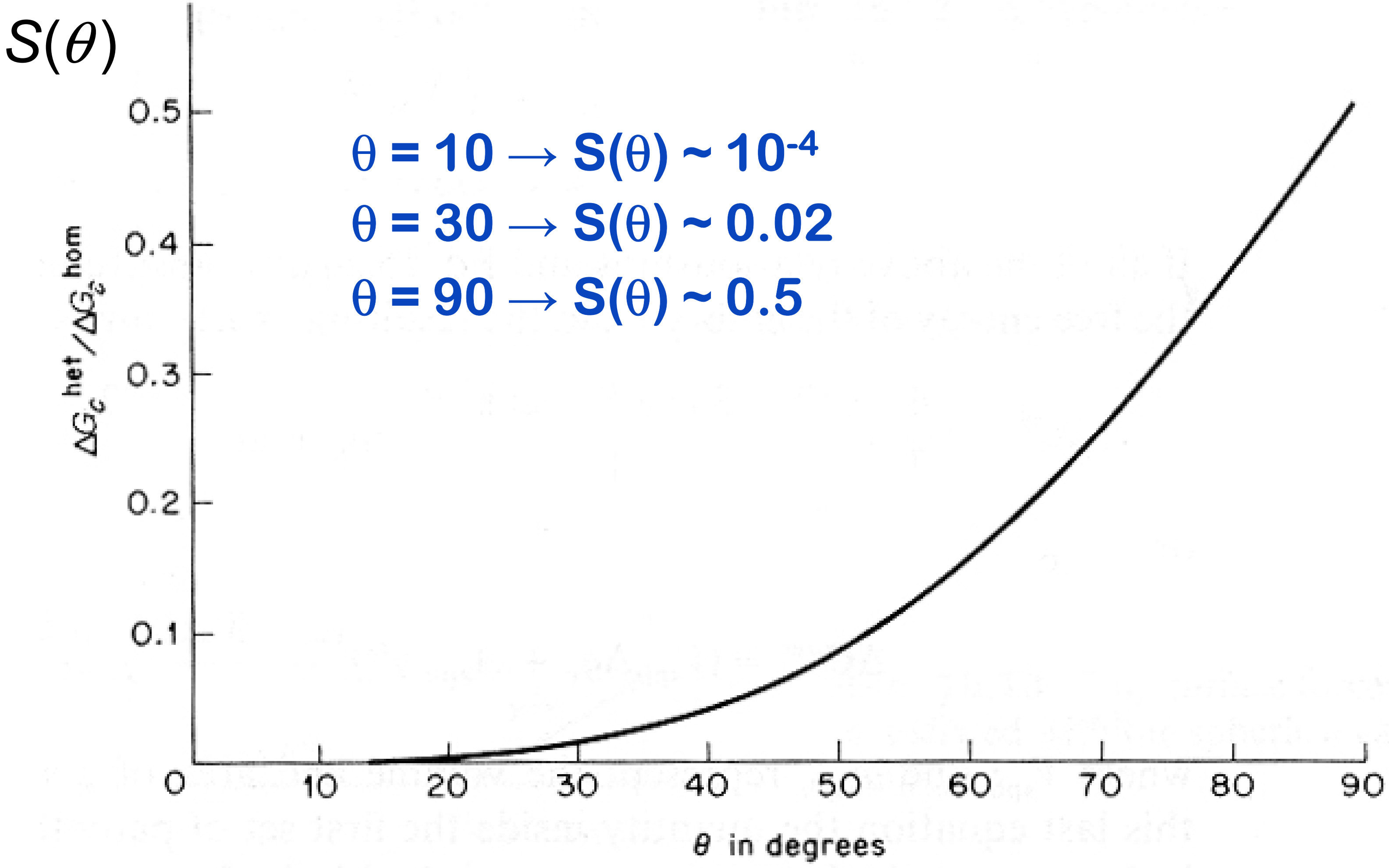
In terms of the wetting angle (θ) and the cap radius (r) (Exercies 4.6)

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

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

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

$$\boxed{\Delta G^*_{het} = S(\theta)\Delta G^*_{\mathrm{hom}}} \Rightarrow \quad r^* = \frac{2\,\gamma_{SL}}{\Delta G_V} \quad and \quad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}\cdot S(\theta)$$



θ = 10 → S(θ) ~ 10^{-4}

θ = 30 → S(θ) ~ 0.02

θ = 90 → S(θ) ~ 0.5

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

$$\Delta G^*_{het} = S(\theta)\Delta G^*_{hom} \Rightarrow r^* = \frac{2\gamma_{SL}}{\Delta G_V} \quad and \quad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}\cdot S(\theta)$$

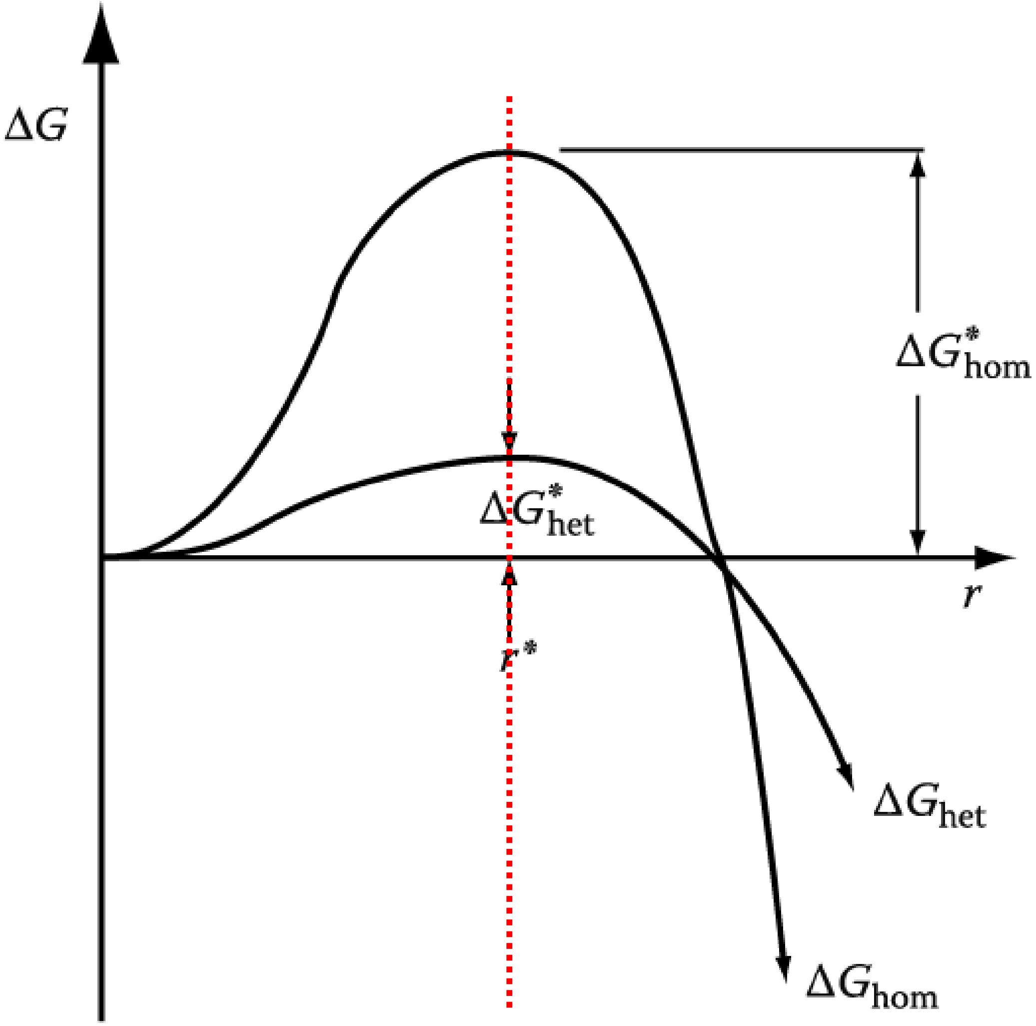


Fig. 4.8 The excess free energy of solid clusters for homogeneous and heterogeneous nucleation. Note r* is independent of the nucleation site.

The Effect of ΔT on ΔG^*_{het} & ΔG^*_{hom}?

Plot ΔG^*_{het} & ΔG^*_{hom} vs ΔT and N vs ΔT.

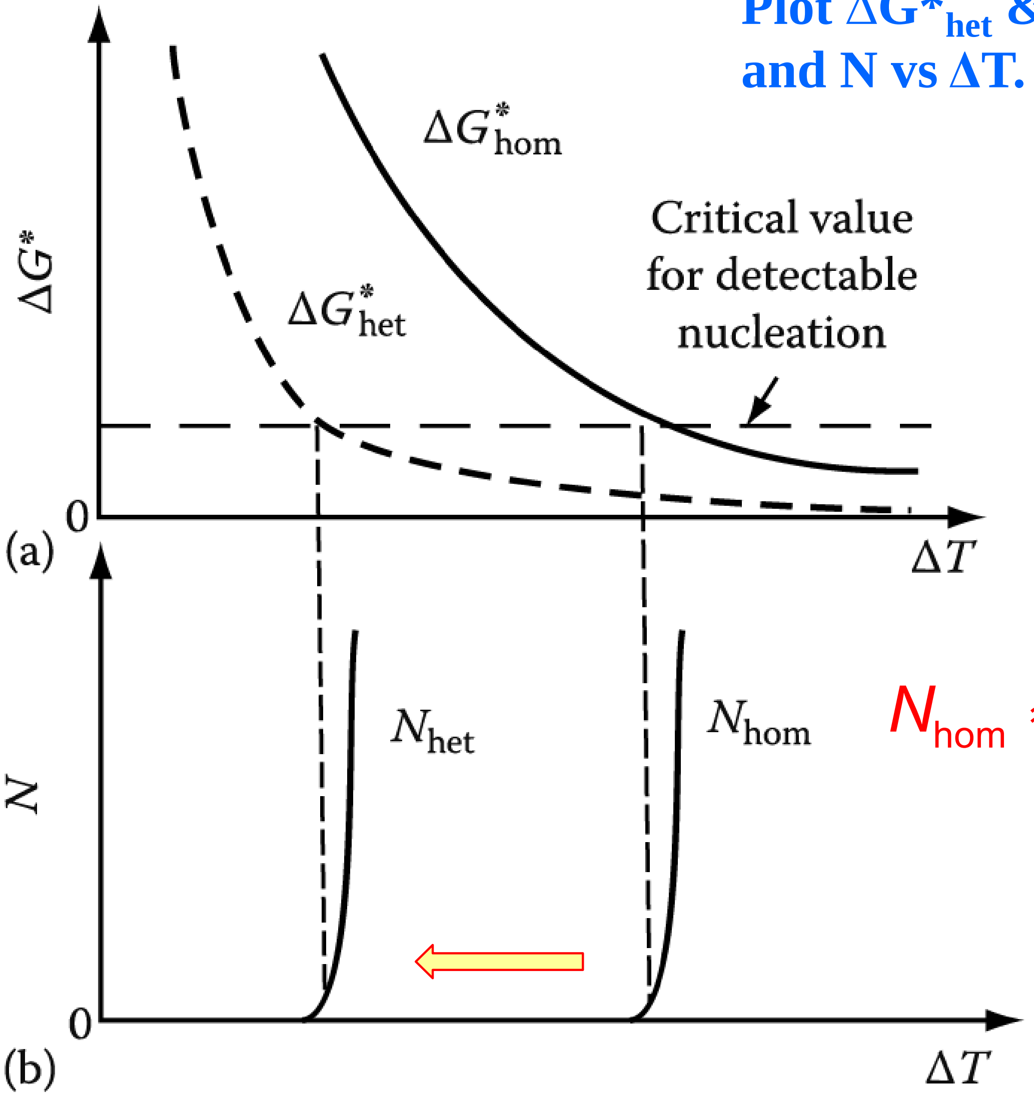
$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_V)^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3\ \ L_V^2}\right)\frac{1}{(\Delta T)^2}$$

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

n_1 atoms in contact with the mold wall

$$n^* = n_1 \exp\left(-\frac{\Delta G^*_{het}}{kT}\right)$$

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



$N_{hom} \approx 1\ \mathrm{cm}^{-3}s^{-1}$

Fig. 4.9 (a) Variation of ΔG* with undercooling (ΔT) for homogeneous and heterogeneous nucleation. (b) The corresponding nucleation rates assuming the same critical value of ΔG*

θ ↓→ V_c / V ↓ → embryo radius (r_{max}) ↑

→ condition for heterogeneous nucleation as a function of θ

Assumption 1: angle of contact is independent of temp.
2: substrate is flat.

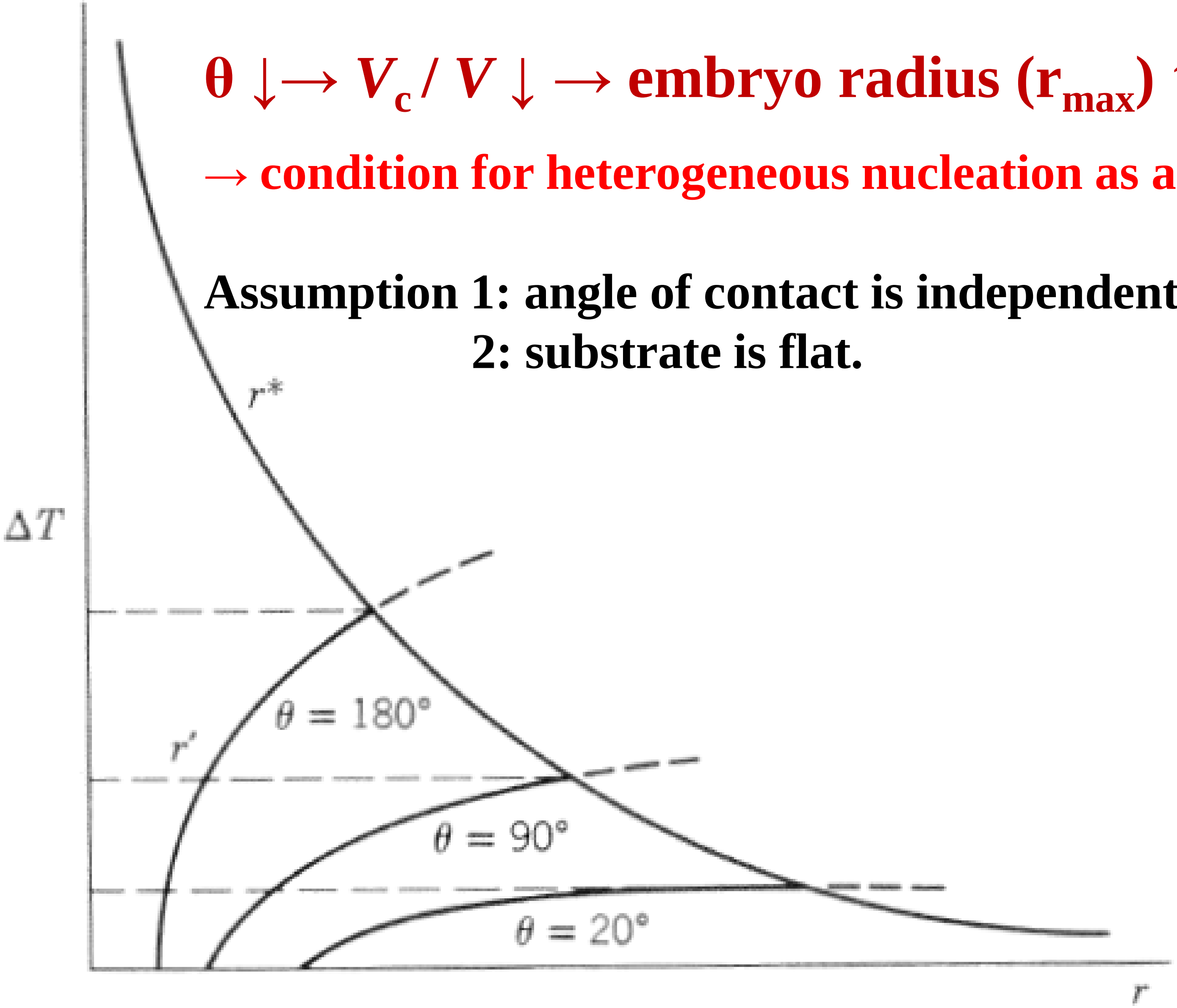
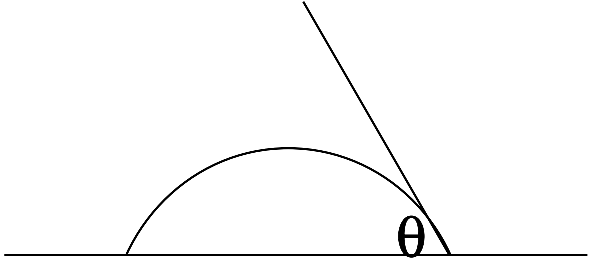


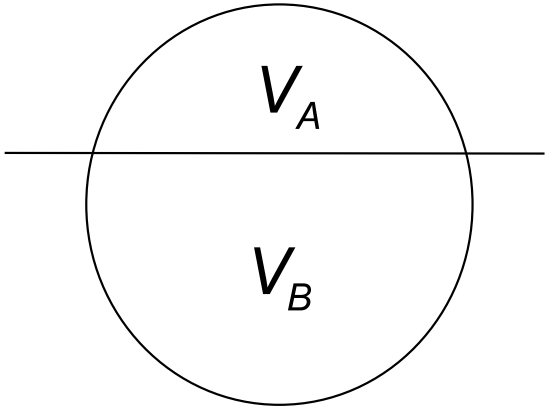
Fig. 3.15. Condition for heterogeneous nucleation (schematic).

Barrier of Heterogeneous Nucleation

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}\cdot S(\theta) = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}\cdot\frac{(2-3\cos\theta+\cos^3\theta)}{4}$$



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



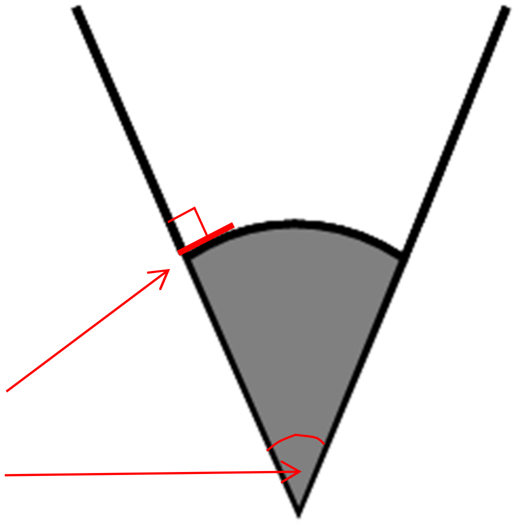
$$\Delta G^*_{sub} = \Delta G^*_{homo}\left(\frac{2-3\cos\theta+\cos^3\theta}{4}\right)$$

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

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

Nucleation Barrier at the crevice

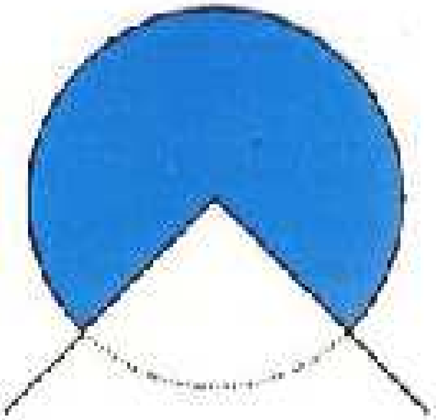
What would be the shape of nucleus and the nucleation barrier for the following conditions?



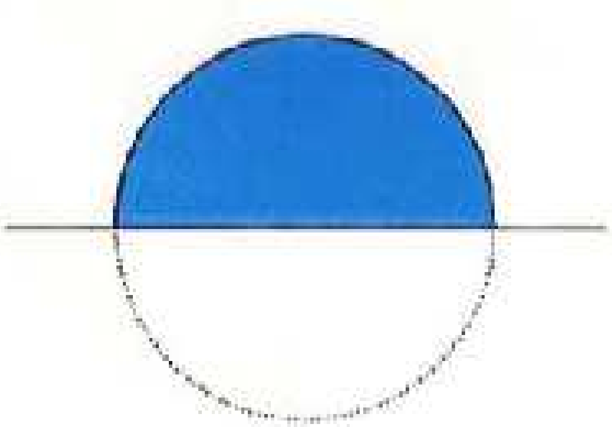
$$\frac{1}{6}\Delta G^{*}_{\text{homo}}$$

contact angle = 90

groove angle = 60



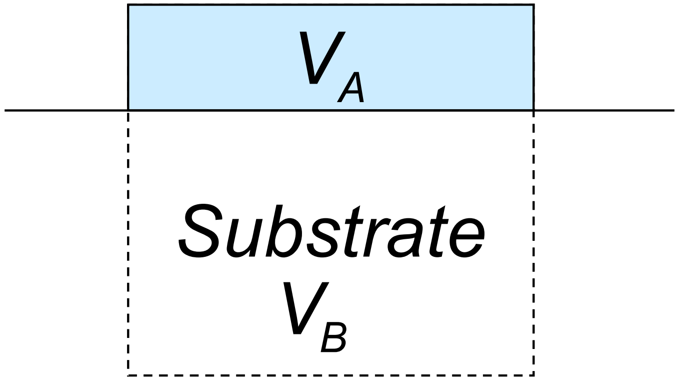
$$\frac{3}{4}\Delta G^{*}_{\text{homo}}$$



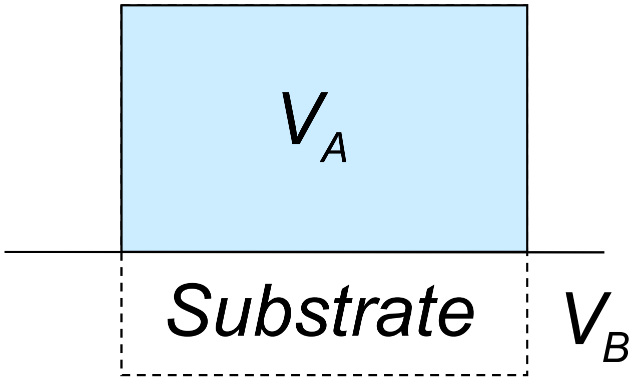
$$\frac{1}{2}\Delta G^{*}_{\text{homo}}$$

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

How do we treat the non-spherical shape?



Good Wetting



Bad Wetting

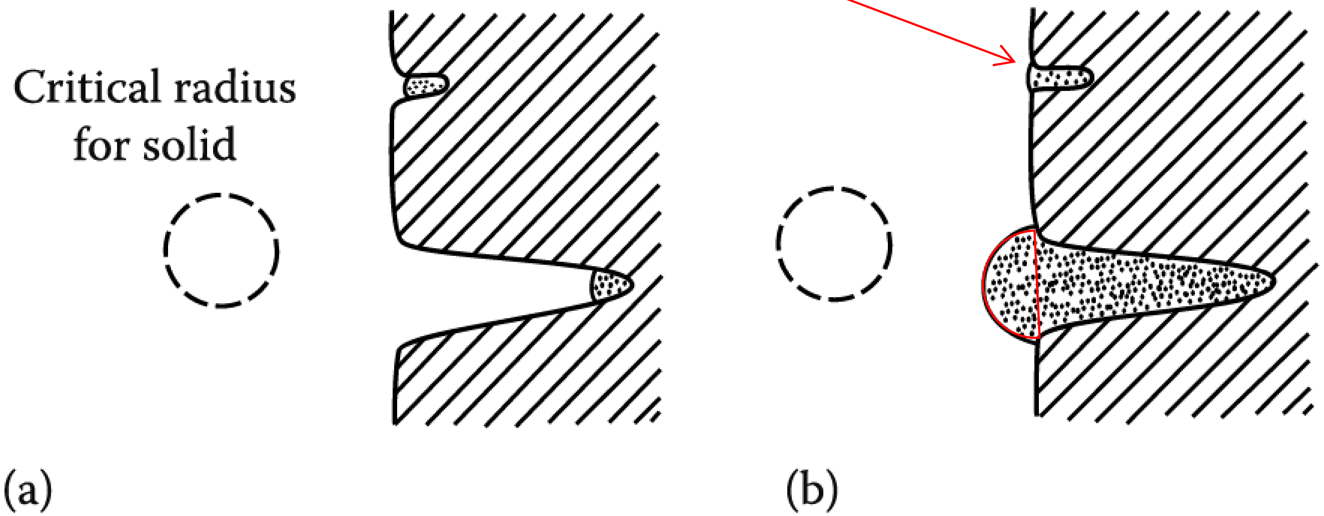
$$\Delta G^*_{sub} = \Delta G^*_{homo}\left(\frac{V_A}{V_A + V_B}\right)$$

Effect of good and bad wetting on substrate

Extreme form of a concave substrate: Nucleation inside the crevice

So far it has been assumed that the mold wall is microscopically flat.
In practice, however, it is likely to contain many microscopic cracks or crevices.

Nucleation from cracks or crevices should be able to occur at very small undercoolings even when the wetting angle θ is relatively large. However, that for the crack to be effective the crack opening must be large enough to allow the solid to grow out without the radius of the solid/liquid interface decreasing below r*.



In both of the nucleation types considered so far it can be shown that

Formation of a nucleus on such a surface

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

몰드 표면에서 핵생성 될 때 필요한 에너지

V* : volume of the critical nucleus (cap or sphere)

Inoculants ~ **low values of θ → low energy interface, fine grain size**

4.1.4 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.

Because, melting can apparently, start at crystal surfaces without appreciable superheating.

Why?

$$\boxed{\gamma_{SL}+\gamma_{LV}<\gamma_{SV}}$$ (commonly)

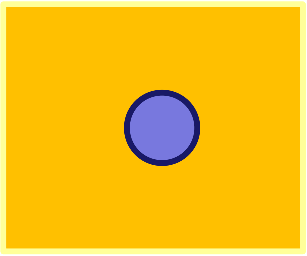
In the case of gold,

γ_{SL}	solid-liquid	132 ergs/cm
γ_{LV}	liquid-vapor	1128 ergs/cm
γ_{SV}	solid-vapor	1400 ergs/cm

In general, wetting angle = 0 ⇨ No superheating required!

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



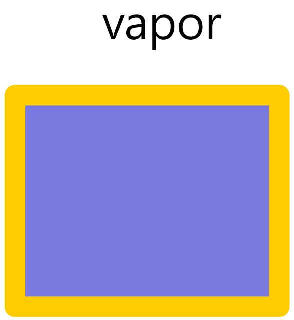
<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

No superheating required!

- Interfacial energy ⇨ No ΔT_N

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



Melting: Liquid ← Solid

Solidification: Liquid ⟶ Solid

- **Nucleation in Pure Metals**
- **Homogeneous Nucleation**

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

r* & ΔG* ↓ as ΔT ↑

$$\boxed{N_{\text{hom}} \approx f_0 C_o \exp\{-\frac{A}{(\Delta T)^{2}}\} \sim \frac{1}{\Delta T^{2}}}$$

- **Heterogeneous Nucleation**

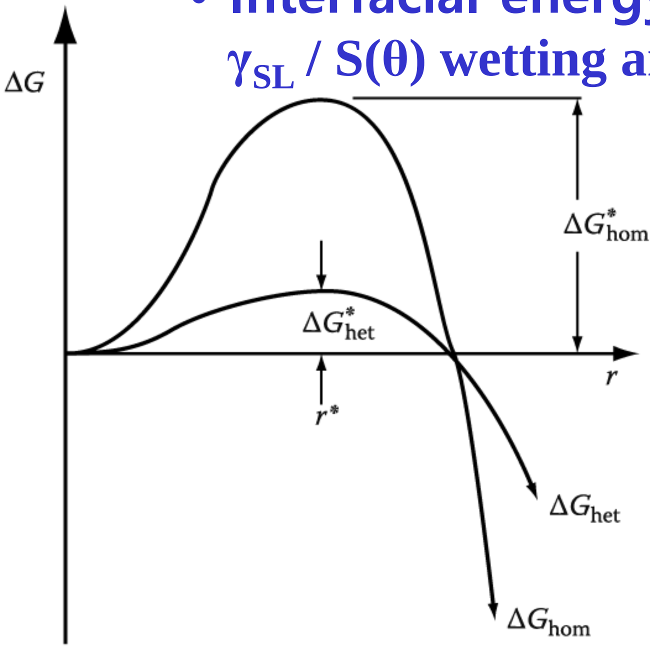
$$\boxed{\Delta G_{het}^{*} = S(\theta)\Delta G_{\text{hom}}^{*}}$$

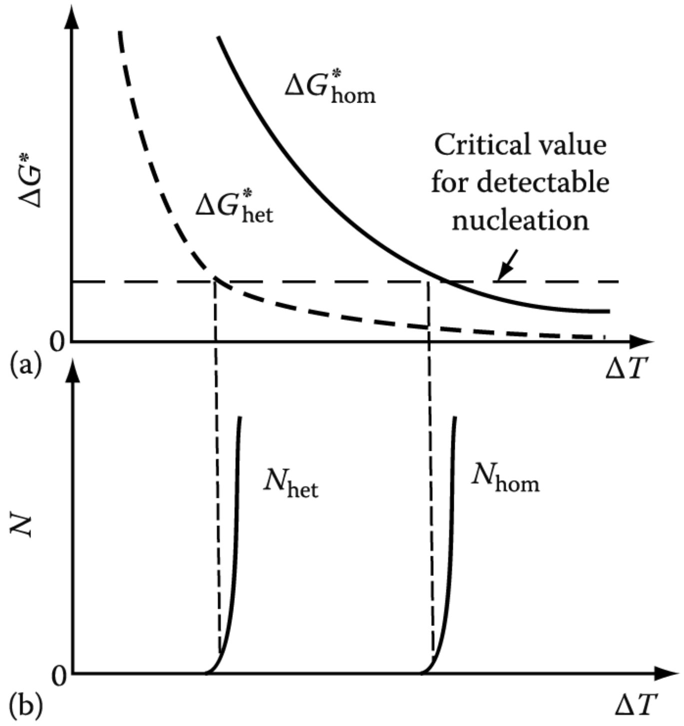
$$\boxed{\frac{V_A}{V_A + V_B} = \frac{2 - 3\cos\theta + \cos^{3}\theta}{4} = S(\theta)}$$

- **Nucleation of melting**

$$\boxed{\gamma_{SL} + \gamma_{LV} < \gamma_{SV}} \quad \textbf{(commonly)}$$

- **Undercooling ΔT**
- **Interfacial energy**
  γ_{SL} / S(θ) wetting angle





Contents for today's class

Solidification: Liquid → Solid

< Nucleation >
&
< Growth >

- Nucleation in Pure Metals

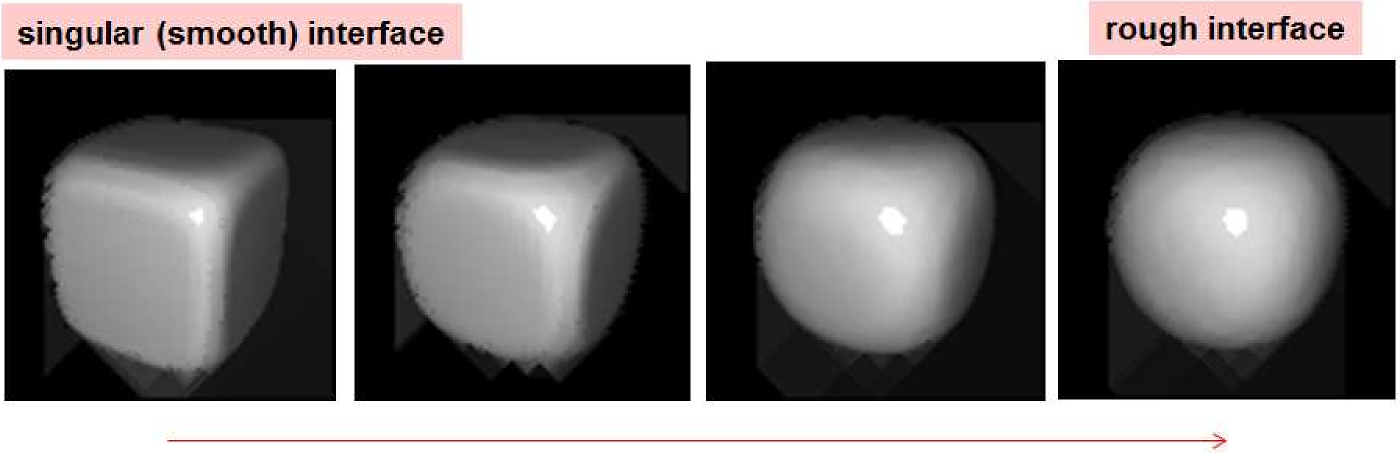
- Equilibrium Shape and Interface Structure on an Atomic Scale
- Growth of a pure solid
  - 1) Continuous growth
    : Atomically rough or diffuse interface
  - 2) Lateral growth
    : Atomically flat of sharply defined interface
- Heat Flow and Interface Stability

4.3 Alloy solidification

- Solidification of single-phase alloys
- Eutectic solidification
- Off-eutectic alloys
- Peritectic solidification

Q: Rough interface vs Singular interface?

Thermal Roughening



Heating up to the roughening transition.

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

Do not vary with crystallographic orientation,
i.e, γ-plots are spherical

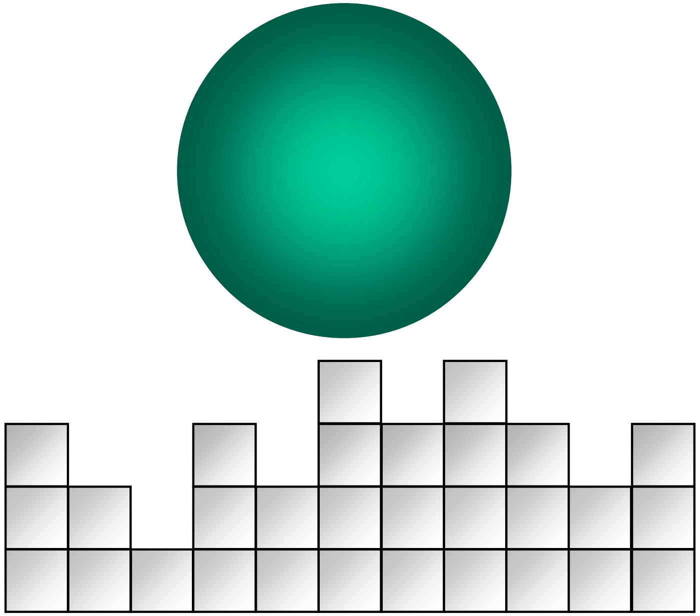
Strong crystallographic effects,
: solidify with low-index close-packed facets

Water Drops ⟷ Natural Minerals

Topaz (황옥) **Stibnite** (휘안광)

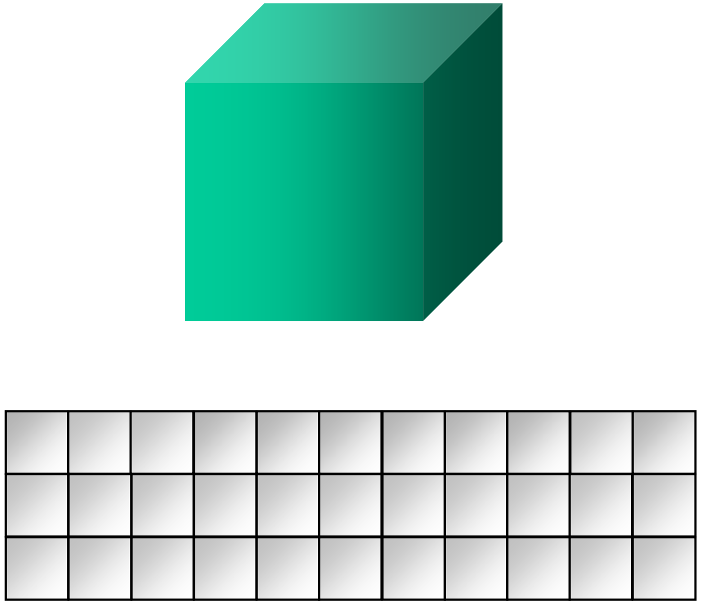
How differ the structure of the surface on an atomic scale?

Equilibrium Shape and Interface Structure on an Atomic Scale



atomically-disordered

Ex) metallic systems



atomically-flat

nonmetals

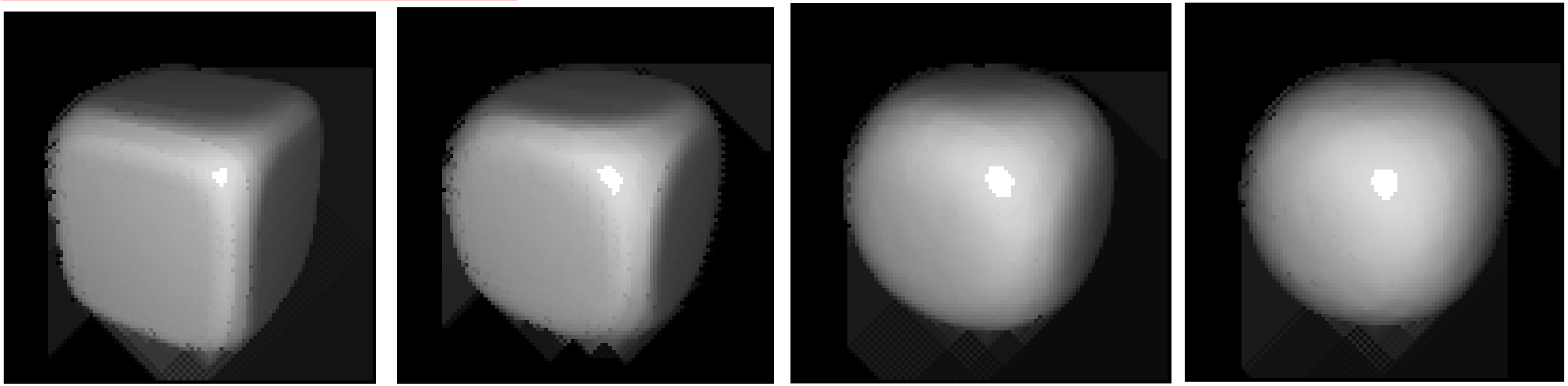
Apply thermodynamics to this fact and derive more information.

stable at high T	←	**stable at low T**
Entropy-dominant		**Enthalpy-dominant**
weak bonding energy		**strong bonding energy**

Thermal Roughening

singular (smooth) interface

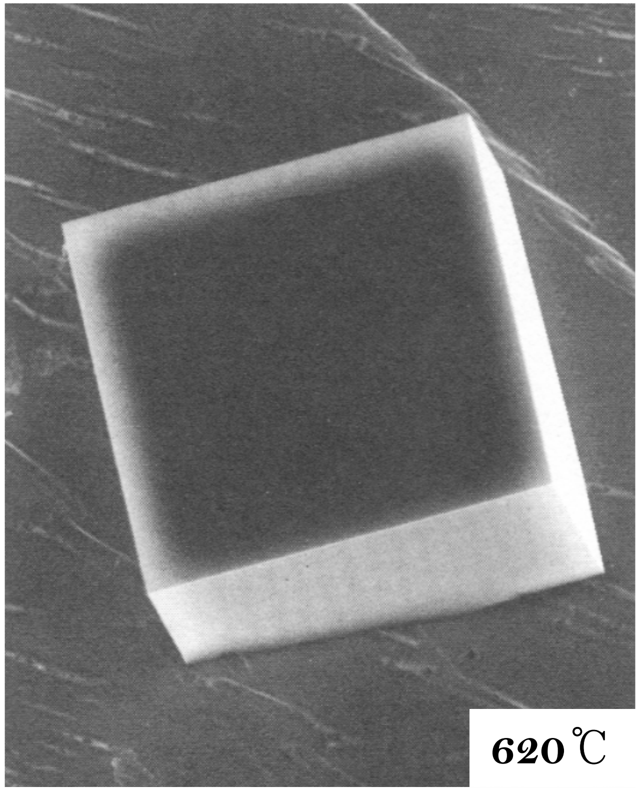
rough interface



Enthalpy-dominant → **Entropy-dominant**

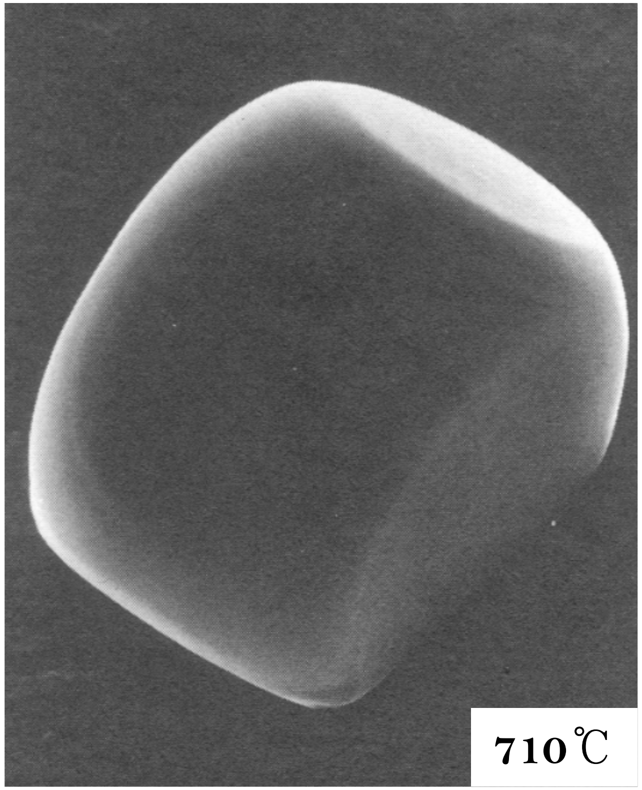
Heating up to the roughening transition.

✓ Equilibrium shape of NaCl crystal



620℃

Thermal Roughening



710℃

J.C. Heyraud, J.J. Metois, J. Crystal Growth , 84, 503 (1987)

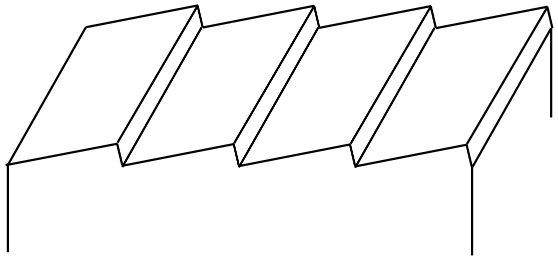
Compare the kinetic barrier for atomic attachment.

Which has a low growth barrier?

Atomic View

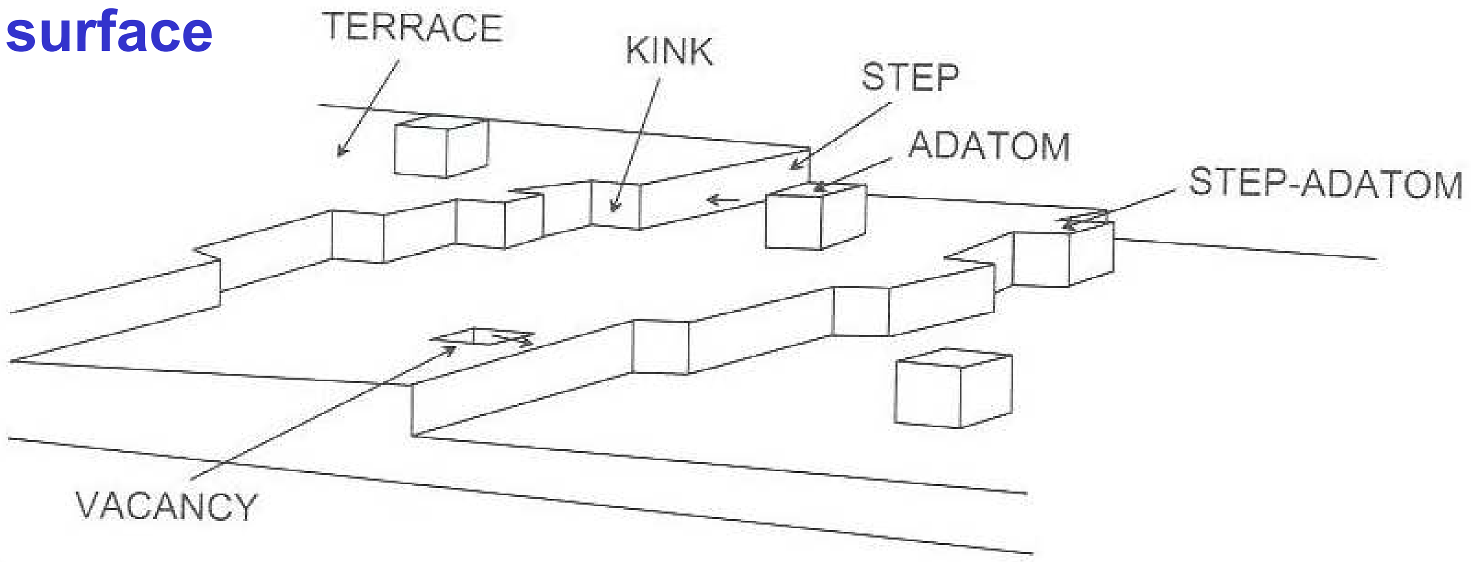
Ideal Surfaces

singular



vicinal

More realistic surface



- **Realistic surfaces of crystals typically look like this at low temperature**

→ - **At sufficiently high temperature, the structure becomes atomically rough**

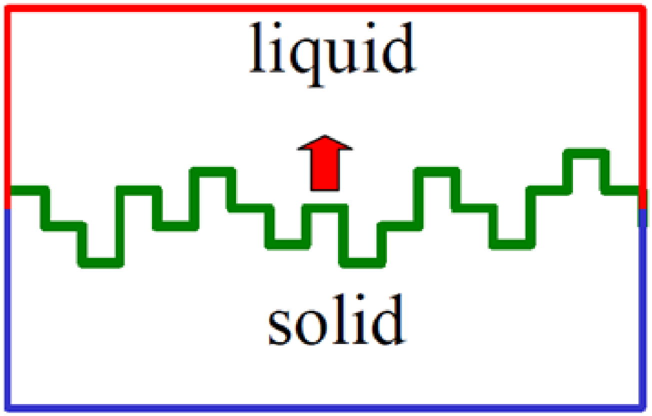
(Thermal Roughening)

Q: What kinds of Growth in a pure solid exist?

Two types of solid-liquid interface

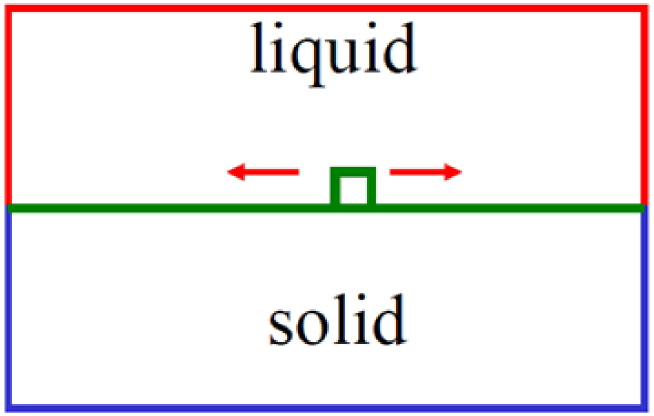
a) Continuous growth

: Atomically rough or diffuse interface



b) Lateral growth

: Atomically flat of sharply defined interface



4.2. Growth of a pure solid

: The next step after the nucleation is growth.

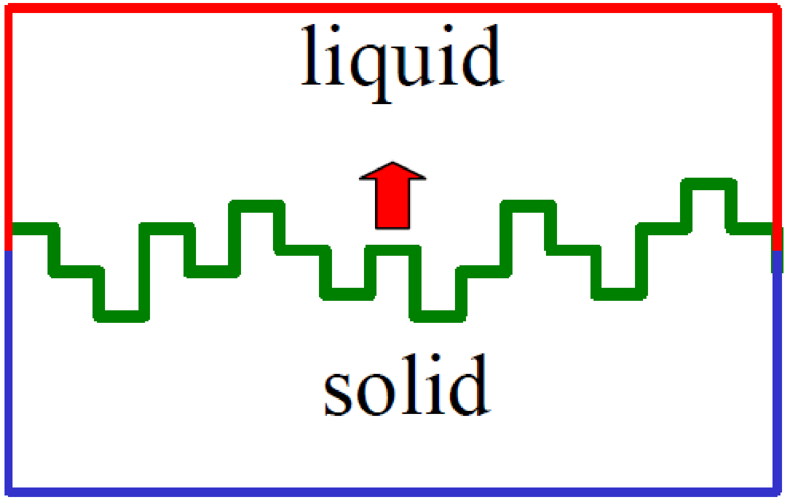
Two types of solid-liquid interface

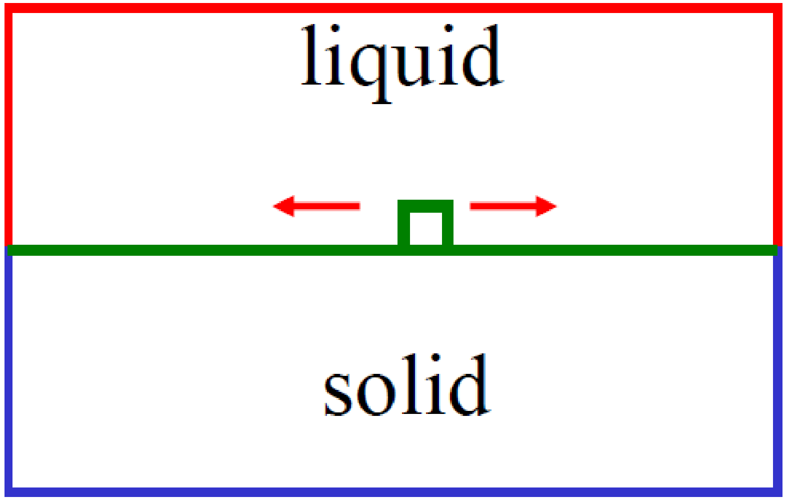
a) Continuous growth

: Atomically rough or diffuse interface

b) Lateral growth

: Atomically flat of sharply defined interface





4.2. Growth of a pure solid

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Two types of solid-liquid interface

a) Continuous growth

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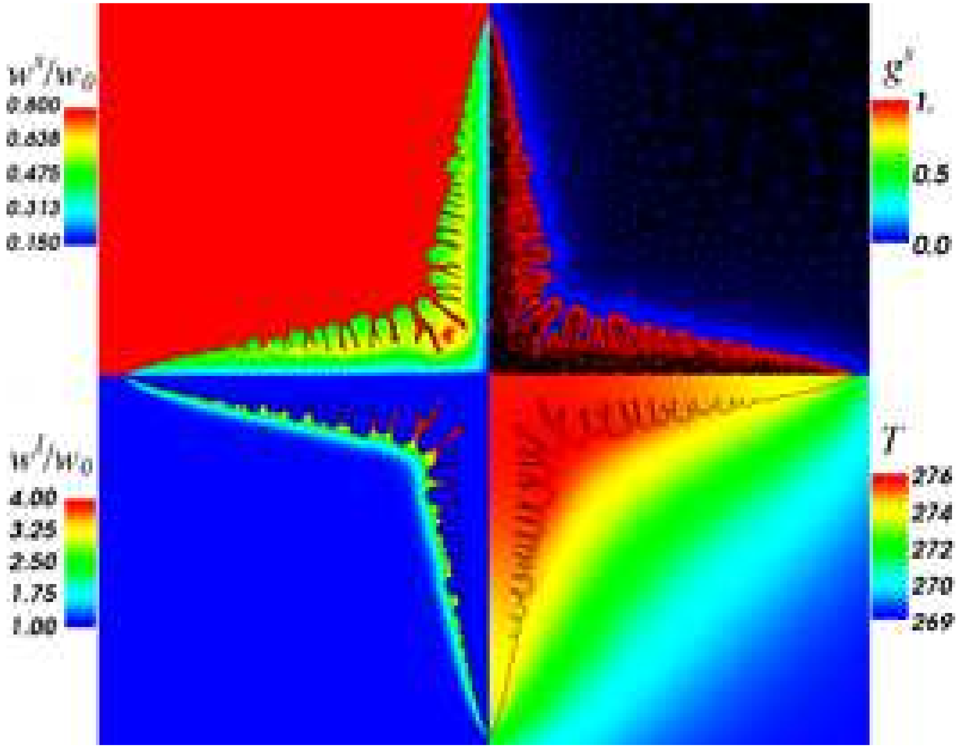

b) Lateral growth

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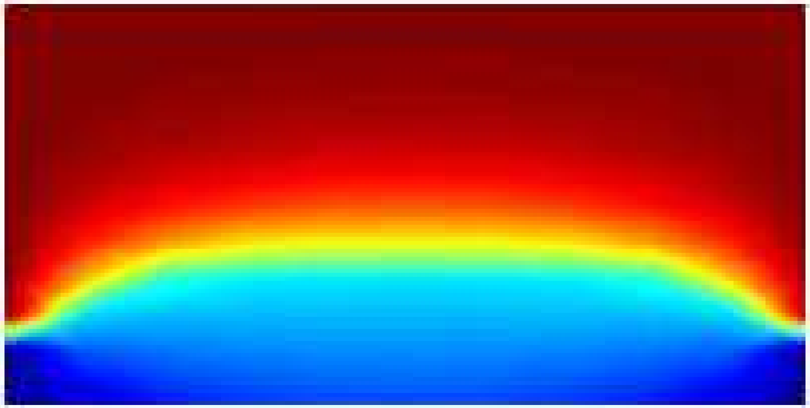
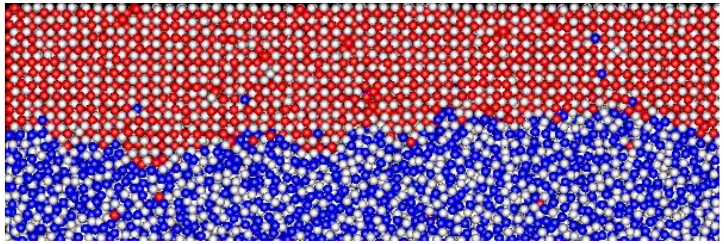


a) Continuous growth

The migration of a rough solid/liquid interface can be treated in a similar way to the migration of a random high angle grain boundary.

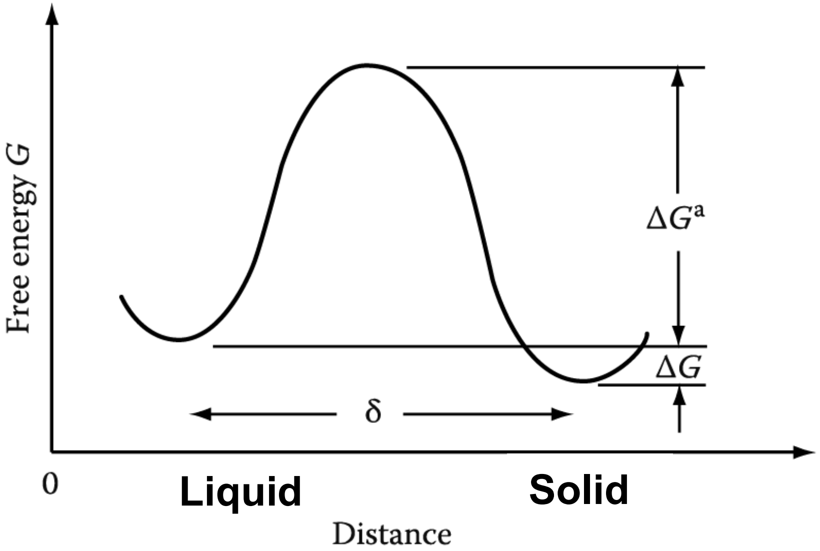


- Driving force for solidification

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

L: latent heat of melting

ΔT_i : undercooling of the interface



- Net rate of solidification

$$\boxed{v = k_1 \boxed{\Delta T_i}}$$

k_1: properties of boundary mobility

Reference (eq. 3.21) $v = M \cdot \Delta G / V_m$

The rate of the continuous growth (typical for metals) is usually a "diffusion controlled process".

- Pure metal grow at a rate controlled by heat transfer to the interfacial region.
- Alloy grow at a rate controlled by solute diffusion.

b) Lateral growth

- Materials with a high entropy of melting (~high T_m) prefer to form atomically smooth, closed-packed interfaces.
- For this type of interface the minimum free energy also corresponds to the minimum internal energy, i.e. a minimum number of broken 'solid' bonds.

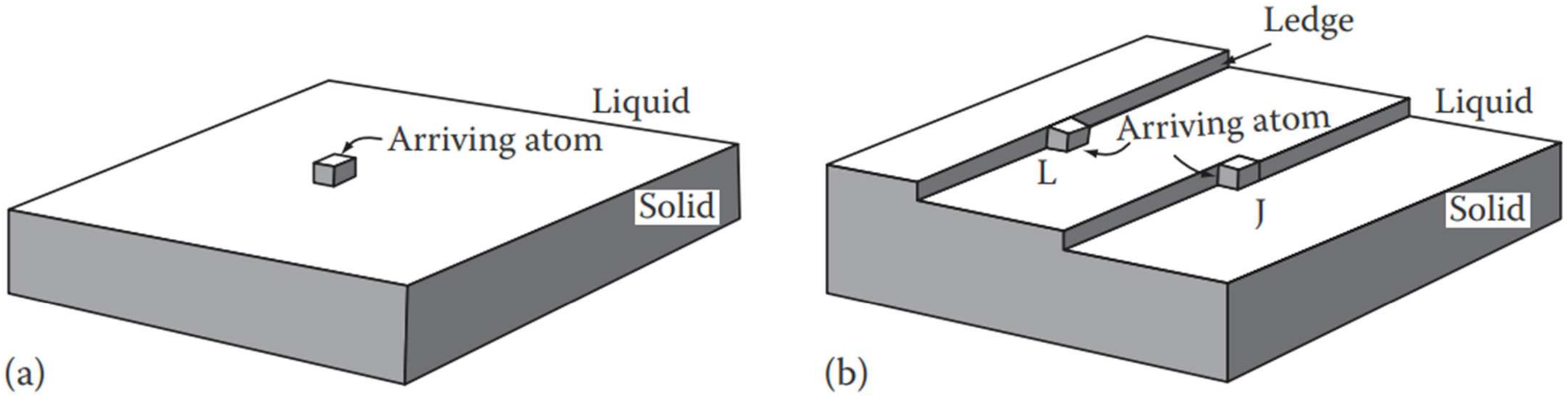


FIGURE 4.11 Atomically smooth solid/liquid interfaces with atoms represented by cubes. (a) Addition of a single atom onto a flat interface increases the number of 'broken bonds' by four. (b) Addition to a ledge (L) only increases the number of broken bonds by two, whereas at a jog in a ledge (J) there is no increase.

b) Lateral growth

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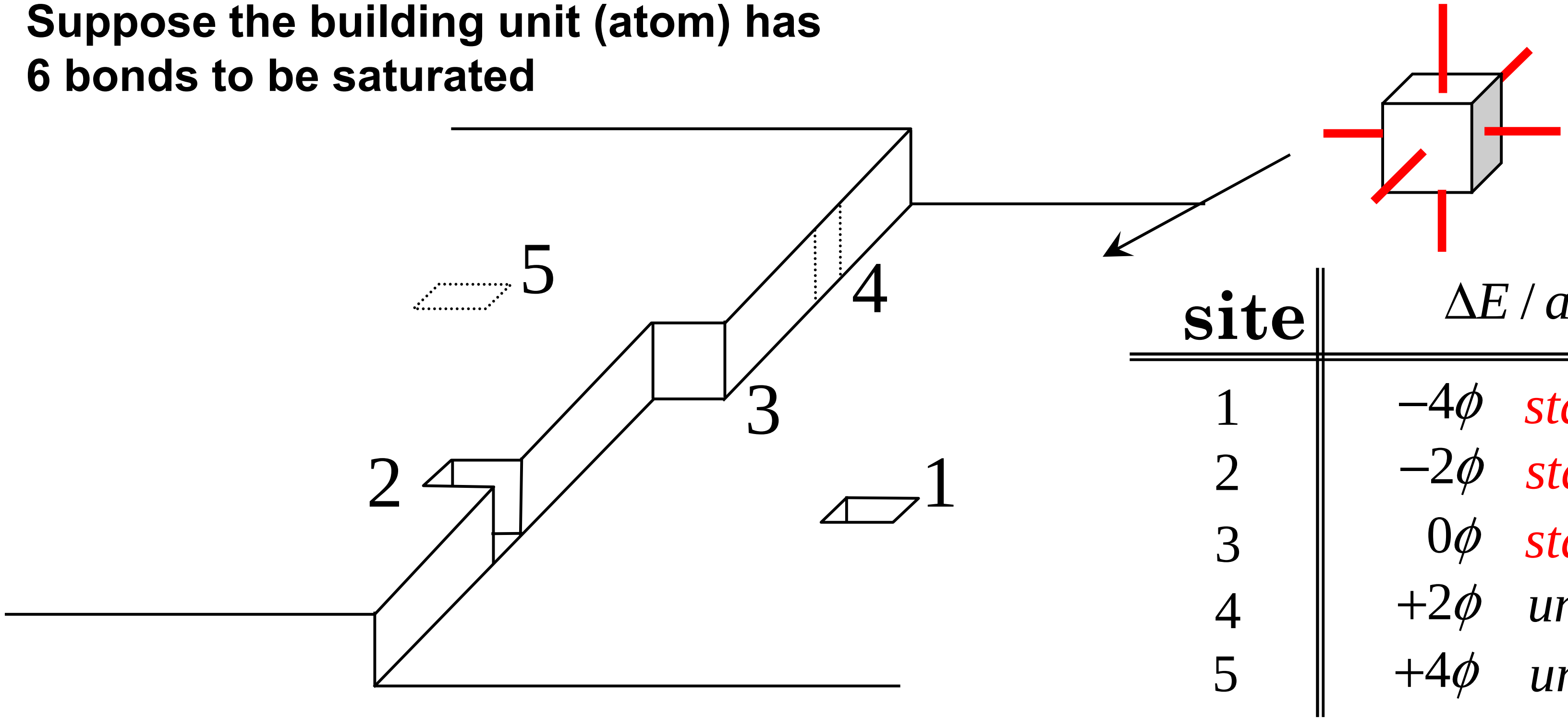
- For this type of interface the minimum free energy also corresponds to the minimum internal energy, i.e. a minimum number of broken 'solid' bonds.

Two ways in which ledges and jogs (kinks) can be provided.

① Surface (2-D) nucleation ② Spiral growth

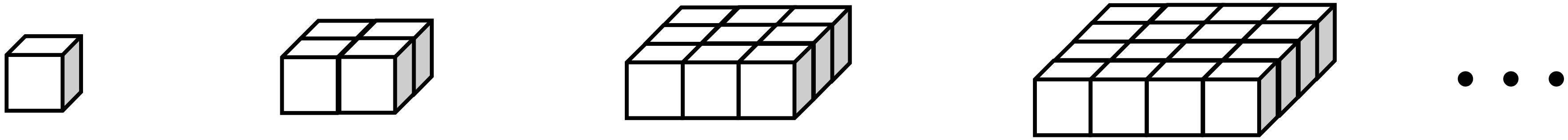
Condition for Atomic Attachment

Suppose the building unit (atom) has
6 bonds to be saturated



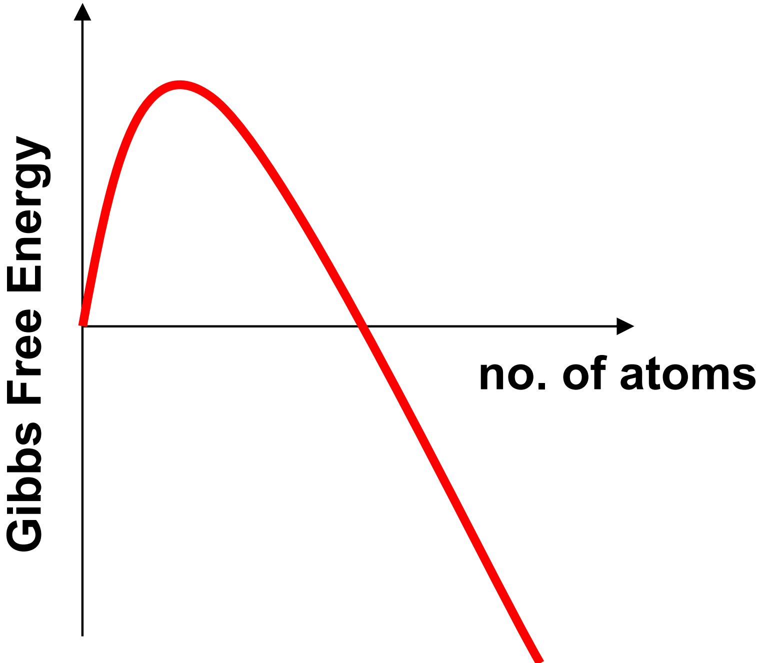
site	ΔE / atom			
1	-4ϕ	*stable*		
2	-2ϕ	*stable*		
3	0ϕ	*stable*	:	*kink*
4	$+2\phi$	*unstable*		
5	$+4\phi$	*unstable*		

How many unsaturated bonds are there if they are epitaxial to the underneath atomic layer?



$+4\phi / atom$	$+8\phi / 4\ atoms$	$+12\phi / 9\ atoms$	$+16\phi / 16\ atoms$
$\Delta f = -kT\ln(P/P_e)$	**$4\Delta f$**	**$9\Delta f$**	**$16\Delta f$**
$+4\phi / atom$	$+2\phi / atom$	$+\frac{4}{3}\phi / atom$	$+1\phi / atom$
ΔE/atom	**ΔE/atom**	**ΔE/atom**	**ΔE/atom**

Draw the plot showing how the free energy varies with the number of atoms in the presence of supersaturation (driving force) for growth.



→ 2-Dimensional Nucleation ①

- **If large # of atoms form a disc-shaped layer,**

→ self-stabilized and continue to grow.

- **ΔT becomes large, r* ↓.**
- $v \infty \exp(-k_2/\Delta T_i)$

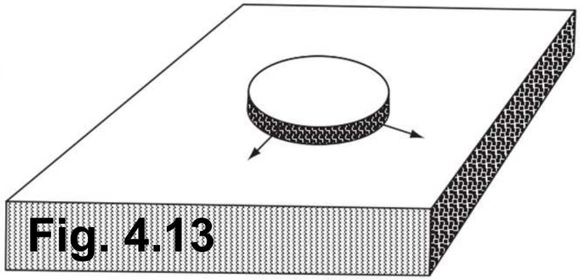


Fig. 4.13

② Spiral growth: Growth by Screw Dislocation

Crystals grown with a low supersaturation were always found to have a 'growth spirals' on the growing surfaces.

- addition of atoms to the ledge cause it to rotate around the axis of screw dislocation
- If atoms add at an equal rate to all points along the step, the angular velocity of the step will be initially greatest nearest to the dislocation core.
- the spiral tightens until it reaches a minimum radius of r*
- $\boxed{v = k_3(\Delta T_i)^2}$

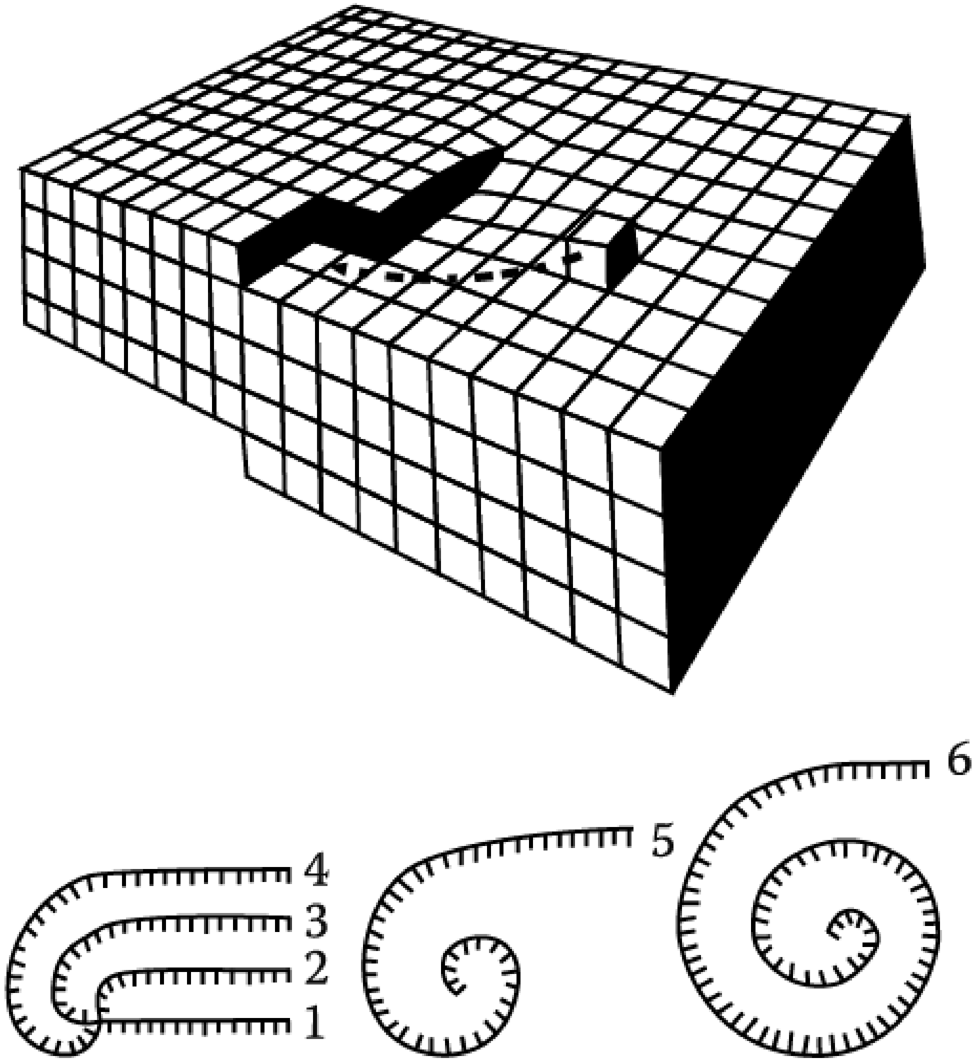
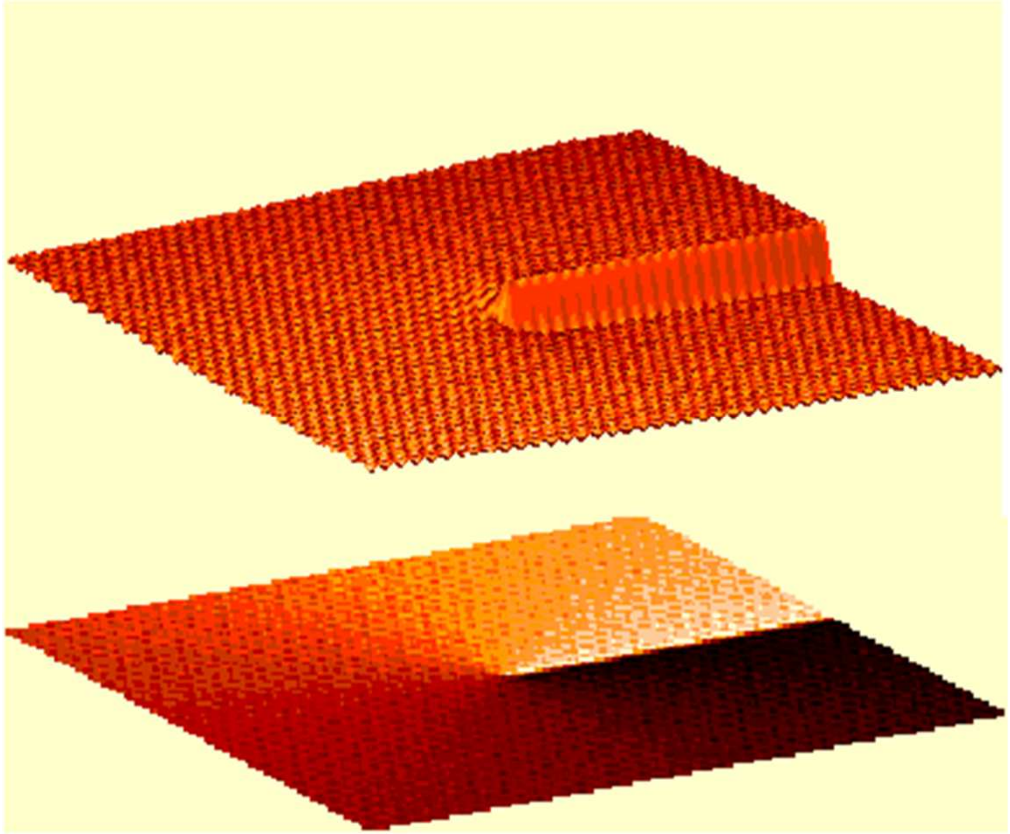


Fig. 4. 13 Spiral growth. (a) A screw dislocation terminating in the solid/liquid interface showing the associated ledge. Addition of atoms at the ledge causes it to rotate with an angular velocity decreasing away from the dislocation core so that a growth spiral develops as shown in (b).

Growth by Screw Dislocation



Burton, Cabrera and Frank (BCF, 1948) elaborated the spiral growth mechanism, assuming steps are atomically disordered...

Their interpretation successfully explained the growth velocity of crystals as long as the assumption is valid…

③ Growth from twin boundary → "feather crystal" under small ΔT

- **another permanent source of steps like spiral growth**

  → not monoatomic height ledge but macro ledge

Kinetic Roughening

Rough interface - Ideal Growth → diffusion-controlled → dendritic growth

Smooth interface - Growth by Screw Dislocation
Growth by 2-D Nucleation

Small ΔT → "feather" type of growth ↔ Large ΔT → cellular/dendritic growth

The growth rate of the singular interface cannot be higher than ideal growth rate.

When the growth rate of the singular Interface is high enough, it follows the ideal growth rate like a rough interface.

→ kinetic roughening

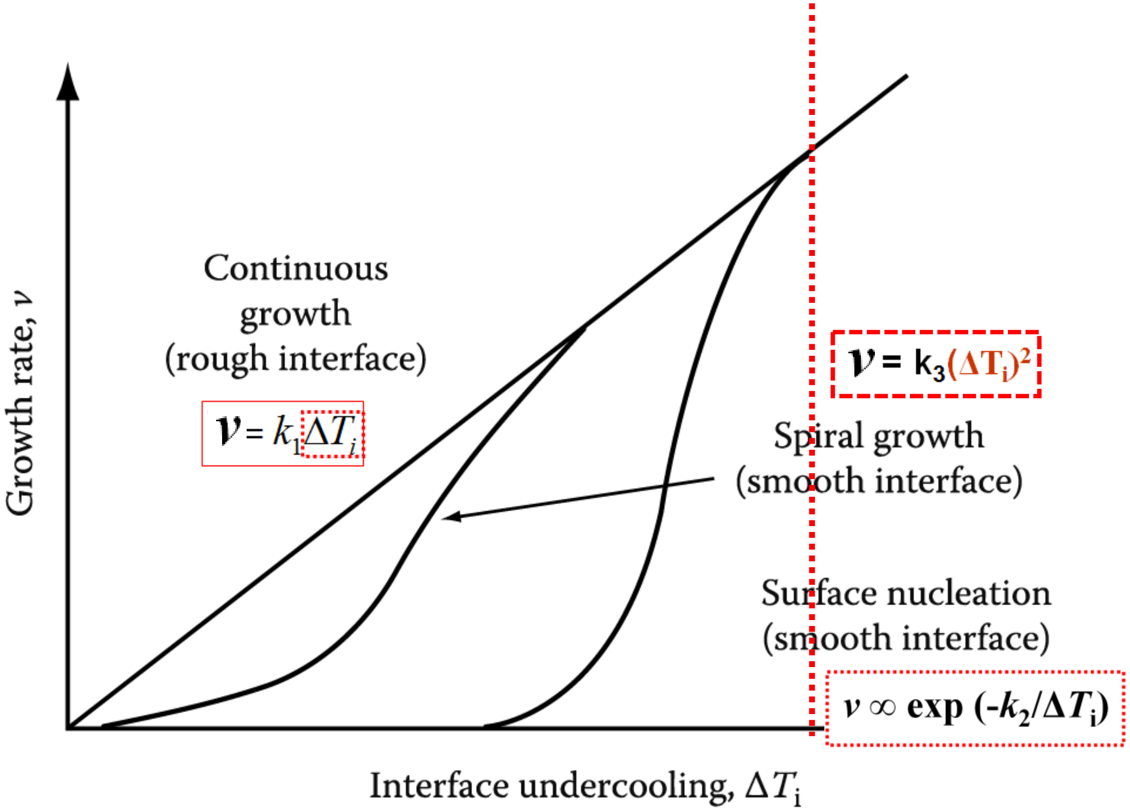
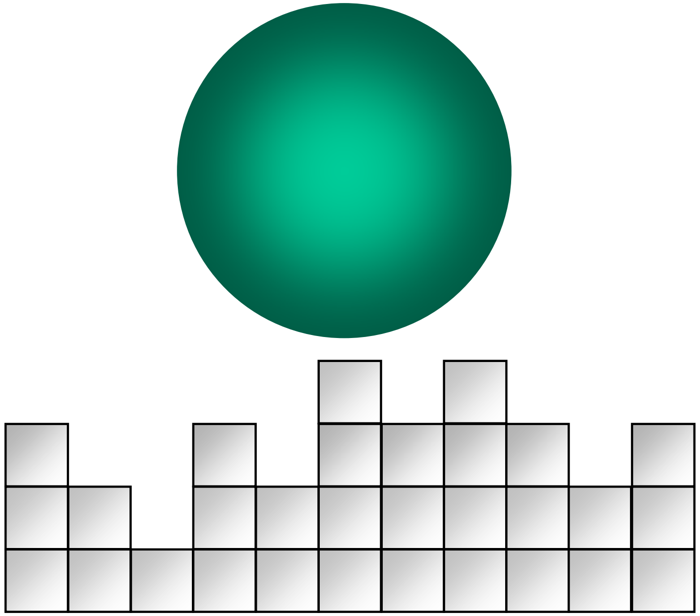


Fig.4.14 The influence of interface undercooling (ΔT_i) on growth rate

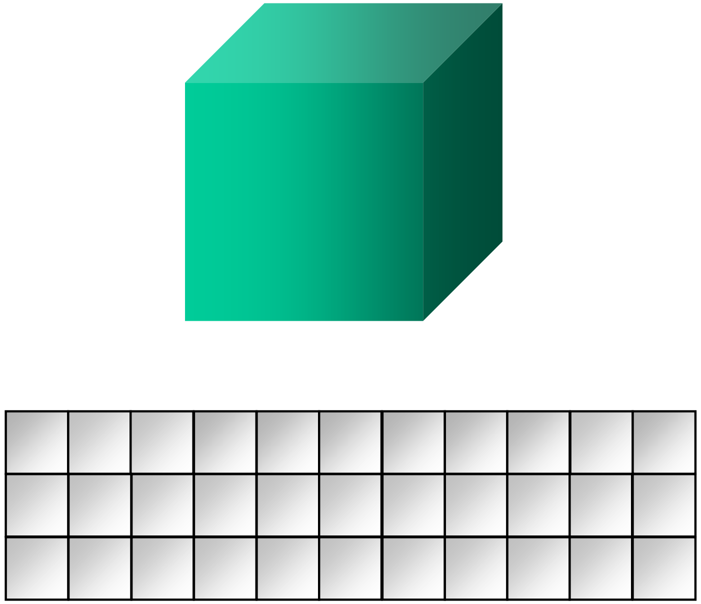
* Growth

Equilibrium Shape and Interface Structure on an Atomic Scale



atomically-disordered

Ex) metallic systems



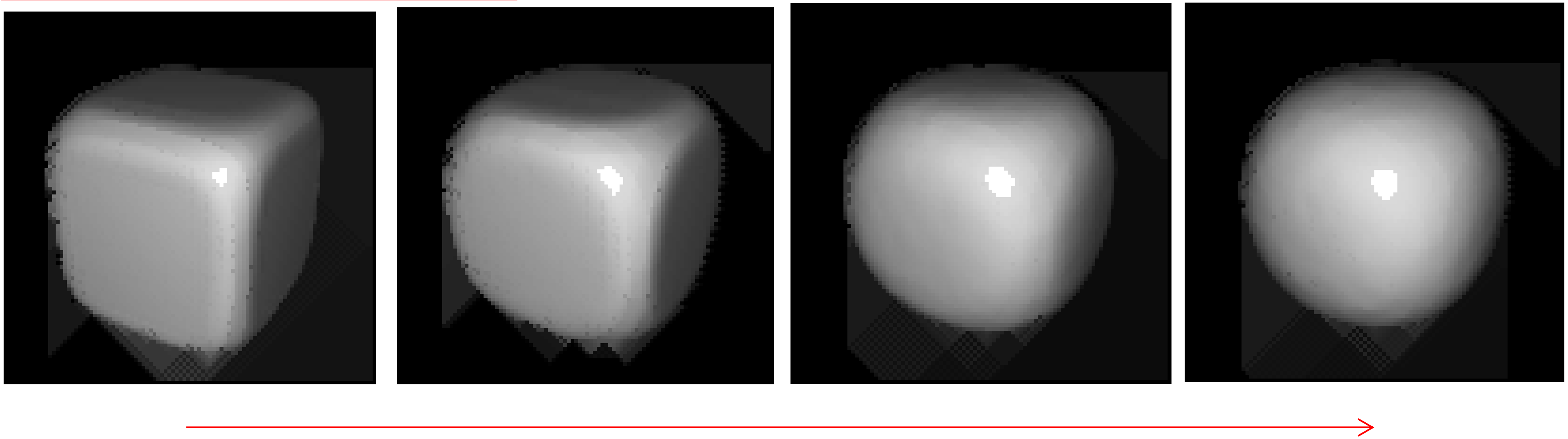
atomically-flat

nonmetals

Apply thermodynamics to this fact and derive more information.

Entropy-dominant	**Enthalpy-dominant**
weak bonding energy	**strong bonding energy**
stable at high T ←	**stable at low T**

Thermal Roughening



singular (smooth) interface

rough interface

Enthalpy-dominant

Entropy-dominant

Heating up to the roughening transition.

Kinetic Roughening

Rough interface - Ideal Growth → diffusion-controlled → dendritic growth

Smooth interface - Growth by Screw Dislocation
Growth by 2-D Nucleation

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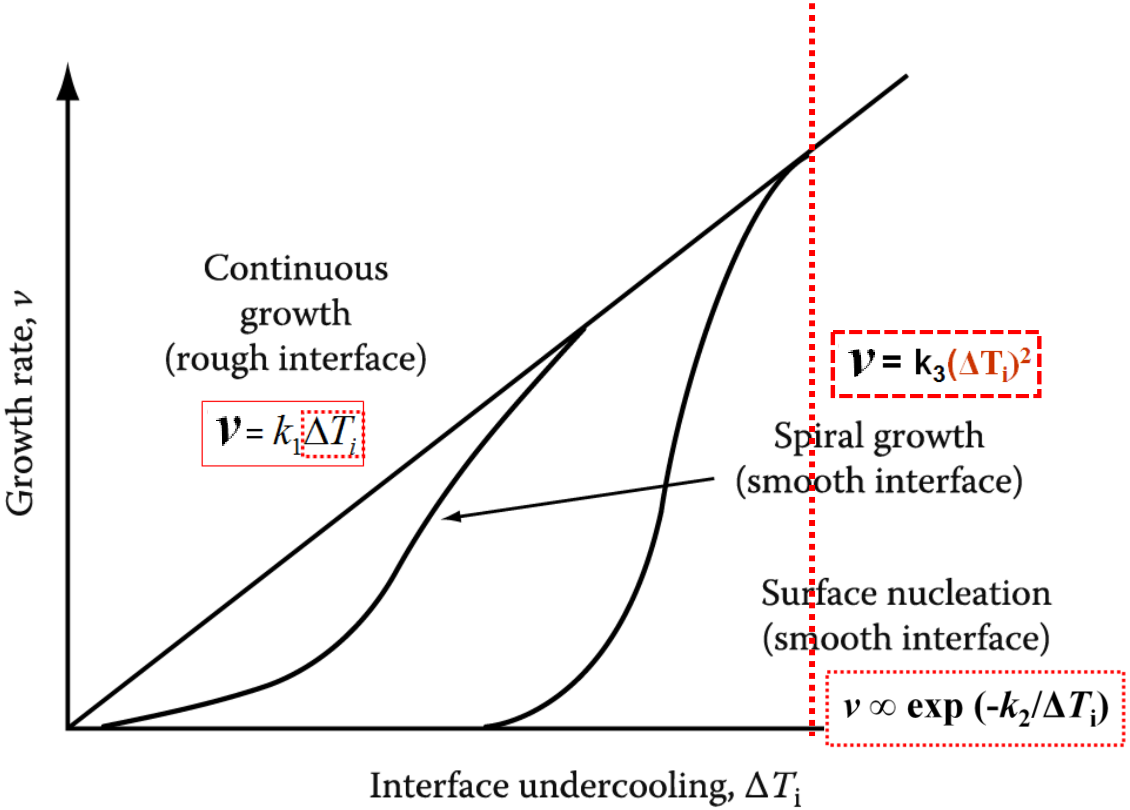

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