2017 Spring

“Calculation and Applications Phase Equilibria”

Principles *of* Solidification

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Contents for previous class: Liquid ↔ Solid transformation at T_m

Chapter 3. Nucleation

Solidification: Liquid → Solid

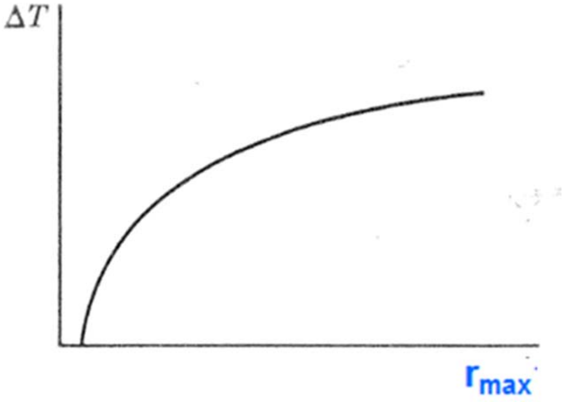
Presence of metastable supercooled liquid

1) Atomic consideration

→ If it is curved, "escape angle" changes with curvature.

$$\therefore\ T_{E,\ \text{small crystal}} < T_{E,\ \text{large crystal}}$$

Thus, at any temperature below T_E , there is a radius of curvature at which the rates of melting and of freezing are equal. = critical radius r*



2) Thermodynamic treatment of equilibrium access a curved interface

Extra pressure ΔP due to curvature

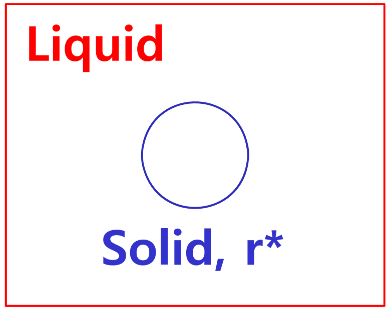
Gibbs-Thomson effect (capillarity effect)

Free energy increase due to interfacial energy

$$\Delta G = \Delta P \cdot V \Rightarrow \Delta G = \frac{2\gamma V_m}{r}$$

For incompressible solid,

$$\frac{L\Delta T}{T_E} = \frac{2\gamma_{SL}}{r^*}, \quad \text{or} \quad r^* = \frac{2\sigma T_E}{L\Delta T}$$

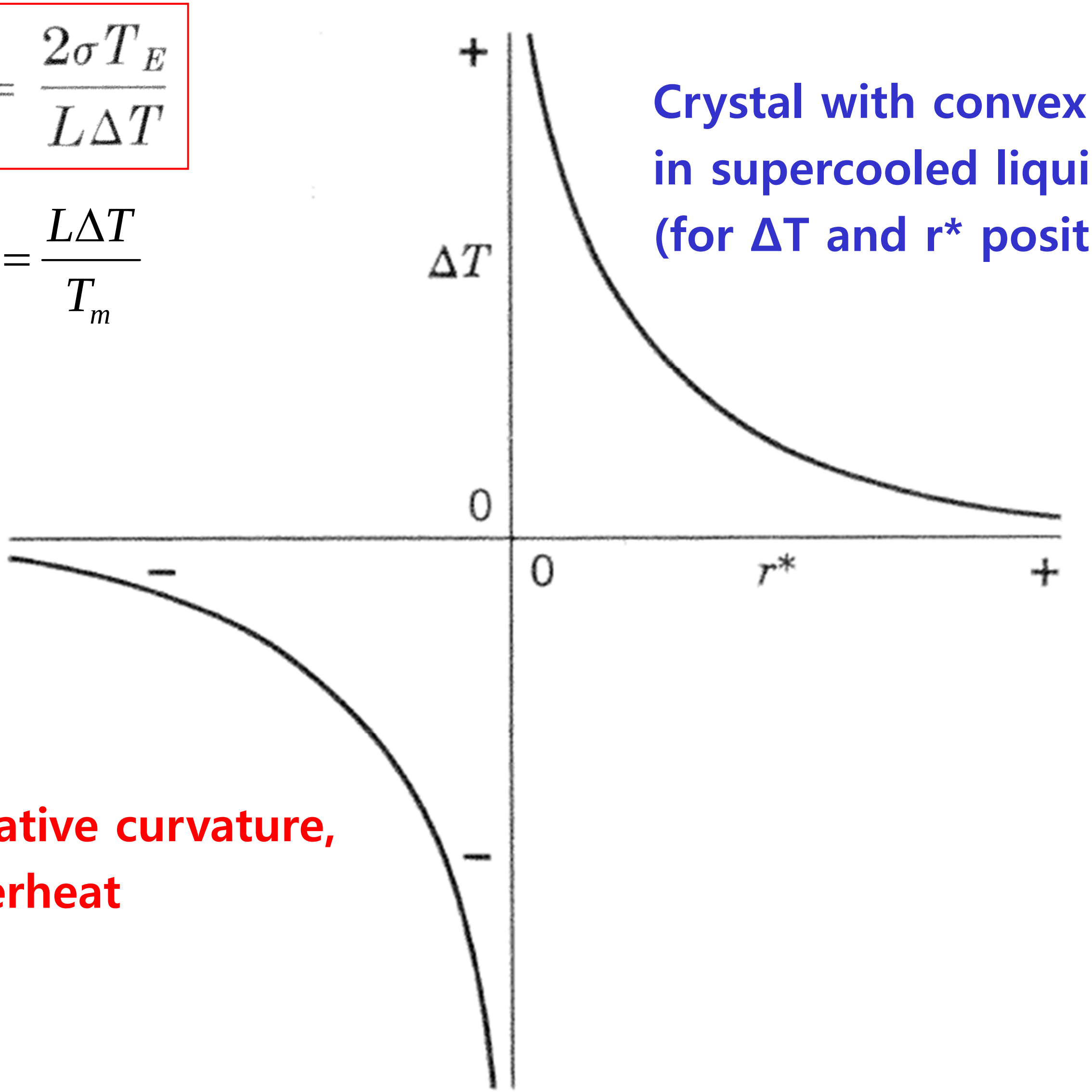


ΔH, ΔS : independent of temperature

- Critical condition of Nucleation → Depends on the curvature of the crystal surface
- To calculate r* under a given ΔT: $\sigma = \gamma_{SL}$ (Sol.-Liq. Interfacial E) measurement required

$$\boxed{r^* = \frac{2\sigma T_E}{L\Delta T}}$$

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

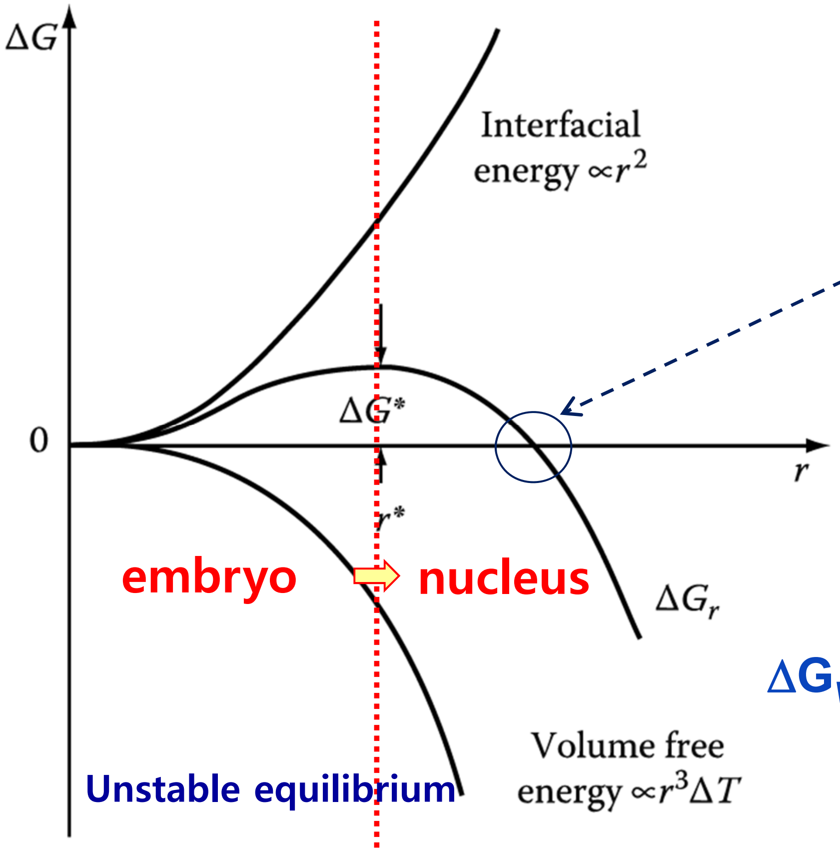


Crystal with convex surface
in supercooled liquid
(for ΔT and r* positive)

Negative curvature,
superheat

Fig. 3.3. Relationship between critical radius and supercooling.

Calculation of critical radius, r*



$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

Why r^* is not defined by $\Delta G_r = 0$?

r < r* : unstable (lower free E by reduce size)

r > r* : stable (lower free E by increase size)

r* : critical nucleus size

$\Delta G_V = \Delta G_P$ **$r^* \Rightarrow dG=0$**

Gibbs-Thompson Equation

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

$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

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

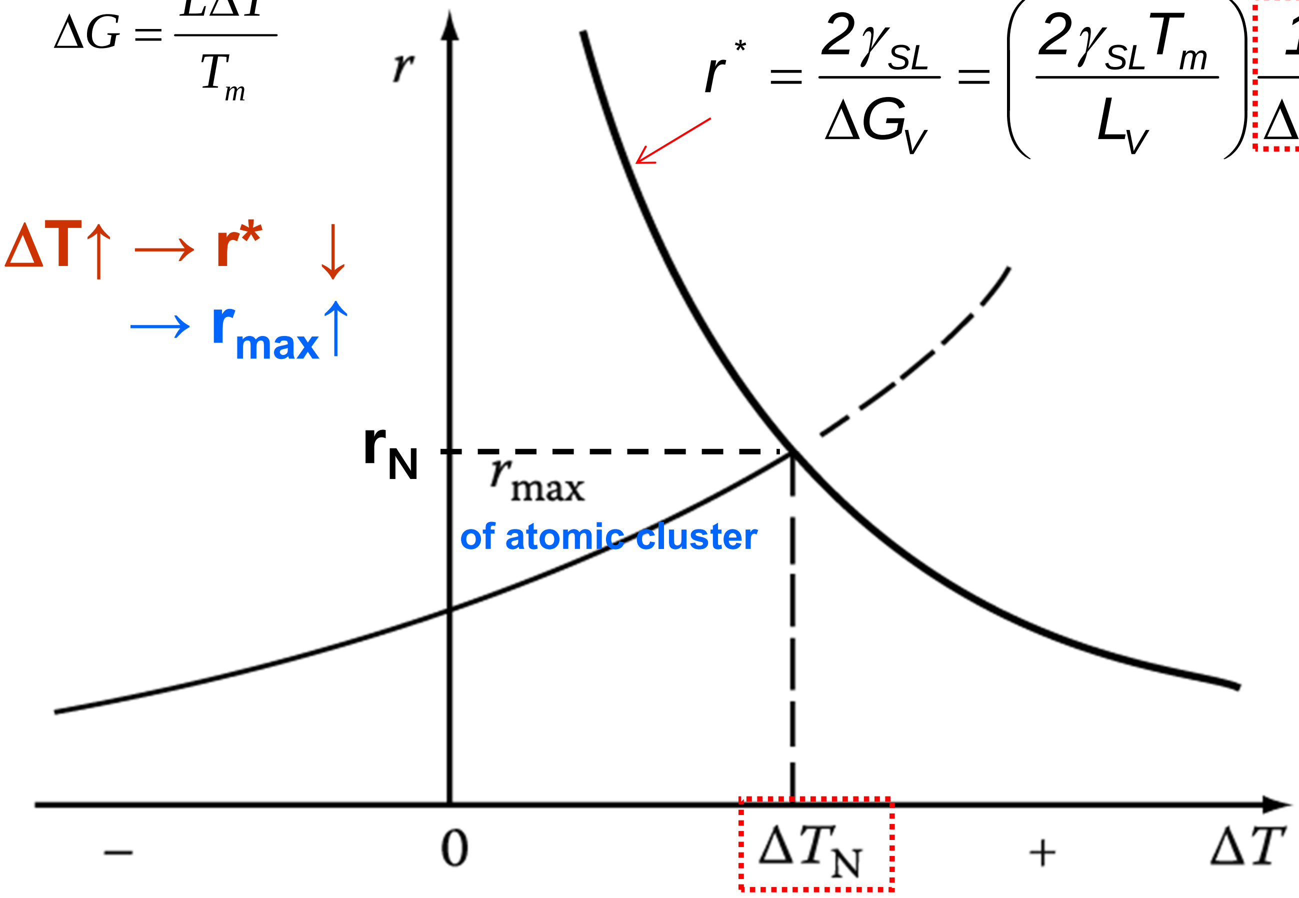
The creation of a critical nucleus ~ thermally activated process

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

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

$\Delta T\uparrow \rightarrow r^* \downarrow$

$\rightarrow r_{max}\uparrow$



ΔT_N is the critical undercooling for homogeneous nucleation.

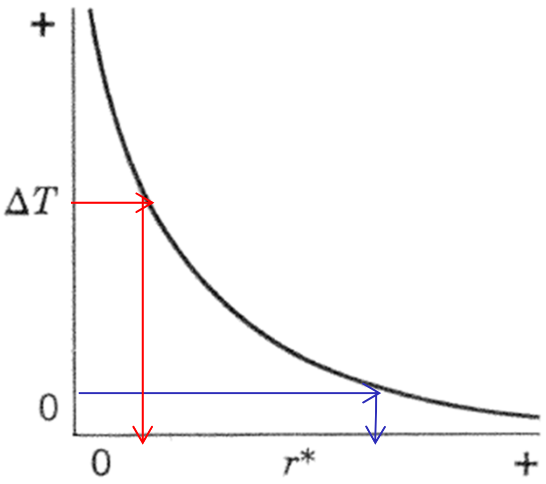
The variation of r* and r_{max} with undercooling ΔT

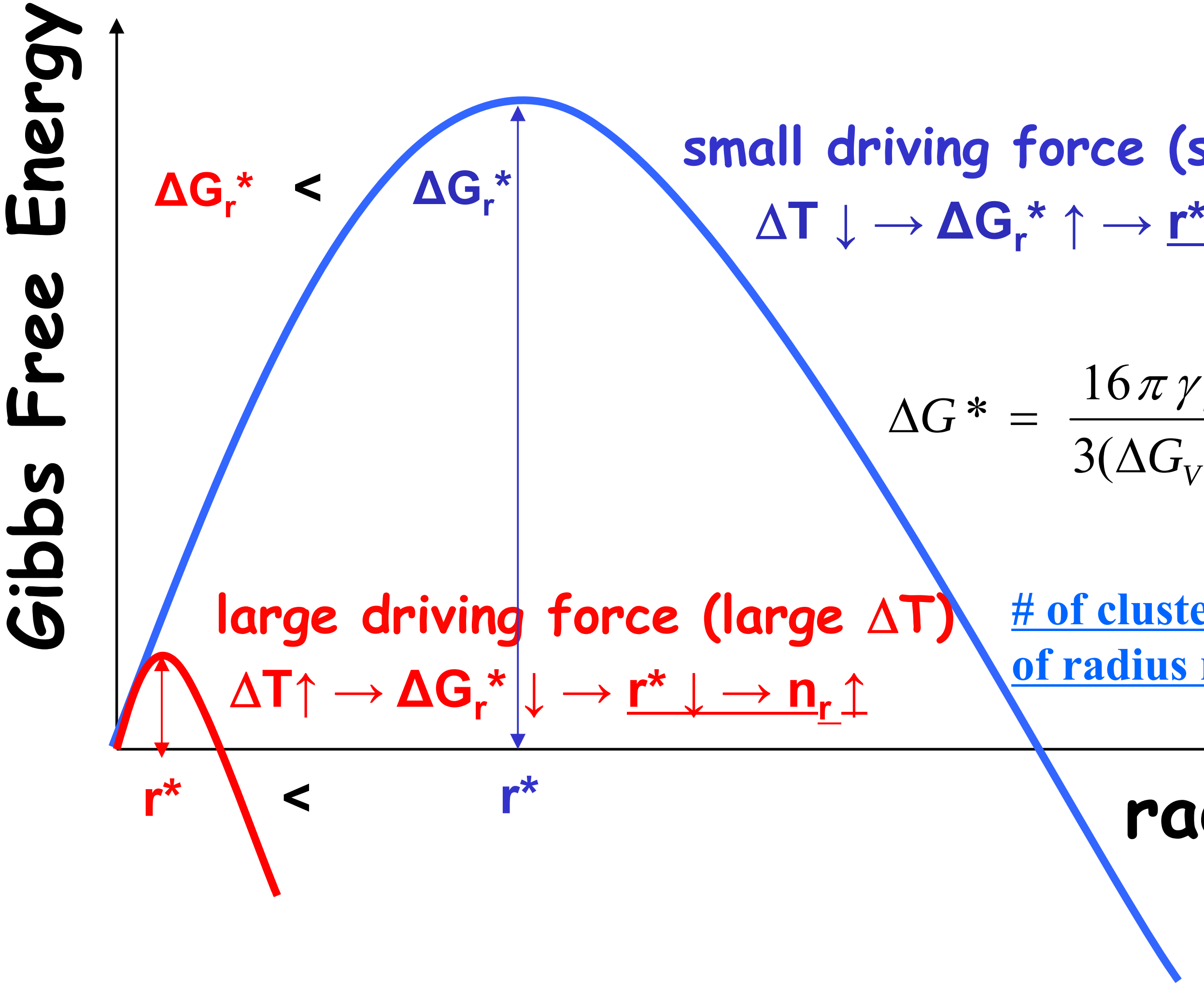
→ The condition for nucleation:

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

Formation of Atomic Cluster

Compare the nucleation curves between small and large driving forces.





small driving force (small ΔT)

$\Delta T \downarrow \rightarrow \Delta G_r^* \uparrow \rightarrow \underline{r^* \uparrow \rightarrow n_r \downarrow}$

large driving force (large ΔT)

$\Delta T \uparrow \rightarrow \Delta G_r^* \downarrow \rightarrow \underline{r^* \downarrow \rightarrow n_r \uparrow}$

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

<u>**# of cluster of radius r**</u>

$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

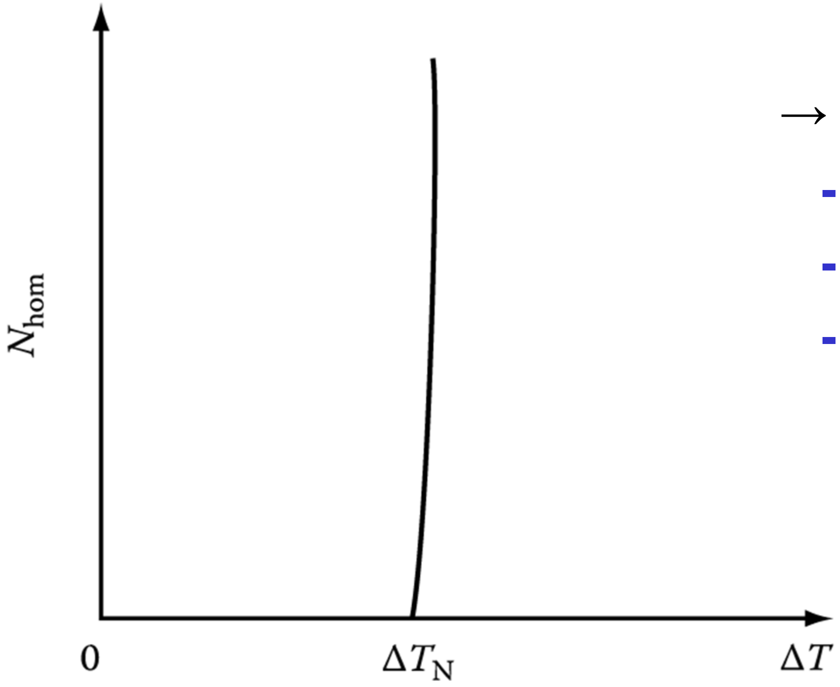
* The homogeneous nucleation rate - kinetics

$$I = \frac{nkT}{h}\exp\left(-\frac{G_A}{kT}\right)\exp\left(-\frac{16\pi\sigma_{SL}{}^3T_E{}^2}{3L^2(\Delta T)^2kT}\right)$$

: insensitive to Temp.

How do we define nucleation temperature, ΔT_N ?

$$\boxed{N_{\text{hom}} \sim \frac{1}{\Delta T^2}}$$



→ critical value for detectable nucleation

- critical supersaturation ratio
- critical driving force
- critical supercooling

→ for most metals, ΔT_N~0.2 T_m (i.e. ~200K)

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

* Comparison between experiment and theory

Most metal ΔT_N < several K

but Turnbull and his coworker ΔT_N → larger (~several hundreds K)

by formation of large number of very small drops

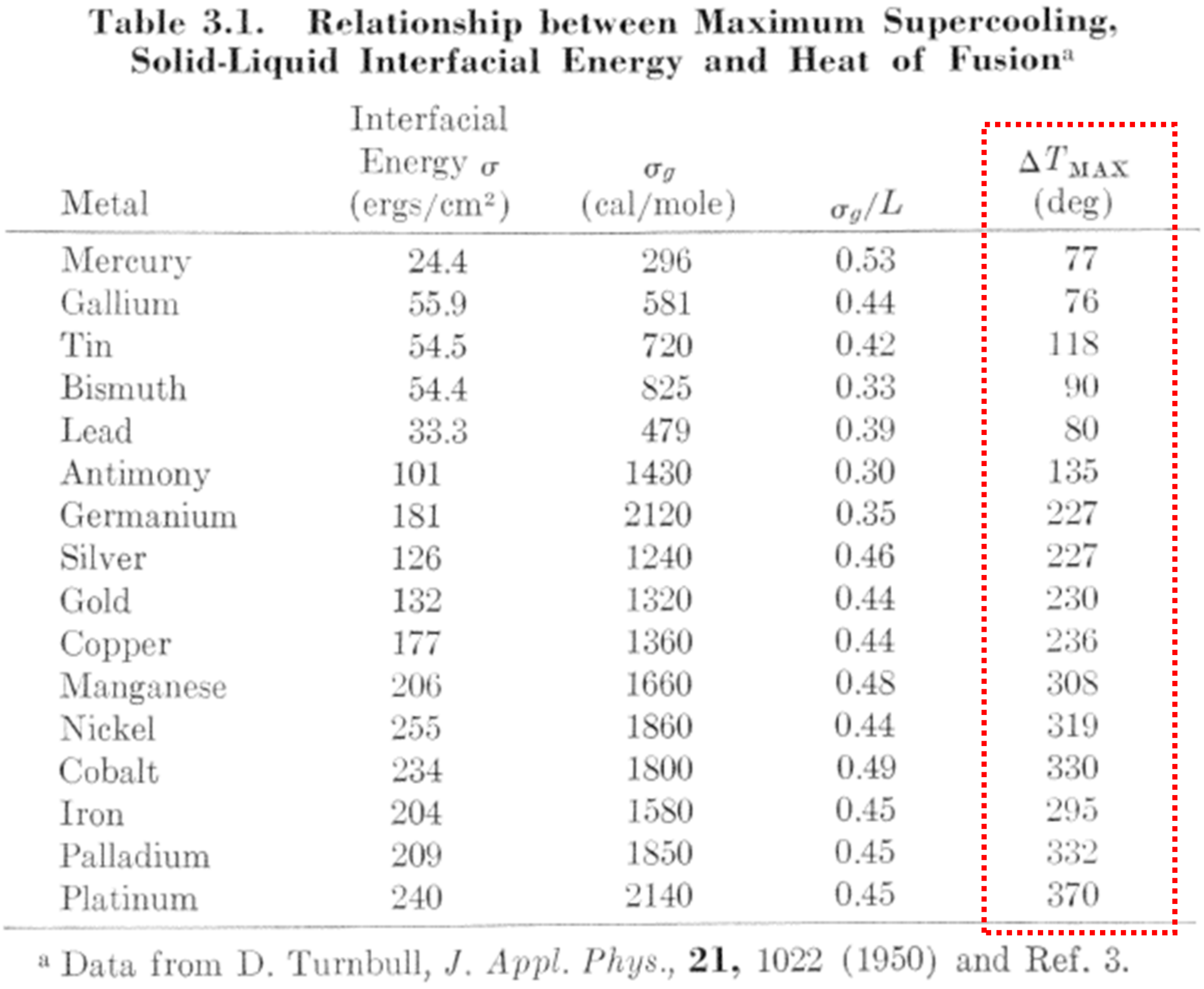


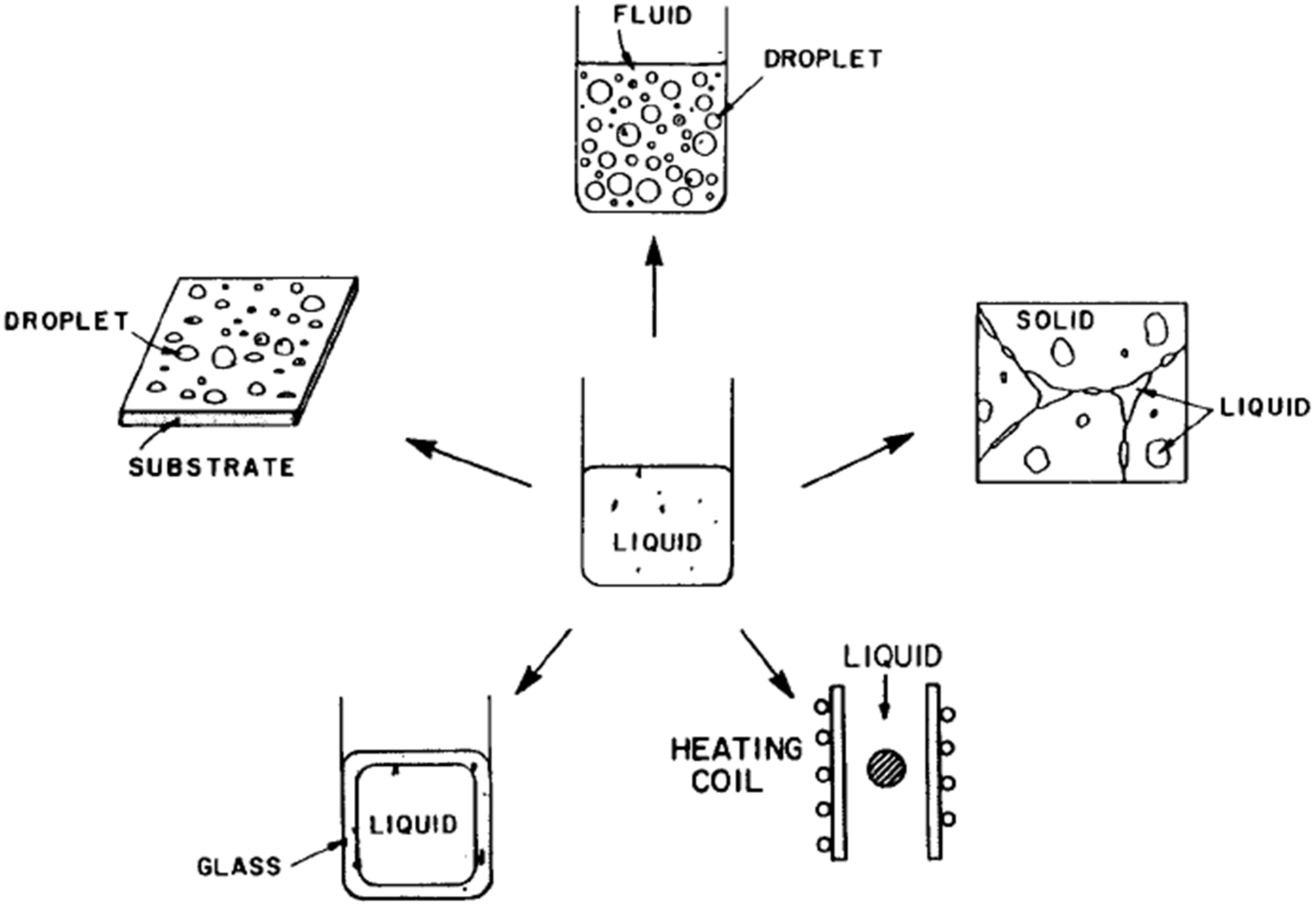
Table 3.1. Relationship between Maximum Supercooling, Solid-Liquid Interfacial Energy and Heat of Fusion[a]

Metal	Interfacial Energy σ (ergs/cm²)	σ_g (cal/mole)	σ_g/L	ΔT_{MAX} (deg)
Mercury	24.4	296	0.53	77
Gallium	55.9	581	0.44	76
Tin	54.5	720	0.42	118
Bismuth	54.4	825	0.33	90
Lead	33.3	479	0.39	80
Antimony	101	1430	0.30	135
Germanium	181	2120	0.35	227
Silver	126	1240	0.46	227
Gold	132	1320	0.44	230
Copper	177	1360	0.44	236
Manganese	206	1660	0.48	308
Nickel	255	1860	0.44	319
Cobalt	234	1800	0.49	330
Iron	204	1580	0.45	295
Palladium	209	1850	0.45	332
Platinum	240	2140	0.45	370

[a] Data from D. Turnbull, *J. Appl. Phys.*, **21**, 1022 (1950) and Ref. 3.

How to Obtain Extensive Undercooling

John H. PEREPEZKO, MSE, 65 (1984) 125-135



By dispersing a liquid into a large number of small droplets within a suitable medium, the catalytic effects of active nucleants may be restricted to a small fraction of the droplets so that many droplets will exhibit extensive undercooling.

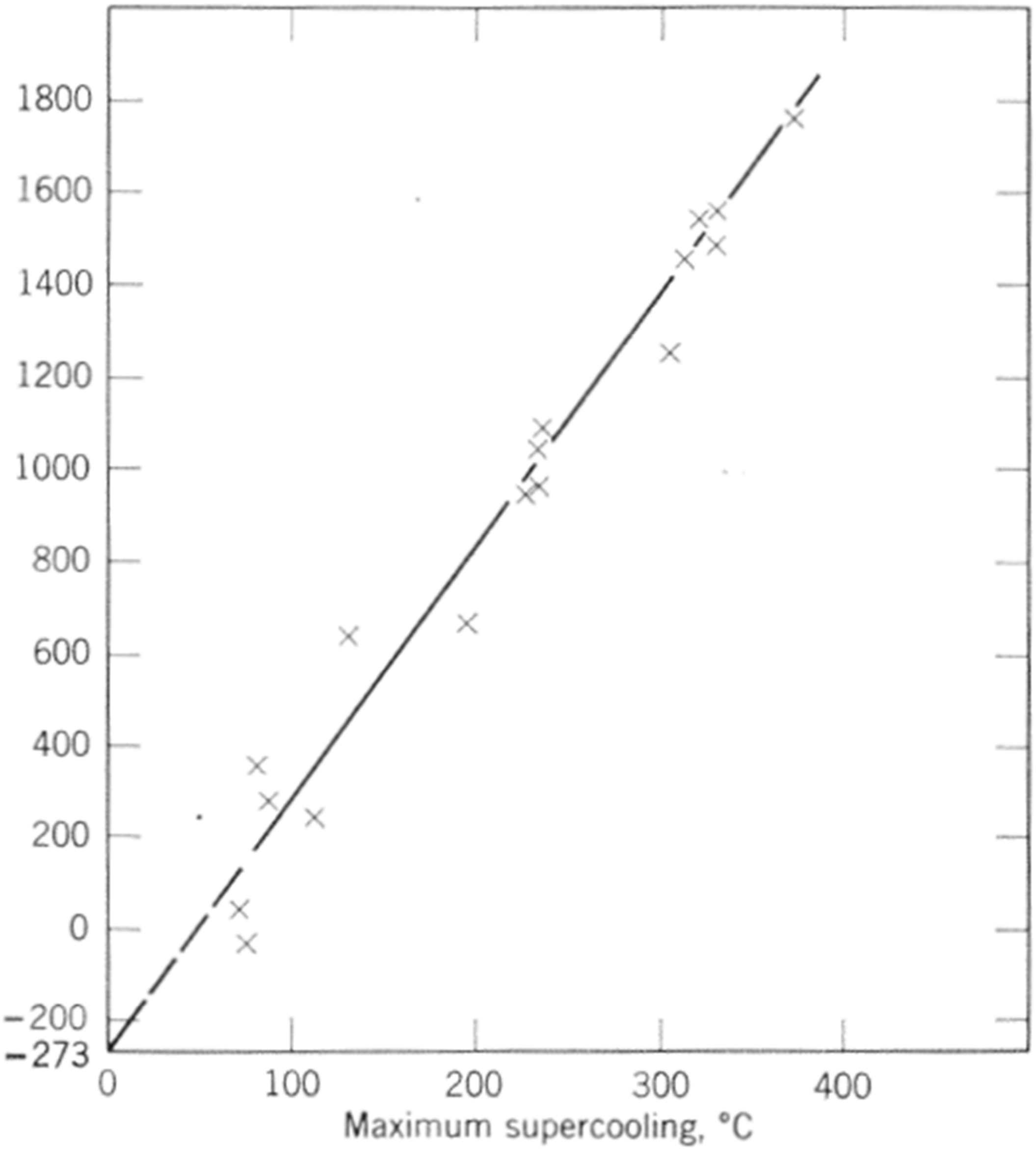
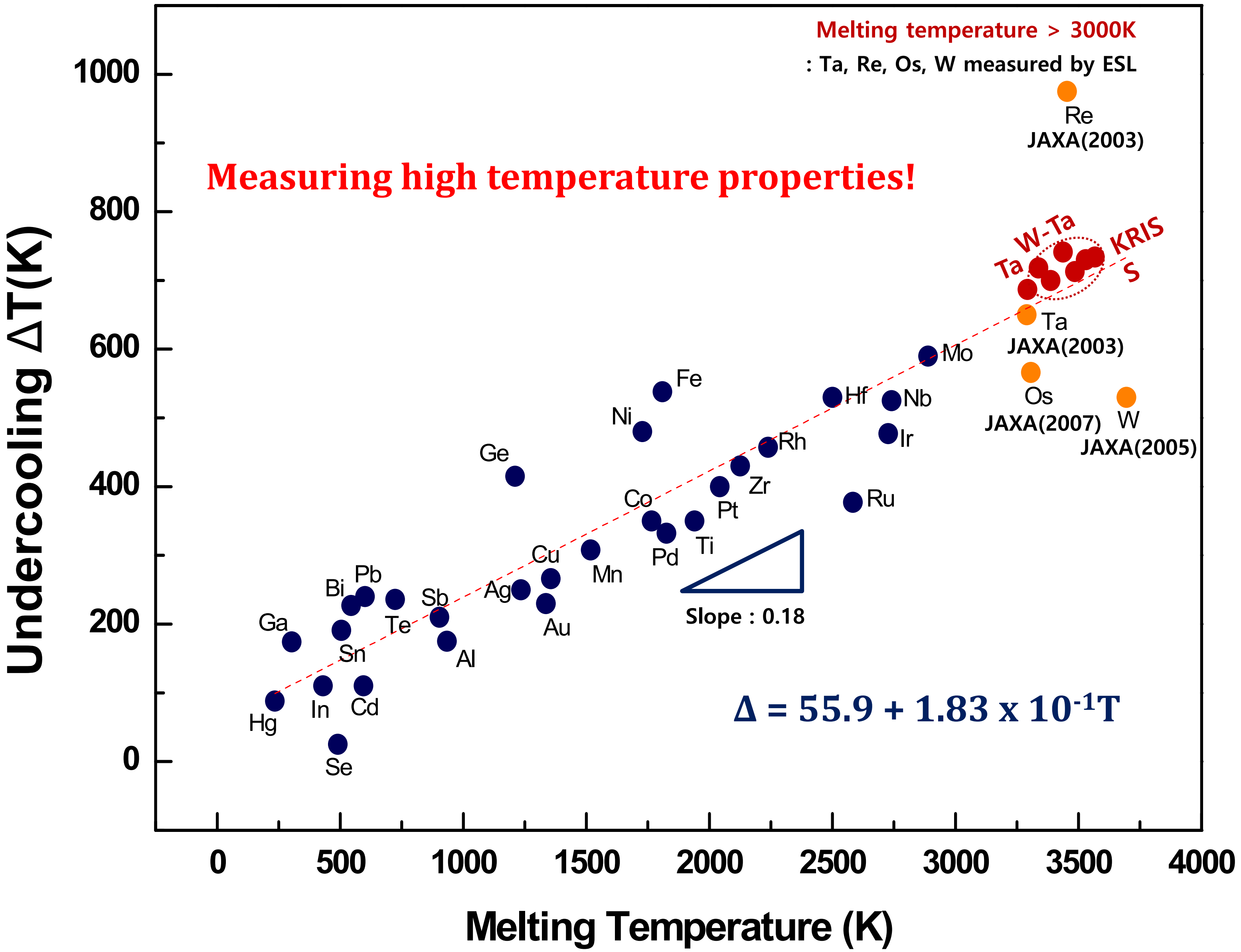


Fig. 3.7. Maximum supercooling as a function of melting point. (From *Thermodynamics in Physical Metallurgy,* American Society for Metals, Cleveland, 1911, p. 11.)

Maximum undercooling vs. Melting temperature



* **If Max supercooling is considered a temperature definition for homogeneous nucleation,**

Interfacial E, σ can be calculated by

$$I = \frac{nkT}{h}\exp\left(-\frac{G_A}{kT}\right)\exp\left(-\frac{16\pi\boxed{\sigma_{SL}}^3 T_E{}^2}{3L^2(\Delta T)^2 kT}\right)$$

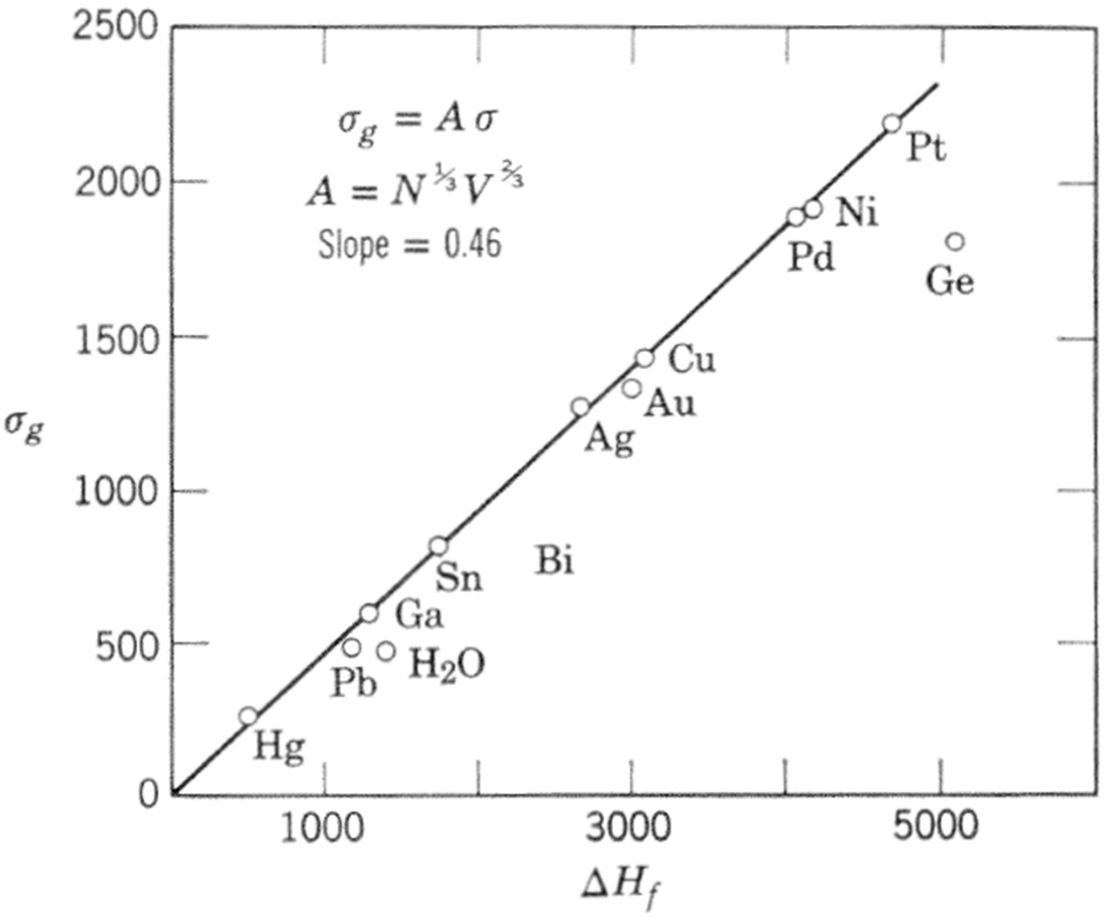


Fig. 3.8. Relationship between surface free energy and heat of fusion. (From Ref. 3, p. 294.)

For (111) plane

"Surface energy calculated by nearest-neighbor bond"

# of broken bond at surface : 3 broken bonds

Bond Strength: $\varepsilon \rightarrow$ for each atom : $\varepsilon/2$

Extra energy per atom on surface: $3\varepsilon/2$

Heat of Sublimation (승화) in terms of ε? → $L_S = 12 N_a \varepsilon/2$

(Latent heat of melting + vaporization)

(1 mole of solid = $12 N_a$)

Energy per atom of a {111} Surface?

Difference by T-dependent entropy effect

$E_{SV} = 3\varepsilon/2 = 0.25 L_S/N_a$ (¼ of L_s/N_a) ⇨ E_{SV} vs γ ?

"Approximated value" due to assumptions, 1) 2nd nearest neighbors have been ignored and 2) strengths of the remaining bonds in the surface are unchanged from the bulk values.

γ interfacial energy = surface free energy ← Gibb's free energy (J/m^2)

$\rightarrow \gamma = G = H - TS$

$= E + PV - TS$ (if PV is ignored) ($E_{SV} \uparrow \rightarrow \gamma \uparrow$)

$\rightarrow \gamma = E_{sv} - TS_{sv}$ (S_{sv} thermal entropy, configurational entropy)

surface>bulk Extra configurational entropy due to vacancies

$\rightarrow \boxed{\partial\gamma/\partial T = -S}$: surface free energy decreases with increasing T

0< S < 3 ($mJ/m^{-2}K^{-1}$) due to increased contribution of entropy

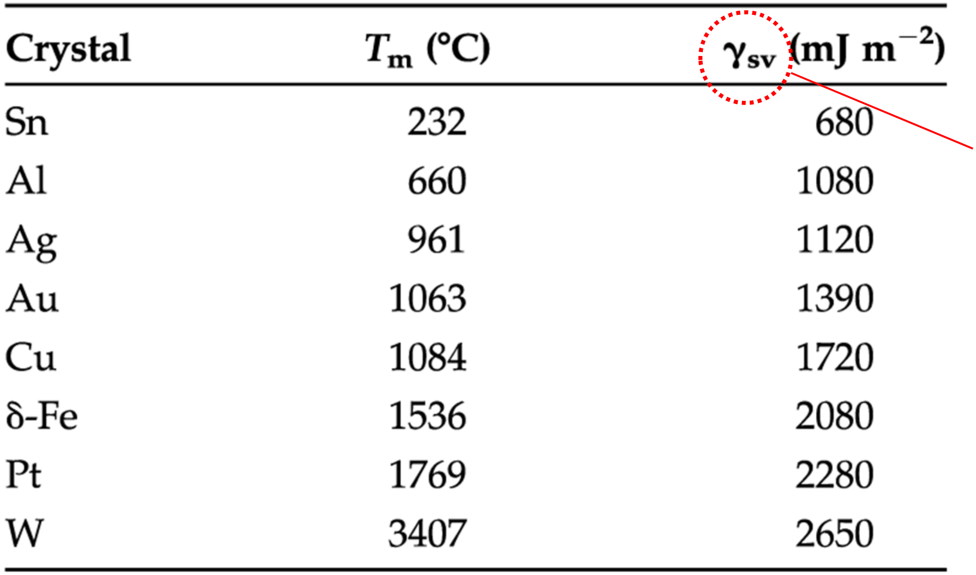
* E_{SV} vs γ ?

- The measured γ values for pure metals near the melting temperature

$E_{SV} = 3\ \varepsilon/2 = 0.25\ L_S\ /N_a$ ⇨ $\gamma_{SV} = 0.15\ L_S\ /N_a$ J / surface atom

(∵ surface free E averaged over many surface plane, S effect at high T)

- **Average Surface Free Energies of Selected Metals**



Crystal	T_m (°C)	γ_{sv} (mJ m^{-2})
Sn	232	680
Al	660	1080
Ag	961	1120
Au	1063	1390
Cu	1084	1720
δ-Fe	1536	2080
Pt	1769	2280
W	3407	2650

Difficult to measure, near T_m

γ of Sn : 680 mJ/m^2 (T_m : 232°C)
γ of Cu : 1720 mJ/m^2 (T_m : 1083°C)

cf) G.B. energy γ_{gb} is about one third of γ_{sv}

*** Higher T_m → stronger bond (large L_S) → larger surface free energy (γ_{SV})**

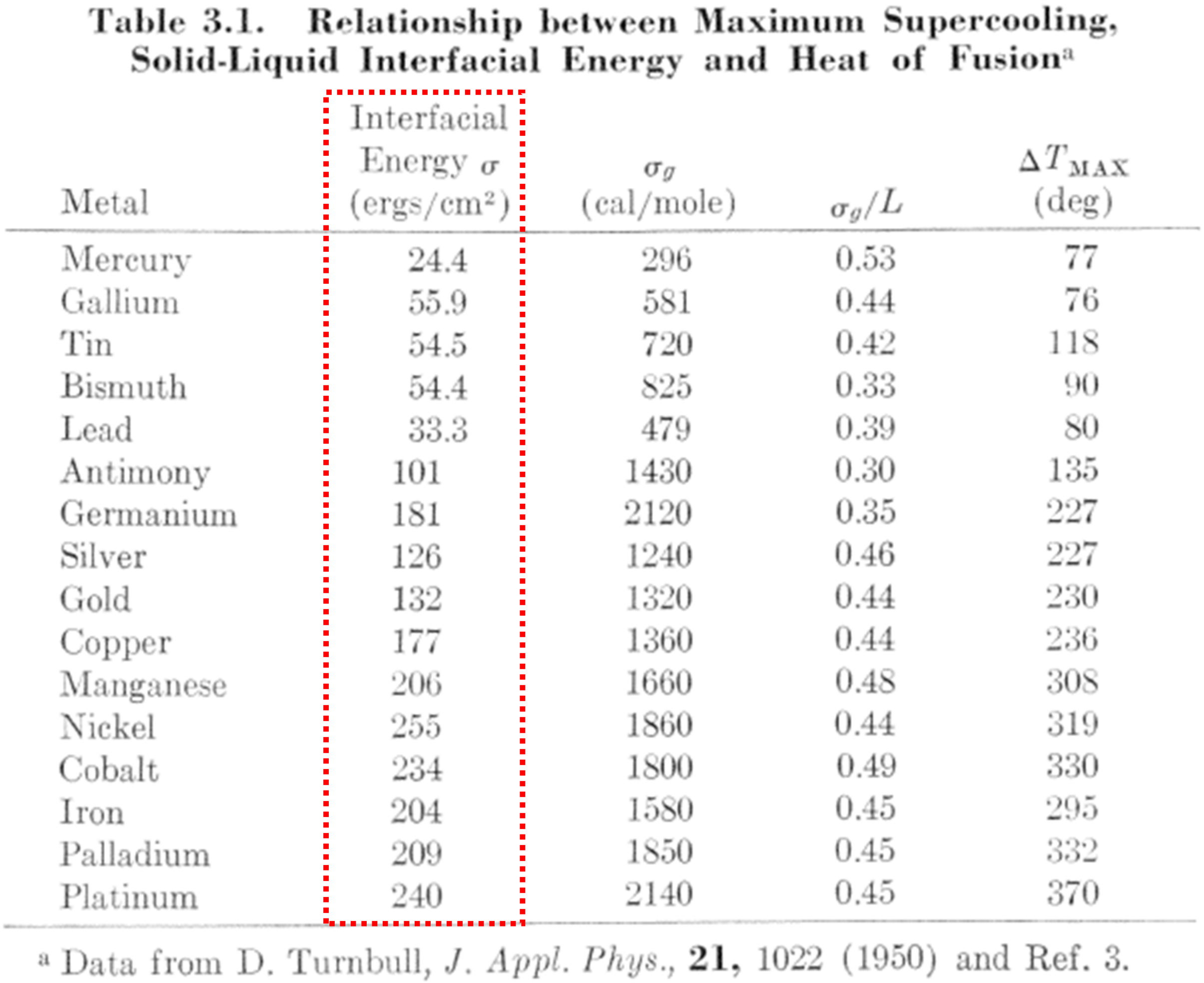
$$\boxed{high\ T_m \rightarrow high\ L_s \rightarrow high\ \gamma_{sv}}$$

* Convexity of surface ↑ → E/unit area ↑

→ # of nearest neighbor at each atom in a spherical particle are smaller than average # in the flat surface. → higher E for the flat surface

∴ If the crystal is as small as the critical nucleus

Surface E/Area > 0.25 (Theoretical value) → 0.46 (Experimental value)



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[a] Data from D. Turnbull, *J. Appl. Phys.*, **21**, 1022 (1950) and Ref. 3.

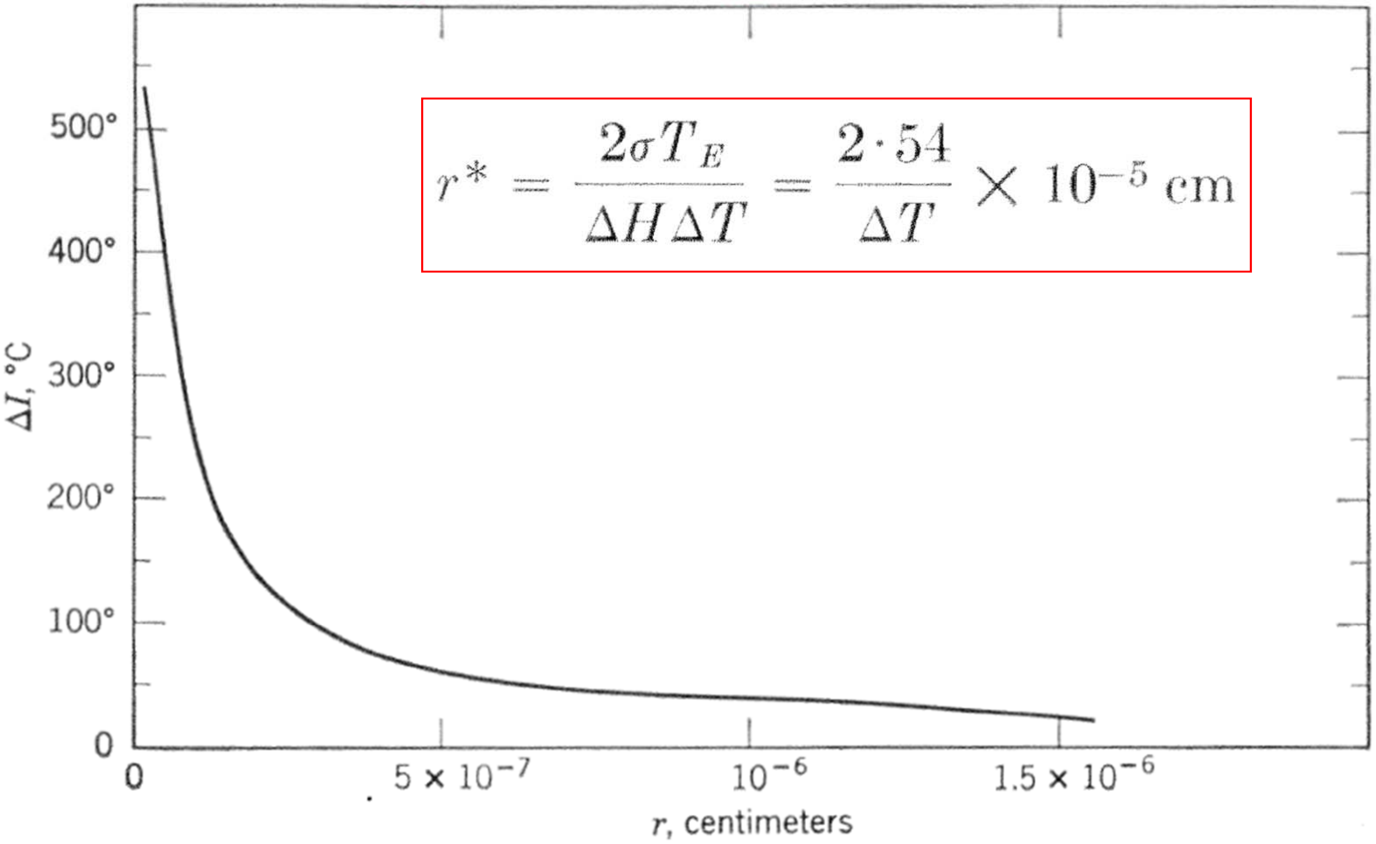
* Size of the critical nucleus

$$r^* = \frac{2\sigma T_E}{L\Delta T}$$

→ **If you know the interfacial energy (σ), you can calculate the critical nucleus size at a given ΔT**

Copper $L = 50$ cal/gm or $1.88 * 10^{10}$ ergs/cm^2

$T_m = 1356$ K, $\sigma_{SL} = 1.44 * 10^2$ ergs/cm^2



$$r^* = \frac{2\sigma T_E}{\Delta H \Delta T} = \frac{2 \cdot 54}{\Delta T} \times 10^{-5} \text{ cm}$$

Fig. 3.9. Critical radius for copper as a function of supercooling.

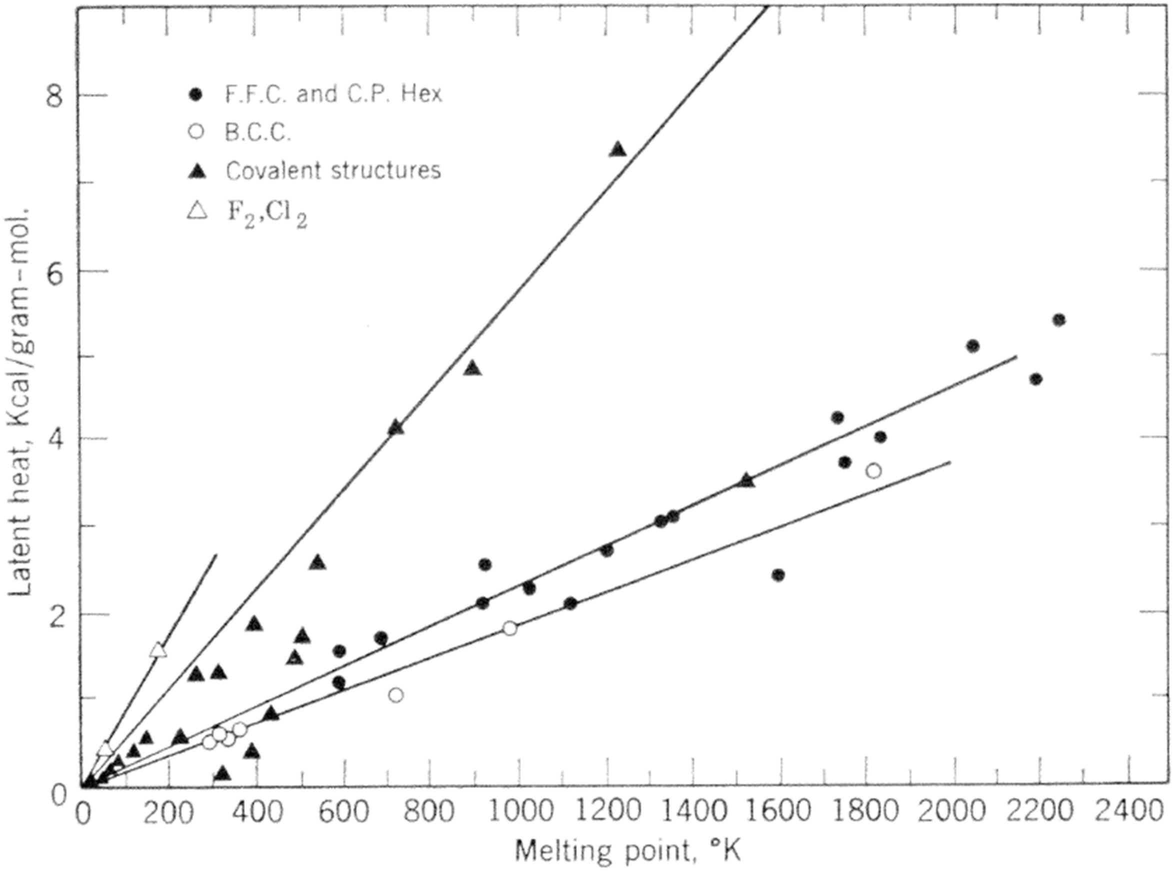
$$\boxed{\frac{L}{RT_E} = \ln\frac{A_M}{A_F}}$$

b) A_M ~ 1 for all liquid, A_F depends on crystal structure

- **Metallic structure** (FCC, C.P.H, and BCC, “less localized bonding”) ~ good relationship compared with the structures which are covalently bonded (“specific directional bonds”).
- **Molecular liquid such as F_2, Cl_2 ~ extra condition for A_F**

(∵ molecule must be correctly oriented in order to be accommodated.)

$$\boxed{L \propto T_E}$$



< Relationship between latent heat and melting point>

* **If Max supercooling is considered a temperature definition for homogeneous nucleation,**

Interfacial E, σ can be calculated by

$$I = \frac{nkT}{h}\exp\left(-\frac{G_A}{kT}\right)\exp\left(-\frac{16\pi\boxed{\sigma_{SL}}^3 T_E{}^2}{3L^2(\Delta T)^2 kT}\right)$$

$\boxed{\sigma_g \propto L}$

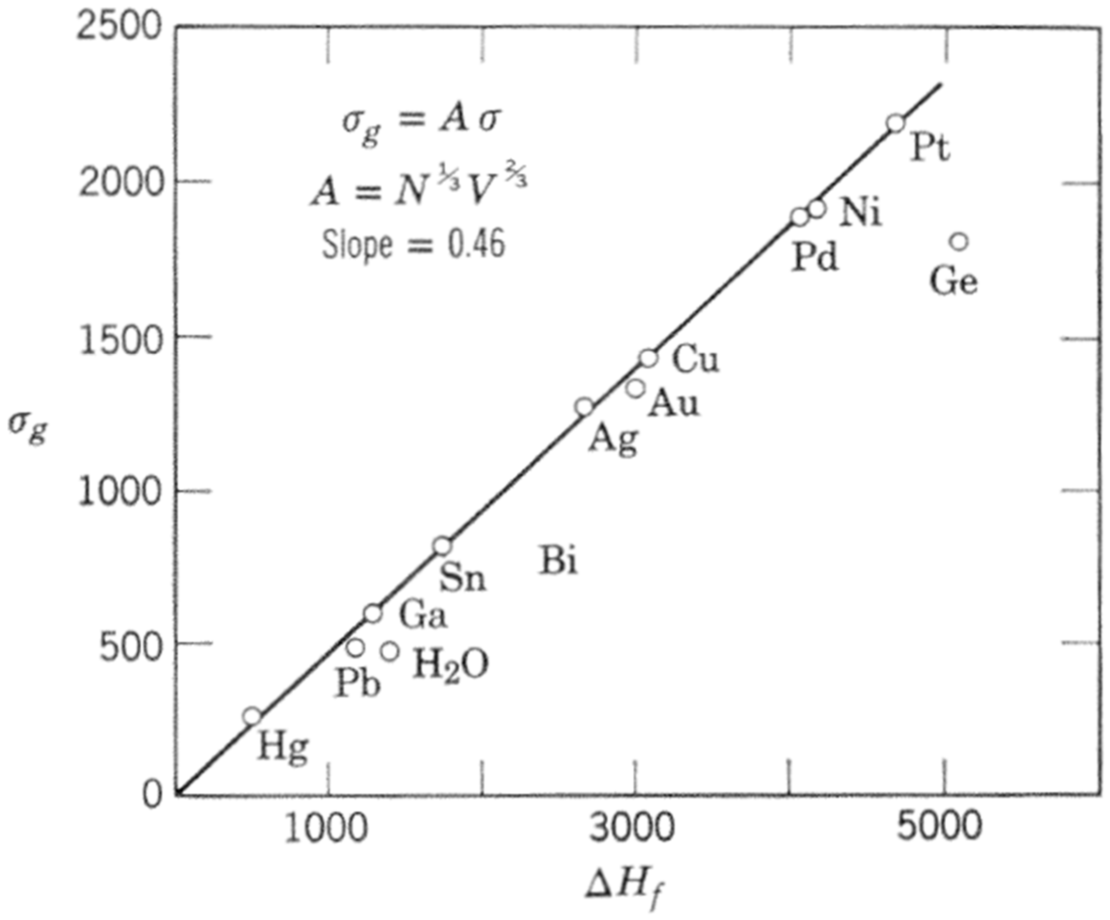


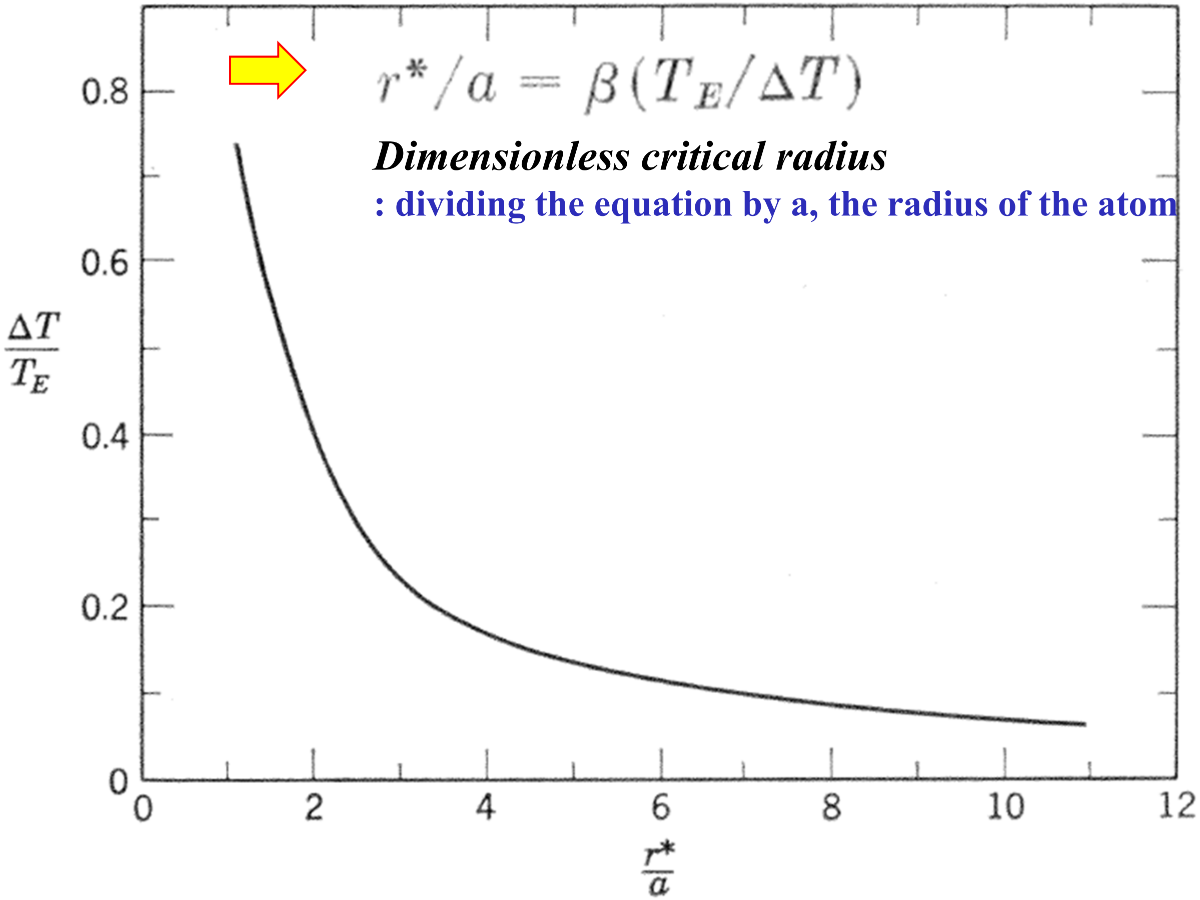
Fig. 3.8. Relationship between surface free energy and heat of fusion. (From Ref. 3, p. 294.)

$\sigma_g \propto L \propto T_E$

high $\gamma \rightarrow$ high $L_s \rightarrow$ high T_m

$$r^* = \frac{2\sigma T_E}{\Delta H \Delta T} \Rightarrow r^* = A\frac{T_E}{\Delta T}$$

A **should be approximately the same for all metals.**



$$r^*/a = \beta(T_E/\Delta T)$$

Dimensionless critical radius

: dividing the equation by a, the radius of the atom

Fig. 3.10. General relationship between ΔT and r^* for metals.

* Copper Homogeneous nucleation

$\Delta T = 230\ \text{K} \rightarrow r^* \sim 10^{-7}\ \text{cm} < 4 *$ (diameter of Cu atom)

if it is spherical,

$V = 4.2 * 10^{-21}\ \text{cm}^3 \sim 360$ atoms ($\because$ one Cu atom $1.16 * 10^{-23}\ \text{cm}^3$)

⇨ "Generalization of metal" $\Delta T^* \sim 0.2\ T_E$ / $\sigma_{SL} \sim 0.4\ L$

→ r^* (critical nucleus for homogeneous nucleation) of metal ~ 200 atoms

But, if Cluster radius ~ (only 4 * atom diameter),

"Not exactly spherical particle"

(Deviation is very large with spherical particle) →

→ Possible structure for the critical nucleus of Cu

: bounded only by {111} and {100} plane

- σ_{SL} may very with the crystallographic nature of the surface.
- The faces of this crystal are close to their critical size for 2D nucleation at the critical temp for the nucleus as a whole.

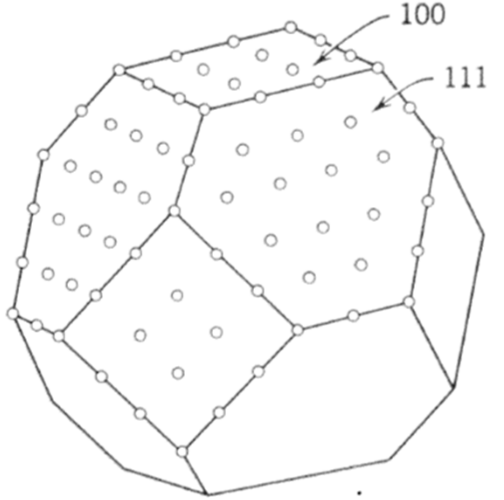


Fig. 3.11. Possible structure for the critical nucleus. (From B. Chalmers, *Physical Metallurgy*, John Wiley and Sons, New York, 1959, p. 246.)

Surface energy for high or irrational {hkl} index

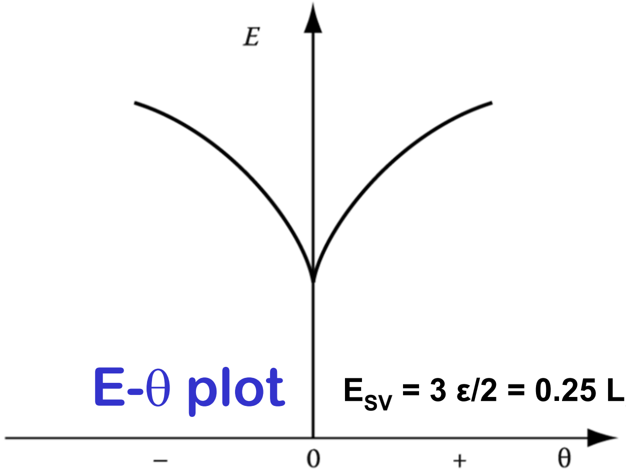
(cosθ/a)(1/a) : broken bonds from the atoms on the steps

(sin|θ|/a)(1/a) : additional broken bonds from the atoms on the steps

Attributing ε/2 energy to each broken bond,

$$E_{SV} = \frac{1}{1\times a}\frac{\varepsilon}{2}\left(\frac{\cos\theta}{a} + \frac{\sin|\theta|}{a}\right)$$

$$= \frac{\varepsilon\left(\cos\theta + \sin\left(|\theta|\right)\right)}{2a^2}$$



E-θ plot

$E_{SV} = 3\,\varepsilon/2 = 0.25\, L_S/N_a$

Fig. 3.4 Variation of surface energy as a function of θ

- **The close-packed orientation (θ = 0) lies at a cusped minimum in the E plot.**
- **Similar arguments can be applied to any crystal structure for rotations about any axis from any reasonably close-packed plane.**
- **All low-index planes should therefore be located at low-energy cusps.**
- **If γ is plotted versus θ similar cusps are found (γ-θ plot), but as a result of entropy effects they are less prominent than in the E-θ plot, and for the higher index planes they can even disappear.**

Equilibrium shape of a crystal?

Equilibrium shape: Wulff surface

* A convenient method for plotting the variation of γ with surface orientation in 3 dimensions

: Polyhedron with the largest facets having the lowest interfacial free energy

* Distance from center : γ_{sv}

→ Construct the surface using γ_{sv} value as a distance between the surface and the origin when measured along the normal to the plane

Several plane A_1, A_2 etc. with energy γ_1 , γ_2

Total surface energy : $A_1\gamma_1 + A_2\gamma_2 \ldots$

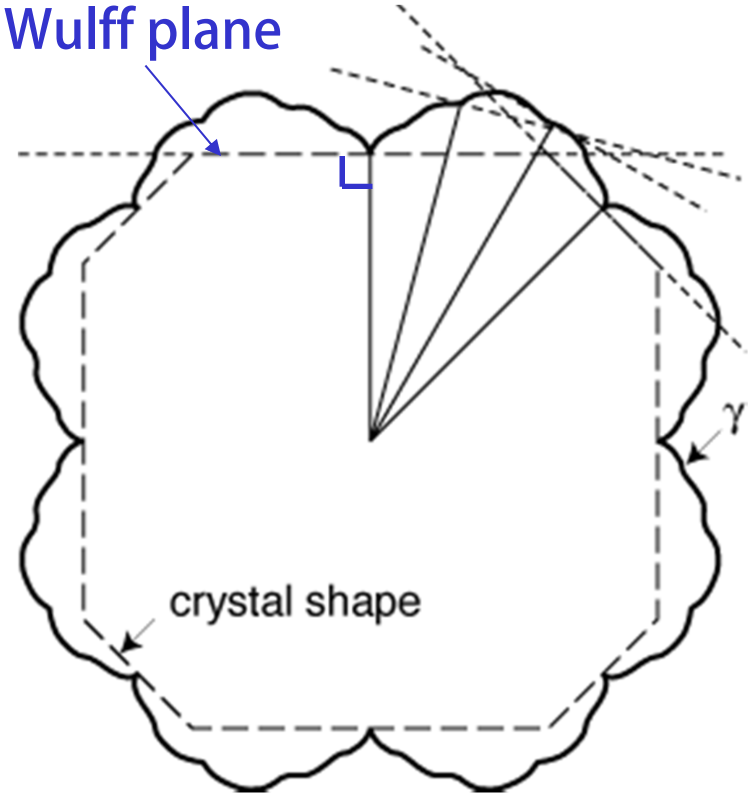
$= \sum A_i \gamma_i \rightarrow$ minimum

→ equilibrium morphology

: can predict the equilibrium shape of an isolated single crystal

How is the equilibrium shape determined?

$$\boxed{\sum_{i=1}^{n} A_i \gamma_j = Minimum}$$



γ-θ plot

Due to entropy effects the plot are less prominent than in the E_{SV}-θ plot, and for the higher index planes they can even disappear

Process of Wulff shape intersection for two cubic Wulff shapes

: Polyhedron with the largest facets having the lowest interfacial free energy

(a) Wulff Shape I (b) Wulff Shape II

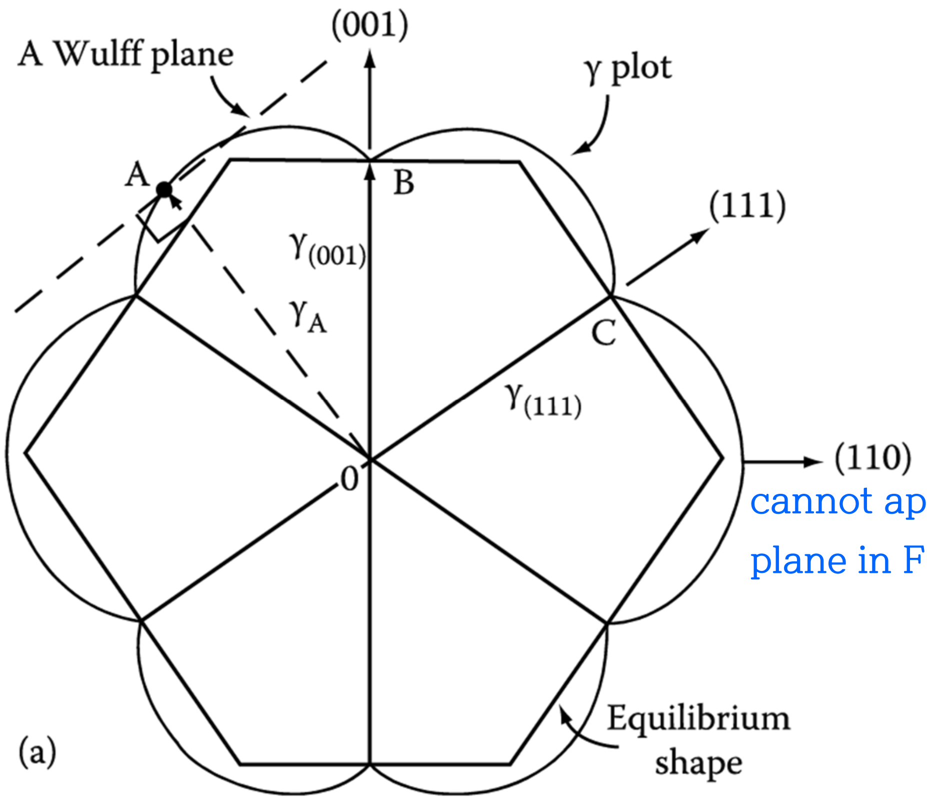
(c) Union of I and II (d) Intersection of I and II

Figure 1: The process of Wulff shape intersection for two cubic Wulff shapes with displaced origins and rotated coordinate systems. Each individual shape has cubic symmetry *m3m* and **[100]** facets.

Equilibrium shape: Wulff surface

Equilibrium shape can be determined experimentally by annealing small single crystals at high temperatures in an inert atmosphere, or by annealing small voids inside a crystal.

Of course when γ is isotropic, as for liquid droplets, both the γ-plots and equilibrium shapes are spheres.



cannot appear {110} plane in FCC crystals

A possible ($\bar{1}10$) section through the γ-plot of an fcc crystal

"Equilibrium shape of FCC crystals"

1) Square faces {100} and

2) Hexagonal faces {111}

The length OA represents the free energy of a surface plane whose normal lies in the direction OA.

3.5 Homogeneous Nucleation in Alloys

* Binary alloys: nucleus and melt ~ different compositions &

problem of equilibrium distribution of embryo sizes

∴ The theory of homogeneous nucleation in alloy melts is complicated and it has not been completely solved.

But, there is experimental evidence that the nucleation of the solid solution crystals from the liquid solutions occurs at approximately the same supercooling, calculated from the liquidus temperature, as would be expected for a pure metal with the same melting point.

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

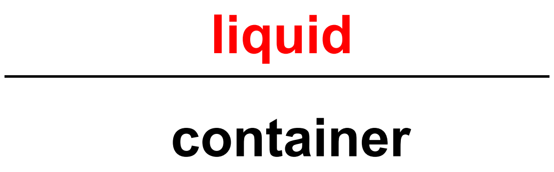
Under suitable conditions, liquid nickel can be undercooled (or supercooled) to 250 K below T_m (1453°C) and held there indefinitely without any transformation occurring.

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)



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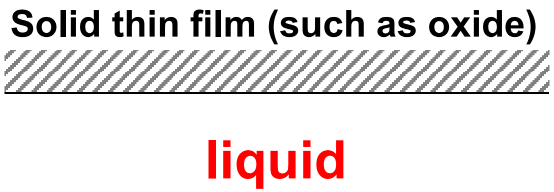


Why this happens? What is the underlying physics?

Which equation should we examine?

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

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

Heterogeneous nucleation

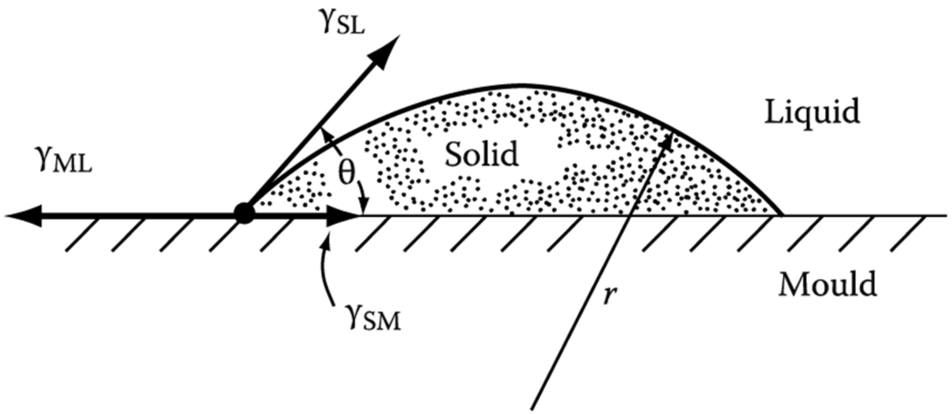
From $$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2}\right)\frac{1}{(\Delta T)^2}$$

Nucleation becomes easy if $\boxed{\gamma_{SL}\downarrow}$ by forming nucleus from the surface of the container.
Its stability depends upon the radius of curvature r.

Heterogeneous nucleation of spherical cap on a flat mold wall.

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

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



***m* : surface E relationship** → describe "wetting" tendency

Any value of *m* between +1 and -1 corresponds to a stable contact angle.

A spherical cap can form on a substrate for which $0 < m < 1$.

Thus, the condition for nucleation –that the radius of curvature of the surface of the largest probable embryo is equal to the critical radius – can occur with less supercooling when a suitable substrate is present than without a substrate.

$$\frac{V_c}{V} = \frac{\frac{1}{3}\pi h^2 (3r - h)}{\frac{4}{3}\pi r^3} = \frac{h^2}{4r^3}\,(3r - h)$$

If the ratio h/r is represented by q, then $V_c/V = q^2(3 - q)/4$. Thus V_s/V can be calculated for various values of h/r, with the following results; the corresponding values of m are also given.

h/r	V_s/V	m
1.	0.5	0.
0.8	0.35	0.21
0.5	0.16	0.50
0.3	0.06	0.72
0.1	0.007	0.9
0.01	0.00007	0.99
0.001	0.000007	0.999

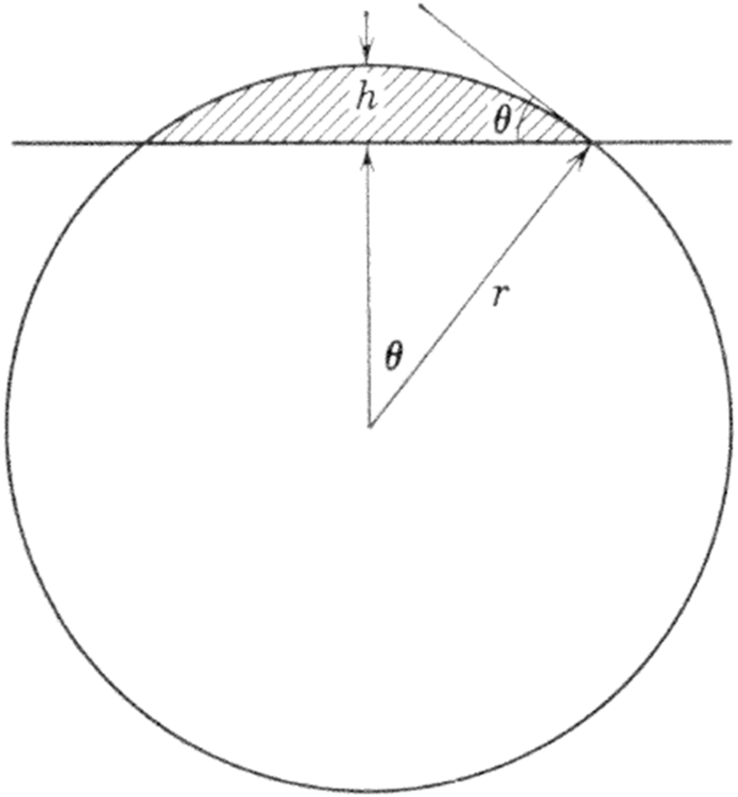
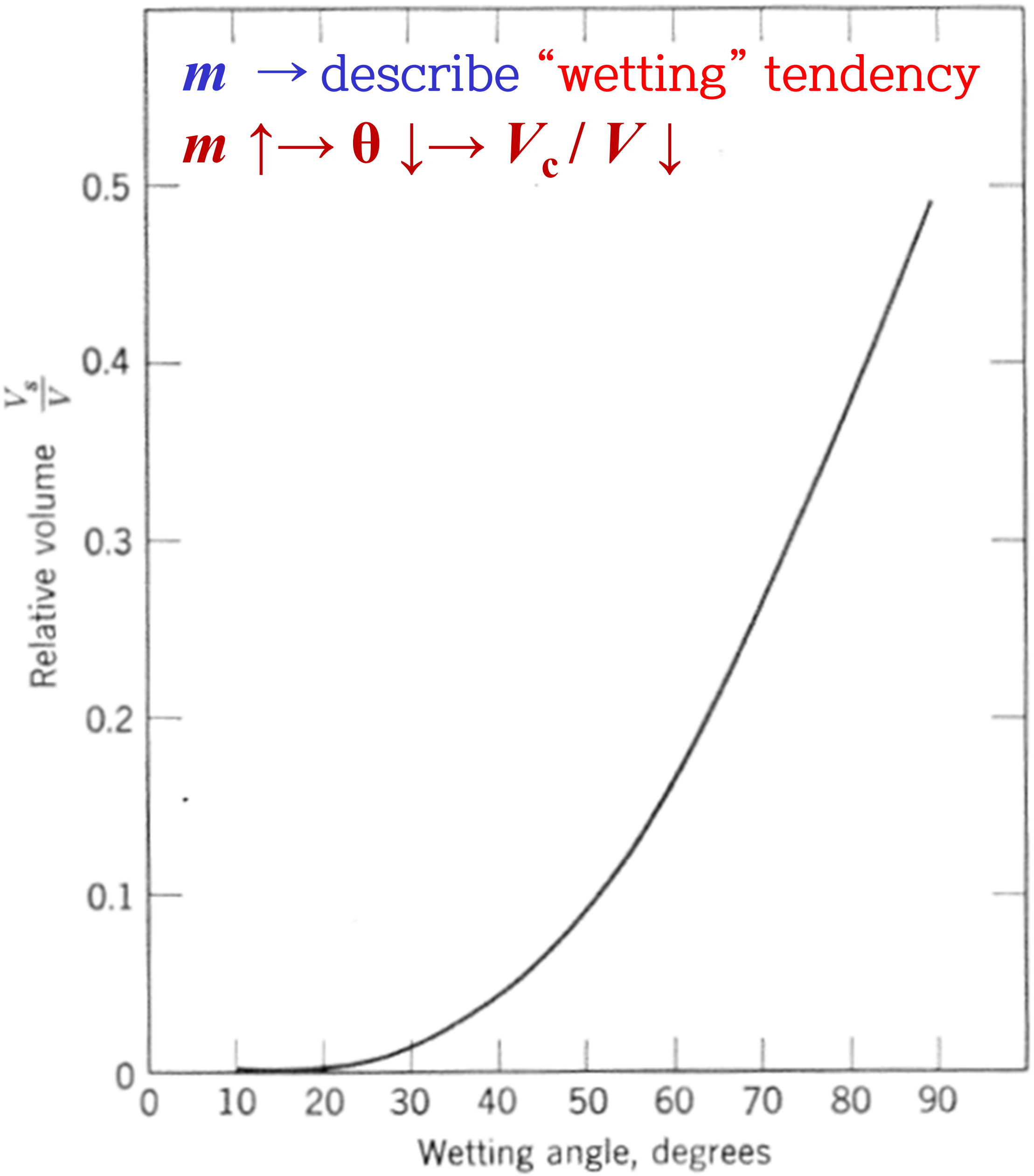


Fig. 3.13. Volume of a spherical cap.



$m \rightarrow$ describe "wetting" tendency

$m \uparrow \rightarrow \theta \downarrow \rightarrow V_c / V \downarrow$

Fig. 3.14. Relation between volume of an embryo and angle of contact.

m ↑→ θ ↓→ V_c / V ↓ → embryo radius ↑

→ condition for heterogeneous nucleation as a function of θ

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

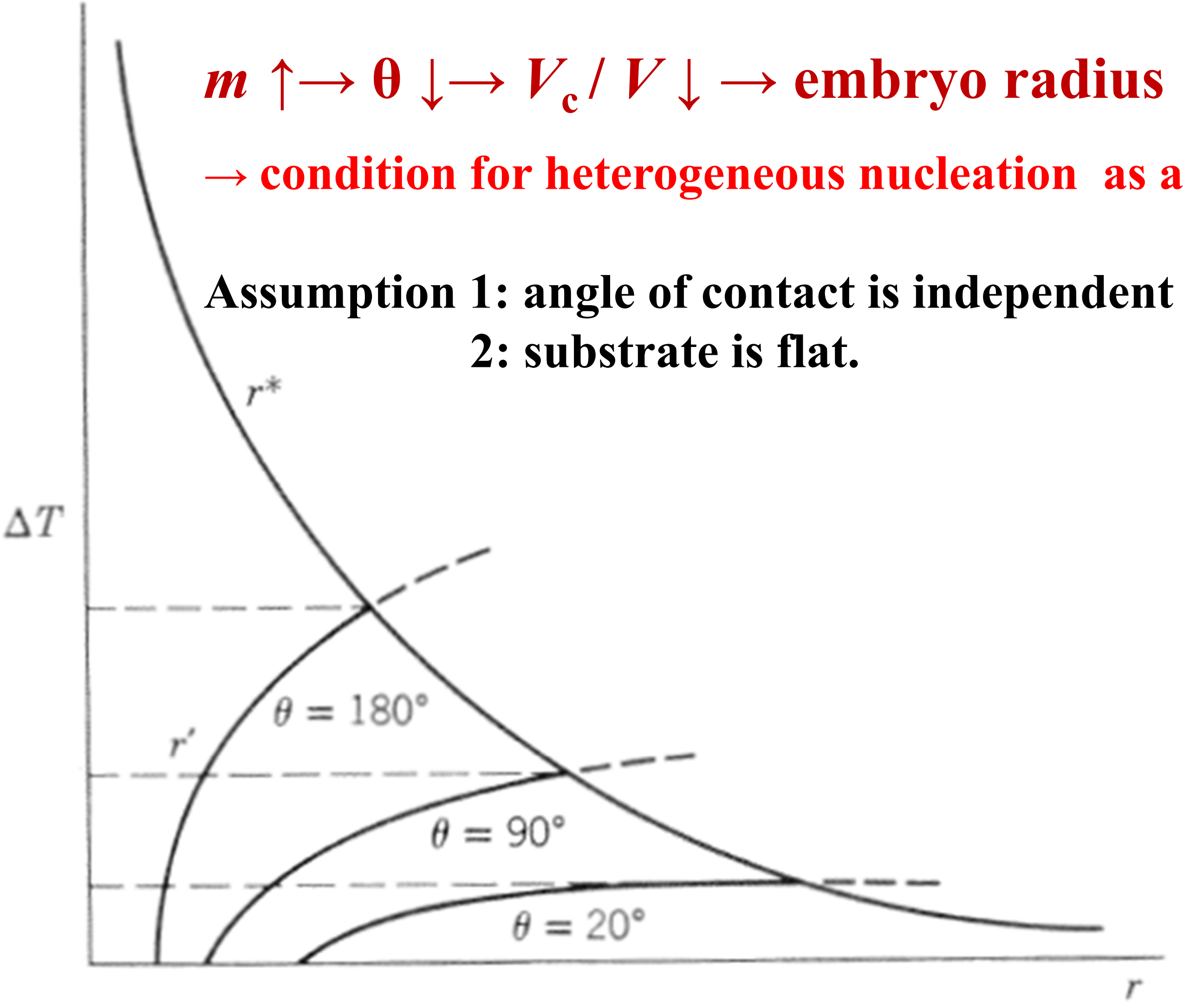


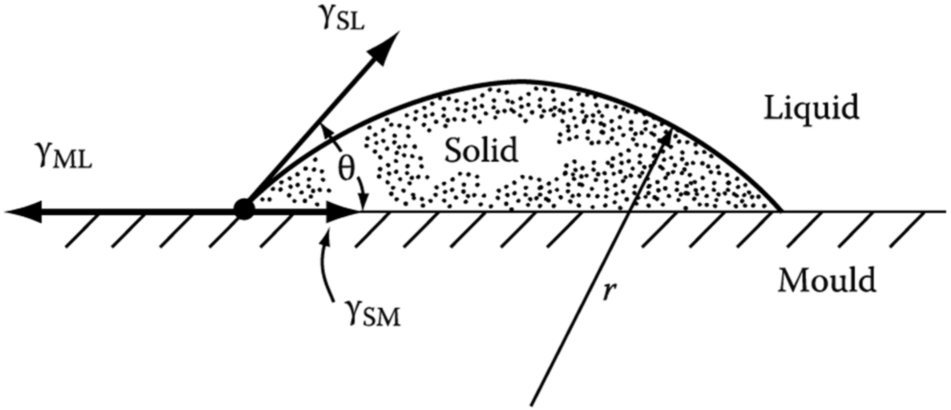
Fig. 3.15. Condition for heterogeneous nucleation (schematic).

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 the surface of the container.

Heterogeneous nucleation of spherical cap on a flat mold wall.



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

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

m **: surface E relationship** → describe "wetting" tendency

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

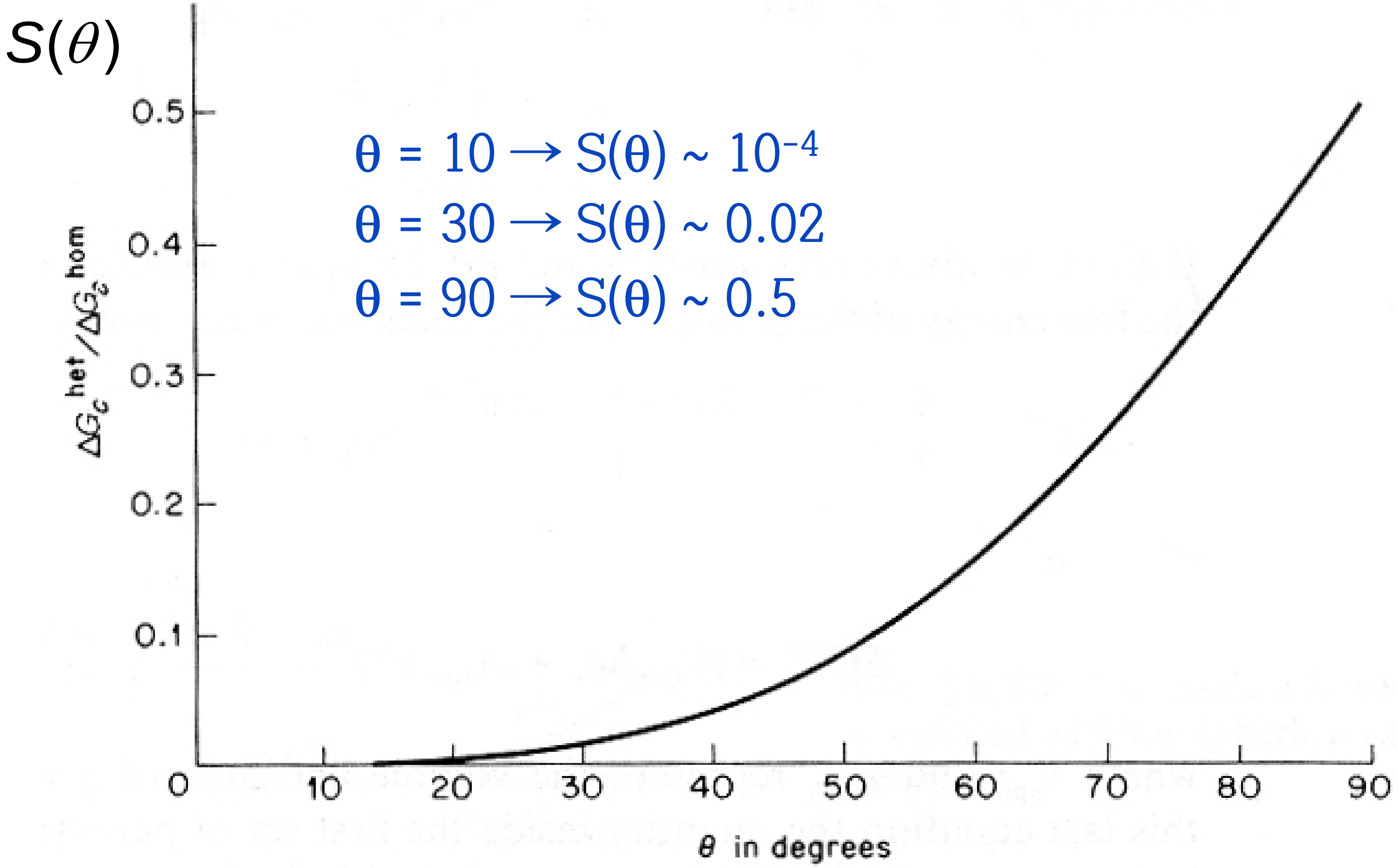
In terms of the wetting angle (θ) and the cap radius (r) **(Exercies 4.6)**

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

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)

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



θ = 10 → S(θ) ~ 10^{-4}

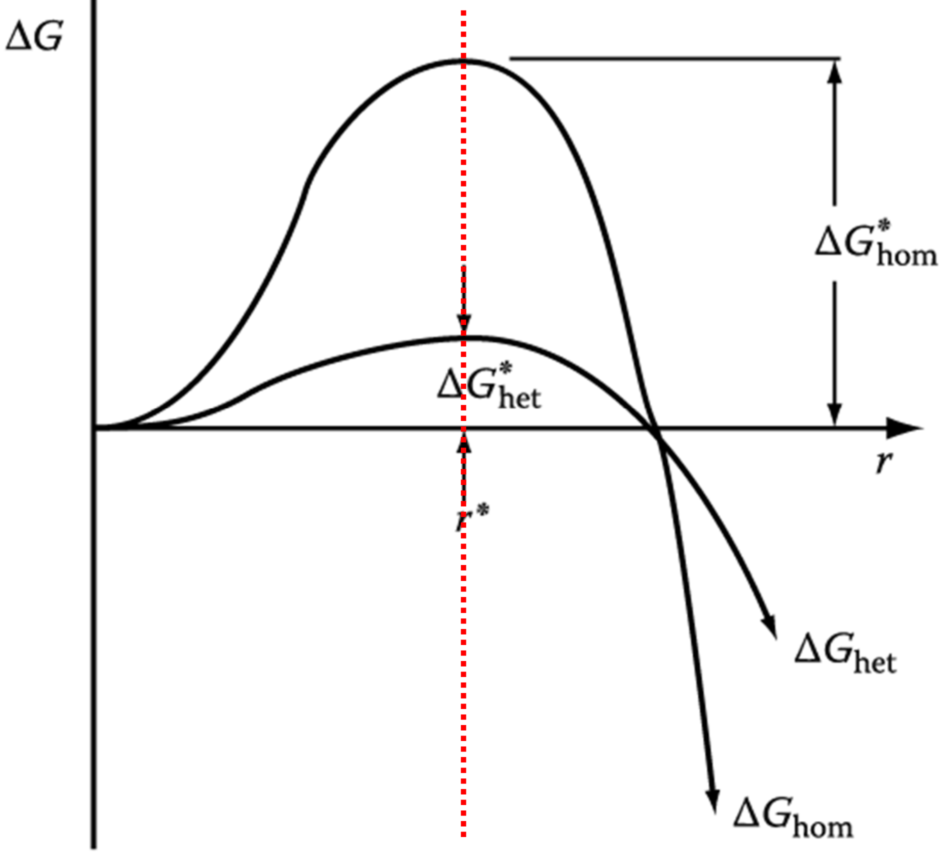
θ = 30 → S(θ) ~ 0.02

θ = 90 → S(θ) ~ 0.5

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

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

$$= \left(\frac{2\gamma_{SL}T_m}{L_V}\right)\boxed{\frac{1}{\Delta T}} \qquad = \left(\frac{16\pi\gamma_{SL}^{3}T_m^{2}}{3L_V^{2}}\right)\boxed{\frac{1}{(\Delta T)^{2}}} \cdot S(\theta)$$



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}?

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

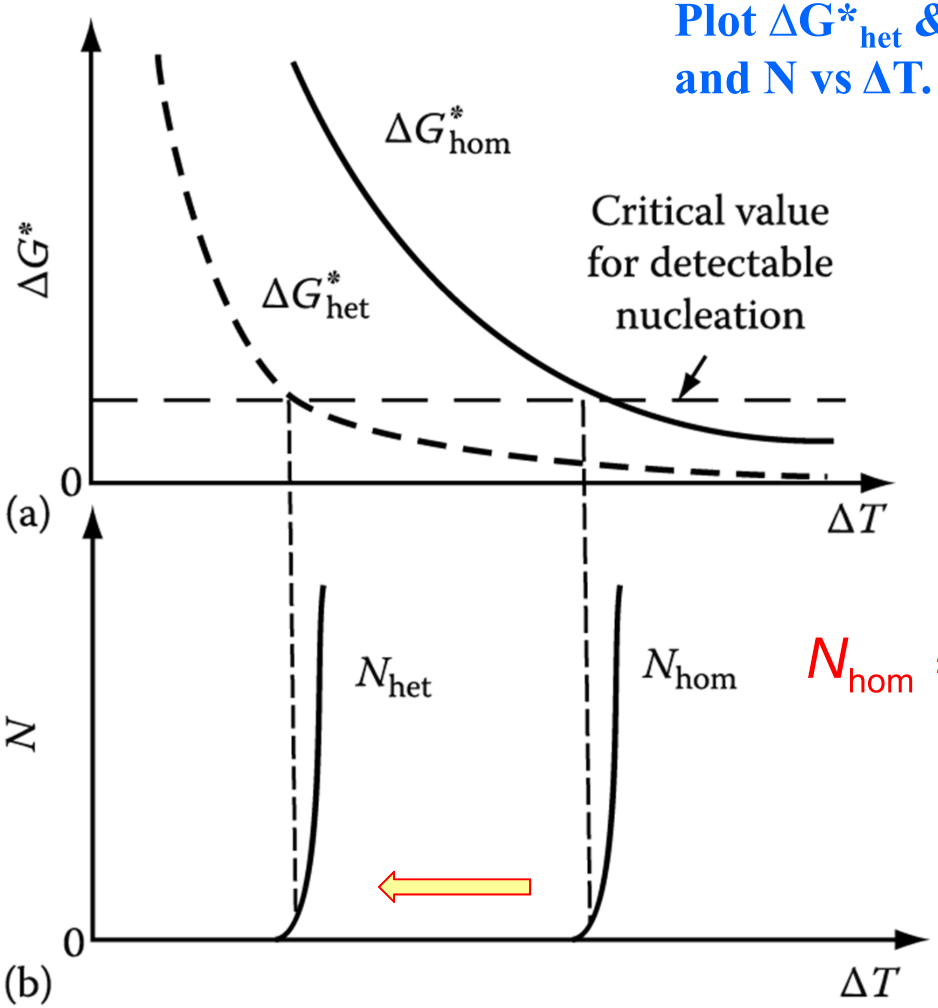
$$\Rightarrow \quad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}\cdot S(\theta)$$

Plot ΔG^*_{het} & $\Delta G^*_{\ hom}$ vs ΔT and N vs ΔT.

n_1 atoms in contact with the mold wall

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

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

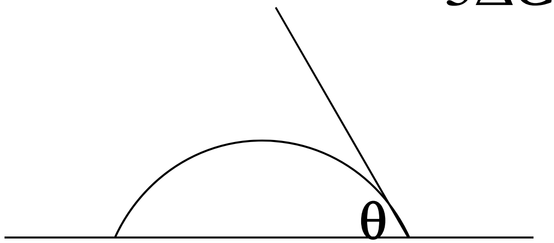


$$N_{hom} \approx 1\ \text{cm}^{-3}\text{s}^{-1}$$

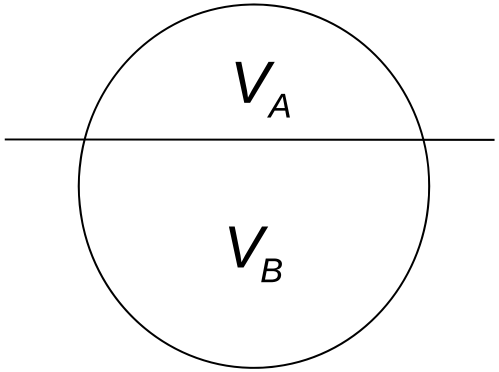
Fig. 4.9 (a) Variation of ΔG* with undercooling (ΔT) for homogeneous and heterogeneous nucleation. (b) The corresponding nucleation rates assuming the same critical value of ΔG*

Barrier of Heterogeneous Nucleation

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



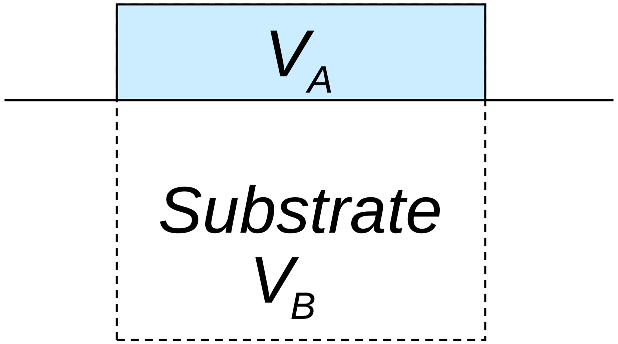
$$\boxed{\Delta G_{het}^* = S(\theta)\Delta G_{\mathrm{hom}}^*}$$



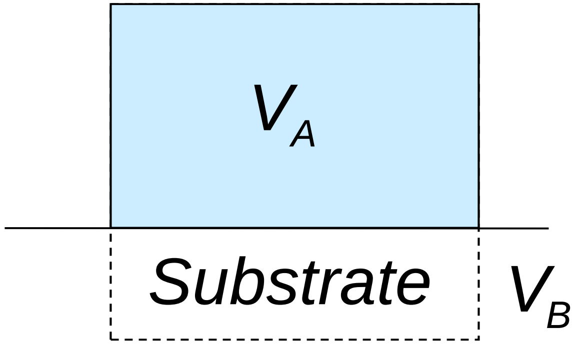
$$\Delta G_{sub}^* = \Delta G_{homo}^* \left(\frac{2-3\cos\theta+\cos^3\theta}{4} \right)$$

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

How 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

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

Assumption 2: substrate is flat.

→ If it is curved, the nucleus has a smaller volume when the substrate is concave, and it therefore requires less undercooling to cause nucleation.

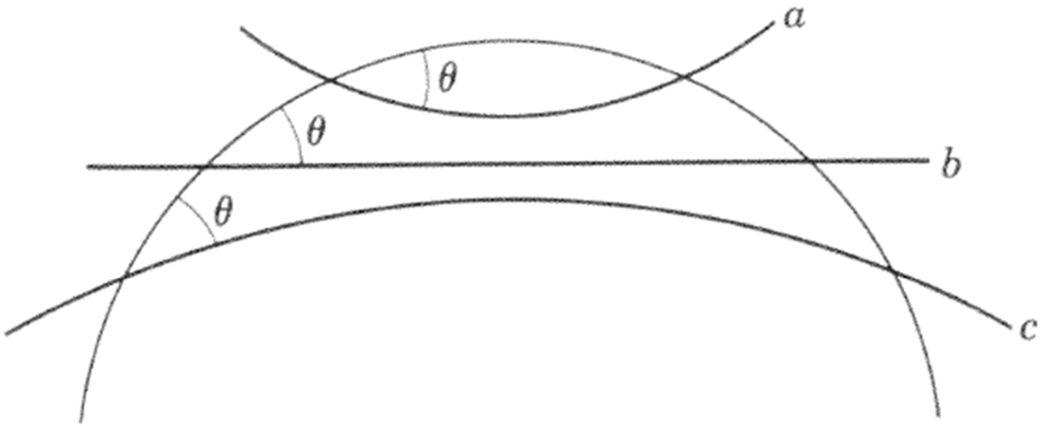
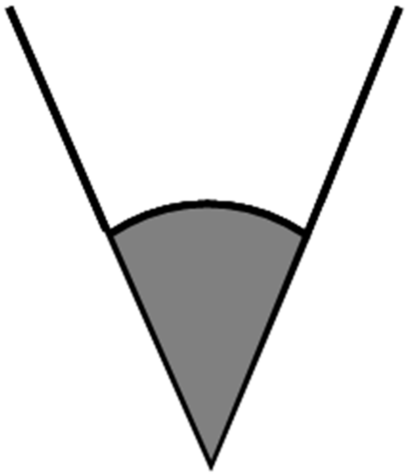


Fig. 3.16. Nucleation on curved (a), flat (b), and concave (c) surfaces, with the same angle of contact θ.

Nucleation Barrier at the crevice

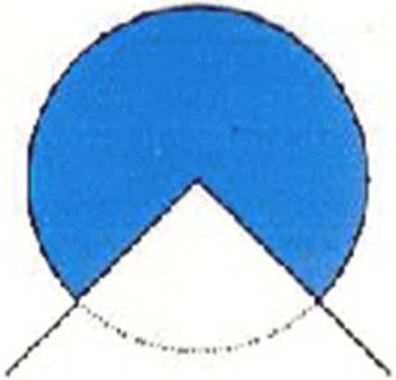


What would be the shape of nucleus and the nucleation barrier for the following conditions?

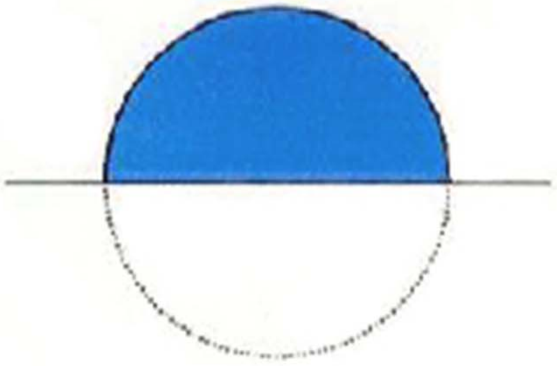
contact angle = 90

groove angle = 60

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



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



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

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

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.

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

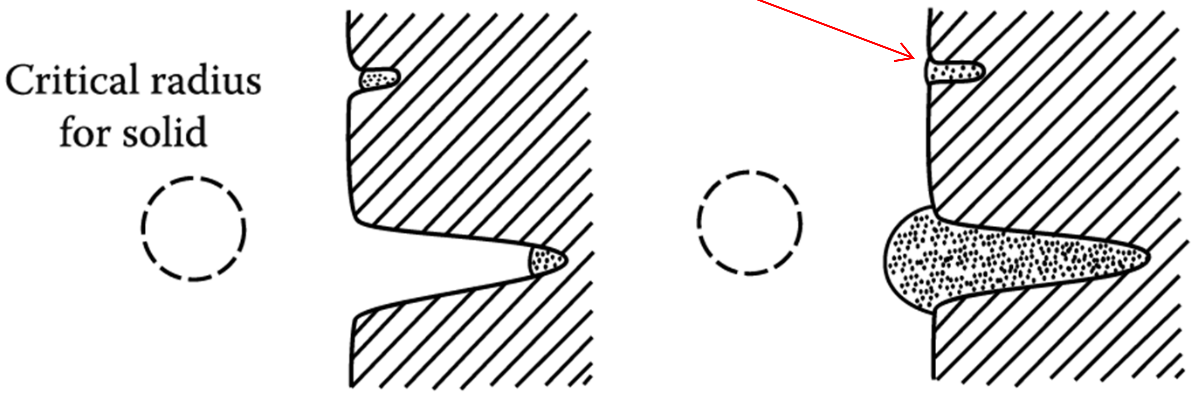
Formation of a nucleus on such a surface

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

Energy required for nucleation at the mold surface

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

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 inteface decreasing below r*.



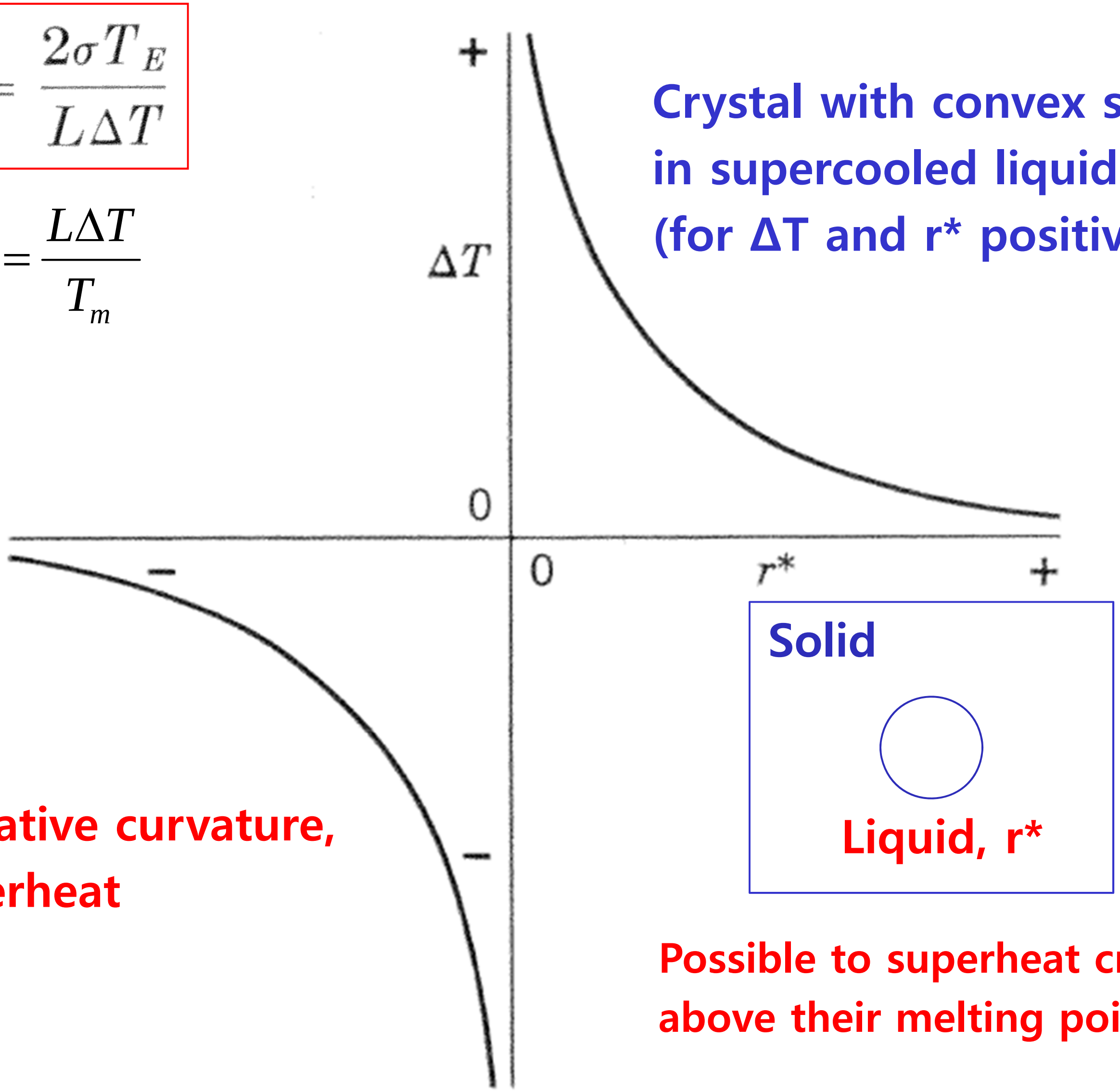
(a) (b)

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

3.7 The Nucleation of Melting

$$r^* = \frac{2\sigma T_E}{L\Delta T}$$

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



Crystal with convex surface
in supercooled liquid
(for ΔT and r* positive)

Negative curvature,
superheat

Possible to superheat crystals
above their melting points

Fig. 3.3. Relationship between critical radius and supercooling.

3.7 The 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, stat at crystal surfaces without appreciable superheating.

Why?

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

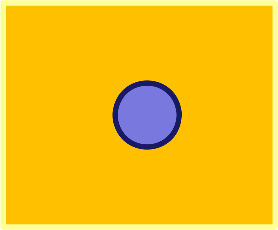
In the case of gold,

solid-liquid	132 ergs/cm
liquid-vapor	1128 ergs/cm
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

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

Melting: Liquid ← Solid