2019 Fall

Introduction to Materials Science and Engineering

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Contents for previous class

Chapter 11 Phase Diagrams Summary

- Phase diagrams are useful tools to determine:
  -- the number and types of phases present,
  -- the composition of each phase,
  -- and the weight fraction of each phase
  given the temperature and composition of the system.

- The microstructure of an alloy depends on
  -- its composition, and
  -- whether or not cooling rate allows for maintenance of equilibrium.

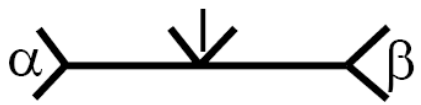
- Important phase diagram phase transformations include eutectic, eutectoid, and peritectic.

Review of Invariant Binary Reactions

Eutectic Type

Eutectic

$l \rightleftarrows \alpha + \beta$



Al-Si, Fe-C

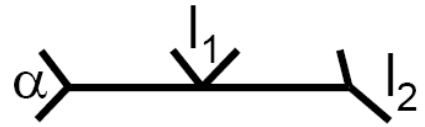
Eutectoid

$\gamma \rightleftarrows \alpha + \beta$

Fe-C

Monotectic

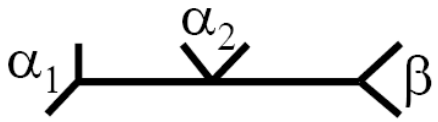
$l_1 \rightleftarrows \alpha + l_2$



Cu-Pb

Monotectoid

$\alpha_2 \rightleftarrows \alpha_1 + \beta$



Al-Zn, Ti-V

On cooling one phase going to two phases

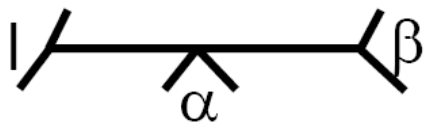
Metatectic reaction: $\beta \leftrightarrow L + \alpha$ **Ex. Co-Os, Co-Re, Co-Ru**

Review of Invariant Binary Reactions

Peritectic Type

Peritectic

$l + \beta \rightleftarrows \alpha$



Fe-C

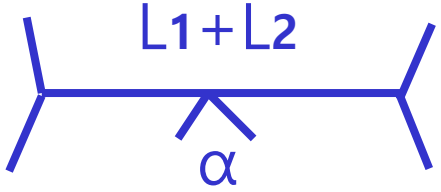
Peritectoid

$\alpha + \beta \rightleftarrows \gamma$

Cu-Al

Syntectic reaction

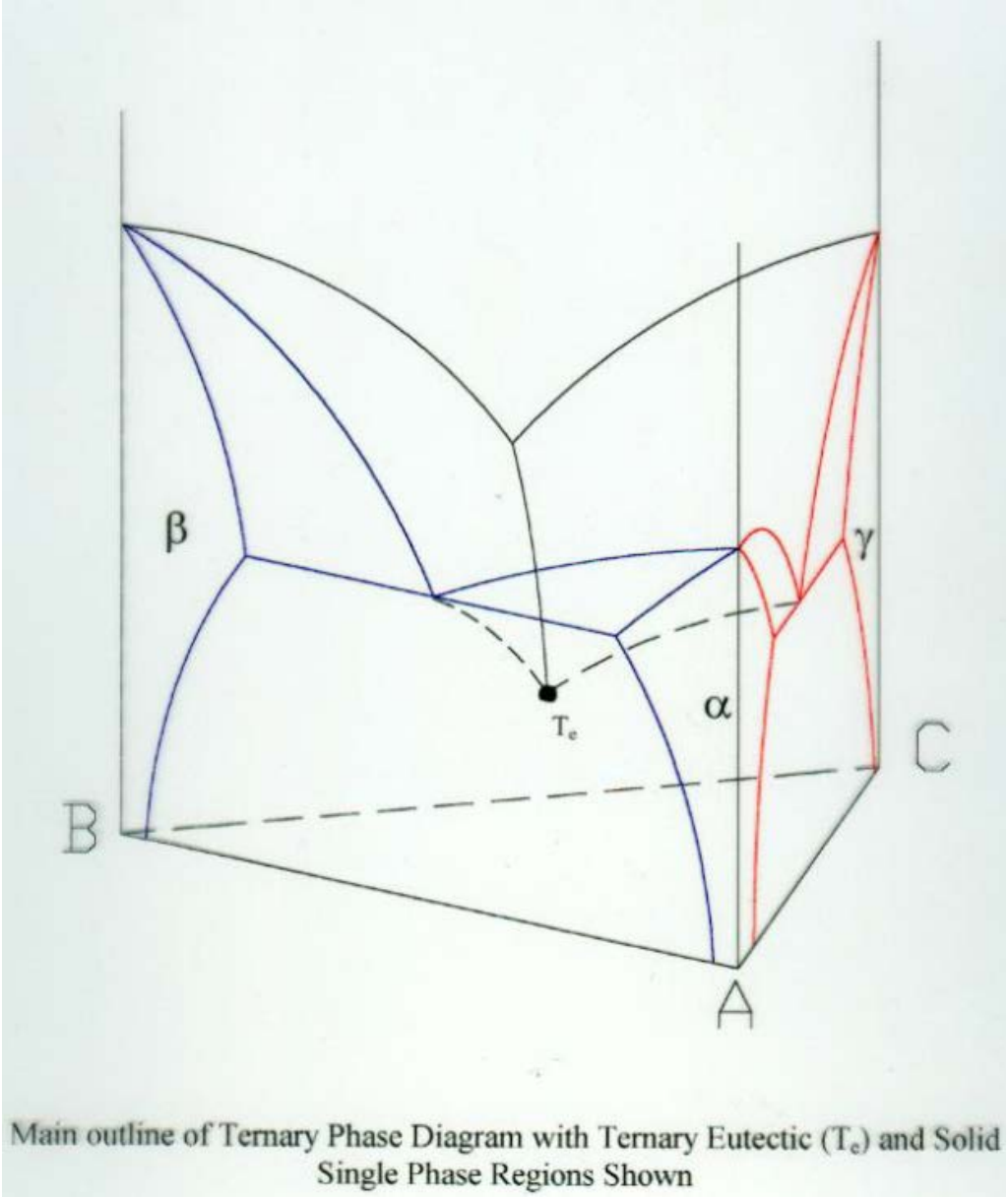
Liquid1+Liquid2 ↔ α



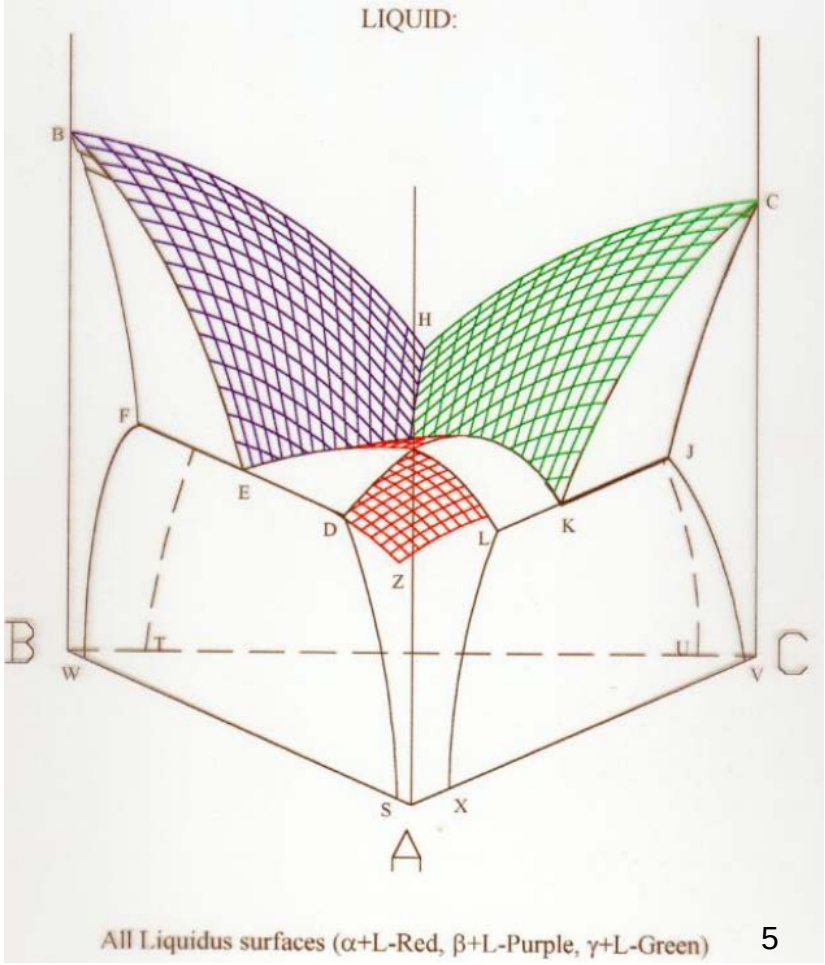
K-Zn, Na-Zn,
K-Pb, Pb-U, Ca-Cd

On cooling two phases going to one phase

Ternary Eutectic System
(with Solid Solubility)



Main outline of Ternary Phase Diagram with Ternary Eutectic (T_e) and Solid Single Phase Regions Shown



All Liquidus surfaces (α+L-Red, β+L-Purple, γ+L-Green)

< Quaternary phase Diagrams >

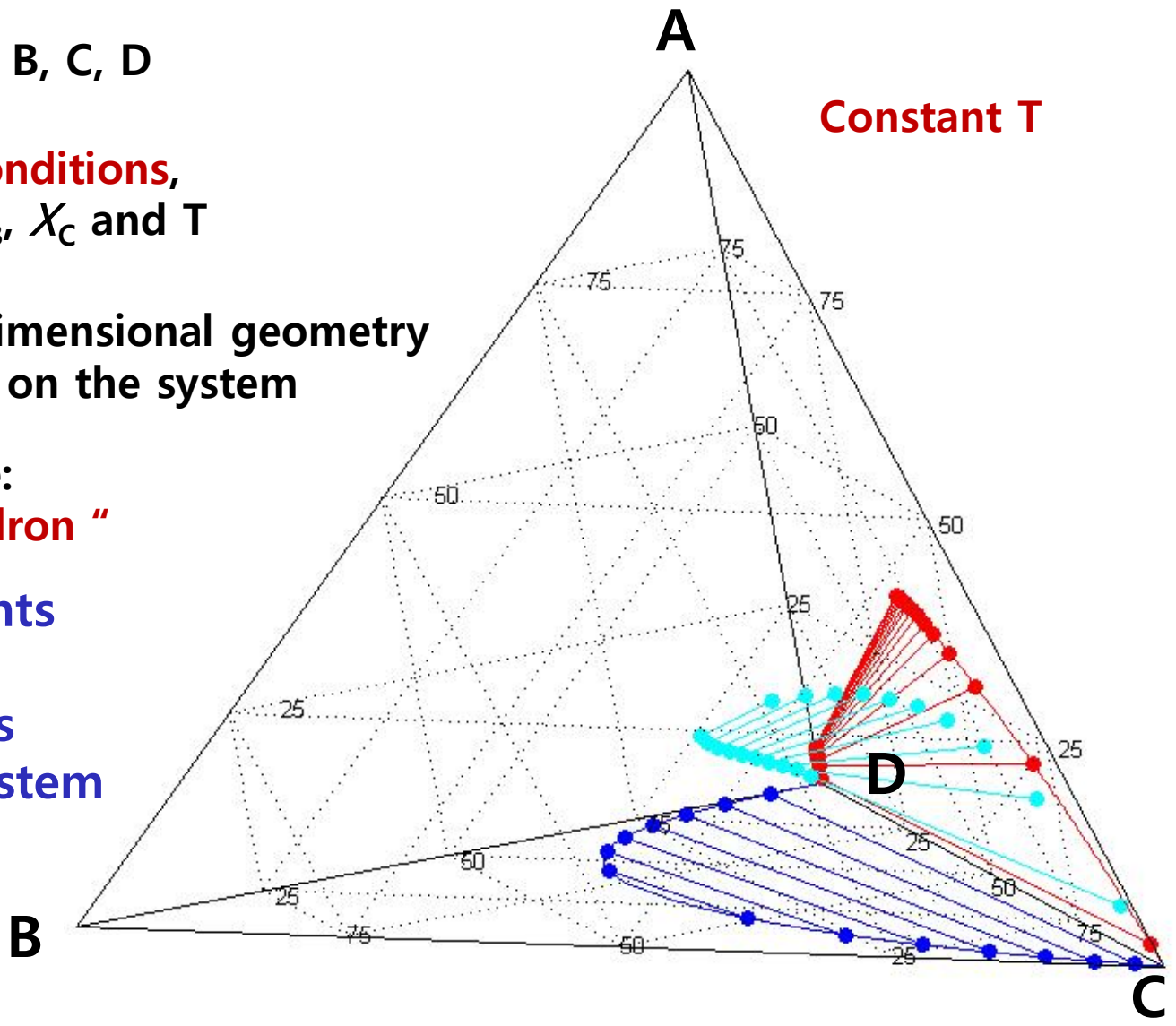
Four components: A, B, C, D

Assuming isobaric conditions,
Four variables: X_A, X_B, X_C and T

A difficulty of four-dimensional geometry
→ further restriction on the system

Most common figure:
" equilateral tetrahedron "

- 4 pure components
- 6 binary systems
- 4 ternary systems
- A quarternary system

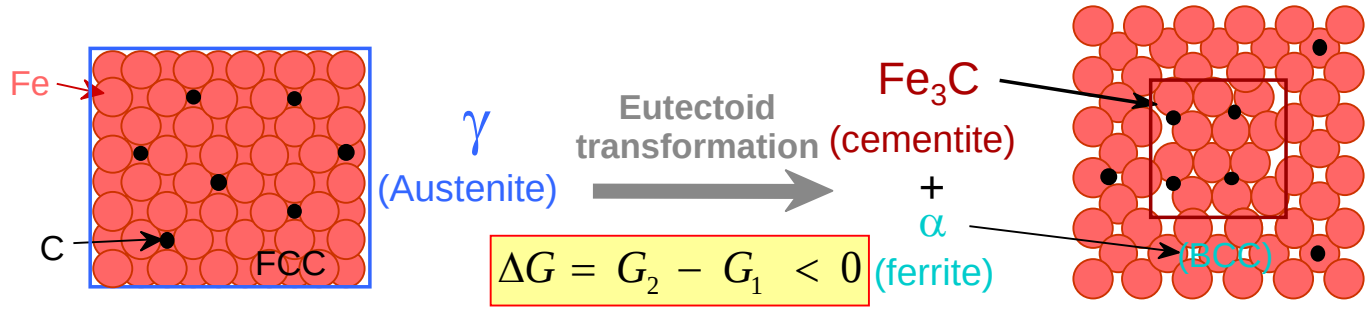


Contents for today's class

Chapter 12. Phase Transformations

ISSUES TO ADDRESS...

- Transforming one phase into another takes **time**.



- How does the rate of transformation depend on **time and *T***?
- How can we slow down the transformation so that we can **engineering non-equilibrium structures**?
- Are the **mechanical properties of non-equilibrium structures** better?

Contents_Phase transformation course

Background to understand phase transformation

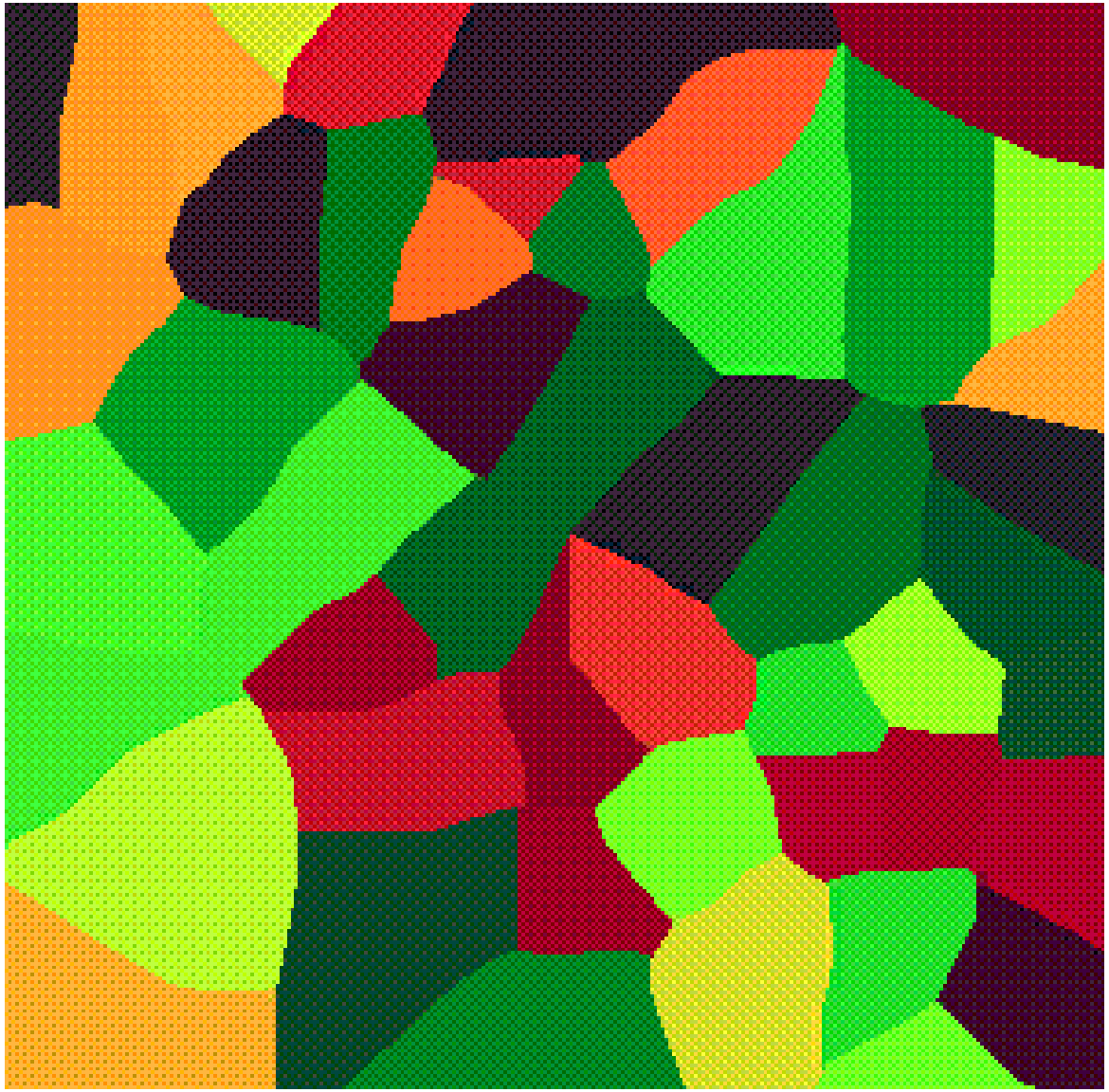
- (Ch1) Thermodynamics and Phase Diagrams
- (Ch2) Diffusion: Kinetics
- (Ch3) Crystal Interface and Microstructure

Representative Phase transformation

- (Ch4) Solidification: Liquid → Solid
- (Ch5) Diffusional Transformations in Solid: Solid → Solid
- (Ch6) Diffusionless Transformations: Solid → Solid

Phase Transformations

Solidification: Liquid → Solid



4 Fold Anisotropic Surface Energy/2 Fold Kinetics, Many Seeds

Solidification: Liquid → Solid

- casting & welding
- single crystal growth
- directional solidification
- rapid solidification

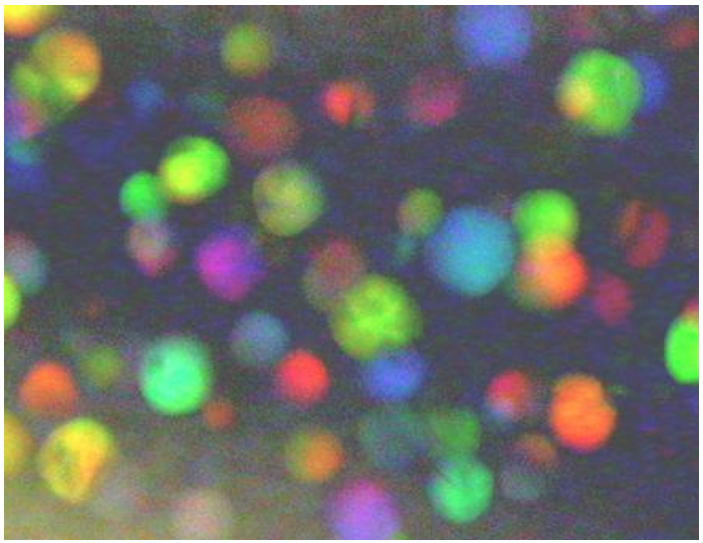
4.1. Nucleation in Pure Metals

T_m : $G_L = G_S$

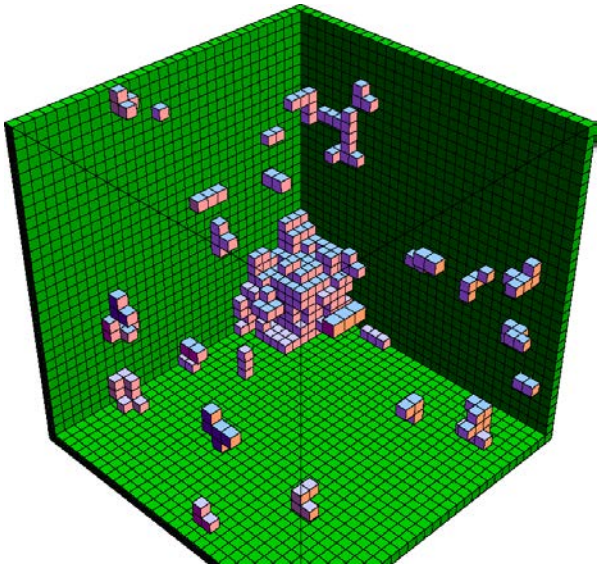
- Undercooling (supercooling) for nucleation: 250 K ~ 1 K

<Types of nucleation>

- Homogeneous nucleation



- Heterogeneous nucleation



4.1.1. Homogeneous Nucleation

Driving force for solidification

$G^L = H^L - TS^L$

$G^S = H^S - TS^S$

$\Delta G = \Delta H - T\Delta S$

$L : \Delta H = H^L - H^S$

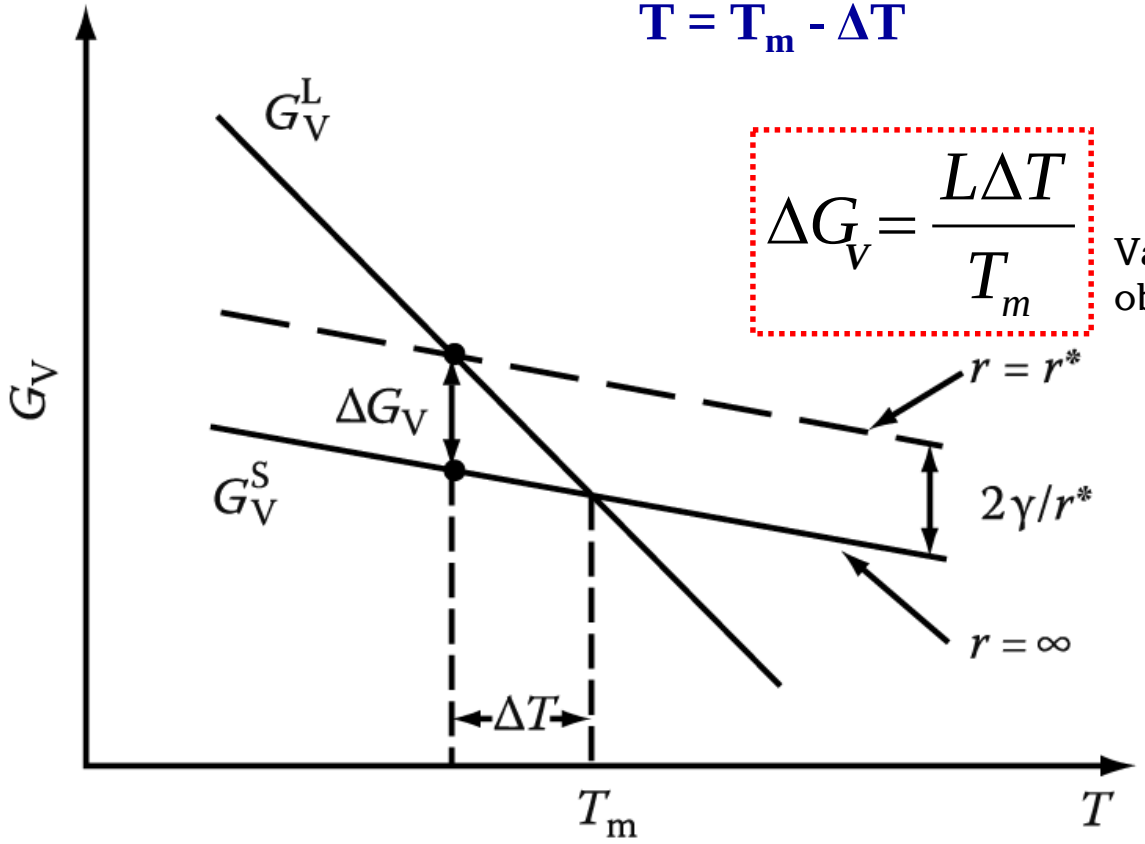
(Latent heat)

$T = T_m - \Delta T$

$\Delta G = 0 = \Delta H - T_m \Delta S$

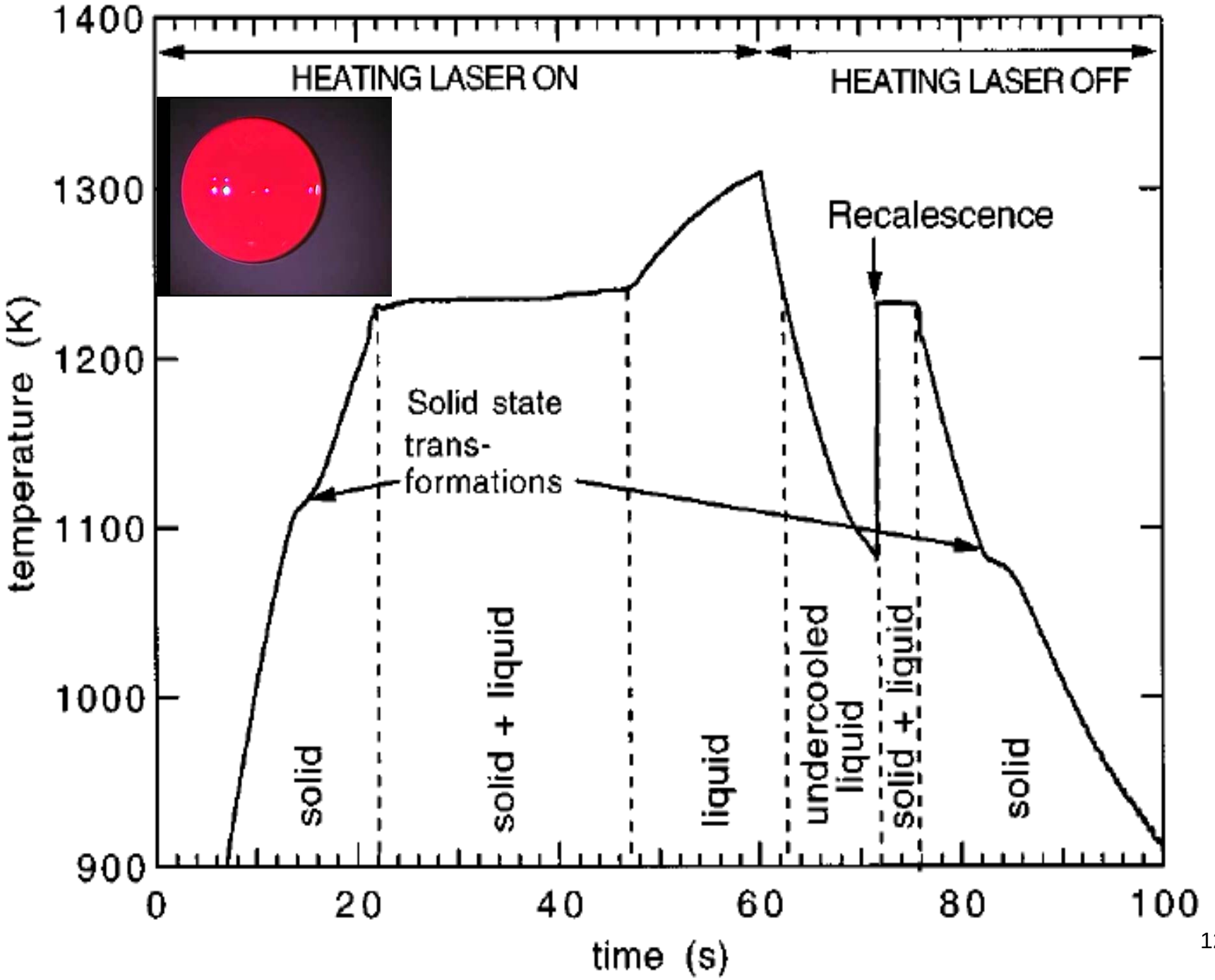
$\Delta S = \Delta H / T_m = L / T_m$

$\Delta G = L - T(L/T_m) \approx (L\Delta T)/T_m$

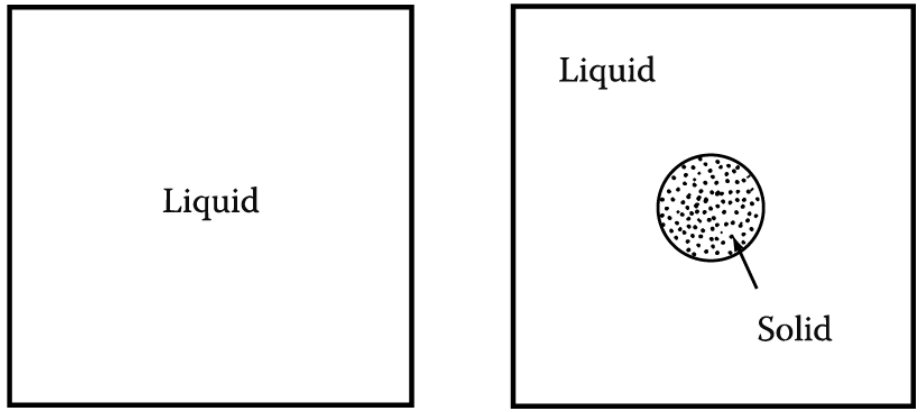


$$\Delta G_V = \frac{L\Delta T}{T_m}$$

Variation of free energy per unit volume obtained from undercooling (ΔT)


HEATING LASER ON
HEATING LASER OFF
Recalescence
Solid state
trans-
formations
solid
solid + liquid
liquid
undercooled
liquid
solid + liquid
solid
temperature (K)
time (s)
1400
1300
1200
1100
1000
900
0
20
40
60
80
100

4.1.1. Homogeneous Nucleation



(a) G_1 (b) $G_2 = G_1 + \Delta G$

$$G_1 = (V_S + V_L)G_V^L \qquad G_2 = V_S G_V^S + V_L G_V^L + A_{SL}\gamma_{SL}$$

G_V^S, G_V^L : **free energies per unit volume**

$$\Delta G = G_2 - G_1 = -V_S(G_V^L - G_V^S) + A_{SL}\gamma_{SL}$$

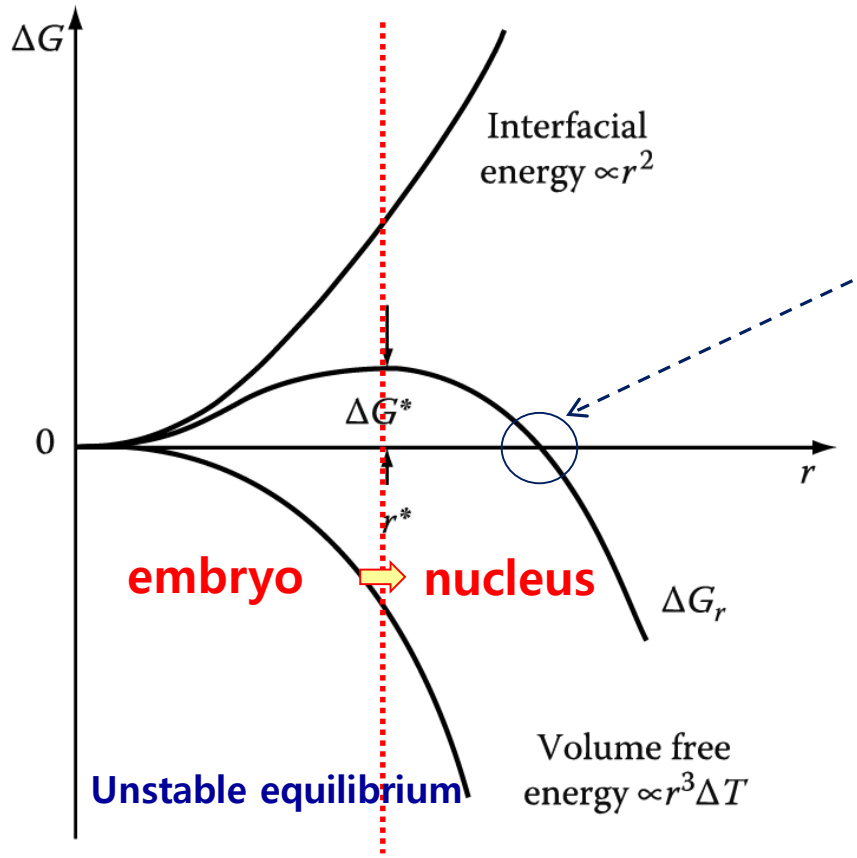
for spherical nuclei (isotropic) of radius : r

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

Volume (Bulk) Free Energy – stabilizes the nuclei (releases energy)

Surface Free Energy- destabilizes the nuclei (it takes energy to make an interface)

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

r* ⇨ **dG=0**

nuclei < r* shrink; nuclei>r* grow (to reduce energy)

Gibbs-Thompson Equation

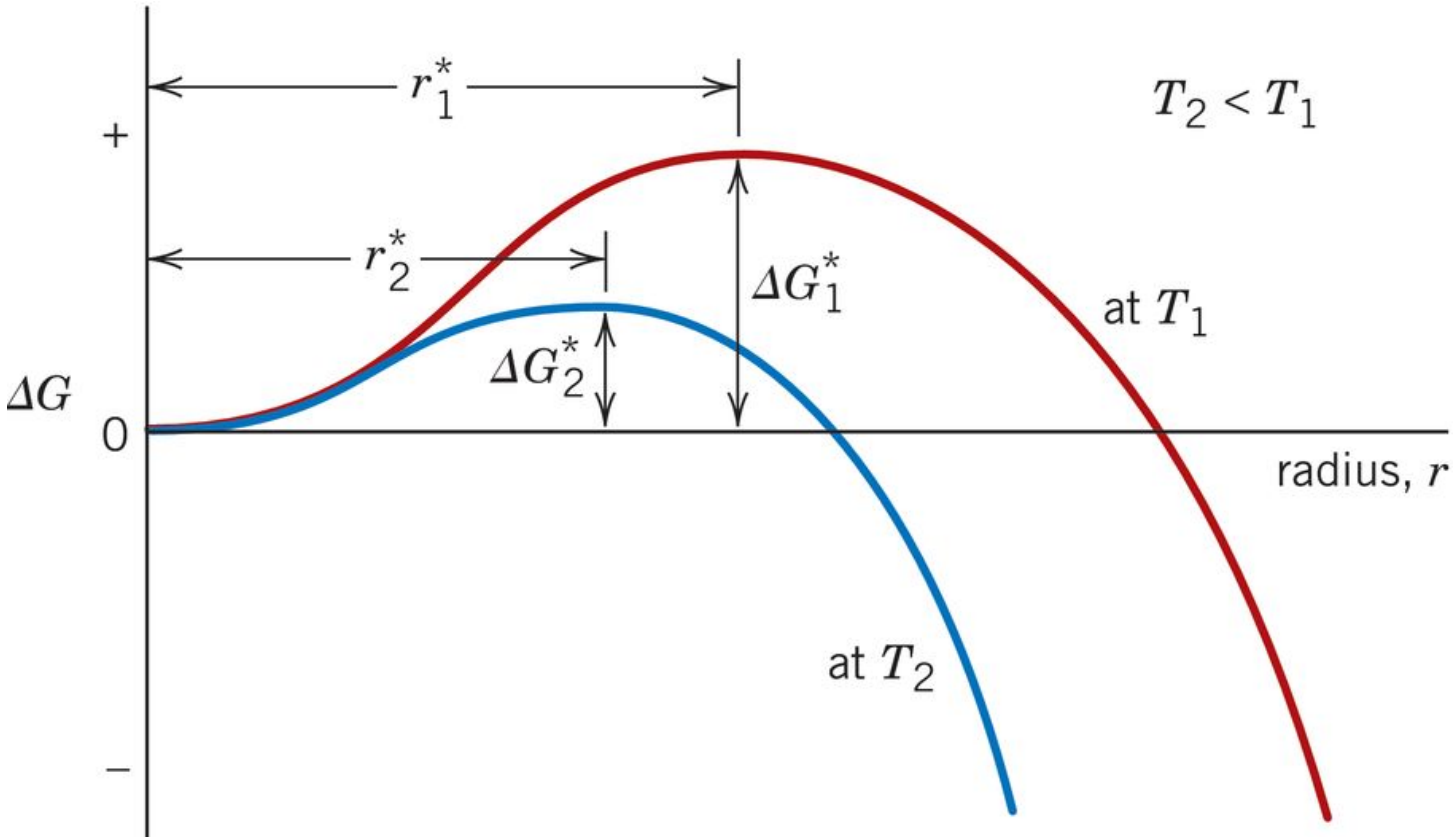
Critical ΔG of nucleation at r*

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

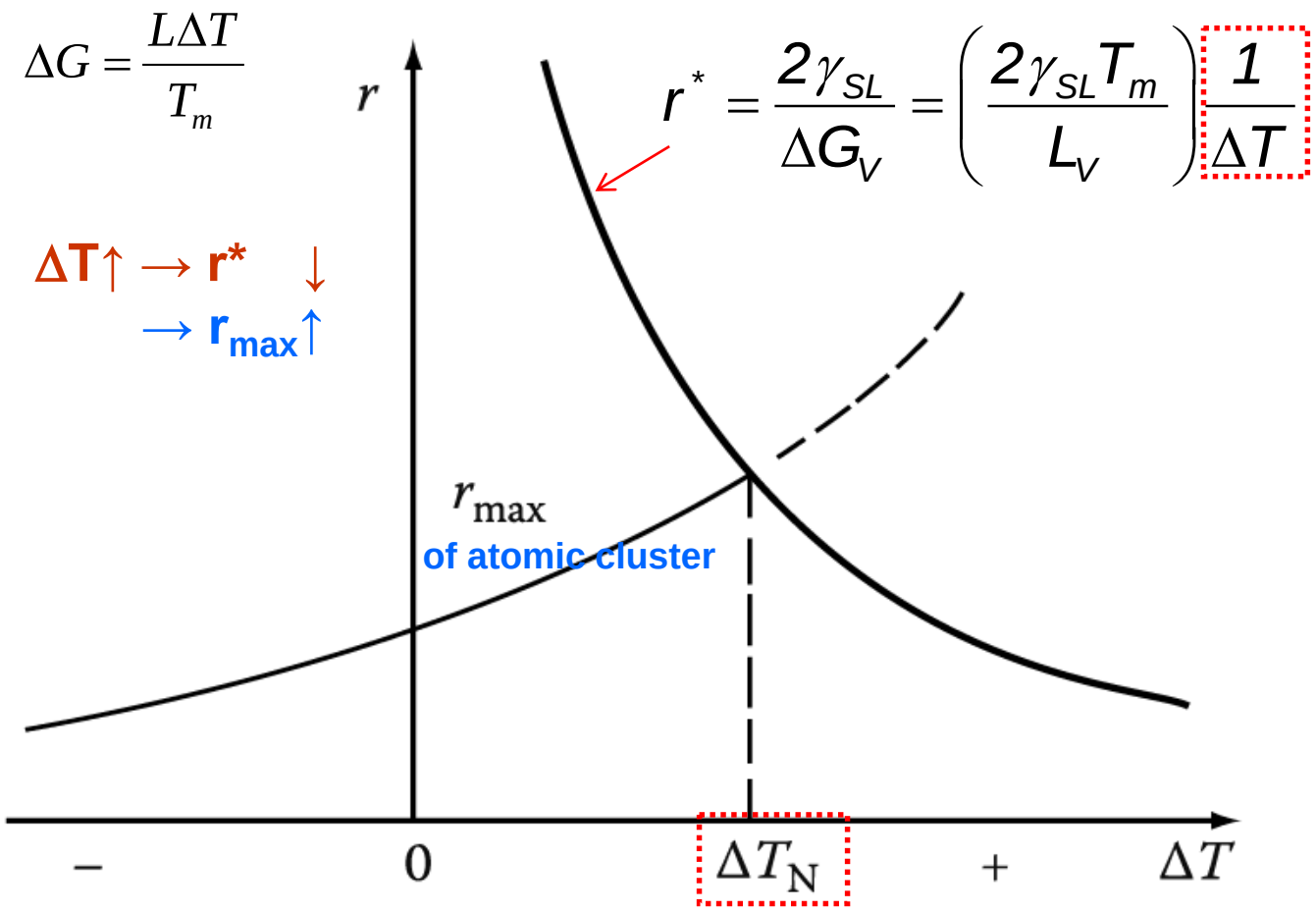
$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL} \qquad \Delta G_V = \frac{L\Delta T}{T_m}$$

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

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



The creation of a critical nucleus ~ thermally activated process



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.

4.1.2. The homogeneous nucleation rate - kinetics

How fast solid nuclei will appear in the liquid at a given undercooling?

C_0 : atoms/unit volume

C^* : # of clusters with size of C* (critical size) 임계핵 크기의 cluster 수

$$C^* = C_0 \exp(-\frac{\Delta G^*_{\text{hom}}}{kT})$$ **clusters / m³**

The addition of one more atom to each of these clusters will convert them into stable nuclei. 한 개 원자 추가로 확산시 핵생성

Homogeneous Nucleation rate

$$N_{\text{hom}} = f_0 C_o \exp(-\frac{\Delta G^*_{\text{hom}}}{kT})$$ **nuclei / m³·s**

$f_o \sim 10^{11}\ s^{-1}$: **frequency ∝ vibration frequency energy of diffusion in liquid surface area (const.)**

$C_o \sim$ **typically** 10^{29} **atoms/m³**

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

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

Reasonable nucleation rate

Homogeneous Nucleation in Solids

Concentration of Critical Size Nuclei per unit volume

$$C^* = C_0 \exp(-\Delta G^* / kT)$$

C_0 : number of atoms per unit volume in the parent phase

Homogeneous Nucleation Rate

If each nucleus can be made supercritical at a rate of f per second,

$$N_{\text{hom}} = f C^*$$

$$f = \omega \exp(-\Delta G_m / kT)$$

: f depends on how frequently a critical nucleus can receive an atom from the α matrix.

$\omega \propto$ *vibration frequency, area of critical nucleus*

ΔG_m : *activation energy for atomic migration*

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

: This eq. is basically same with eq (4.12) except considering temp. dependence of f.

Homogeneous Nucleation rate

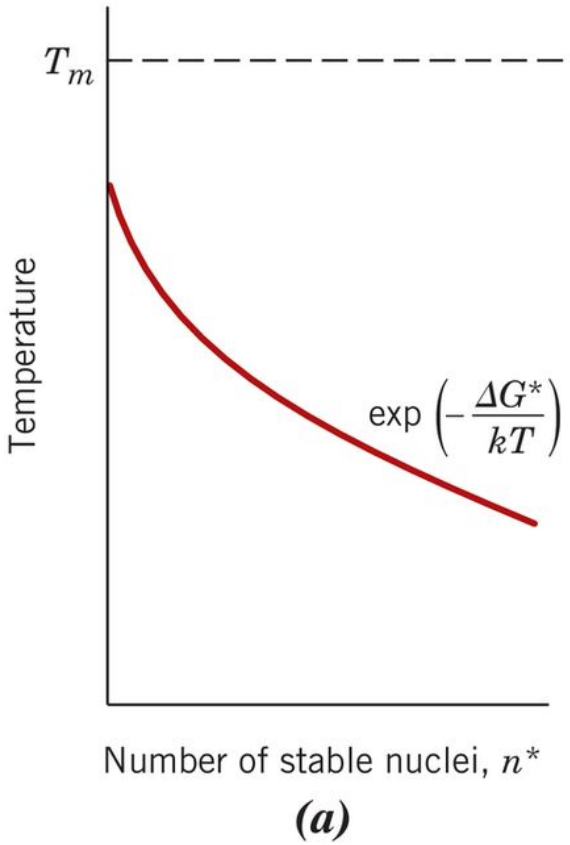
$$N_{\text{hom}} = f_0 C_o \exp\left(-\frac{\Delta G^*_{\text{hom}}}{kT}\right)$$

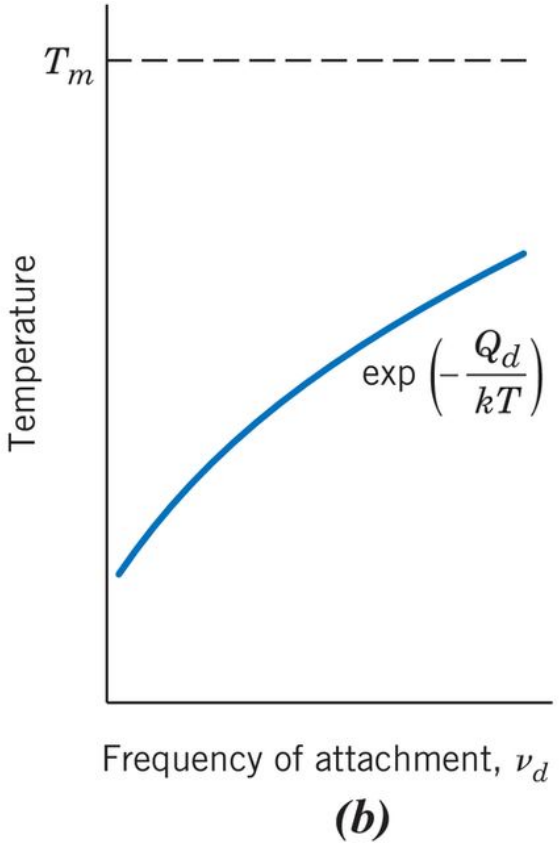
nuclei / m³·s

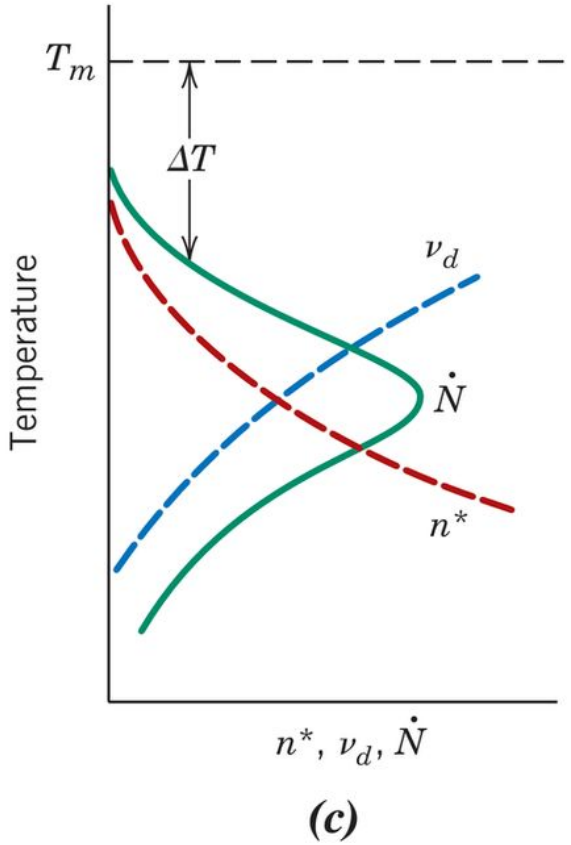
4.1.2. The homogeneous nucleation rate - kinetics

$$= Q_d$$

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







4.1.2. The homogeneous nucleation rate - kinetics

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

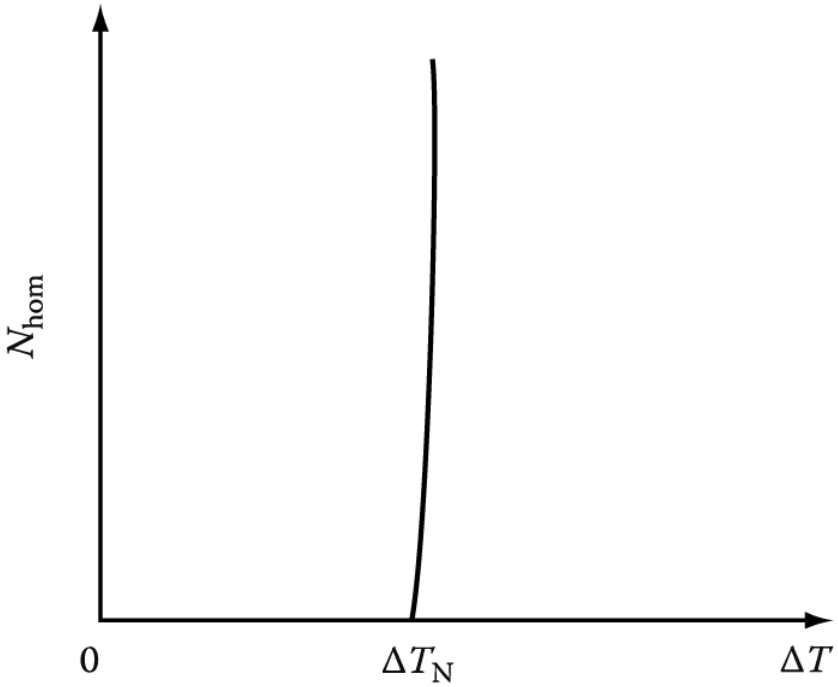
where $A = \frac{16\pi\gamma_{SL}^3 T_m^2}{3 L_V^2 kT}$

A = relatively insensitive to Temp.

How do we define ΔT_N?

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

Changes by orders of magnitude from essentially zero to very high values over a very narrow temperature range



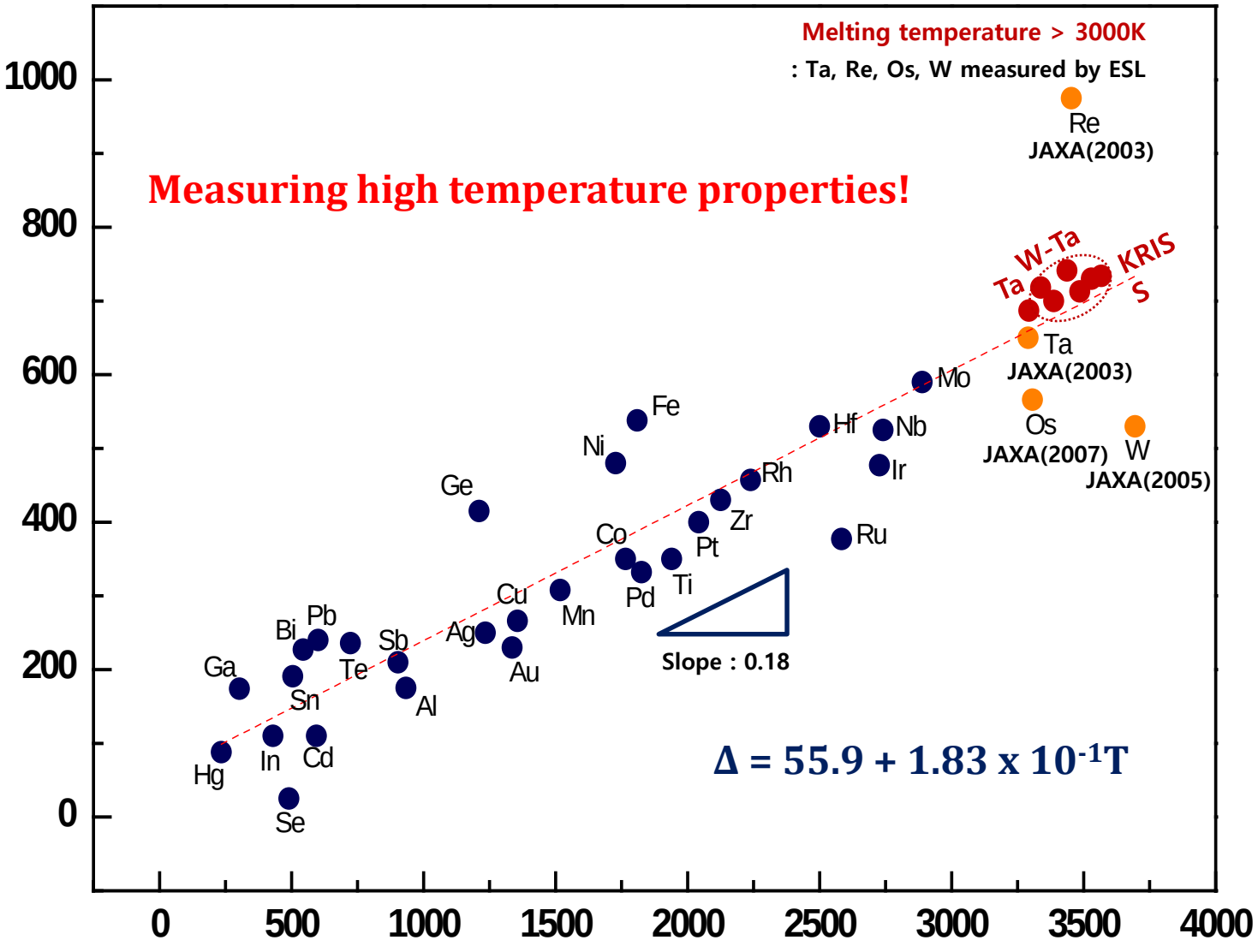
→ **critical value for detectable nucleation**

- **critical supersaturation ratio**
- **critical driving force**
- **critical supercooling**

→ **for most metals, $\Delta T_N \sim 0.2\ T_m$ (i.e. ~200K)**

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

Maximum undercooling vs. Melting temperature



* Copper Homogeneous nucleation

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

If nucleus is spherical shape,

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

"Typically in case 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),

"no spherical shape"

(large deviation from spherical shape) →

→ 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.**

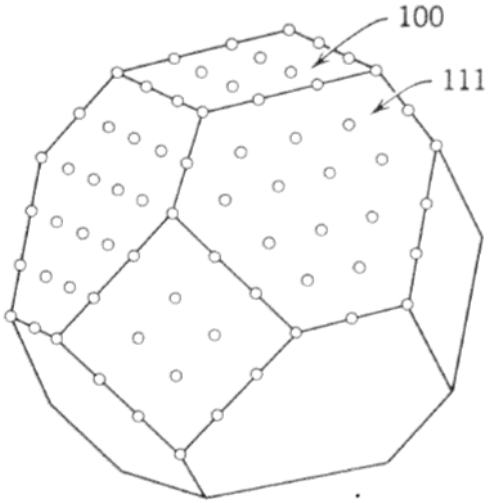


Fig. 3.11. Possible structure for the critical nucleus. (From B. Chalmers, *Physical Metallurgy*, John Wiley and Sons, New York, 1959, p. 246.)

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) liquid / container

or

Solid thin film (such as oxide) / liquid

Why this happens? What is the underlying physics?

Which equation should we examine?

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

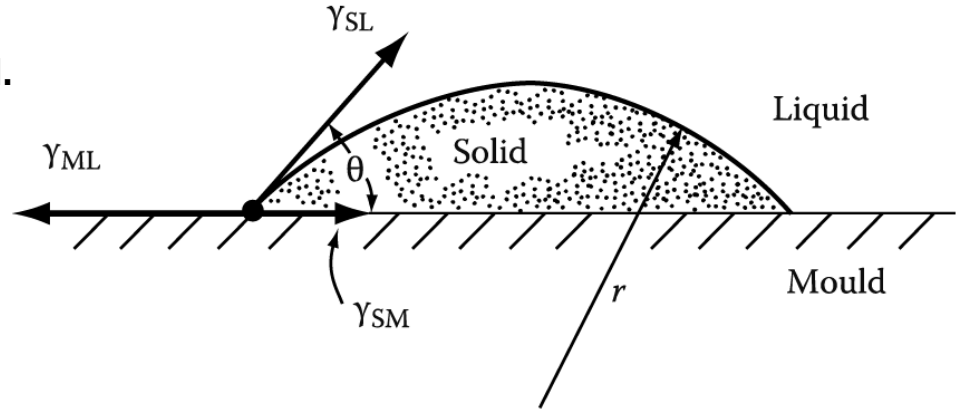
$$N_{\text{hom}} = f_0 C_o \exp\left(-\frac{\Delta G^*_{\text{hom}}}{kT}\right)$$

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 $\gamma_{SL}\downarrow$ by forming nucleus from mould wall.

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



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

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

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

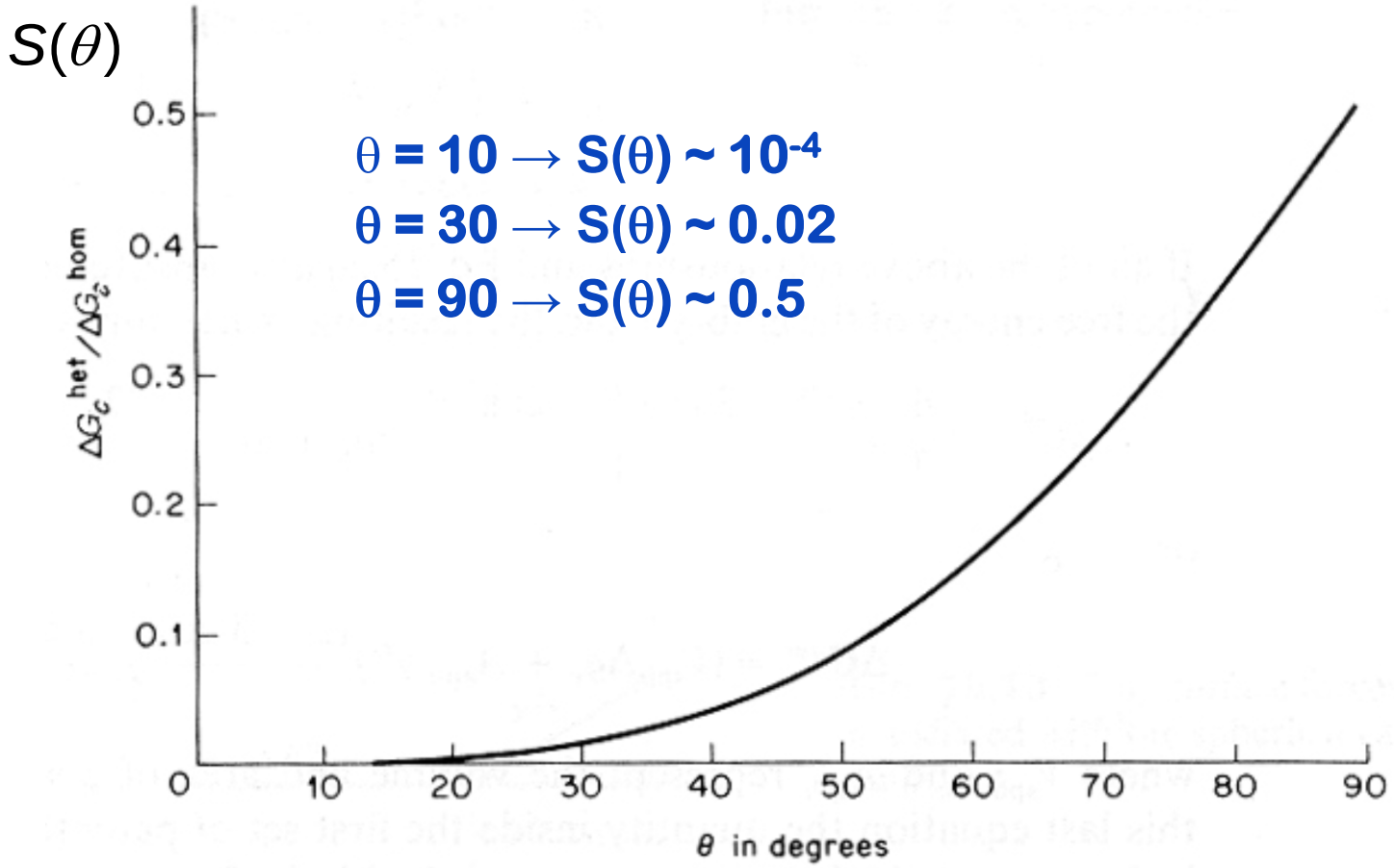
In terms of the wetting angle (θ) and the cap radius (r) **(Exercies 4.6)**

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

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)

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



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

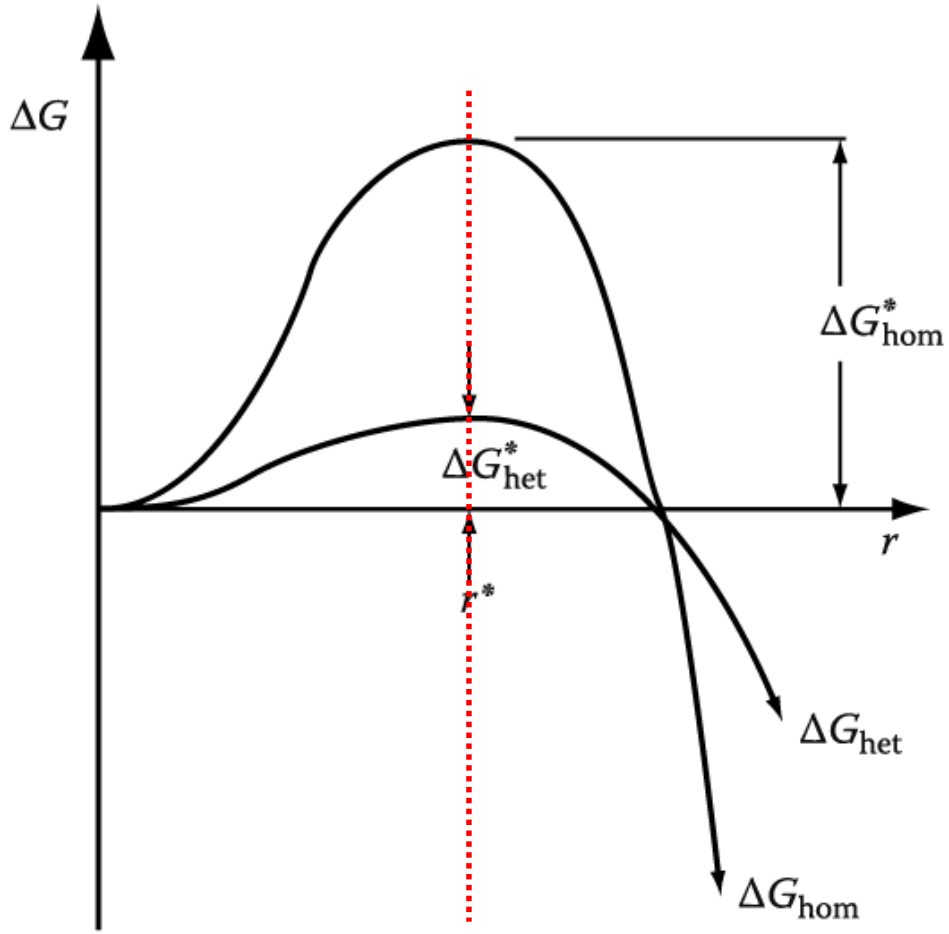
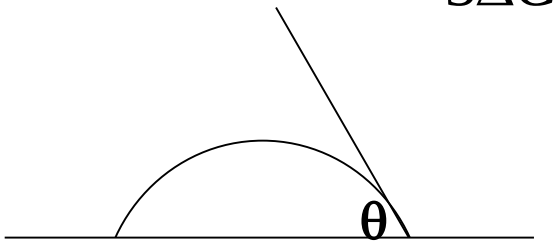


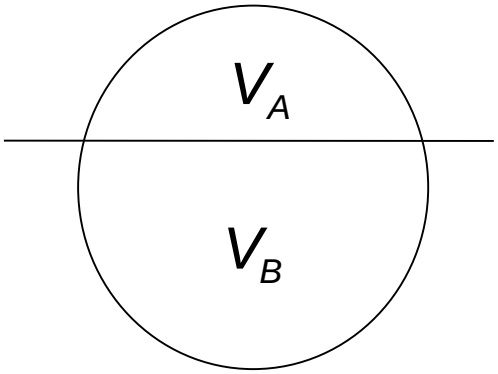
Fig. 4.8 The excess free energy of solid clusters for homogeneous and heterogeneous nucleation. Note r* is independent of the nucleation site.

Barrier of Heterogeneous Nucleation

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



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



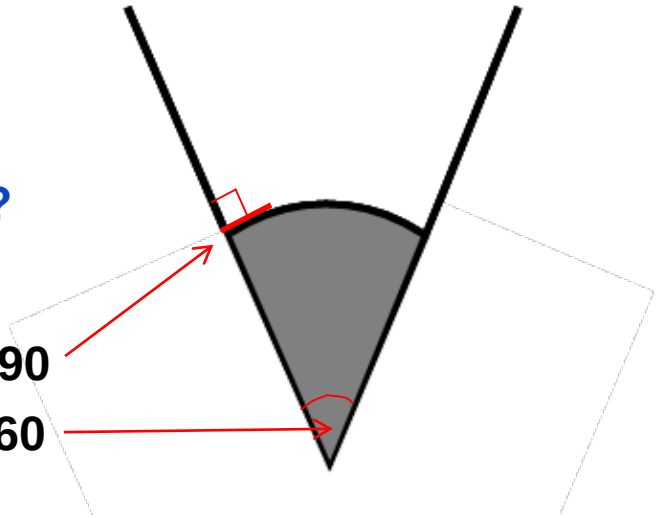
$$\Delta G_{sub}^* = \Delta G_{homo}^* \left(\frac{2-3\cos\theta+\cos^3\theta}{4} \right)$$

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

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

Nucleation Barrier at the crevice

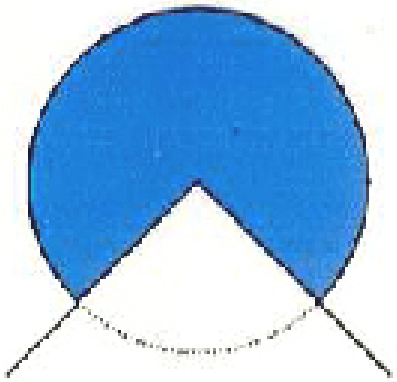
What would be the shape of nucleus and the nucleation barrier for the following conditions?



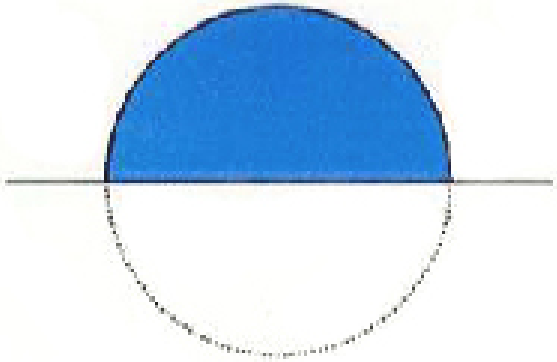
$$\frac{1}{6}\Delta G^*_{\text{homo}}$$

contact angle = 90

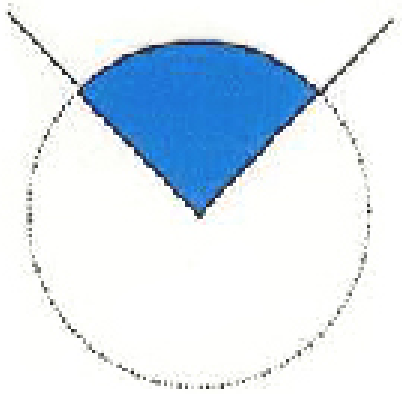
groove angle = 60



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

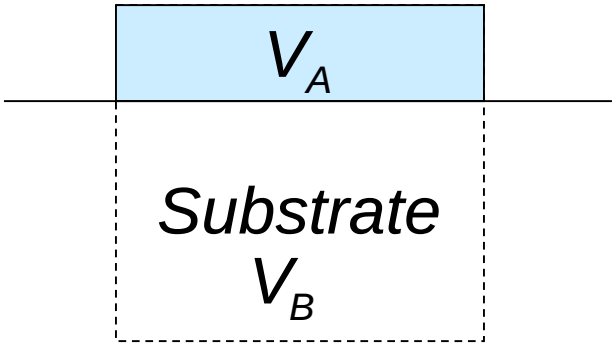


$$\frac{1}{2}\Delta G^*_{\text{homo}}$$

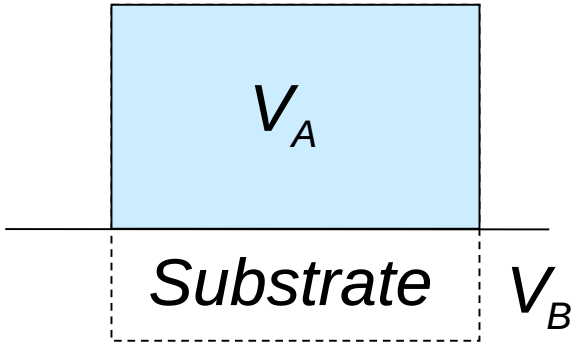


$$\frac{1}{4}\Delta G^*_{\text{homo}}$$

How do we treat the non-spherical shape?



Good Wetting



Bad Wetting

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

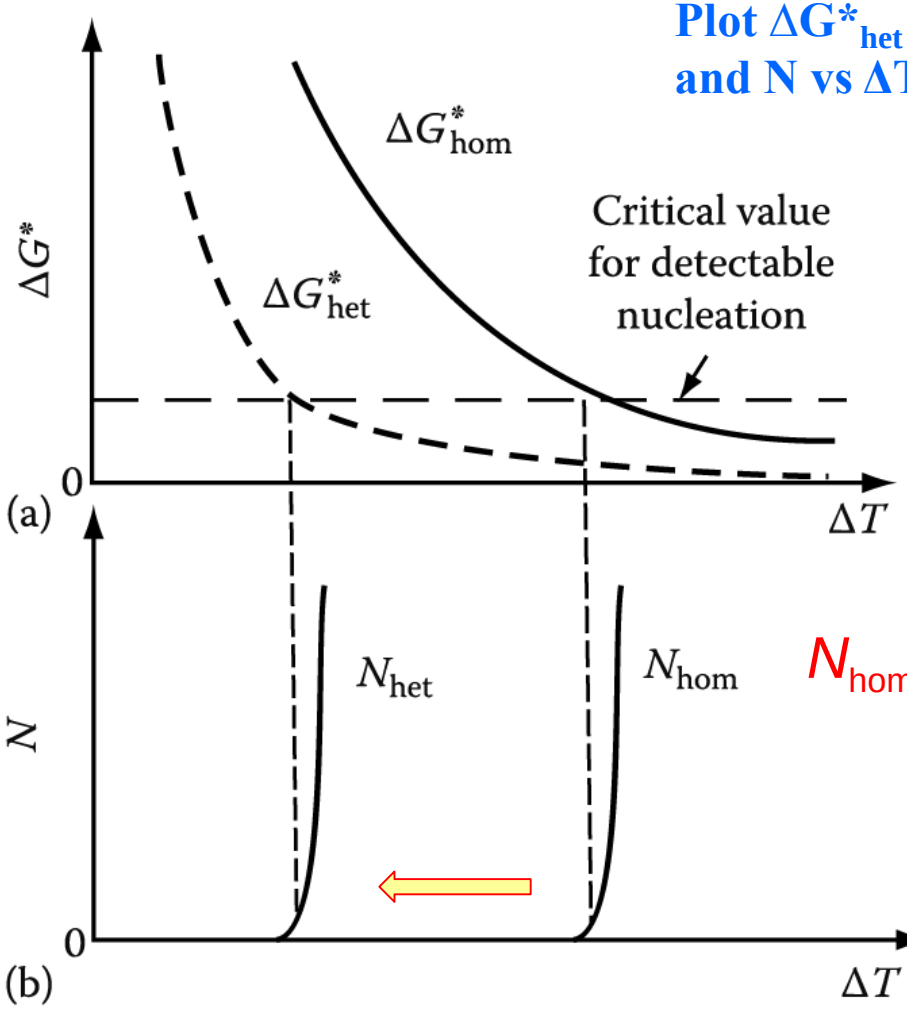
Effect of good and bad wetting on substrate

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} & ΔG^*_{hom} vs ΔT and N vs ΔT.



n_1 atoms in contact with the mold wall

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

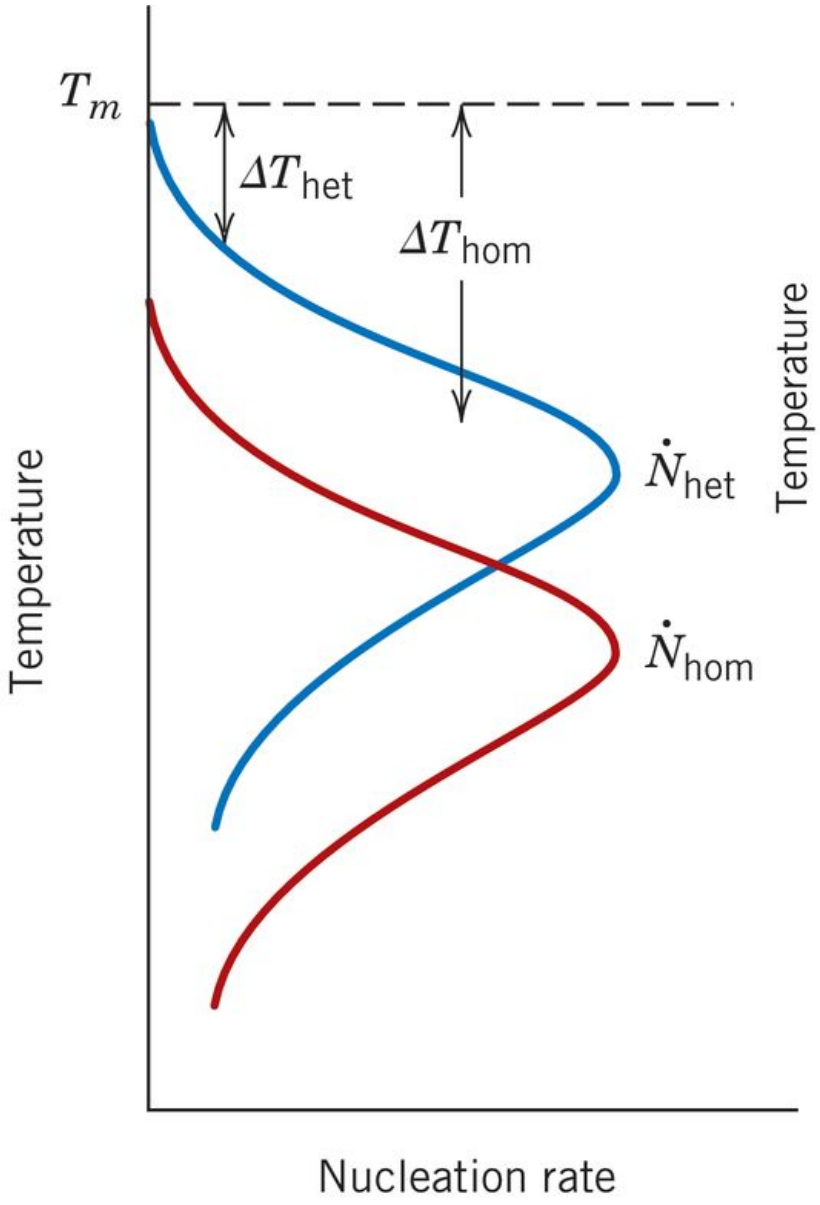
$$N_{het} = f_1 C_1 \exp\left(-\frac{\Delta G^*_{het}}{kT}\right)$$

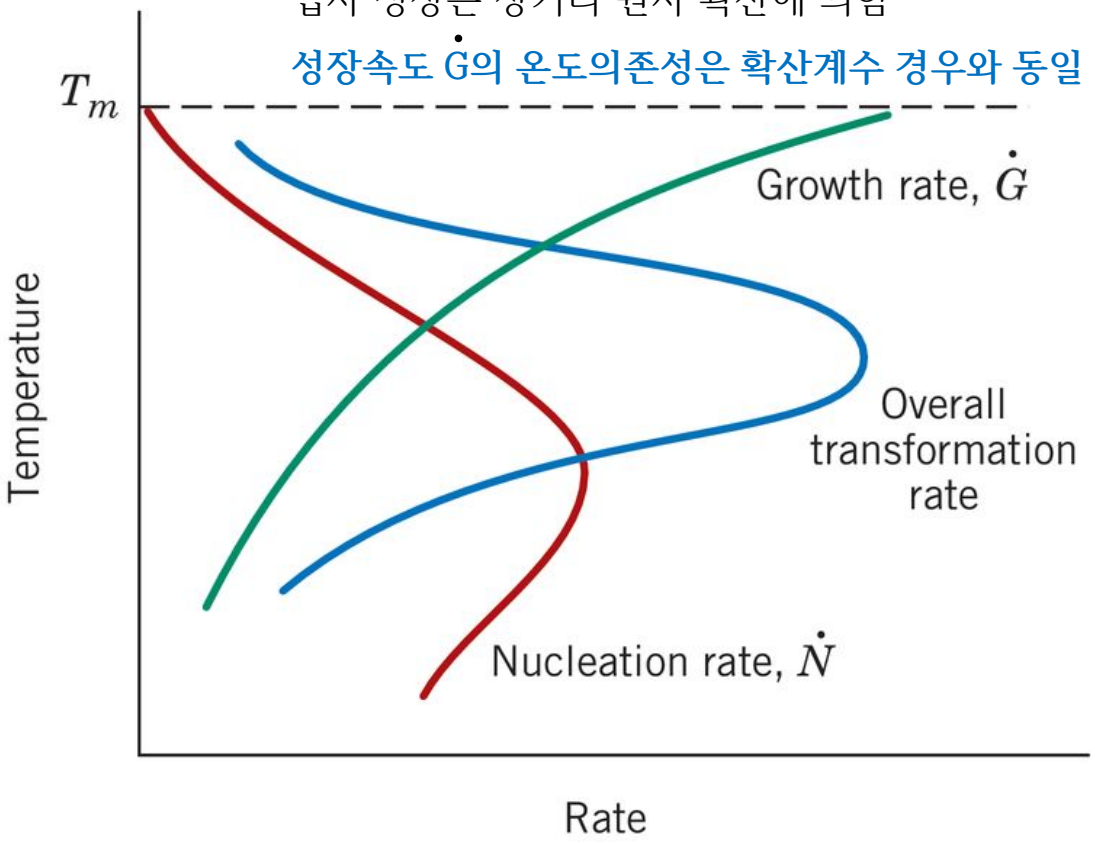
$N_{hom} \approx 1\ \text{cm}^{-3}\text{s}^{-1}$

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*

입자 성장은 장거리 원자 확산에 의함

성장속도 $\dot{G}$의 온도의존성은 확산계수 경우와 동일





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, start at crystal surfaces without appreciable superheating.

Why?

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

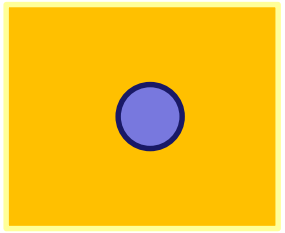
In the case of gold,

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

Liquid | T_m | Undercooled Liquid | Solid

No superheating required!

- Interfacial energy ⇨ No ΔT_N

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

vapor

Melting: Liquid ← Solid

5.4 Overall Transformation Kinetics – TTT Diagram

If isothermal transformation,

The fraction of Transformation as a function of Time and Temperature

$\rightarrow \quad f(t,T)$

Plot f vs log t.

- isothermal transformation
- f ~ volume fraction of β at any time; 0~1

Plot the fraction of transformation (1%, 99%) in T-log t coordinate.

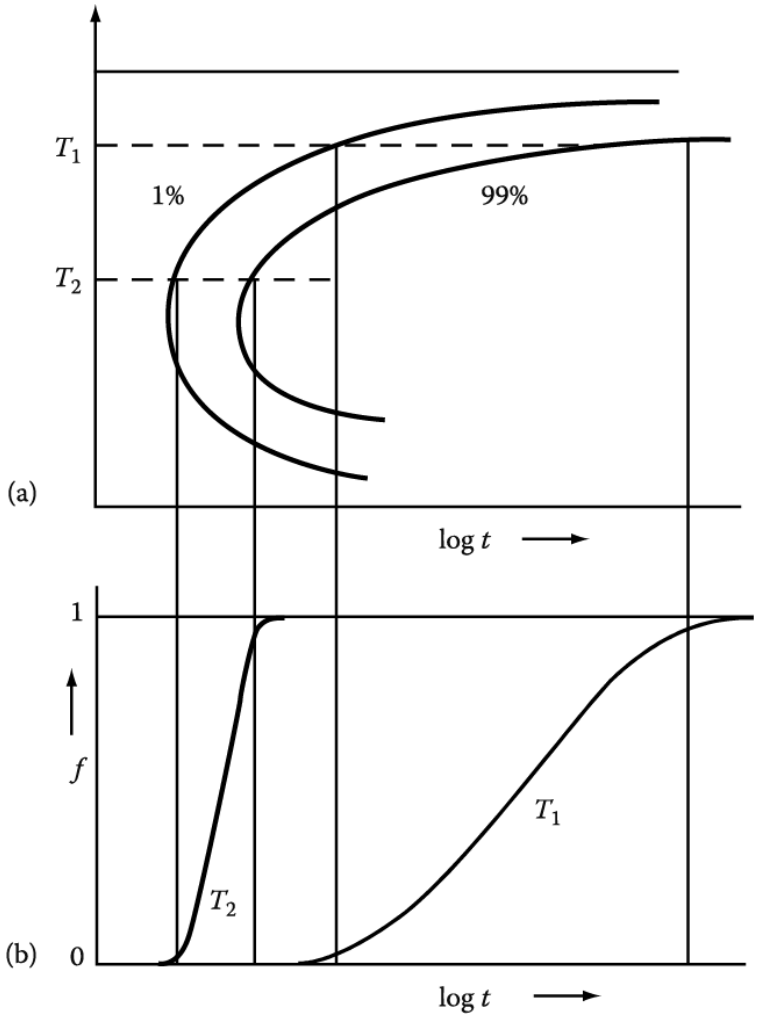


Fig. 5.23 The percentage transformation versus time for different transformation temperatures.

Transformation Kinetics

- Avrami proposed that for a three-dimensional nucleation and growth process kinetic law

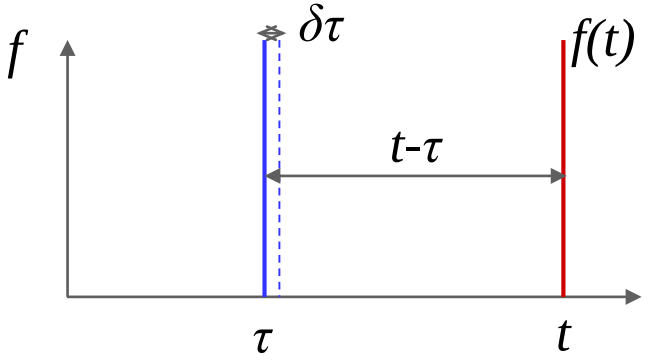
$$f = 1 - \exp\left(-kt^n\right)$$ Johnson-Mehl-Avrami equation

f : volume fraction transformed $= \dfrac{\text{Volume of new phase}}{\text{Volume of specimen}}$

- Assumption :
  - √ reaction produces by nucleation and growth
  - √ nucleation occurs randomly throughout specimen
  - √ reaction product grows rapidly until impingement

Constant Nucleation Rate Conditions

- Nucleation rate (I) is **constant.**
- Growth rate (v) is constant.
- No compositional change



$$df_e = \frac{\left(\begin{array}{l}\text{Vol. of one particle nucleated}\\ \text{during } d\tau \text{ measured at time t}\end{array}\right) \times \left(\begin{array}{l}\text{number of nuclei}\\ \text{formed during } d\tau\end{array}\right)}{\text{Volume of specimen}}$$

$$df_e = \frac{\frac{4}{3}\pi\left[v(t-\tau)\right]^3 \times (IV_0 d\tau)}{V_0}$$

$$f_e(t) = \int_o^t I \cdot \frac{4}{3}\pi\left[v(t-\tau)\right]^3 d\tau$$

$$= I \cdot \frac{4}{3}\pi v^3 \left[-\frac{1}{4}(t-\tau)^4\right]_0^t = \boxed{\frac{1}{3}\pi I v^3 t^4}$$

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi (vt)^3$$

$$V' = \frac{4}{3}\pi v^3 (t-\tau)^3$$

- do not consider impingement & repeated nucleation
- only true for $f \ll 1$

As time passes the β cells will eventually impinge on one another and the rate of transformation will decrease again.

Constant Nucleation Rate Conditions

- **consider impingement + repeated nucleation effects**

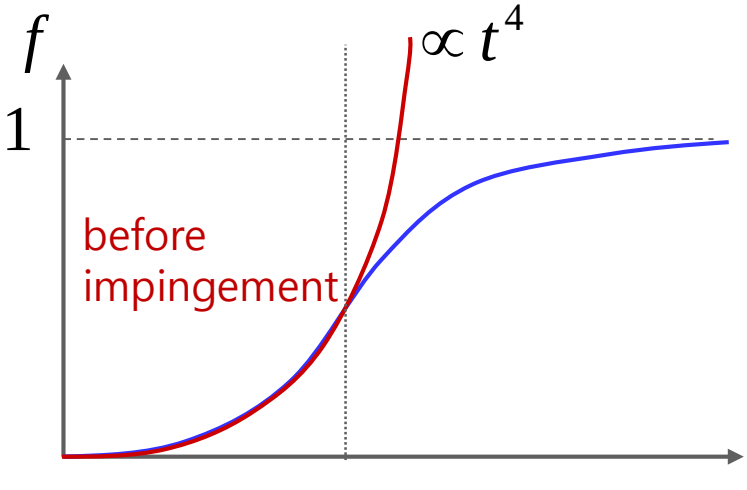
$$df = (1-f)\,df_e \longrightarrow df_e = \frac{df}{1-f}$$

$$f_e = -\ln(1-f)$$

$$f(t) = 1-\exp(-f_e(t)) = 1-\exp\left(-\frac{\pi}{3} I v^3 t^4\right)$$

* Short time:
  1-exp(z)~Z (z ≪1)
* Long time:
  t→∞, f →1

Johnson-Mehl-Avrami Equation



$$f = 1-\exp(-kt^n)$$

k: T sensitive $f(I, v)$ $\quad -\frac{\pi}{3} I v^3$

n: 1 ~ 4 (depend on nucleation mecnanism)

Growth controlled. **Nucleation-controlled.**

If no change of nucleation mechanism during phase transformation, n is not related to T.

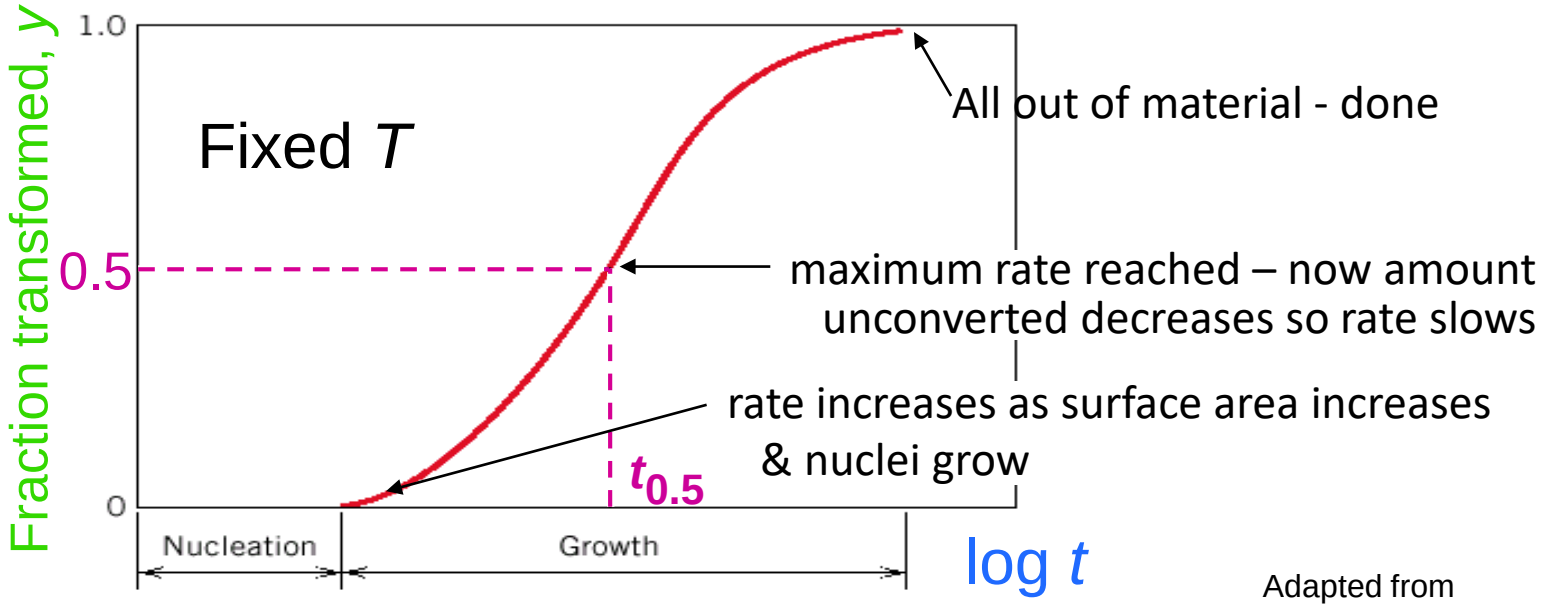
i.e. 50% transform

Exp (-0.7) = 0.5

$$kt_{0.5}^n = 0.7 \quad t_{0.5} = \frac{0.7}{k^{1/n}} \xrightarrow{\frac{\pi}{3} I v^3} t_{0.5} = \frac{0.9}{N^{1/4} v^{3/4}}$$

Rapid transformations are associated with (large values of k), or (rapid nucleation and growth rates)

Rate of Phase Transformation



Adapted from Fig. 10.10, *Callister 7e.*

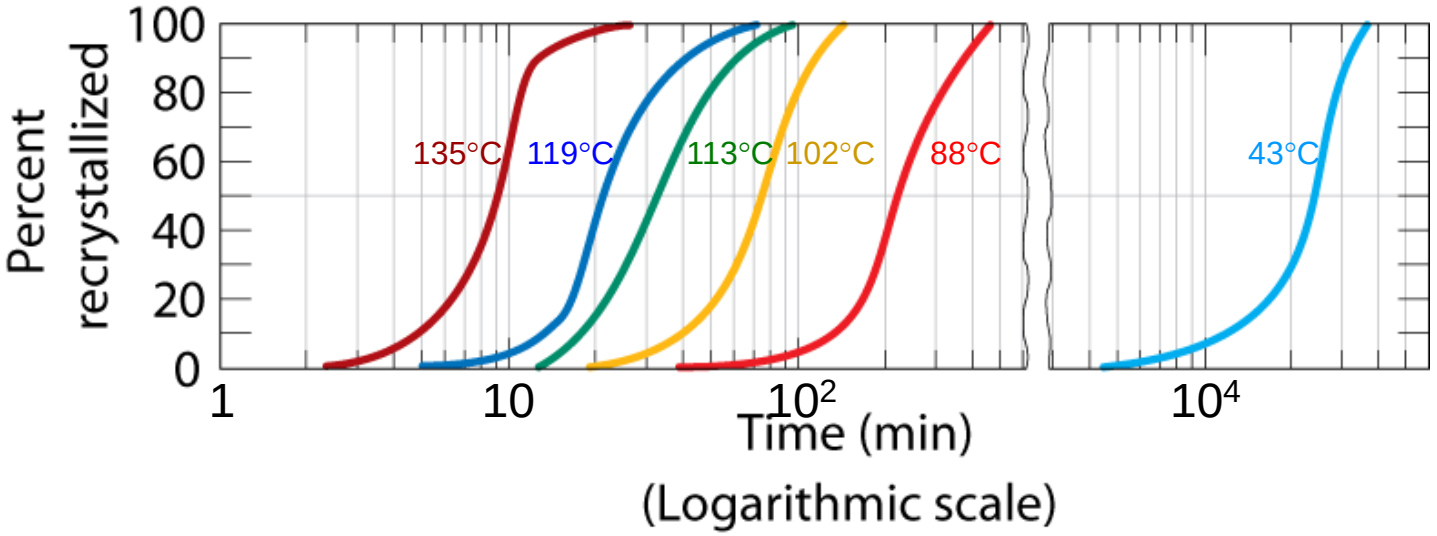
Avrami rate equation → $y = 1 - \exp(-kt^n)$

fraction transformed **time**

– k & n fit for specific sample

By convention $rate = 1 / t_{0.5}$

Rate of Phase Transformations



Adapted from Fig. 10.11, *Callister 7e.* (Fig. 10.11 adapted from B.F. Decker and D. Harker, "Recrystallization in Rolled Copper", *Trans AIME*, **188**, 1950, p. 888.)

- In general, rate increases as $T \uparrow$

$$r = 1/t_{0.5} = A\, e^{-Q/RT}$$

  - R = gas constant
  - T = temperature (K)
  - A = preexponential factor
  - Q = activation energy

Arrhenius expression

- r often small: equilibrium not possible!

Time–Temperature–Transformation Curves (TTT)

- How much time does it take at any one temperature for a given fraction of the liquid to transform (nucleate and grow) into a crystal?

- $f(t,T) \sim \pi I(T) \mu(T)^3 t^4/3$

  where *f* is the fractional volume of crystals formed, typically taken to be 10^{-6}, a barely observable crystal volume.

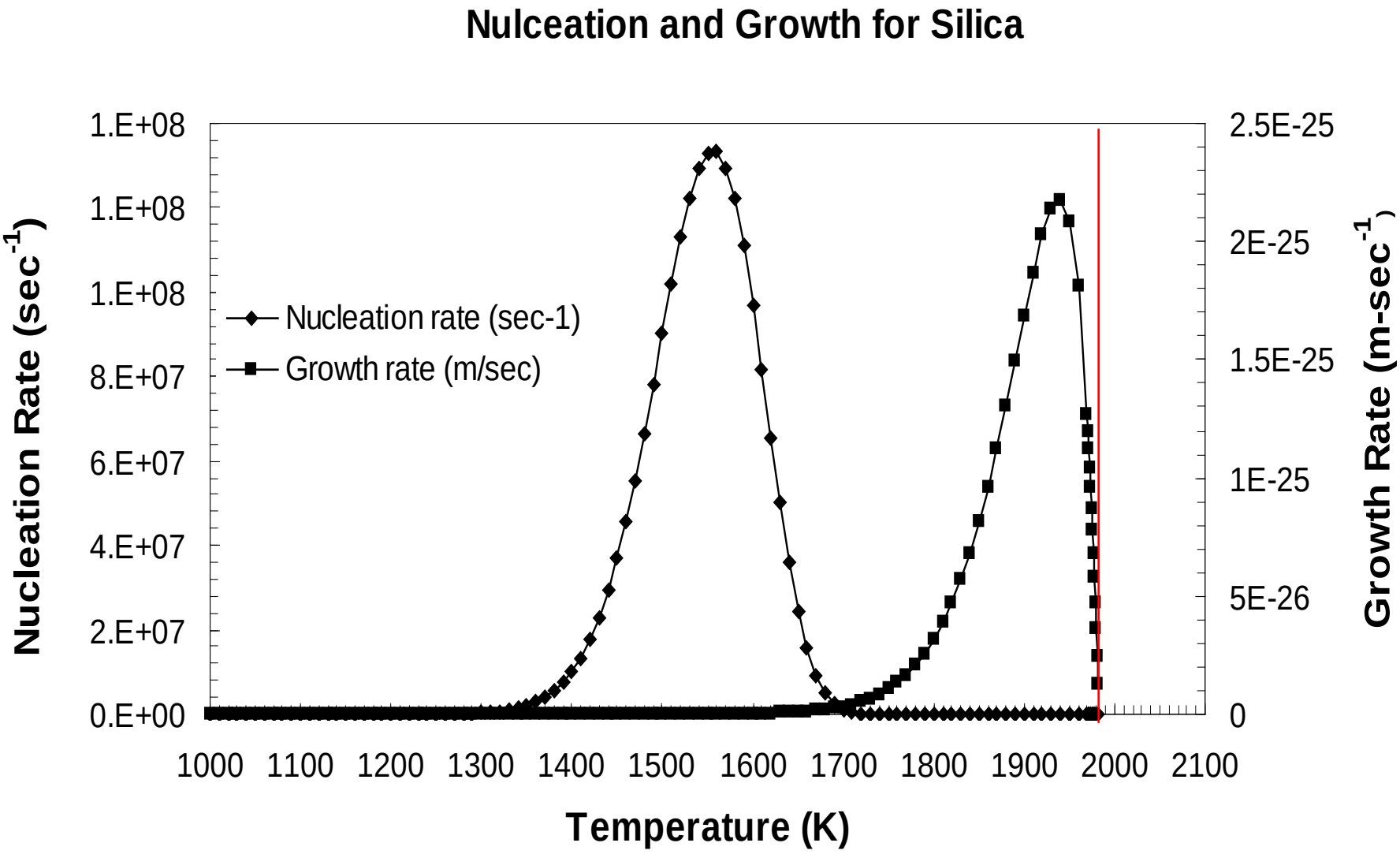
Nucleation rates

$$I = n\nu \exp\left\{\left(\frac{16\pi\Delta H_{cryst}}{81RT}\right)\left(\frac{T_m}{\Delta T}\right)^2\right\}\exp\left\{\frac{-\Delta E_D}{RT}\right\}$$

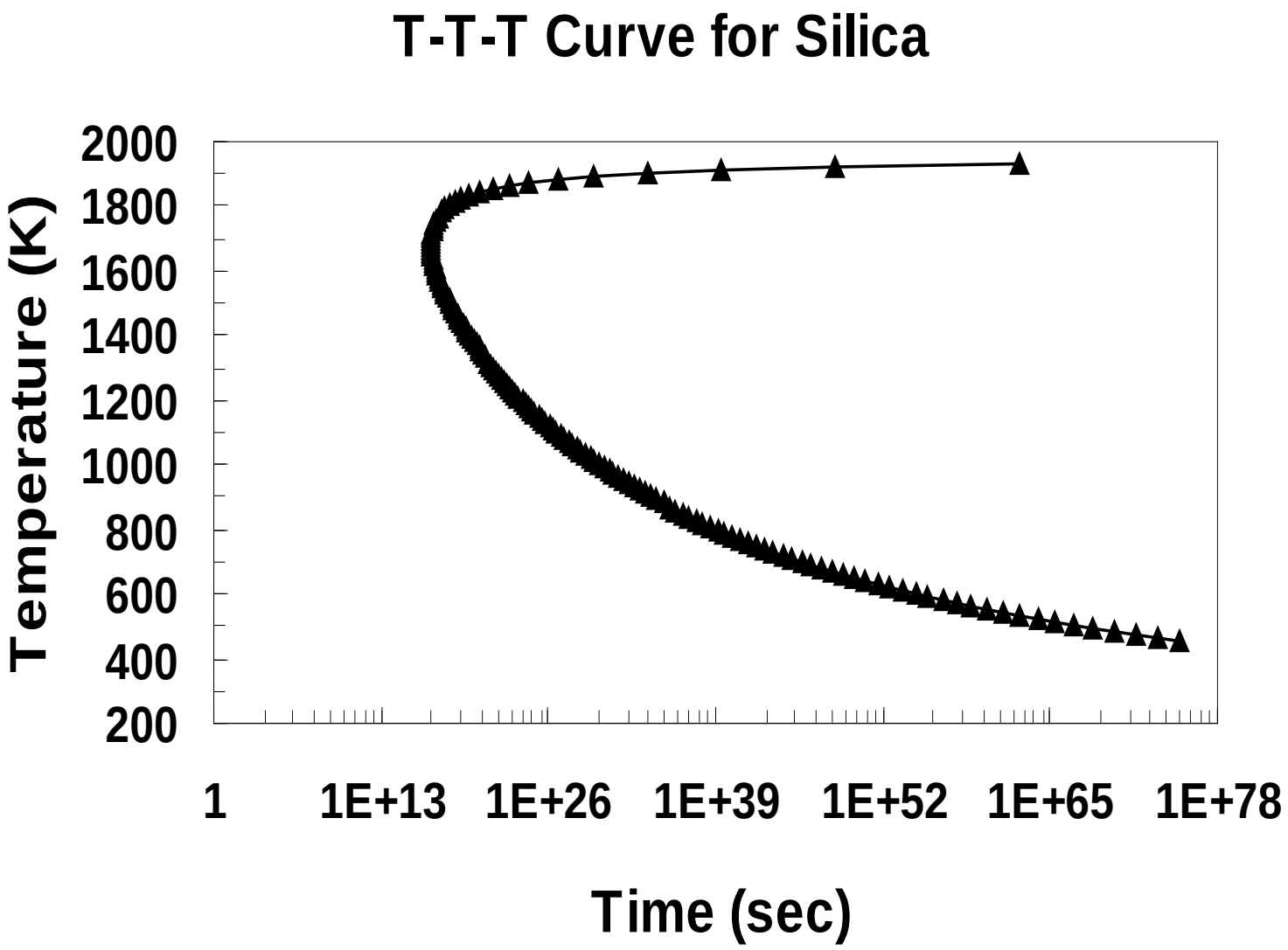
Growth rates

$$\mu(T) = \left(\frac{fRT}{3N\pi a^2\eta(T)}\right)\left(1-\exp\left[\left(\frac{\Delta H_m}{RT}\right)\left(\frac{\Delta T}{T_m}\right)\right]\right)$$

Nucleation and Growth Rates



Time Transformation Curves for Silica



* Time-Temperature-Transformation diagrams

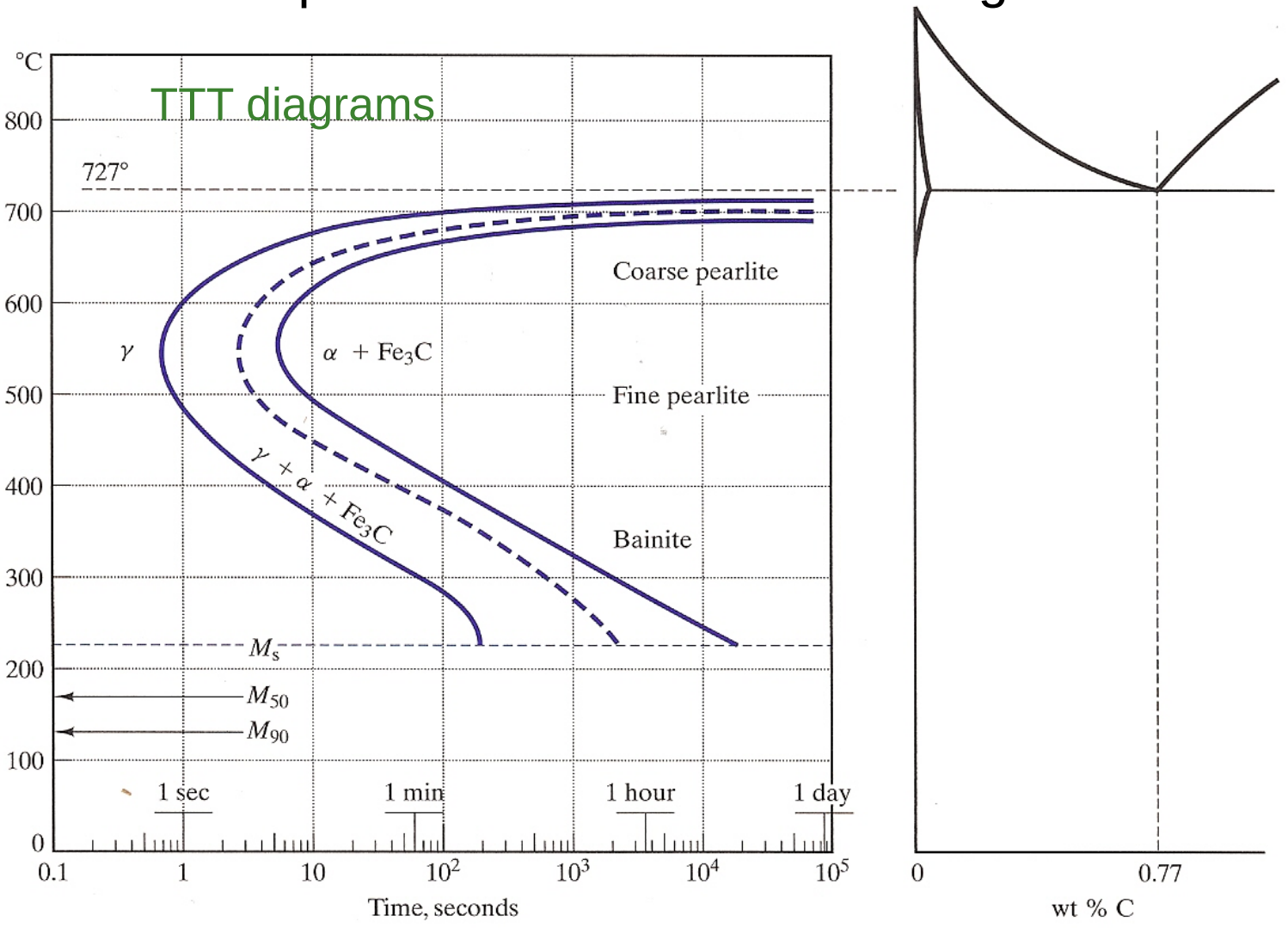


FIGURE 10.11 *A more complete TTT diagram for eutectoid steel than was given in Figure 10.7. The various stages of the time-independent (or diffusionless) martensitic transformation are shown as horizontal lines. M_s represents the start, M_{50} represents 50% transformation, and M_{90} represents 90% transformation. One hundred percent transformation to martensite is not complete until a final temperature (M_f) of −46°C.*

43

* Continuous Cooling Transformation diagrams

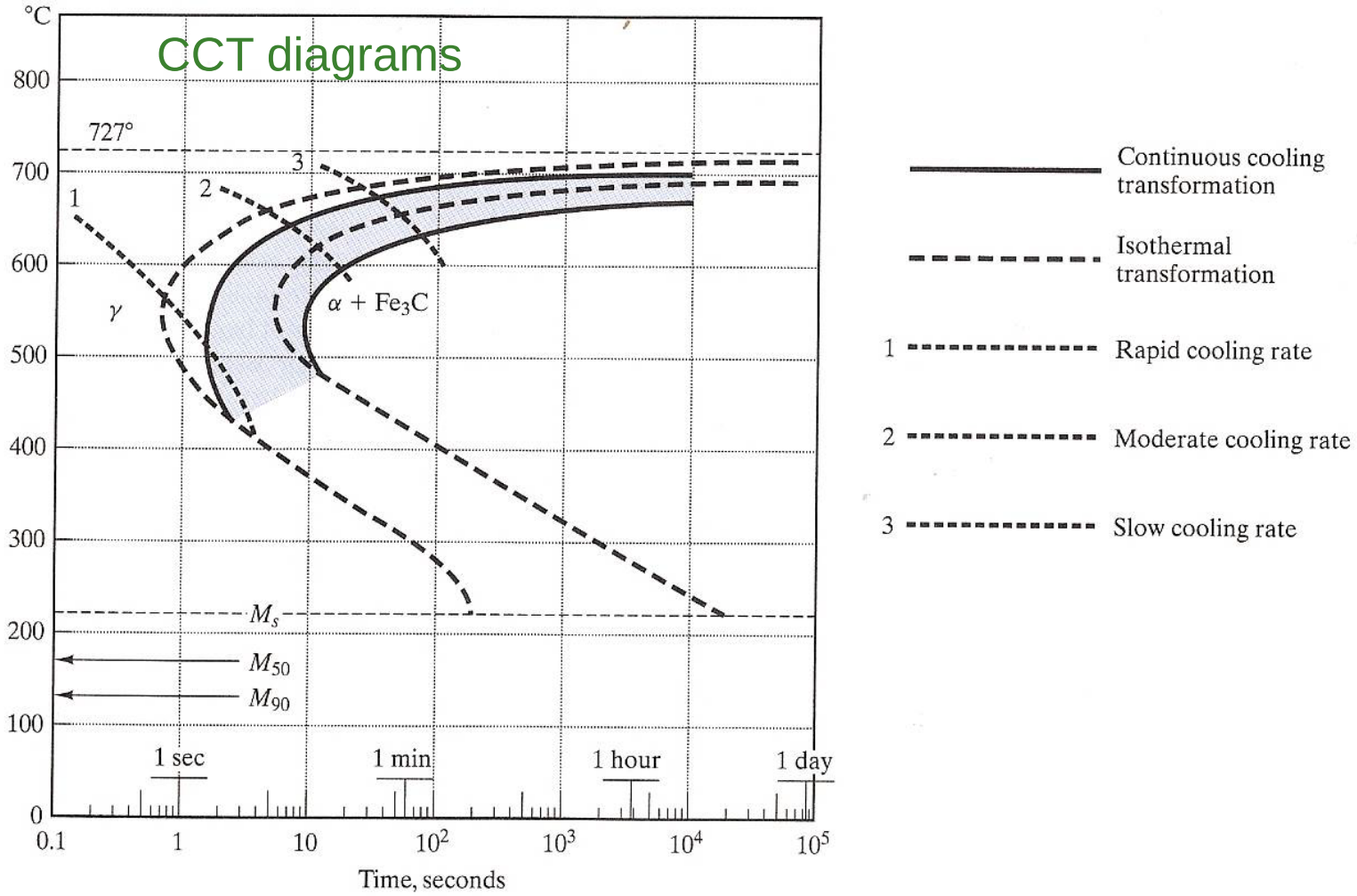


FIGURE 10.14 *A continuous cooling transformation (CCT) diagram is shown superimposed on the isothermal transformation diagram of Figure 10.11. The general effect of continuous cooling is to shift the transformation curves downward and toward the right. (After* Atlas of Isothermal Transformation and Cooling Transformation Diagrams, *American Society for Metals, Metals Park, OH, 1977.)*

44