2020 Spring

Advanced Solidification

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6) 1.5 Ternary and Multicomponent Alloys

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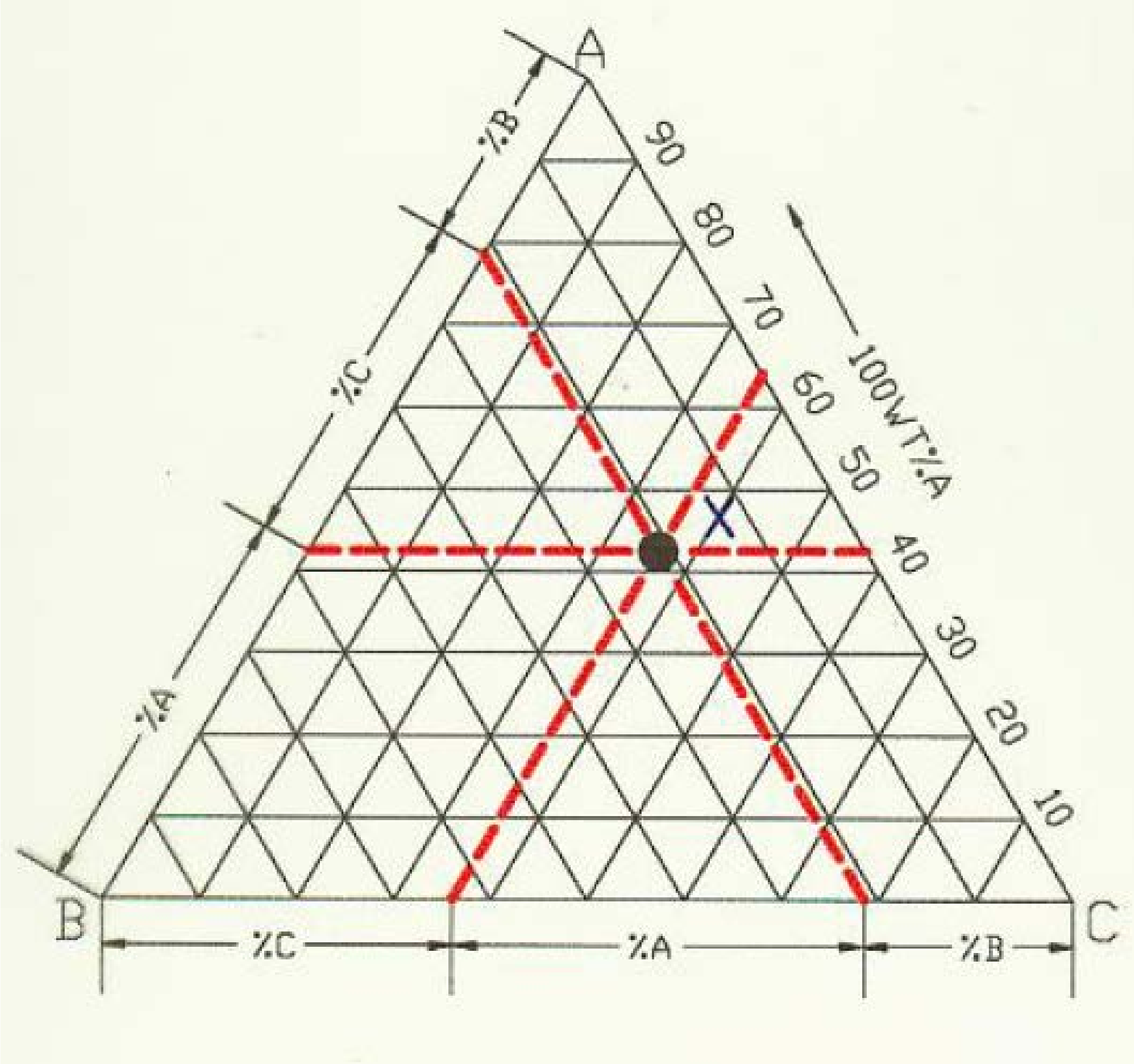
What are ternary phase diagram?

Diagrams that represent the equilibrium between the various phases that are formed between three components, as a function of temperature.

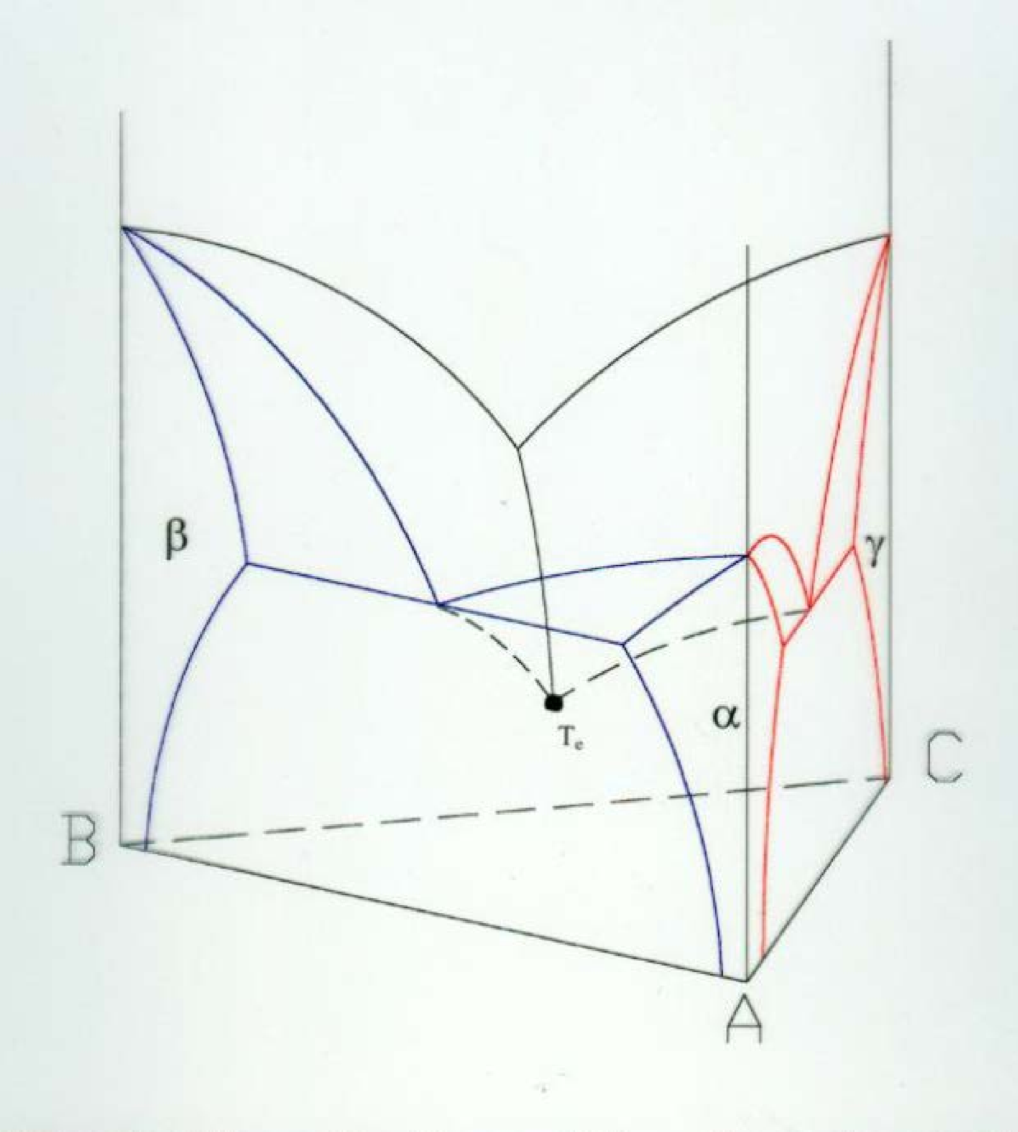
Normally, pressure is not a viable variable in ternary phase diagram construction, and is therefore held constant at 1 atm.

www.sjsu.edu/faculty/selvaduray/page/phase/ternary_p_d.pdf

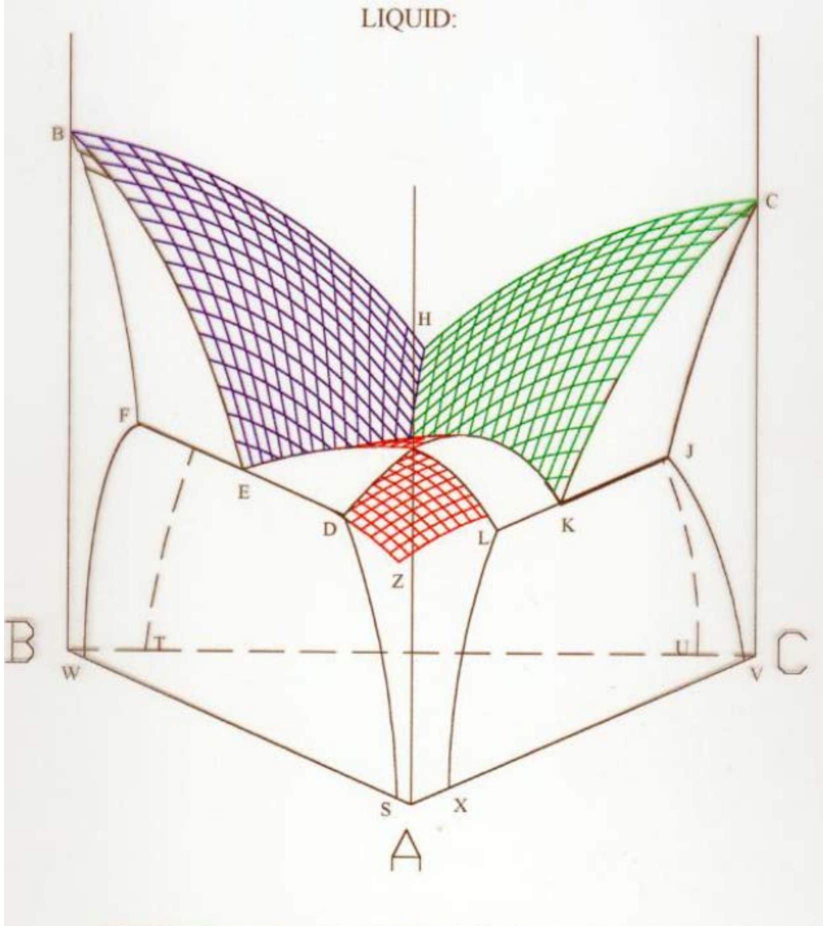
Overall Composition



Ternary Eutectic System
(with Solid Solubility)



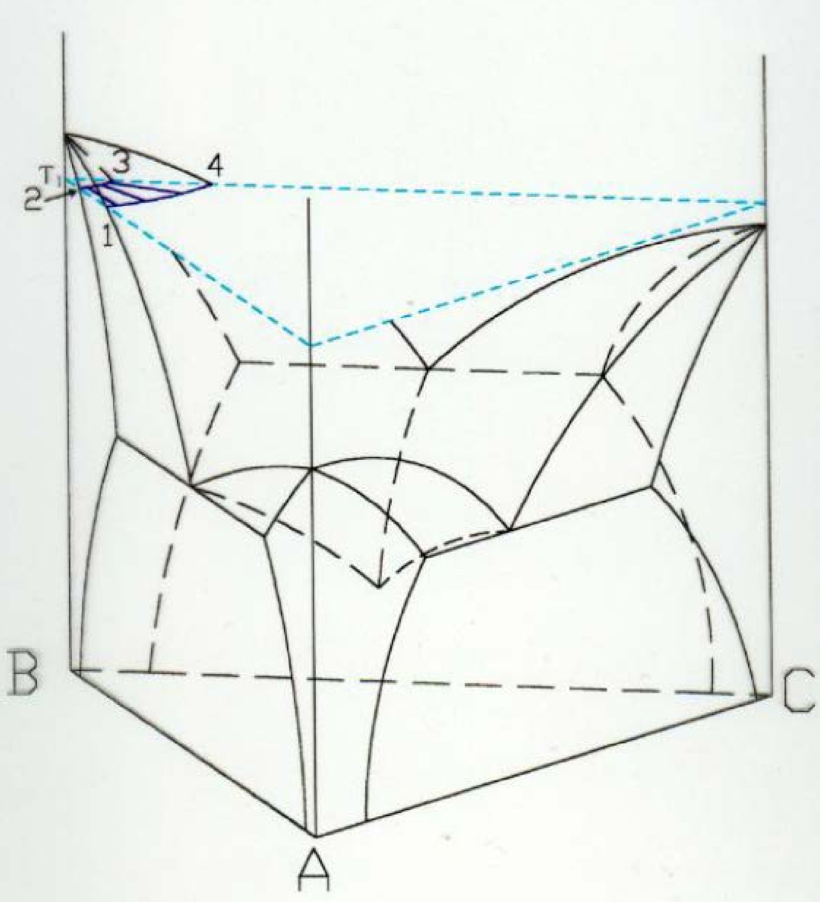
Main outline of Ternary Phase Diagram with Ternary Eutectic (T_e) and Solid Single Phase Regions Shown



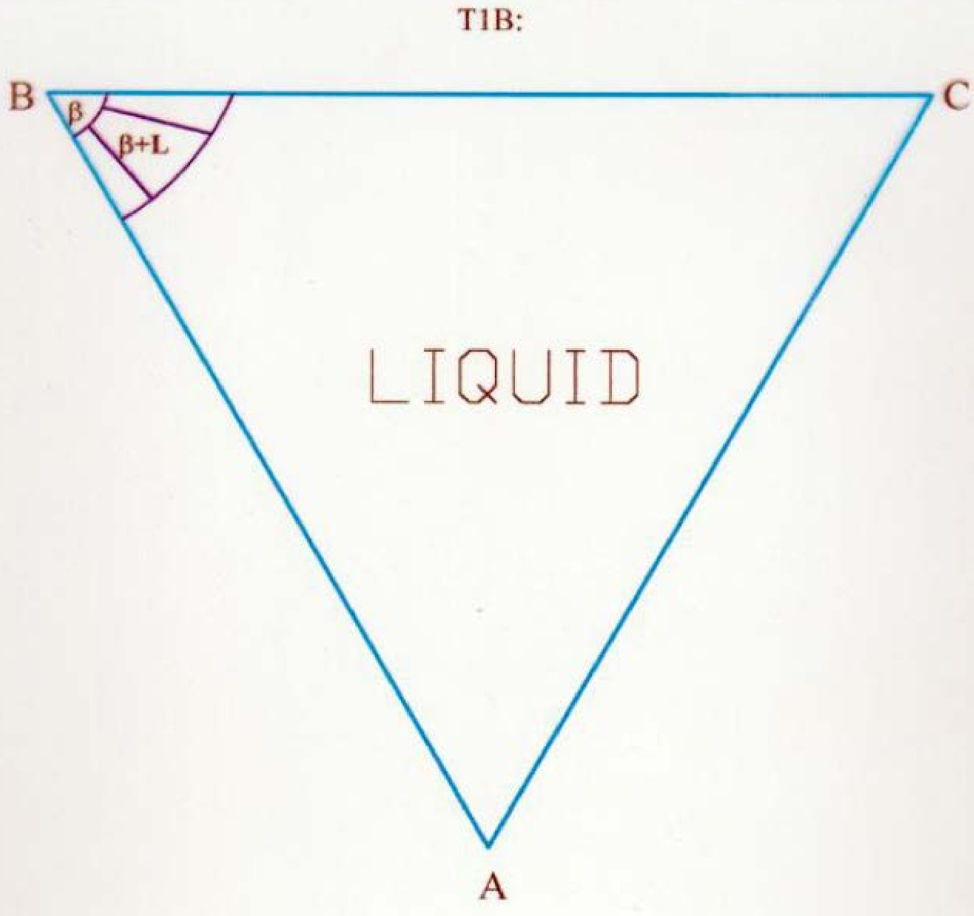
All Liquidus surfaces (α+L-Red, β+L-Purple, γ+L-Green)

Ternary Eutectic System

(with Solid Solubility)



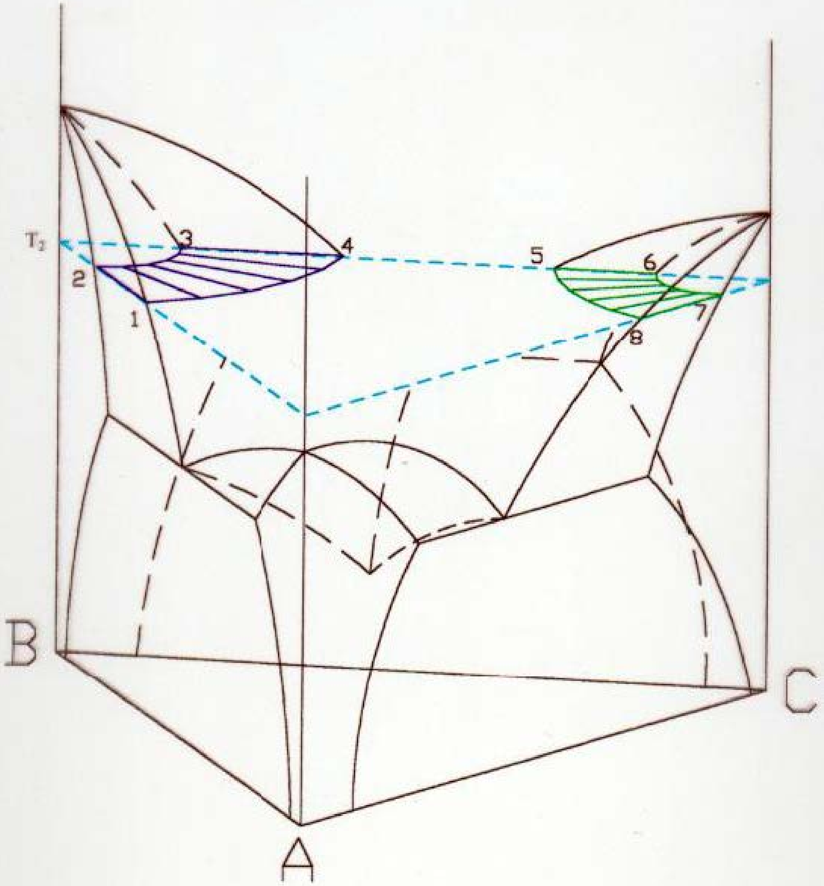
Temperature Slice At $T_1 < T_B$, But $>T_A$, T_C



Isothermal Section At $T=T_1$

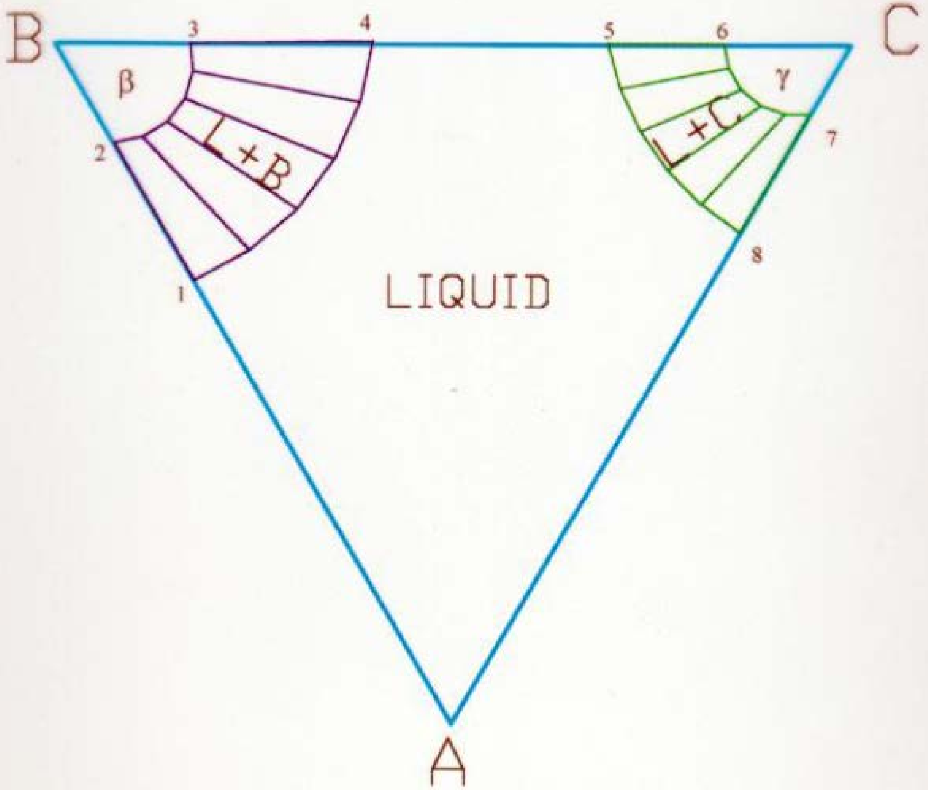
Ternary Eutectic System
(with Solid Solubility)

T2A



Temperature Slice At $T_2 > T_A$ But, $T_2 < T_B$, T_C

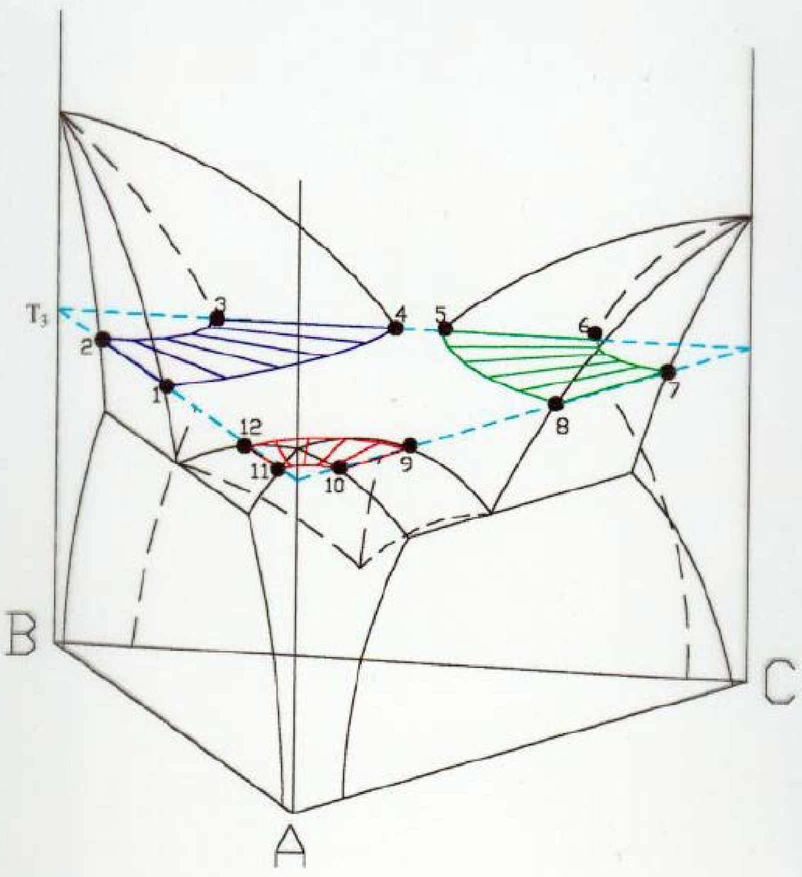
T2B



Isothermal Section At $T=T_2$

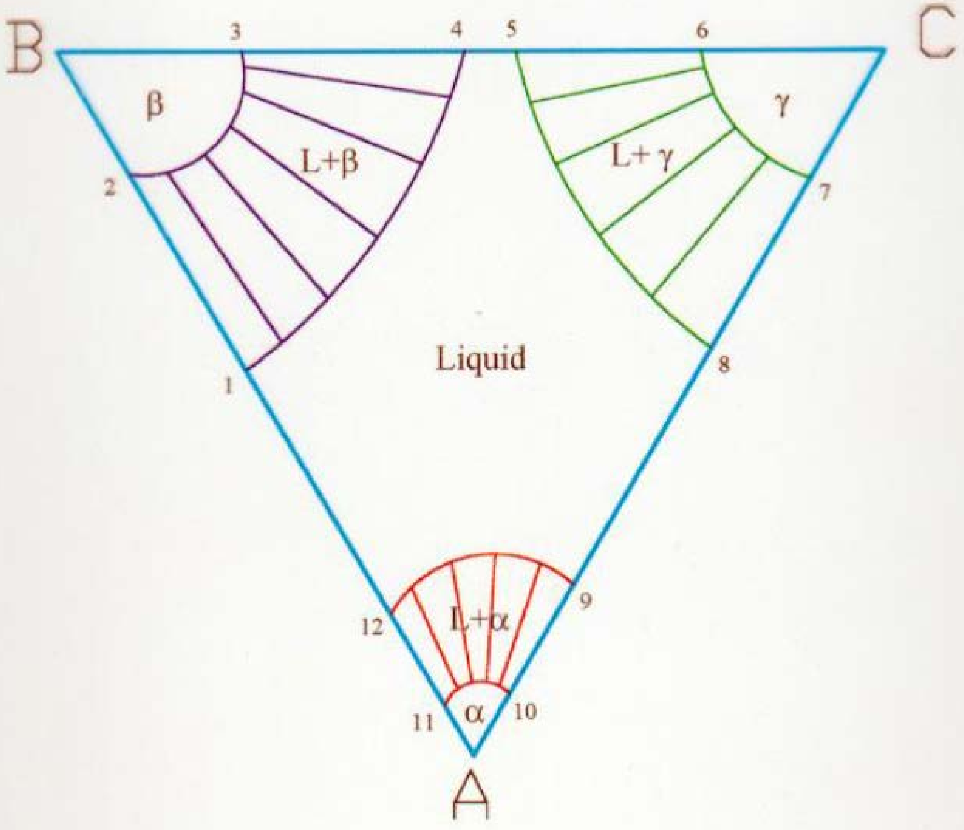
Ternary Eutectic System
(with Solid Solubility)

T3A:



Temperature Slice At $T_3 < T_A, T_B, T_C$, But $T3 > T_{E1}, T_{E2}, T_{E3}$

T3B

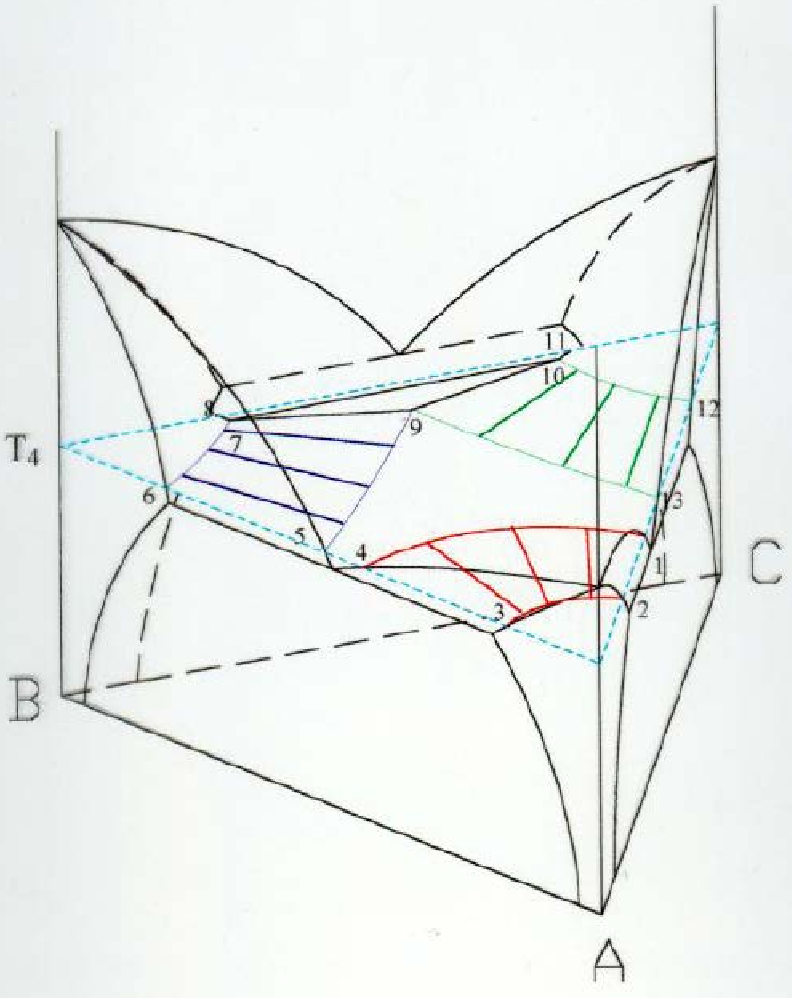


Isothermal Section At $T = T_3$

Ternary Eutectic System

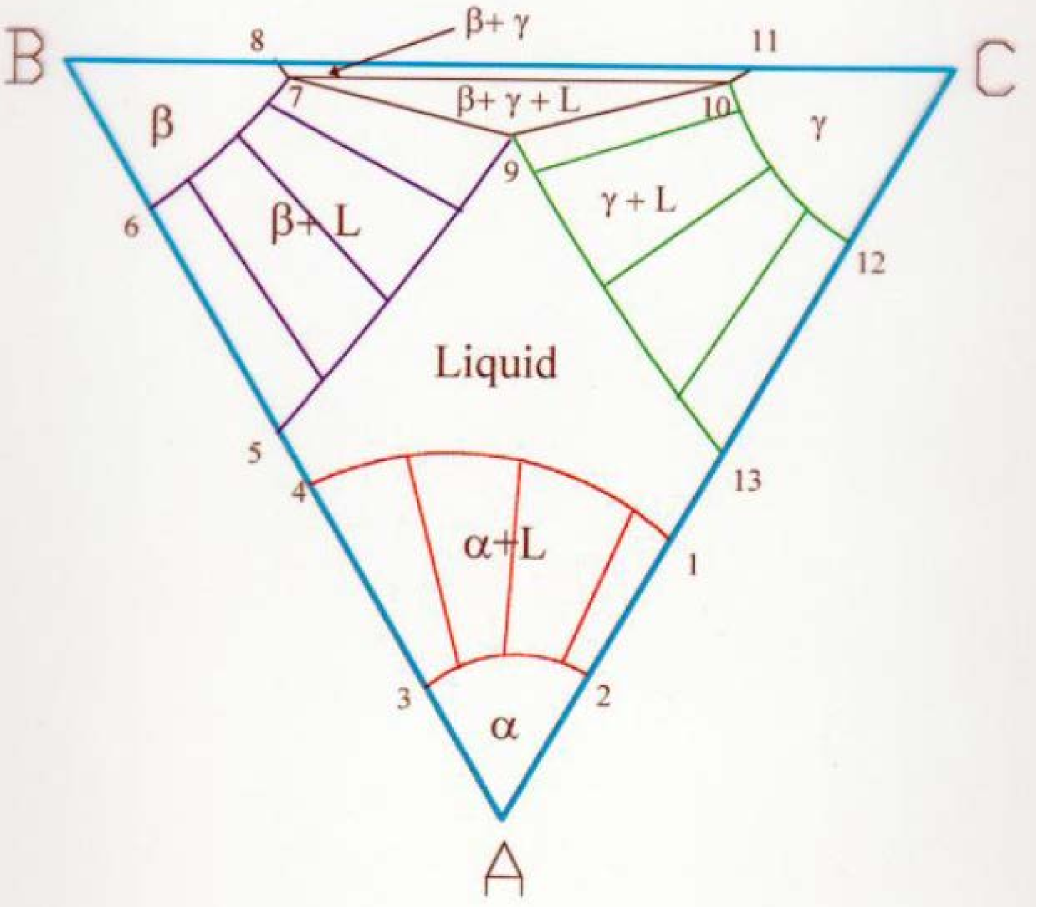
(with Solid Solubility)

T4A:



Temperature Slice At $T_4<T_{E2}$ And $T_4>T_{E1},T_{E3}$

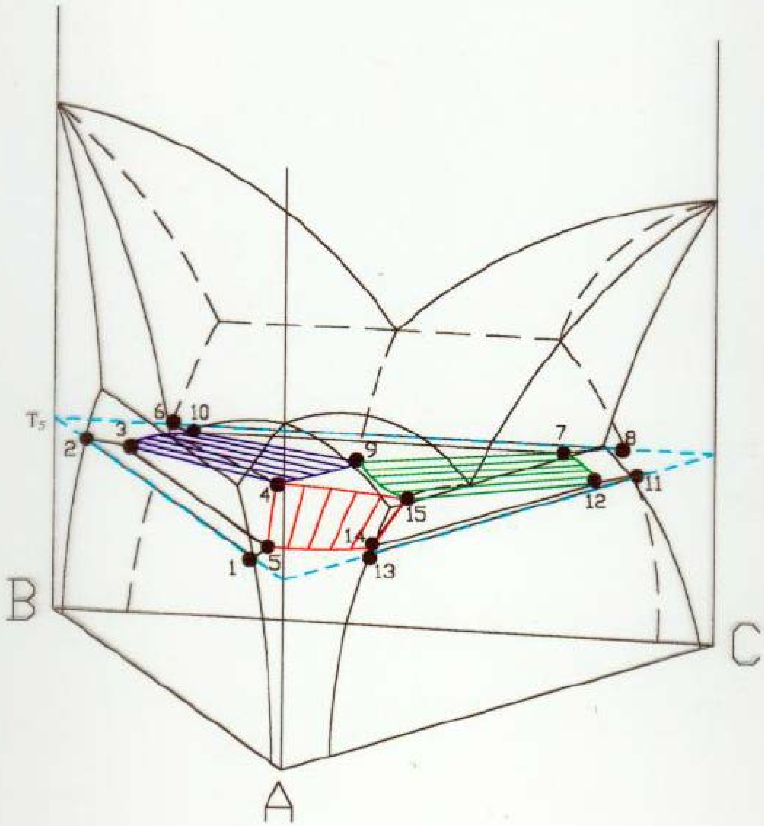
T4B:



Isothermal Section At $T=T_4$

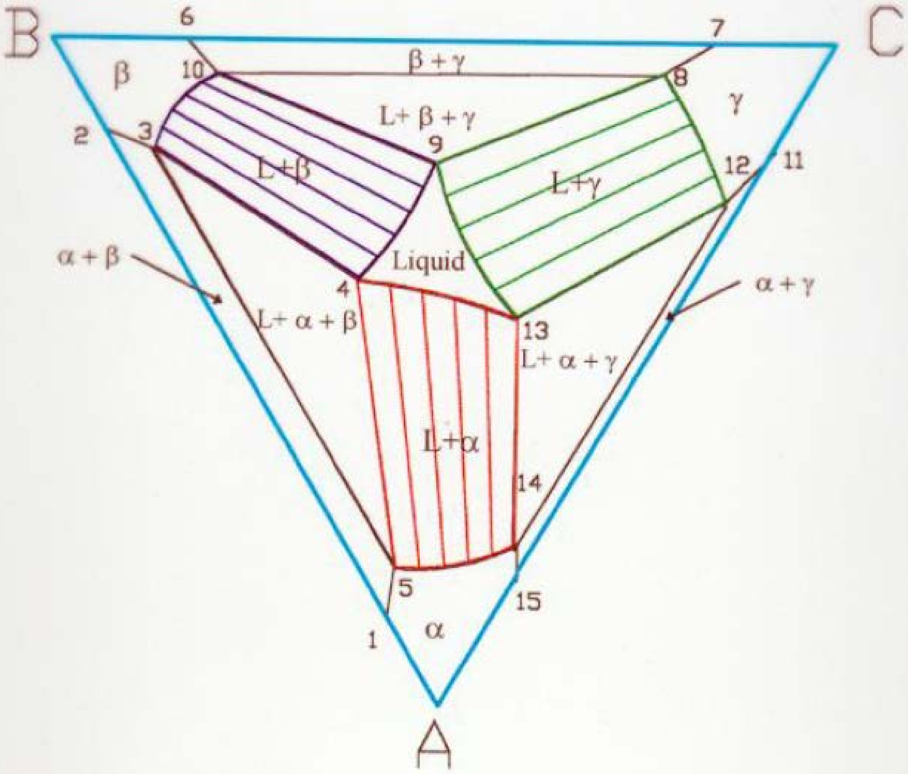
Ternary Eutectic System
(with Solid Solubility)

T5A:



Temperature Slice Below All Binary Eutectics But, Above The Ternary Eutectic

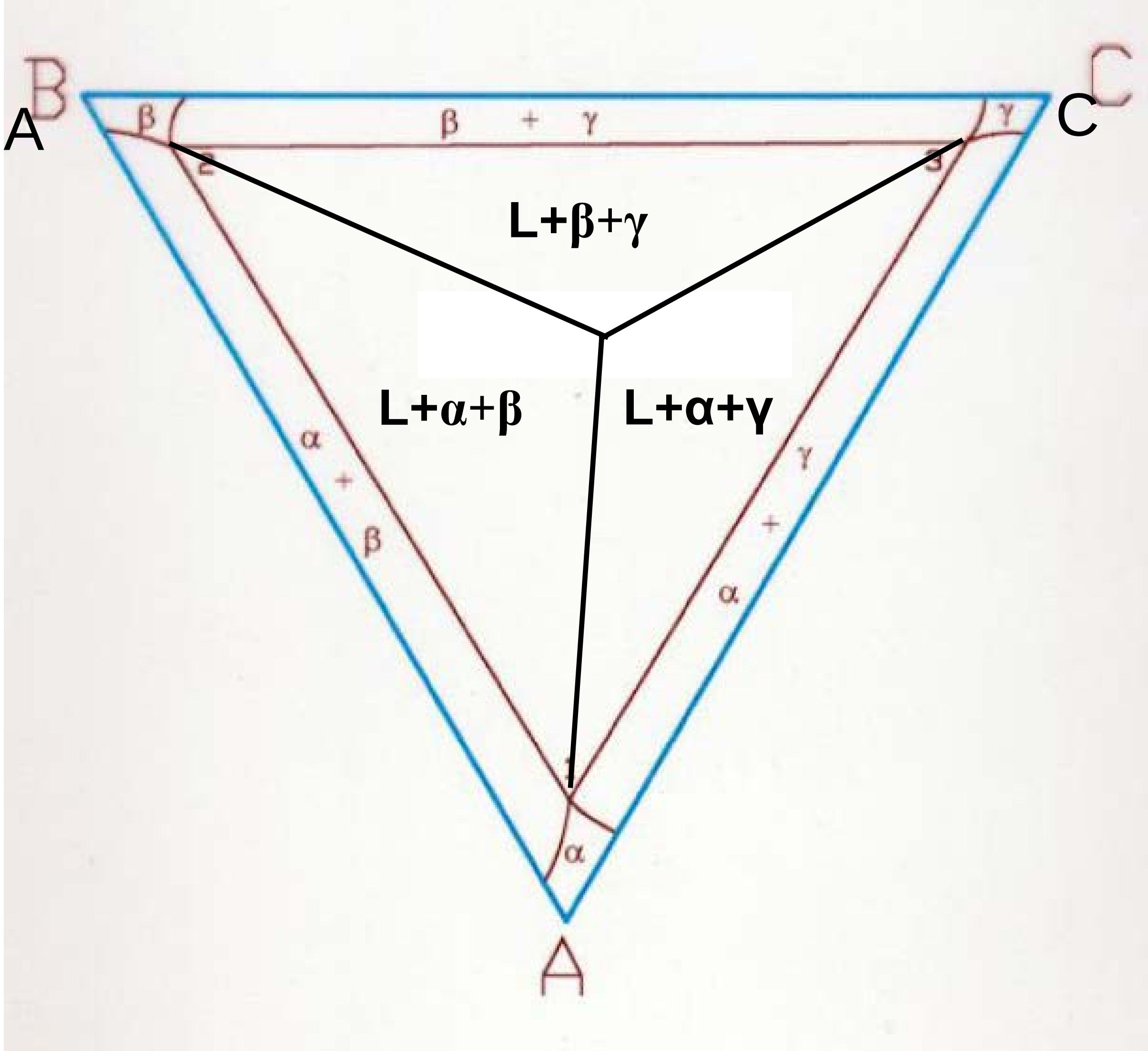
T5B:



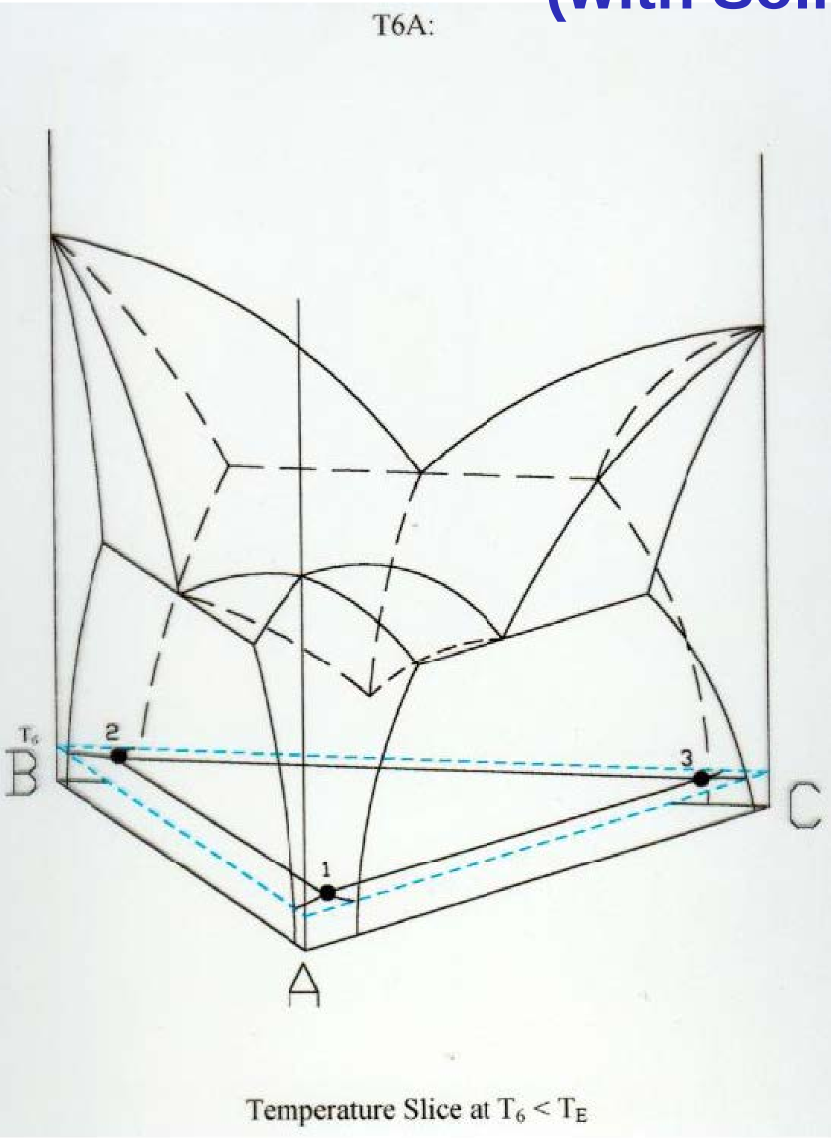
Isothermal Section At T=T_5

Ternary Eutectic System
(with Solid Solubility)

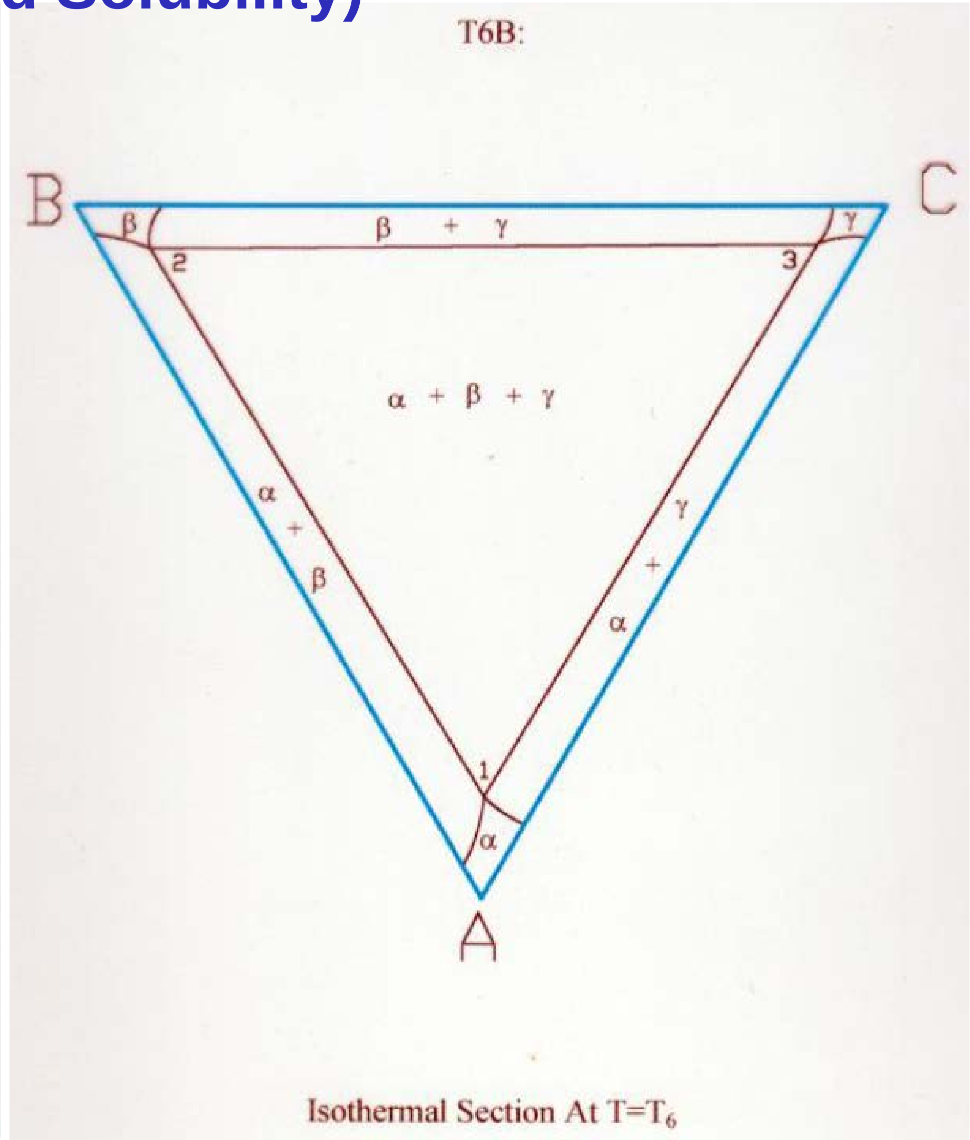
T= ternary eutectic temp.



Ternary Eutectic System
(with Solid Solubility)



Temperature Slice at $T_6 < T_E$



Isothermal Section At $T=T_6$

정해솔 학생 제공 자료 참조: 실제 isothermal section의 온도에 따른 변화
http://www.youtube.com/watch?v=yzhVomAdetM

< Quaternary phase Diagrams >

Four components: A, B, C, D

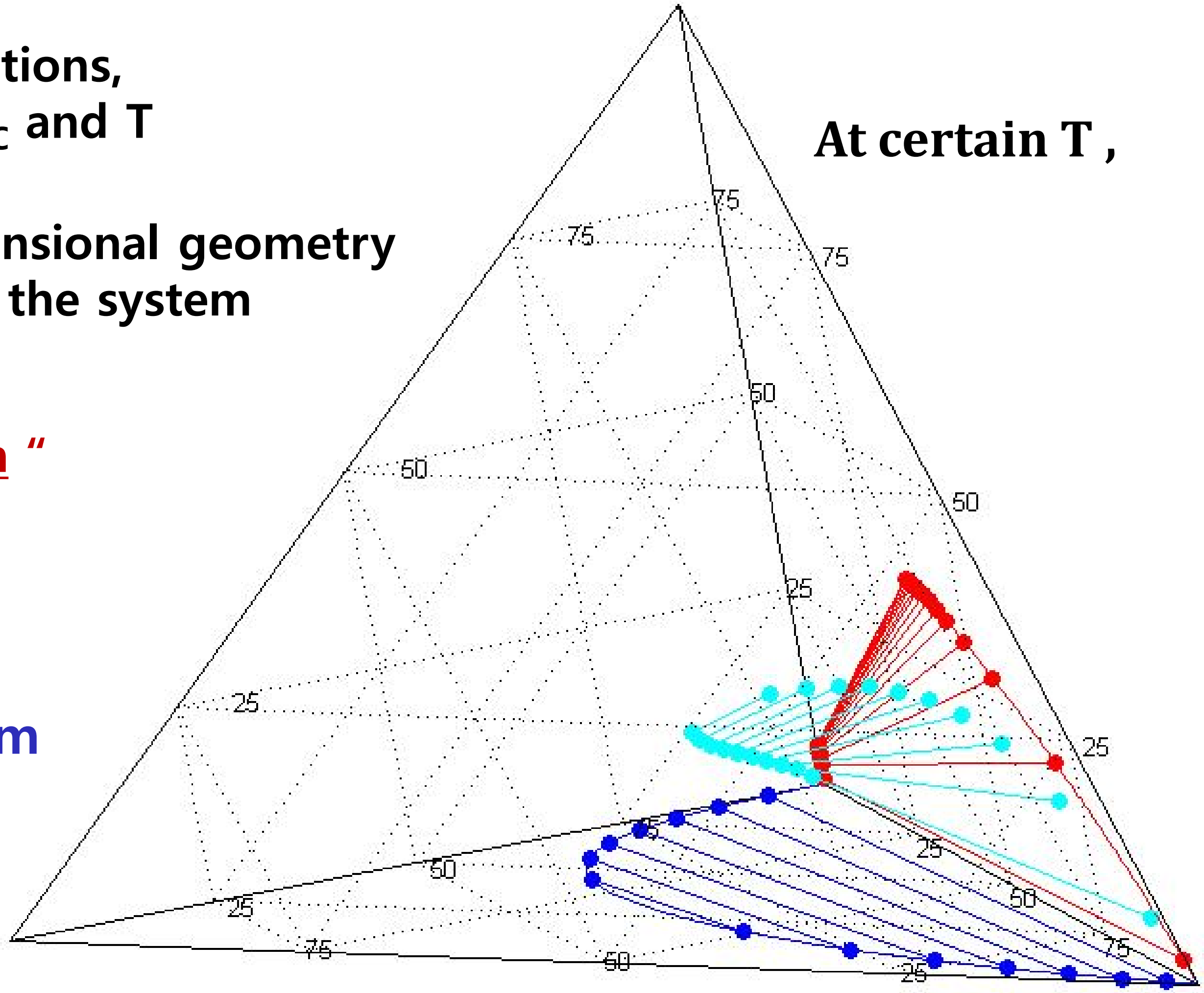
Assuming isobaric conditions,
Four variables: X_A, X_B, X_C and T

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

Isothermal tetrahedron



At certain T ,

*** Draw four small equilateral tetrahedron**

→ **formed with edge lengths of a, b, c, d**

a+b+c+d=100

%A=Pt=c,
%B=Pr=a,
%C=Pu=d,
%D=Ps=b

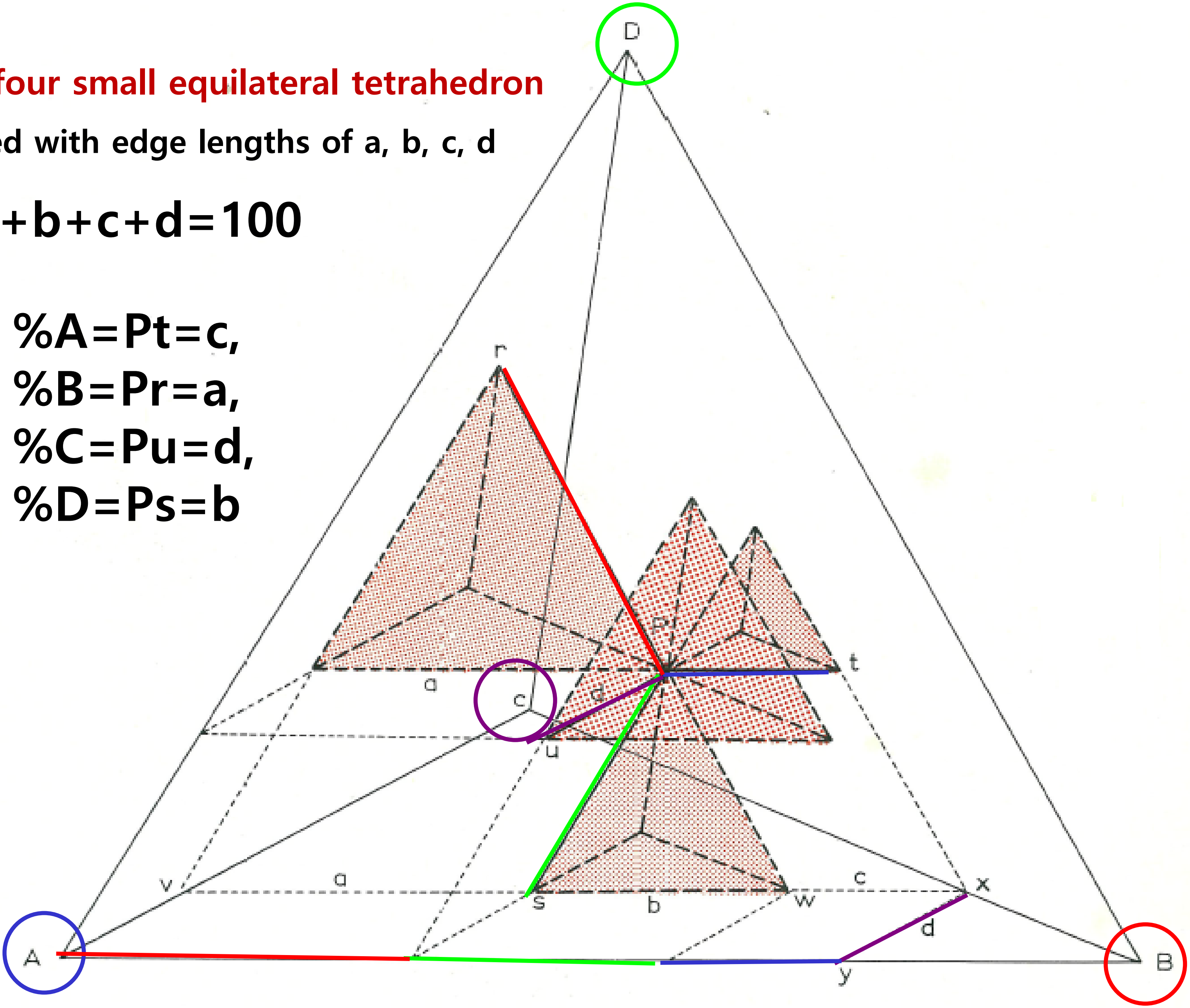


Fig. 247. Representation of a quaternary system by an equilateral tetrahedron.

Define the equilibrium relationships btw solid and liquid :

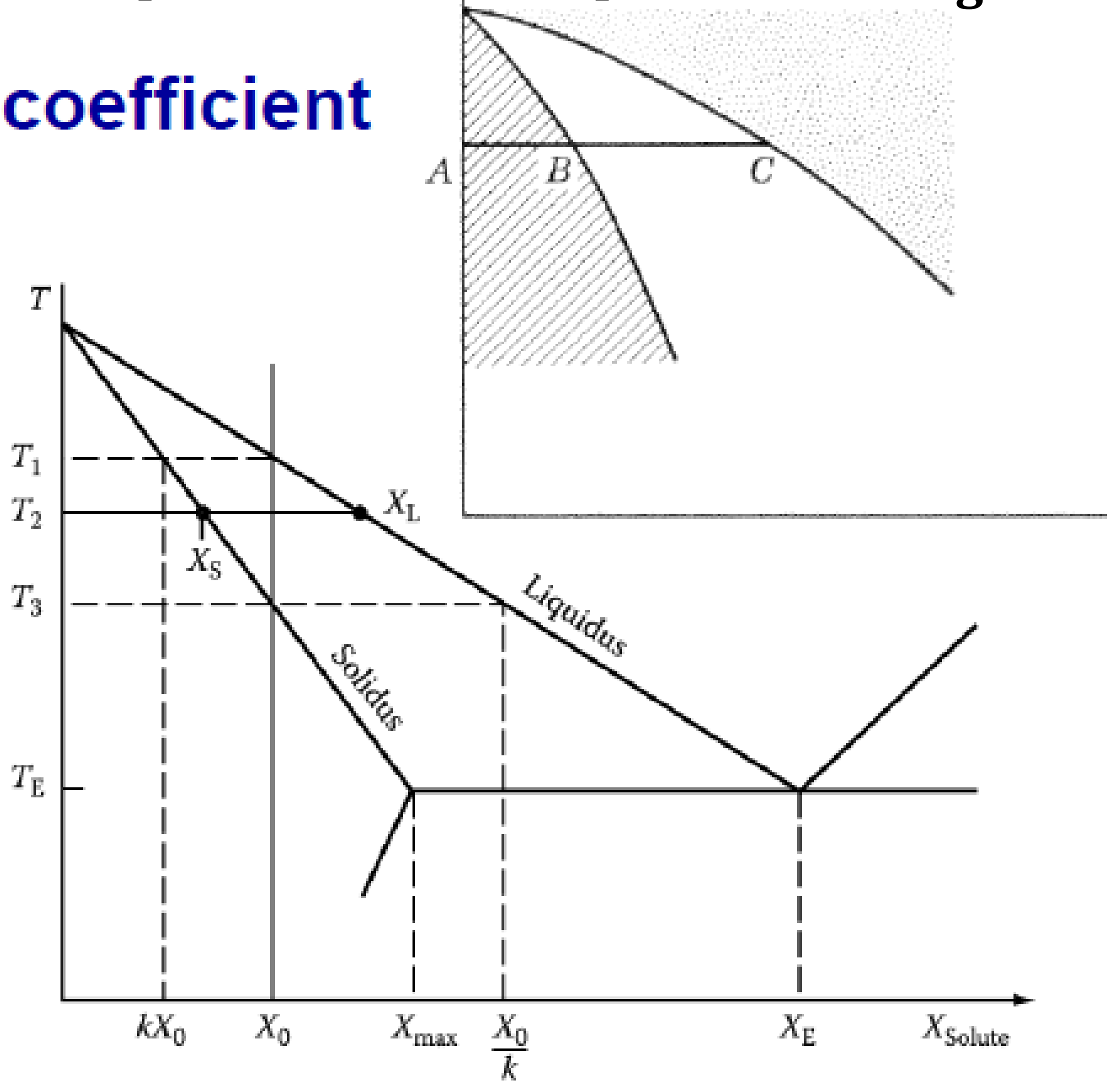
1.7 The Distribution coefficient

$$k_0 = \frac{X_S}{X_L} = AB/AC < 1$$

k_0 : Eq. distribution coefficient

X : mole fraction of solute

In this phase diagram of straight solidus and liquidus, k_0 is independent of T.



A hypothetical phase diagram

$k_0 = X_S/X_L$ is constant.

1.7 The Distribution coefficient

Van't Hoff equation: $\frac{dC_L}{dT_L} - \frac{dC_S}{dT_S} = \frac{L}{RT_E{}^2}$

Van't Hoff equation relates the change in the equilibrium constant, K_{eq}, of a chemical reaction to the change in temperature , T, given the standard enthalpy change ΔH, for the process. The equation has been widely utilized to explore the changes in state functions in the thermodynamic system.

1.7 The Distribution coefficient

Van't Hoff equation: $$\frac{dC_L}{dT_L} - \frac{dC_S}{dT_S} = \frac{L}{RT_E^2}$$

- A useful method of checking the accuracy of the slope dC_s/dT_s of the solidus line from that of the liquidus (which is more reliable)
- This equation applies strictly only at very low concentrations.

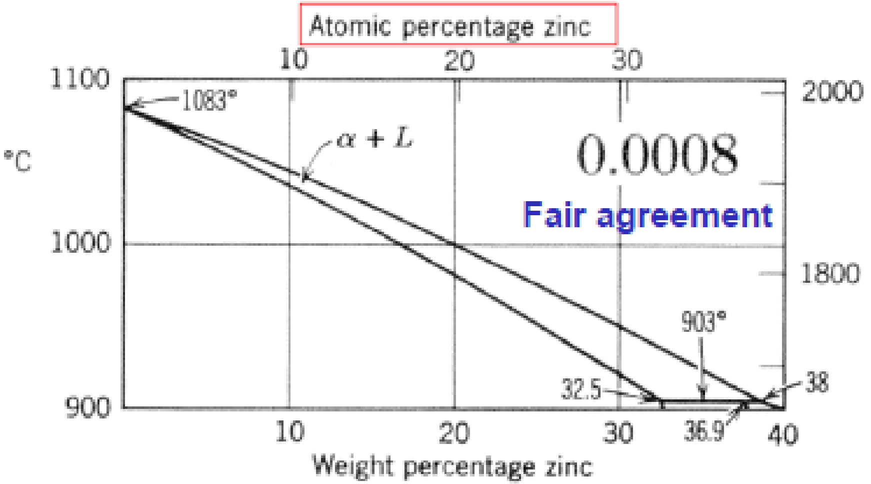
In the case of copper, $$\frac{dC_L}{dT_L} - \frac{dC_S}{dT_S} = 0.0009$$

Atomic weight = 63.5

L = 50.6 cal/gm or 3280 cal/mole

Melting point = 1083°C = 1356°K

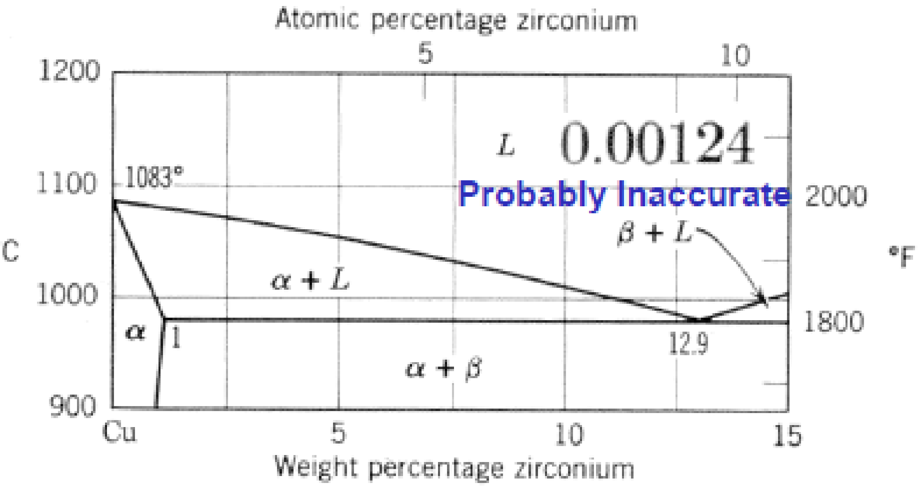
R = 1.98 cal/mole °K



0.0008

Fair agreement

$$\frac{dC_L}{dT_L} = 0.0028 \quad \text{and} \quad \frac{dC_S}{dT_S} = 0.0020$$



0.00124

Probably Inaccurate

0.00133 and 0.00009 atomic per cent per degree

Contents for today’s class I

Chapter 2

Solidification as an Atomic Process

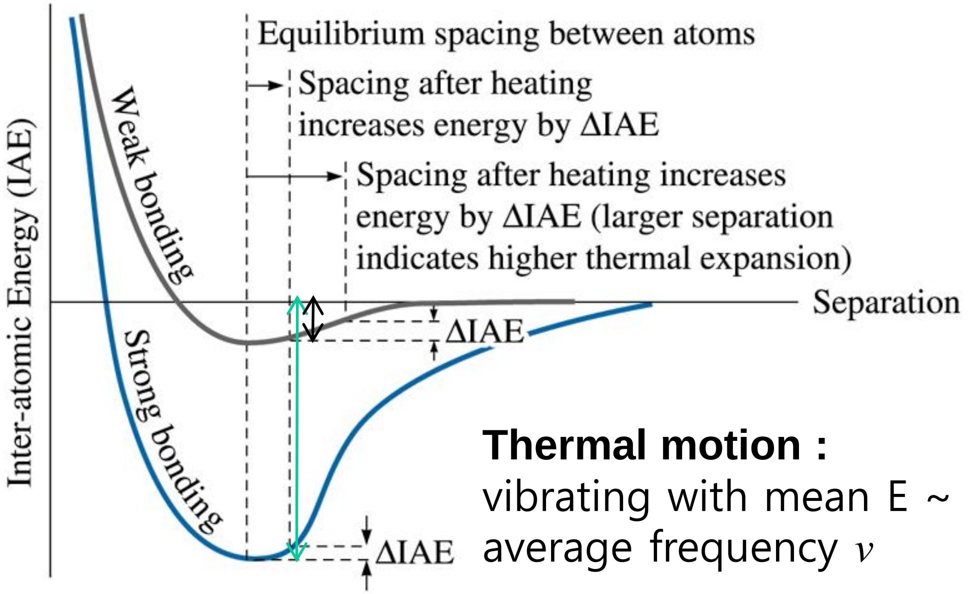
* Solid versus Liquid

2.1 Solids and Liquids

a. The nature of crystalline solids

Correlation between Bonding Strength and Materials Properties

Weakly bonded solids	Strongly bonded solids
Low melting point	High melting point
Low elastic modulus	High elastic modulus
High thermal-expansion coefficient	Low thermal-expansion coefficient



Thermal motion :
vibrating with mean E ~ 3/2 kT
average frequency ν

If E_o is larger,

T_m (melting temp.→ Broken Bonds

E (elastic modulus), ((possibly))

Yield strength is larger,

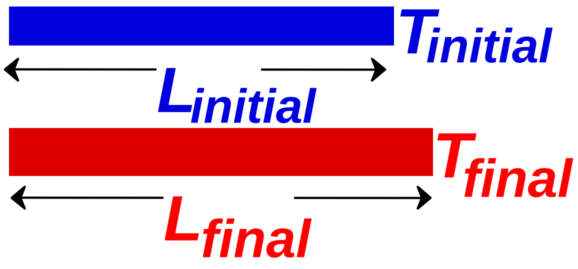
but α is smaller.
(thermal expansion coefficient)

a) Properties from Bonding: Thermal Expansion

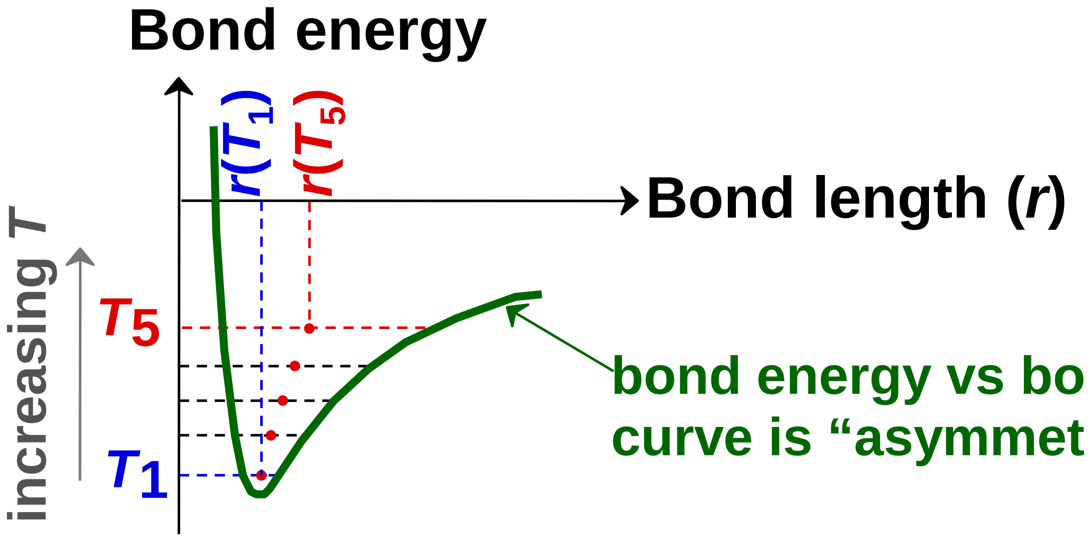
- **Materials change size when heating.**

$$\frac{L_{final} - L_{initial}}{L_{initial}} = \alpha(T_{final} - T_{initial})$$

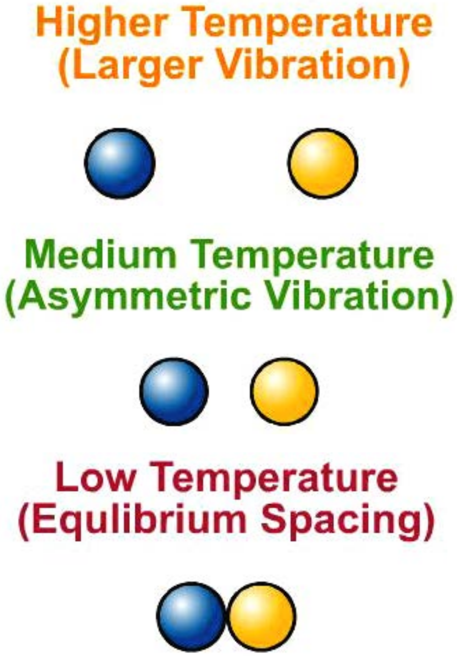
coefficient of thermal expansion (1/K or 1/°C)



- **Atomic view: Mean bond length increases with *T*.**



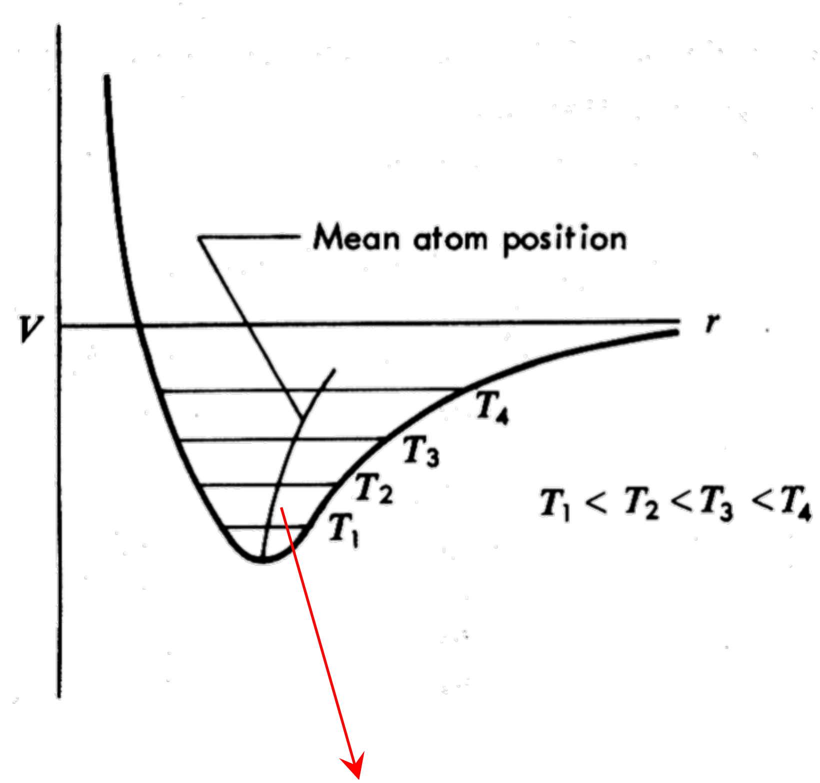
bond energy vs bond length curve is “asymmetric”

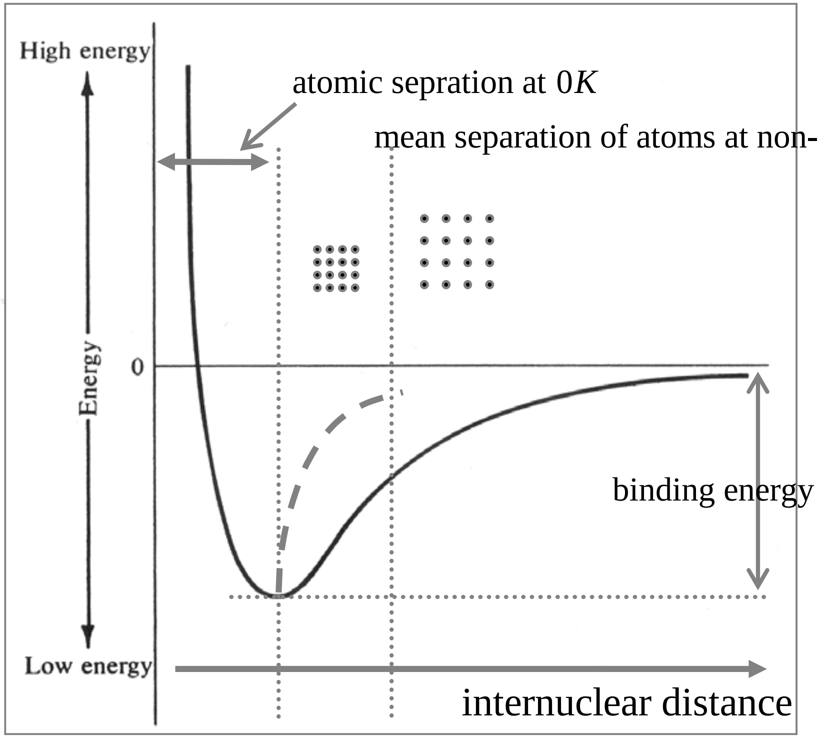


➢ asymmetric nature of the energy well →Thermal expansion

a) Properties from Bonding: Thermal Expansion

Temperature supplies thermal energy into solids → thermal vibration (phonon)

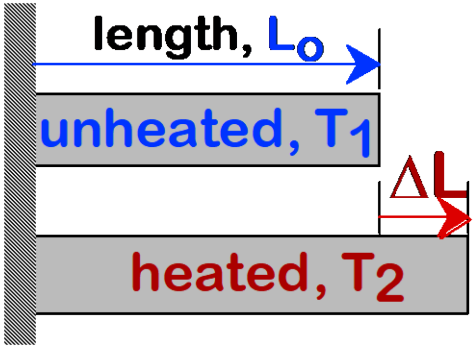




Slope is related to the thermal expansion coefficient of materials

a) Properties from Bonding: Thermal Expansion

- **Coefficient of thermal expansion, α**

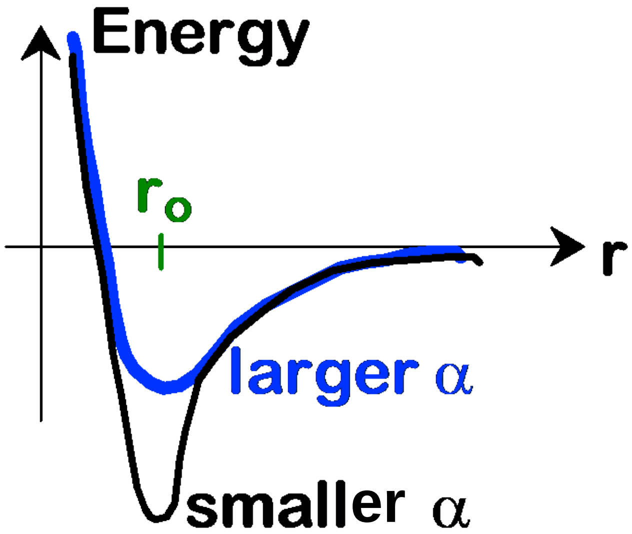


coeff. thermal expansion

$$\frac{\Delta L}{L_o} = \alpha\,(T_2 - T_1)$$

- α ~ 1/bonding energy (E_0) at r_o

$$\alpha_{th} = \frac{1}{l}\frac{dl}{dT}$$



* The greater the bonding energy (E_o), the deeper & more narrow the potential energy well

→ increase in interatomic separation with a given T rise is lower

→ smaller α

- Broad well (generally more asymmetric) → larger expansion

Thermal Expansion: Comparison

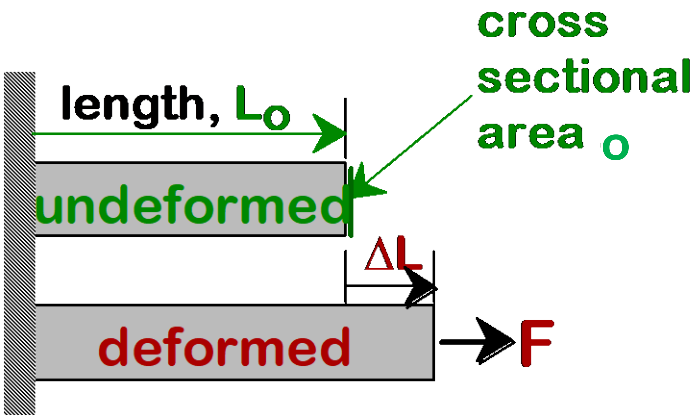
Material	α_ℓ (10^{-6}/K) at room T
- **Polymers**	
Polypropylene	145-180
Polyethylene	106-198
Polystyrene	90-150
Teflon	126-216
- **Metals**	
Aluminum	23.6
Steel	12
Tungsten	4.5
Gold	14.2
- **Ceramics**	
Magnesia (MgO)	13.5
Alumina (Al_2O_3)	7.6
Soda-lime glass	9
Silica (cryst. SiO_2)	0.4

Polymers have large α_ℓ because of weak secondary bonds

Selected values from Table 19.1, *Callister 7e*.

b) Properties from Bonding: E, elastic modulus

- **Elastic (Young's) modulus, E (y)**



Elastic modulus

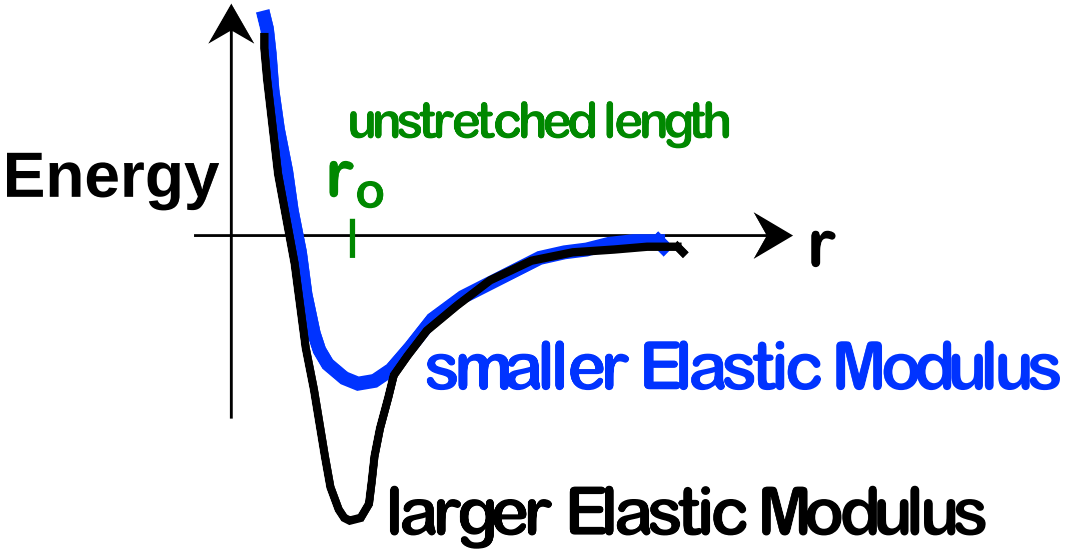
$$\frac{F}{A_o} = E\,\frac{\Delta L}{L_o}$$

$$\sigma = E\varepsilon$$

- **E ~ curvature at r_o (the bottom of the well)**

$$Y \sim \left(\frac{d^2E}{dr^2}\right)_{r_o}$$

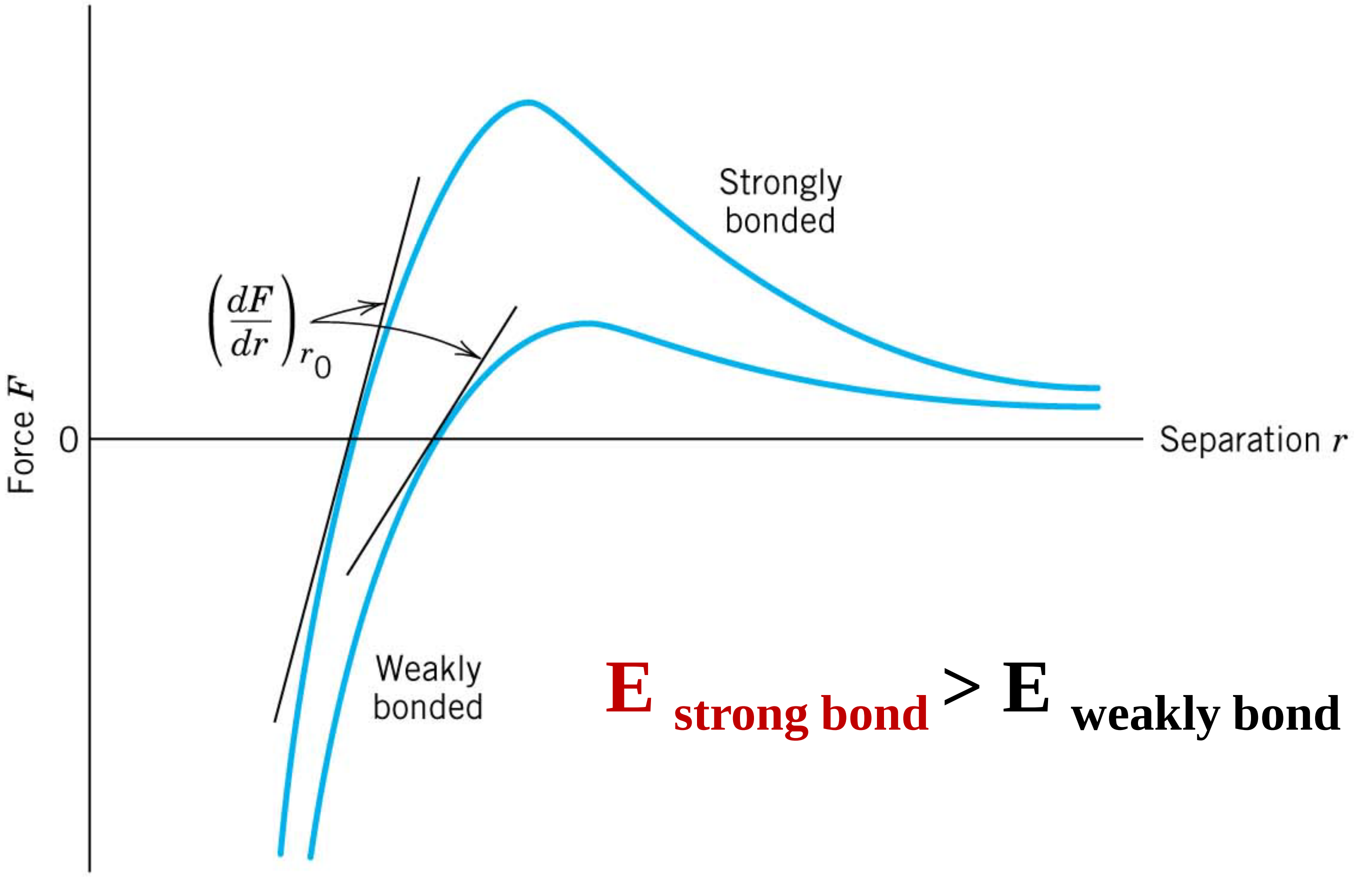
**E is larger
if E_o is larger**



b) Properties from Bonding: E, elastic modulus

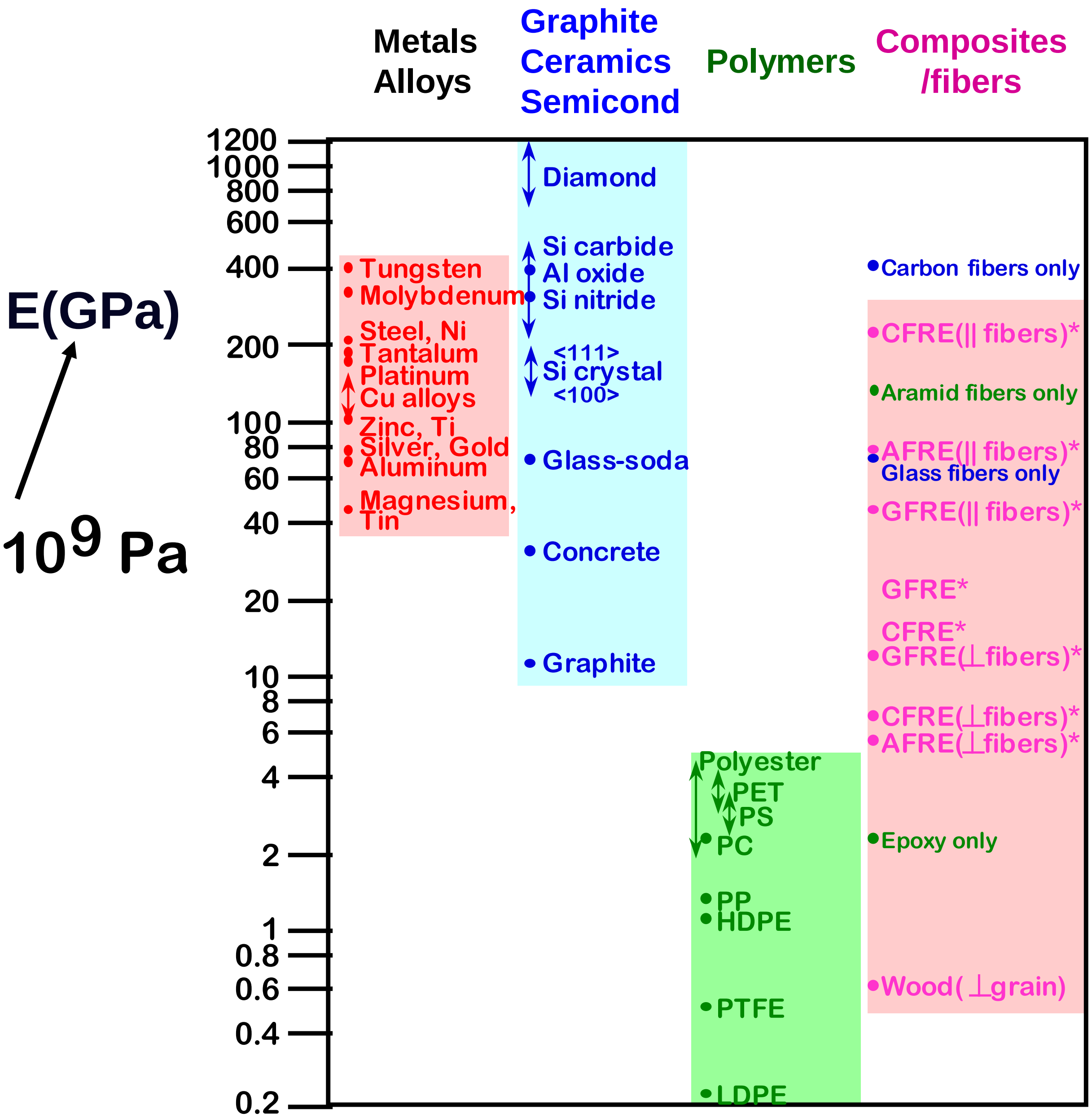
Force versus Interatomic Separation

Figure 6.7 Force versus interatomic separation for weakly and strongly bonded atoms. The magnitude of the modulus of elasticity is proportional to the slope of each curve at the equilibrium interatomic separation r_0.



$E_{\text{strong bond}} > E_{\text{weakly bond}}$

Young's Modulus Comparison



$E_{ceramics}$

$> E_{metals}$

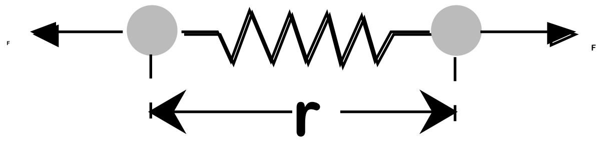
$>> E_{polymers}$

Based on data in Table B2, *Callister 6e*.

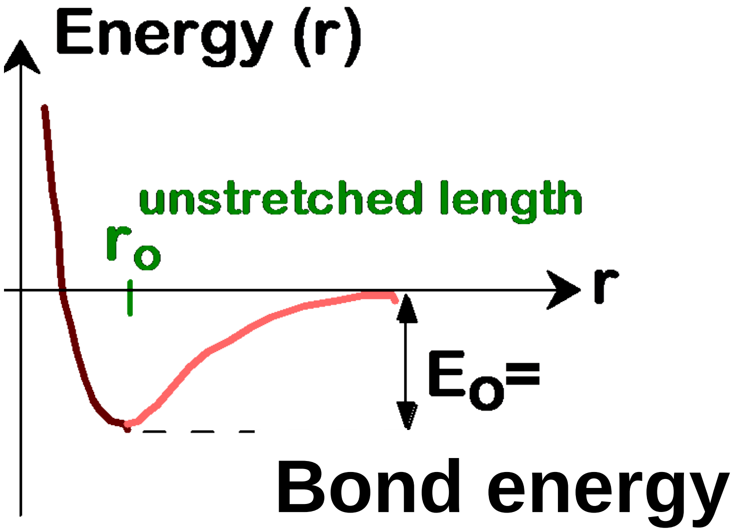
Composite data based on reinforced epoxy with 60 vol% of aligned carbon (CFRE), aramid (AFRE), or glass (GFRE) fibers.

c) Properties from Bonding: T_m, melting point

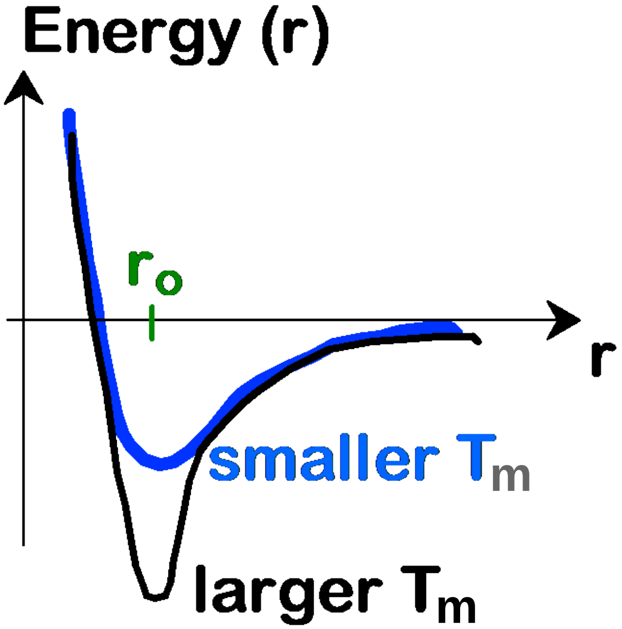
- **Bond length, r_0**



- **Bond energy, E_o**



- **Melting Temperature, T_m**
  - Depth of energy well



T_m is larger if E_o is larger

Imperfections in crystals: external surface/ vacancies/ interstitials/ dislocations/ stacking faults/ sub-boundaries

Bonding

	Type of Bond	Substance	Bond Energy* kcal/mole	Melting Temperature (°C)	Characteristics
Primary bonding	Ionic	CaCl	155	646	Low electrical conductivity; transparent; brittle; high melting temperature
		NaCl	183	801	
		LiF	240	870	
		CuF_2	617	1360	
		Al_2O_3	3618	3500	
	Covalent	Ge	75	958	Low electrical conductivity; very hard; very high melting temperature
		GaAs	≈75	1238	
		Si	84	1420	
		SiC	283	2600	
		Diamond	170	3550	
	Metallic	Na	26	97.5	High electrical and thermal conductivity; easily deformable; opaque
		Al	74	660	
		Cu	81	1083	
		Fe	97	1535	
		W	201	3370	
Secondary	Van der Waals	Ne	0.59	−248.7	Weak binding; low melting and boiling points; very compressible
		Ar	1.8	−189.4	
		CH_4	2.4	−184	
		Kr	2.8	−157	
		Cl_2	7.4	−103	
	Hydrogen	HF	7	−92	Higher melting points than Van der Waals bonding; tendency to form groups of many molecules
		H_2O	12	0	

b. Nature of liquids

* Liquid structure : <u>atom or molecules</u>

→ vibrating with mean E ~ 3/2 kT and average frequency ν

Liquid

Change much more frequently

Free space ⟷

Crystal

Unchanged for relatively long periods

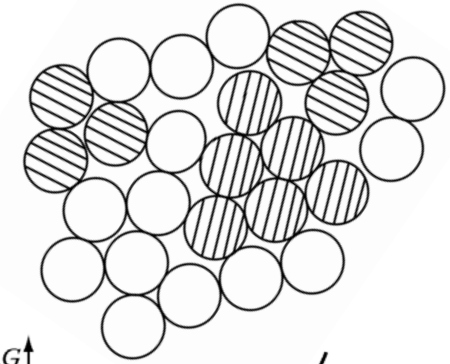
* Instantaneous structure:

crystal-like "cluster" & free space

→ equilibrium mixture of molecules

→ oriented randomly

→ form and disperse very quickly

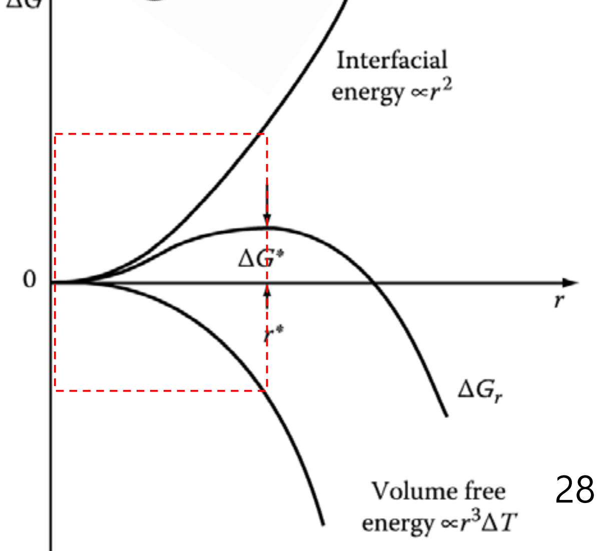


* Thermodynamic point of view

When the free energy of the atomic cluster with radius r is by

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

Cluster size ↑→ free E ↑



② Formation of Atomic Cluster

At the T_m, the liquid phase has a volume 2-4% greater than the solid.

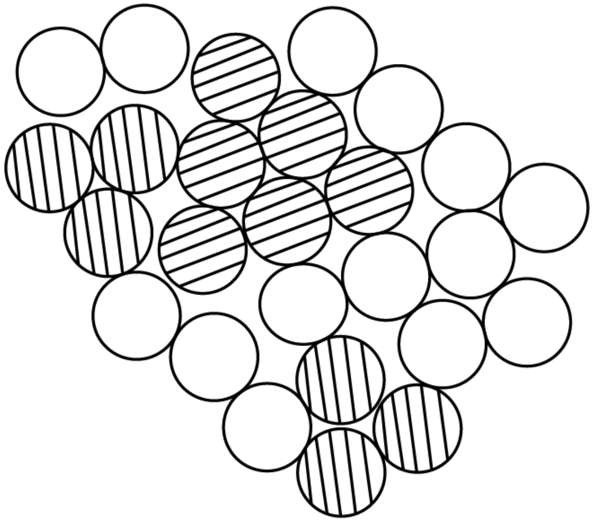
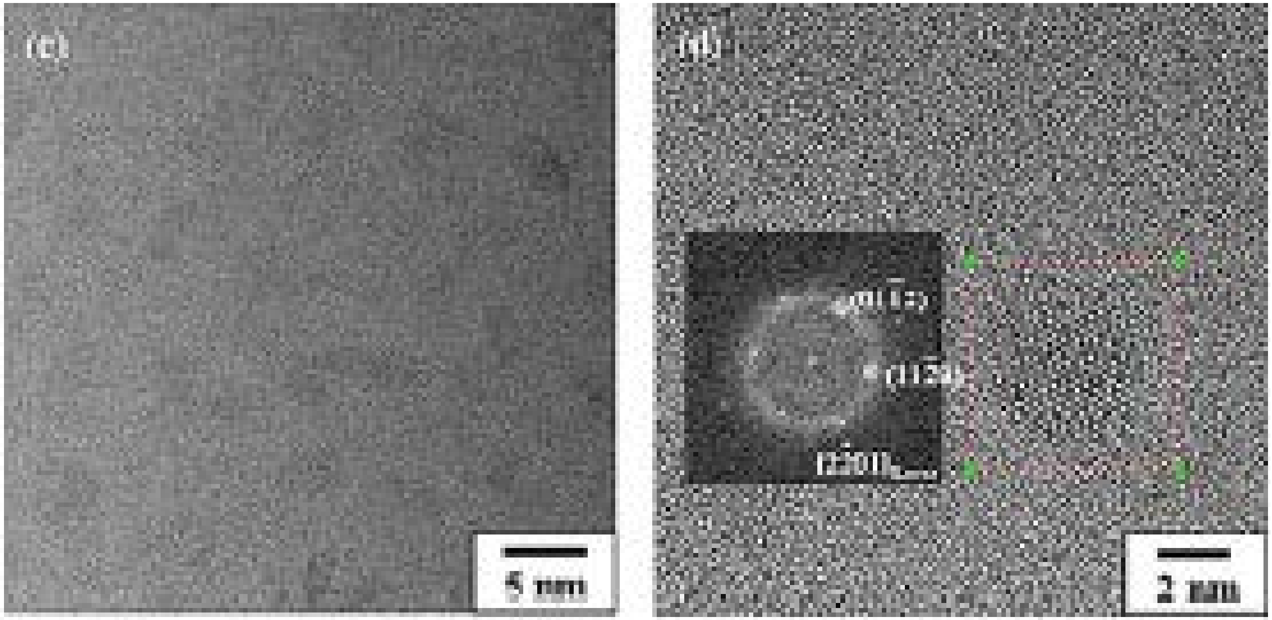


Fig. 4.4 **A two-dimensional representation of an instantaneous picture of the liquid structure. Many close-packed crystal-like clusters (shaded) are instantaneously formed.**



Formation of Atomic Cluster

When the free energy of the atomic cluster with radius r is by

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

how many atomic clusters of radius r would exist in the presence of the total number of atoms, n_0?

$$A_1 \rightarrow A_2 \rightarrow A_3 \rightarrow A_4 \rightarrow \cdots \rightarrow A_{m-1} \rightarrow A_m$$

$$n_2 = n_1 \exp\left(-\frac{\Delta G^{1\rightarrow 2}}{kT}\right)$$

Excess free E associated with the cluster of 1→2 atoms

$$n_3 = n_2 \exp\left(-\frac{\Delta G^{2\rightarrow 3}}{kT}\right)$$

$$n_4 = n_3 \exp\left(-\frac{\Delta G^{3\rightarrow 4}}{kT}\right)$$

$$\vdots$$

$$n_m = n_{m-1} \exp\left(-\frac{\Delta G^{m-1\rightarrow m}}{kT}\right)$$

$$n_m = n_1 \exp\left(-\frac{\Delta G^{1\rightarrow 2} + \Delta G^{2\rightarrow 3} + \cdots + \Delta G^{m-1\rightarrow m}}{kT}\right)$$

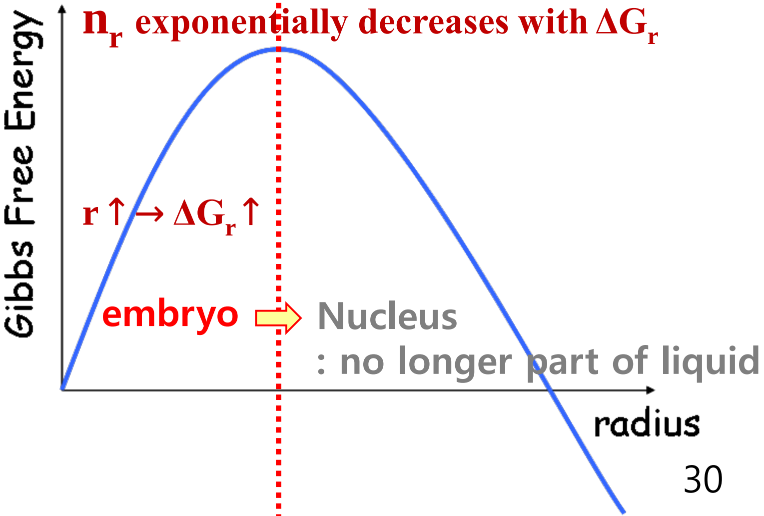
$$n_m = n_1 \exp\left(-\frac{\Delta G^{1\rightarrow m}}{kT}\right)$$

반지름 r인 구상의 군집체 수

# of cluster of radius r

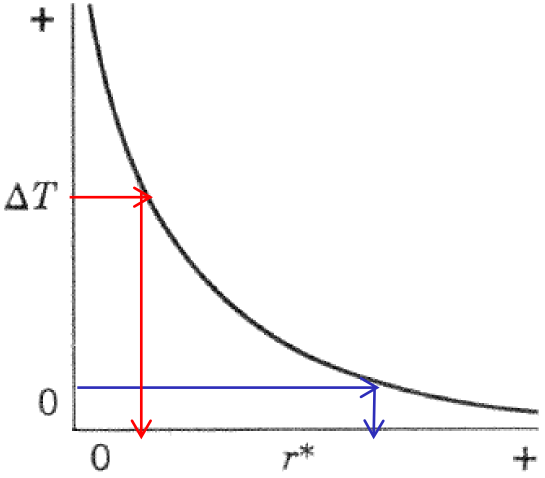
$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

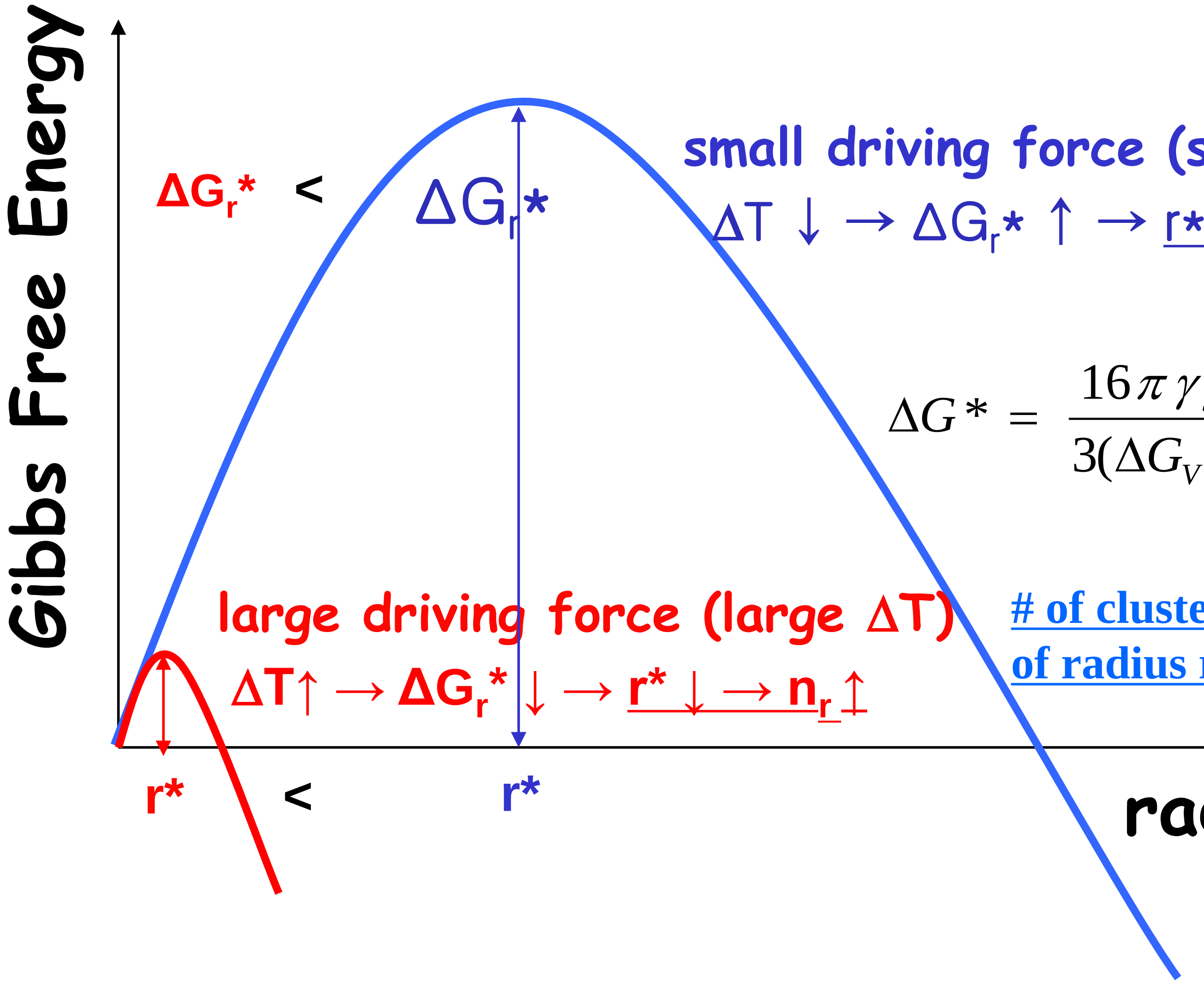
n_r exponentially decreases with ΔG_r



Formation of Atomic Cluster

Compare the nucleation curves between small and large driving forces.





small driving force (small ΔT)

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

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

large driving force (large ΔT)

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

# of cluster of radius r

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

Formation of Atomic Cluster

n_o : total # of atoms.
ΔG_r : excess free energy associated with the cluster
k : Boltzmann's constant

# of cluster of radius r

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

- holds for $T > T_m$ / $T < T_m$ and $r \leq r^*$
  Apply for all r / $r \leq r^*$
  (∵ $r > r^*$: no longer part of the liquid)
- n_r exponentially decreases with ΔG_r

Ex. 1 mm^3 of copper at its melting point (n_0: 10^{20} atoms)

r ↓ → n_r ↑ → ~10^{14} clusters of 0.3 nm radius (i.e. ~ 10 atoms)

r ↑ → n_r ↓ → ~10 clusters of 0.6 nm radius (i.e. ~ 60 atoms)

→ effectively a maximum cluster size, ~ 100 atoms
~ 10^{-8} clusters mm^{-3} or 1 cluster in ~ 10^7 mm^3

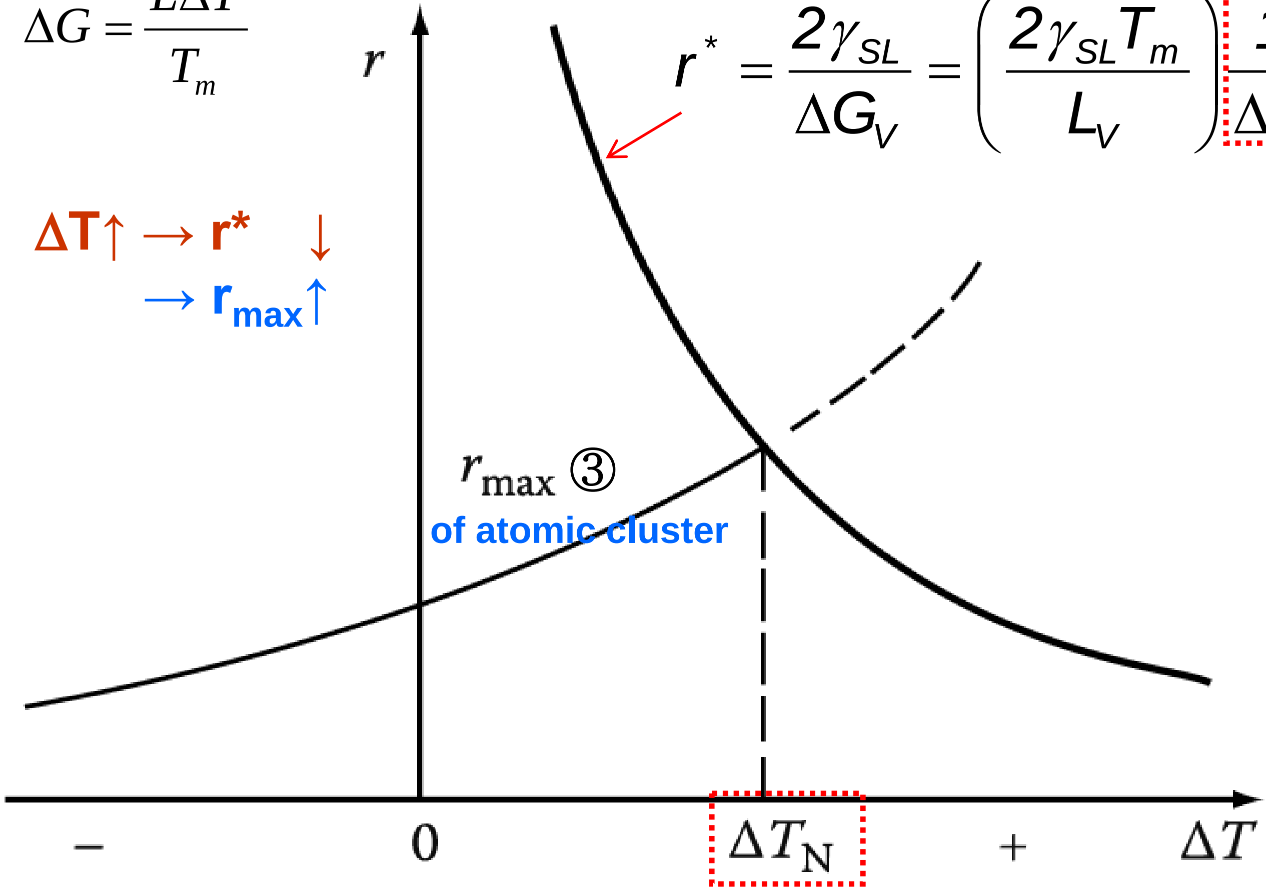
The creation of a critical nucleus ~ thermally activated process

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

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

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

$\rightarrow r_{max} \uparrow$



of atomic cluster

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.

c. The difference between crystals and liquids

1) their behavior when subjected to stress

Liquid

Shape change as response to any shear stress

⟷

Crystal

Elastically deformed

2) Volume change

vibration **2/3kT, ν** **Latent heat** **2/3kT, ν**

→ **relocation of the atom in positions with higher potential E**

Liquid

Less close packed (or more “open”) structure

⟷ **ΔV**

Crystal

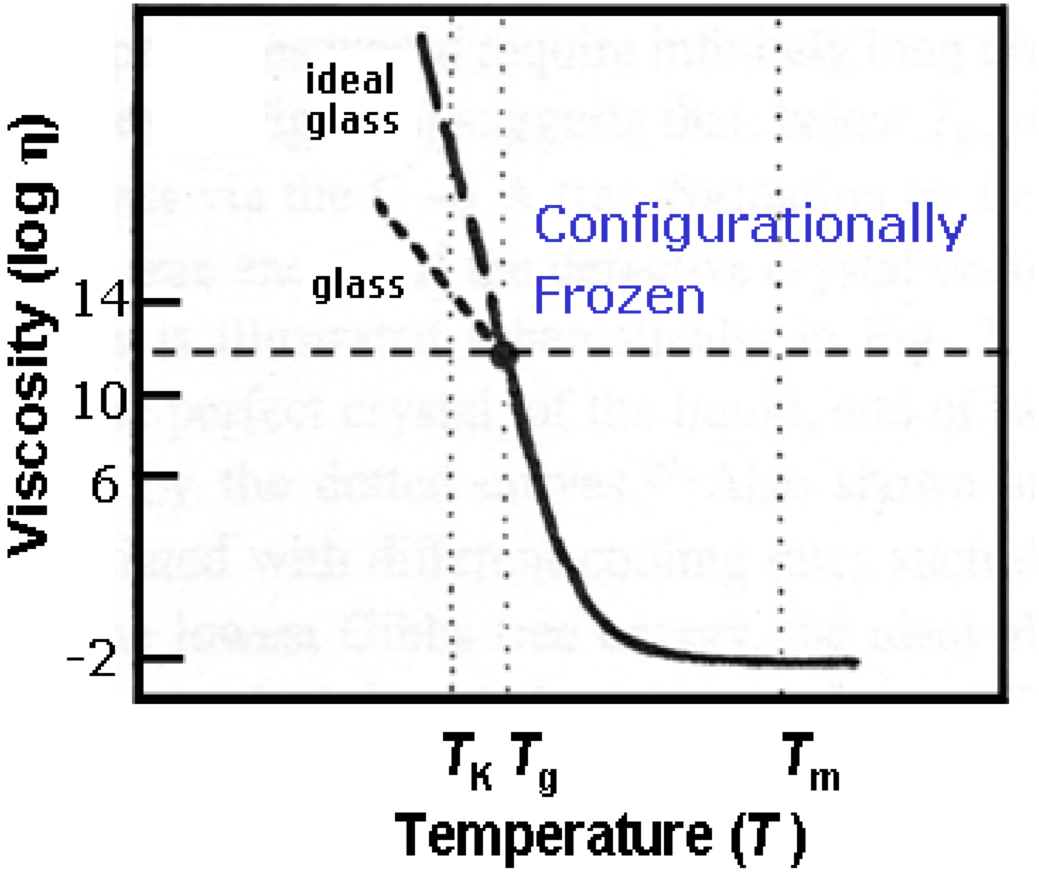
Close-packed or nearly close packed structure

→ **“+” : all metals except gallium and bismuth**

(“borderline” case for classification as metals)

→ **“-” : Silicon and germanium**

1) ***Solid:*** application of small force for one day produces no permanent change.



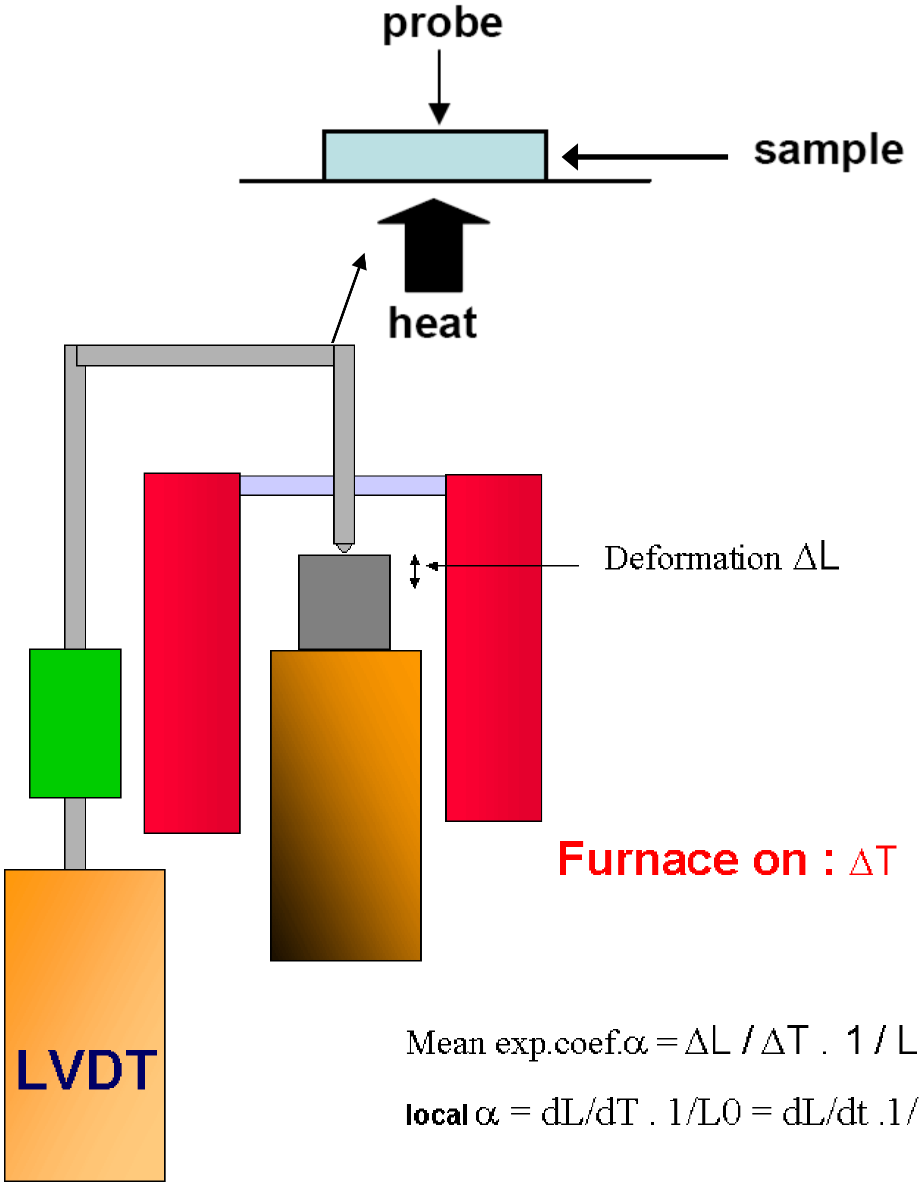
A solid is a materials whose viscosity exceeds $10^{14.6}$ poise

cf) liquid *~10^{-2} poise*

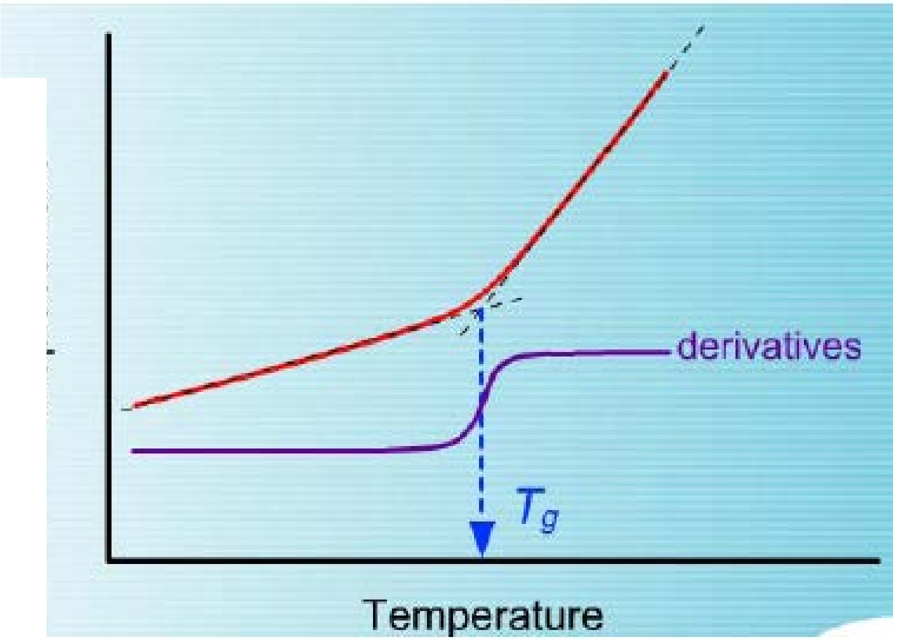
Glass = undercooled liquid with high viscosity

Thermomechanical analysis (TMA):

- measure dimension changes under constant load, as function of temperature



Determination of T_g



Mean exp.coef.$\alpha = \Delta L / \Delta T \cdot 1 / L_0$

local $\alpha = dL/dT \cdot 1/L0 = dL/dt \cdot 1/\beta . L_0$

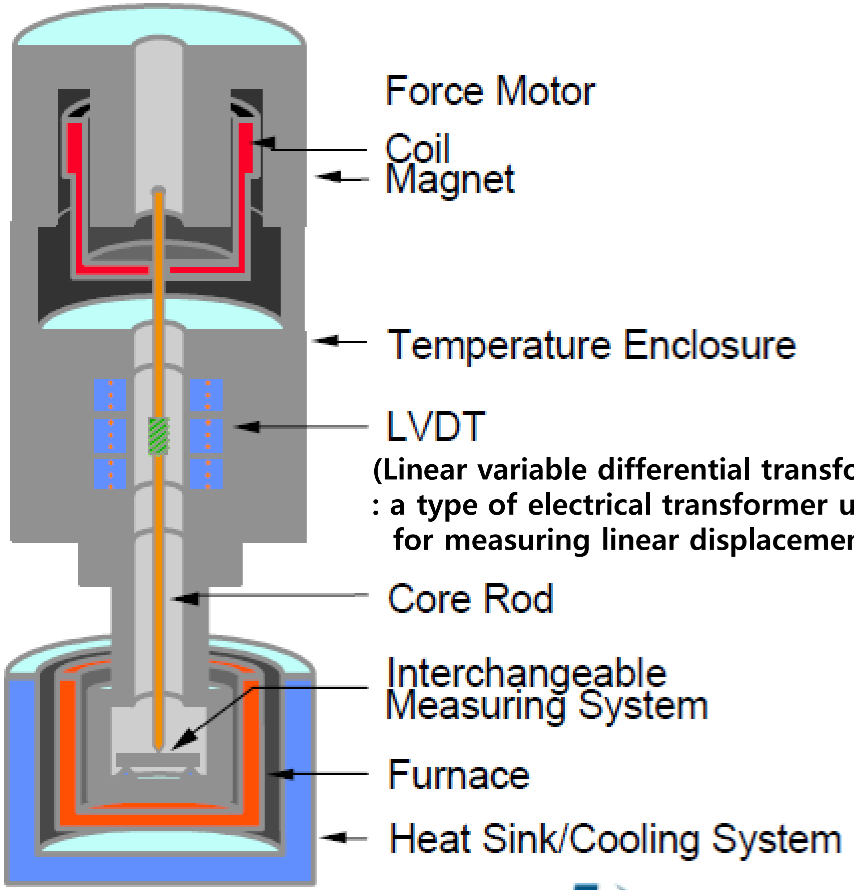
Dynamic Mechanical Analysis (DMA) is a high precision technique for measuring the viscoelastic properties of materials.

- measures the stiffness and damping properties of a materials

- Stiffness depends on mechanical properties and is often converted to a modulus to enable sample inter comparisons.

- Damping is expressed in terms of Tan δ and is related to the amount of energy a material can store.

- DMA is most sensitive for monitoring relaxation events, such as Tg, because mechanical properties change dramatically when relaxation behavior is observed.

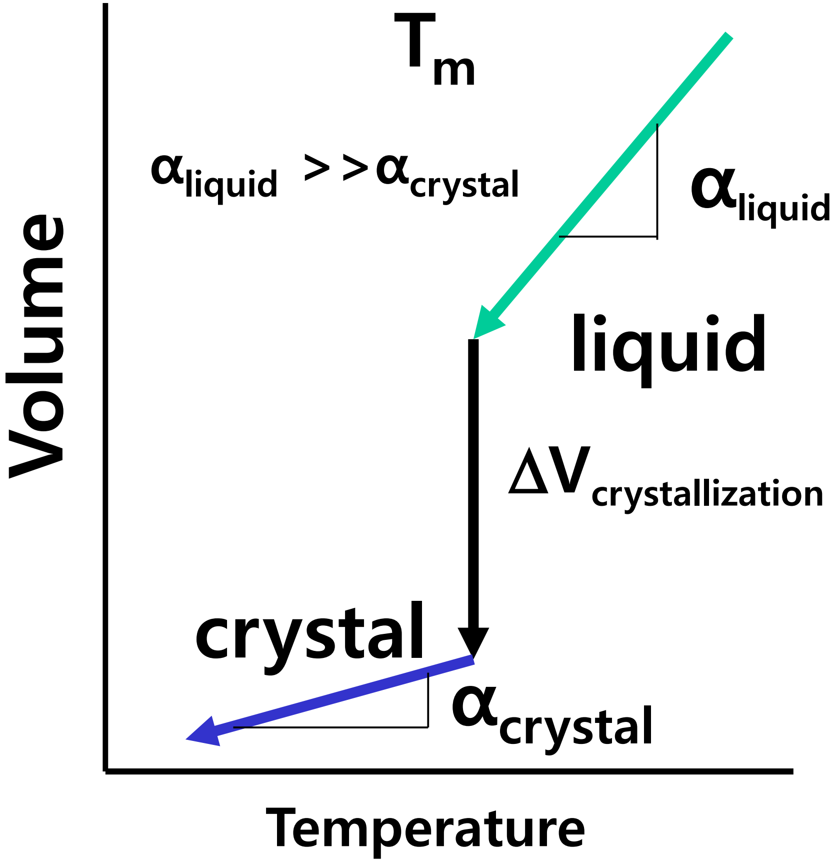


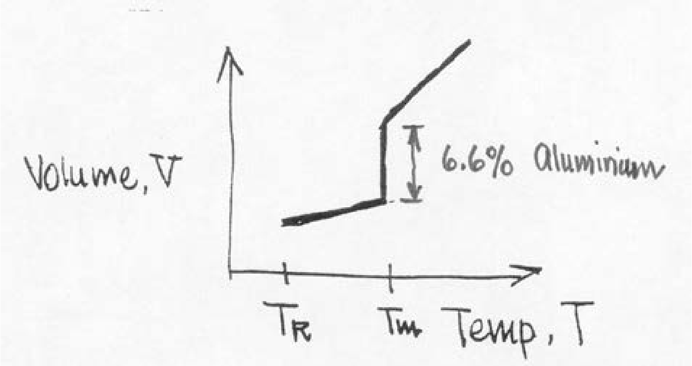
(Linear variable differential transformer)
: a type of electrical transformer used for measuring linear displacement.

PerkinElmer™ instruments.

2) Crystallization is Controlled by Thermodynamics

- Volume is high as a hot liquid
- Volume shrinks as liquid is cooled
- At the melting point, T_m, the liquid crystallizes to the thermodynamically stable crystalline phase
- More compact (generally) crystalline phase has a smaller volume
- The crystal then shrinks as it is further cooled to room temperature
- Slope of the cooling curve for liquid and solid is the thermal expansion coefficient, α





Shrinkage in Solidification and Cooling

- Can amount to 5-10% by volume
- Gray cast iron expands upon solidification due to phase changes
- Need to design part and mold to take this amount into consideration

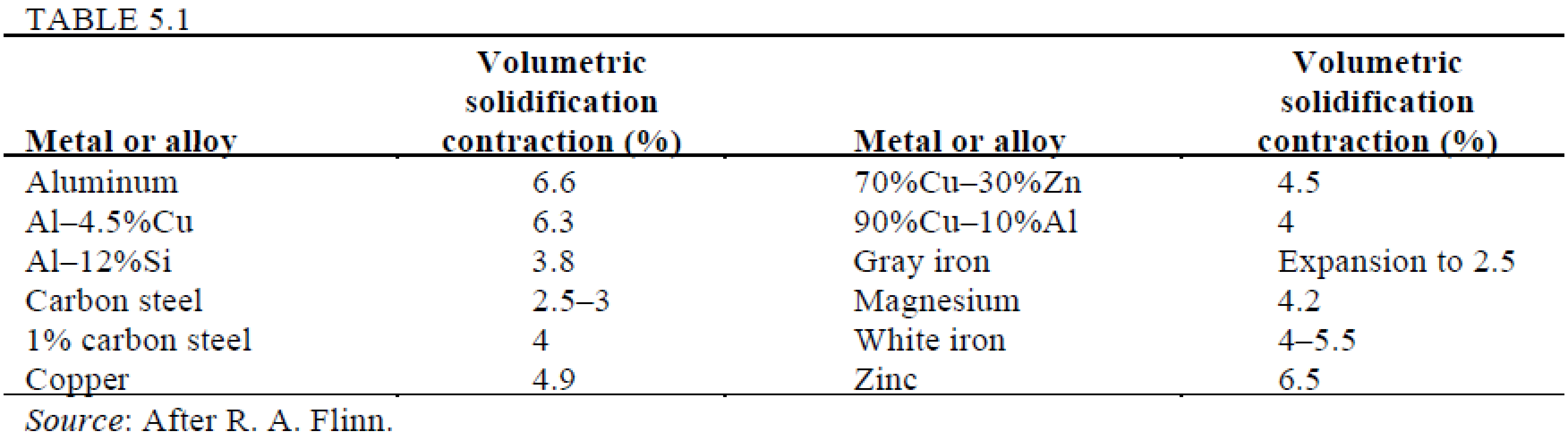


TABLE 5.1

Metal or alloy	Volumetric solidification contraction (%)	Metal or alloy	Volumetric solidification contraction (%)
Aluminum	6.6	70%Cu–30%Zn	4.5
Al–4.5%Cu	6.3	90%Cu–10%Al	4
Al–12%Si	3.8	Gray iron	Expansion to 2.5
Carbon steel	2.5–3	Magnesium	4.2
1% carbon steel	4	White iron	4–5.5
Copper	4.9	Zinc	6.5

Source: After R. A. Flinn.

*** Volumetric solidification expansion: H_2O (10%), Si (20%), Ge**

ex) Al-Si eutectic alloy (casting alloy)→ volumetric solidification contraction of Al substitutes volumetric solidification expansion of Si.

Cast Iron: Fe + Carbon (~ 4%) + Si (~2%)

→ precipitation of graphite during solidification reduces shrinkage.

d. Quasi-chemical approach

Page 25

* Solid: force between pairs of atoms

→ vaporize: break all "pairwise" bonds

For, example: Copper (Cu)

Vaporization **Melting**

Heat of vaporization 80 Kcal/mole vs Heat of fusion 3.1 Kcal/mole

⟷

25 times → 1/25 broken

Melting: each bond is replaced by one with 4 percent less E,

although bond energy of liquid is changed by the positions.

→ Heat of fusion during melting: need to generate weaker liquid bonds

Contents for today's class II

* Free surface (solid/vapor interface)?

* Solid /Liquid Interfaces

*** Broken bond model → calculation of the E of solid/ liquid interface**

2.2 Solid-Liquid Interface

*** An atom at the surface ~ number of nearest neighbors from 3 to 11**

→ missing bonds → low heat of fusion

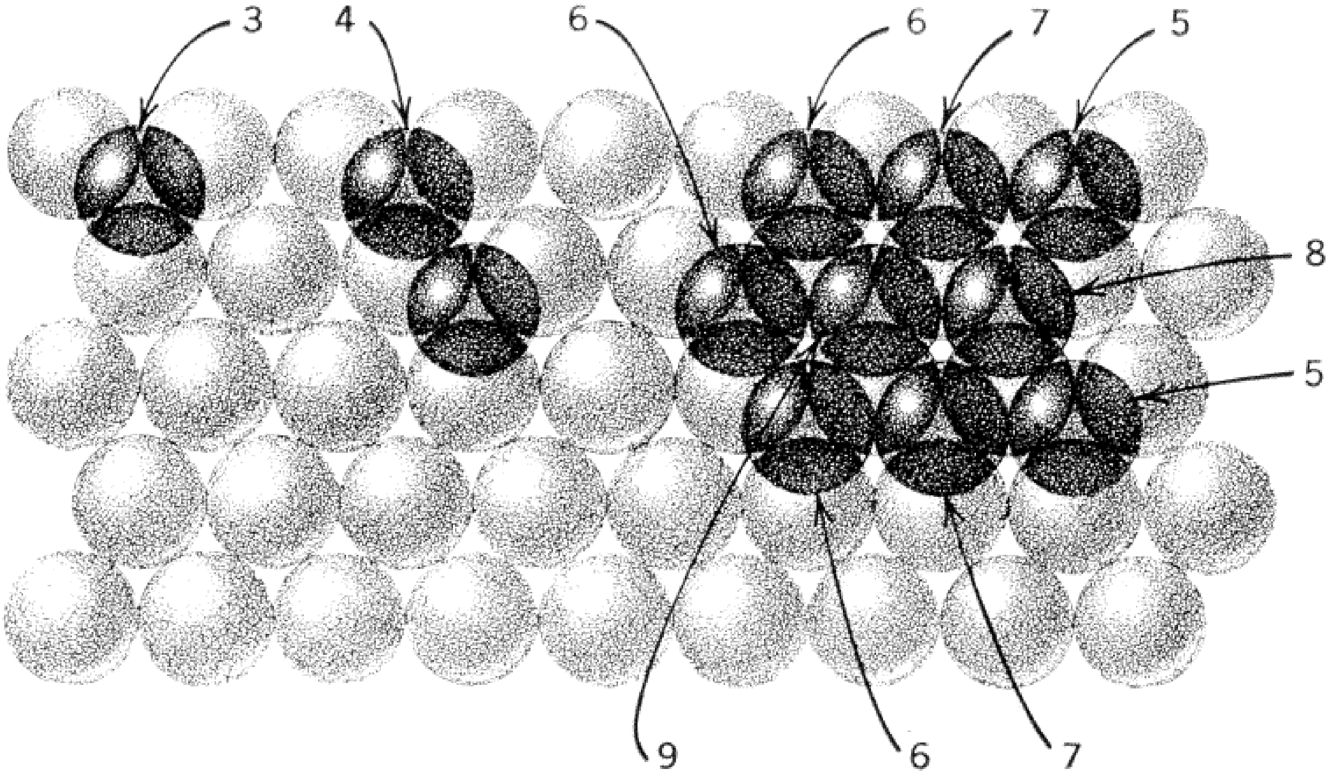


Fig. 2.2. Number of nearest neighbors N of atoms on close-packed surfaces.

Q: Free surface (solid/vapor interface)?

(a) E_{SV} vs γ ?

Extra energy per atom on surface **Interfacial free energy**

- 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

(¼ of L_s/N_a) (∵ surface free E averaged over many surface plane, S effect at high T)

(b) Equilibrium shape: Wulff surface

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

Solid / Vapor Interfaces

*** Assumption: S/V interface → Hard sphere model/ uncontaminated surface**

(In real systems surfaces will reduce their free energies by the adsorption of impurities.)

- Fcc : density of atoms in these planes decreases as $(h^2+k^2+l^2)$ increases

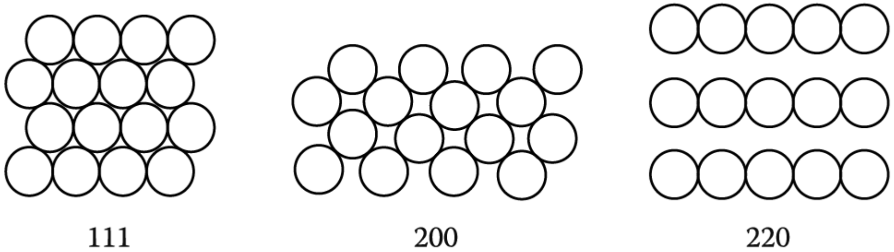
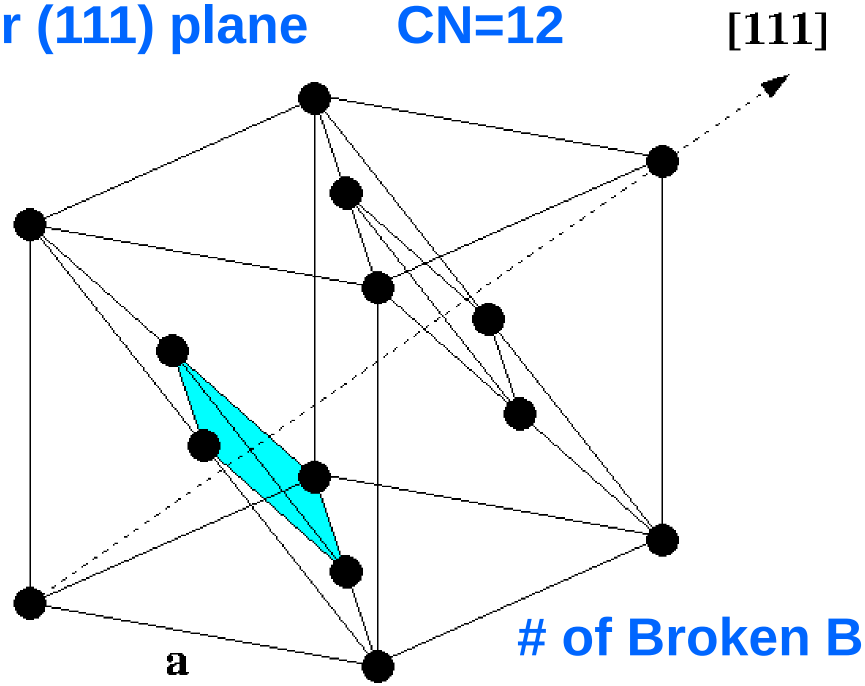


Fig. 3.2 Atomic configurations on the three closest-packed planes in fcc crystals; (111), (200), and (220).

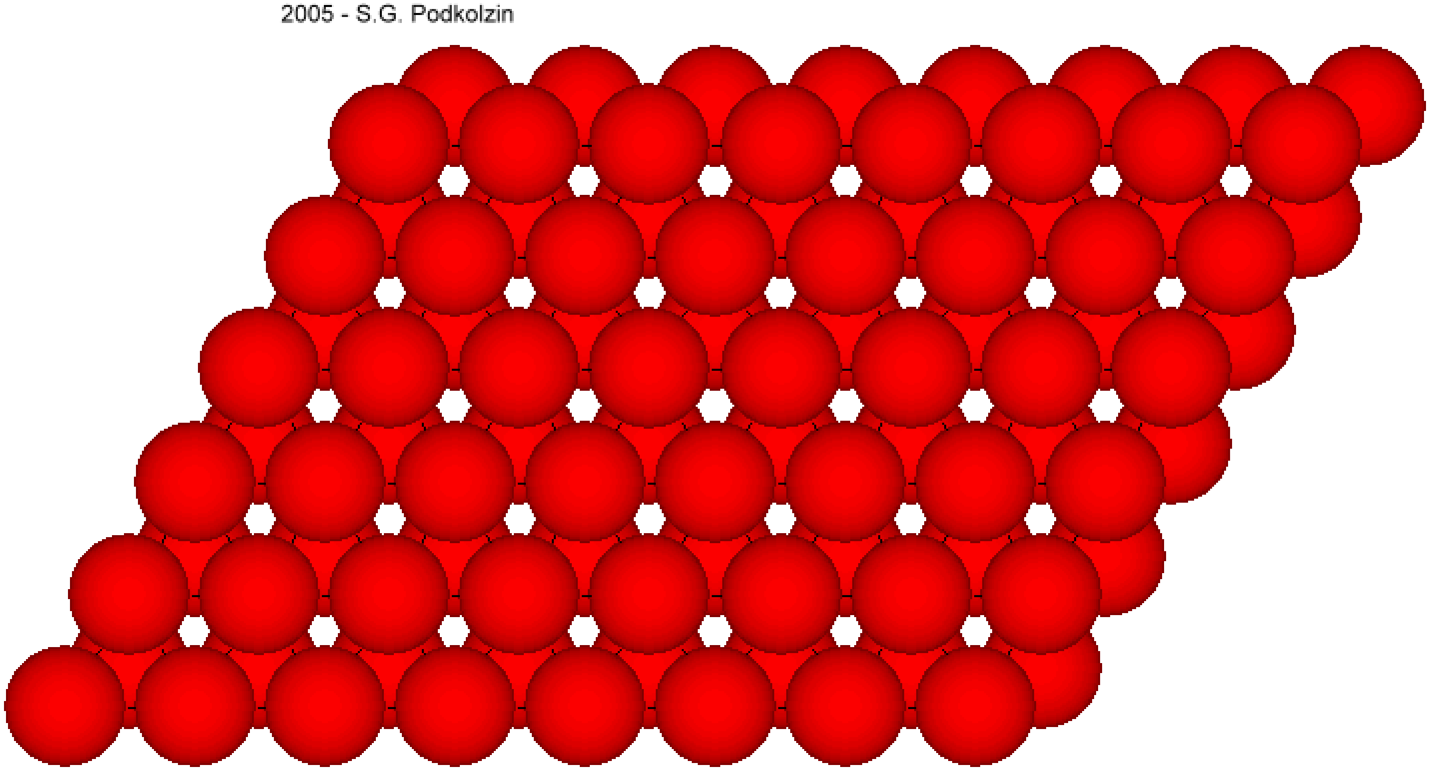
(notation {200} and {220} plane has been used instead of {100} and {110} because the spacing of equivalent atom planes is than given by $a/(h^2+k^2+l^2)^{1/2}$ where a is the lattice parameter.)

For (111) plane CN=12



# of Broken Bonds per atom at surface?

of Broken Bonds per atom at surface? → 3 per atom



For (111) plane

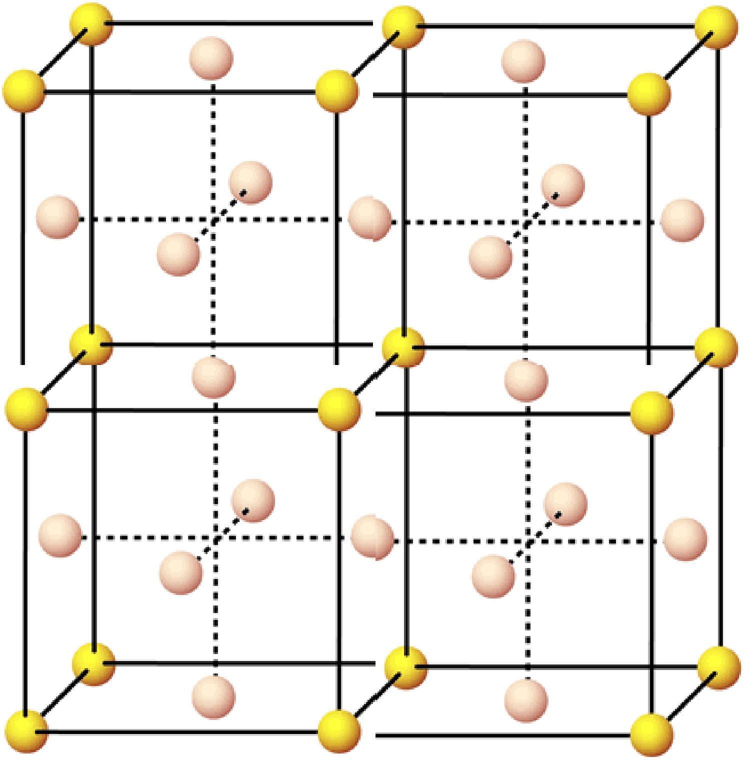
# of broken bond at surface : 3 broken bonds

Bond Strength: ε → for each atom : ε/2

Lowering of Internal Energy per atom on surface: 3ε/2 ↓

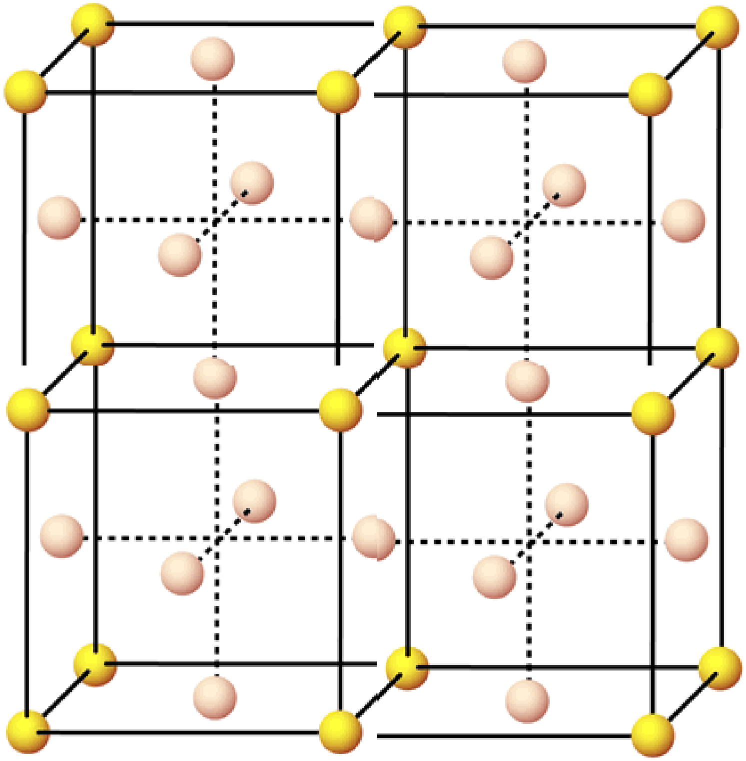
(excess internal energy of 3ε/2 over that of the atoms in the bulk)

For (200) plane CN=12



# of Broken Bonds per atom at surface?

For (200) plane CN=12



# of Broken Bonds per atom at surface?

# of broken bond at surface : 4 broken bonds

Bond Strength: ε ⟶ for each atom : ε/2

Lowering of Internal Energy per atom on surface: 4ε/2 ↓

(excess internal energy of 4ε/2 over that of the atoms in the bulk)

For (111) plane

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? $\rightarrow L_S = 12 N_a \varepsilon/2$

(Latent heat of melting + vaporization)

(1 mole of solid = 12 N_a)

Energy per atom of a {111} Surface?

$E_{SV} = 3\varepsilon/2 = 0.25 L_S / N_a$ (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/m²)

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

$= E + PV - TS$ (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

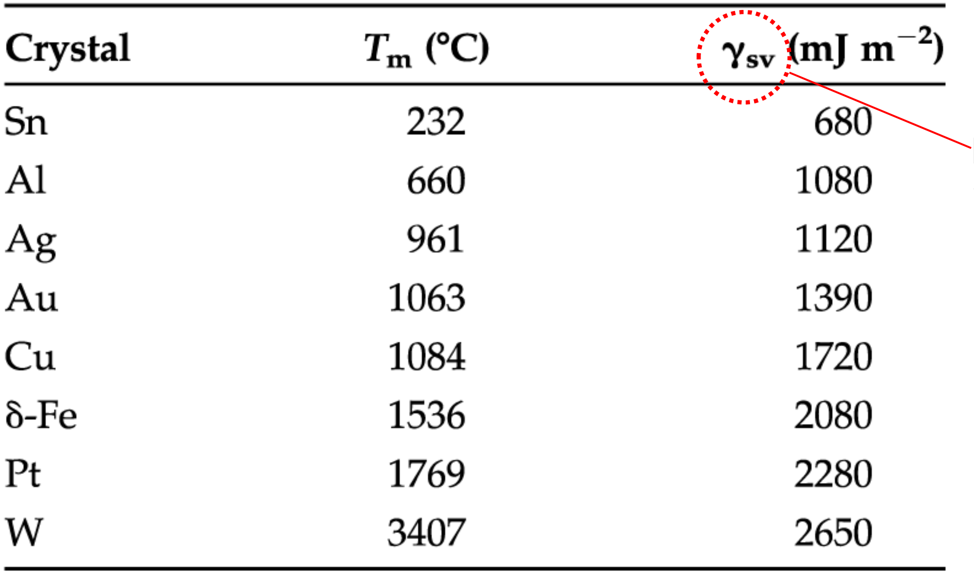
* E_{SV} vs γ ?

- 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})**

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

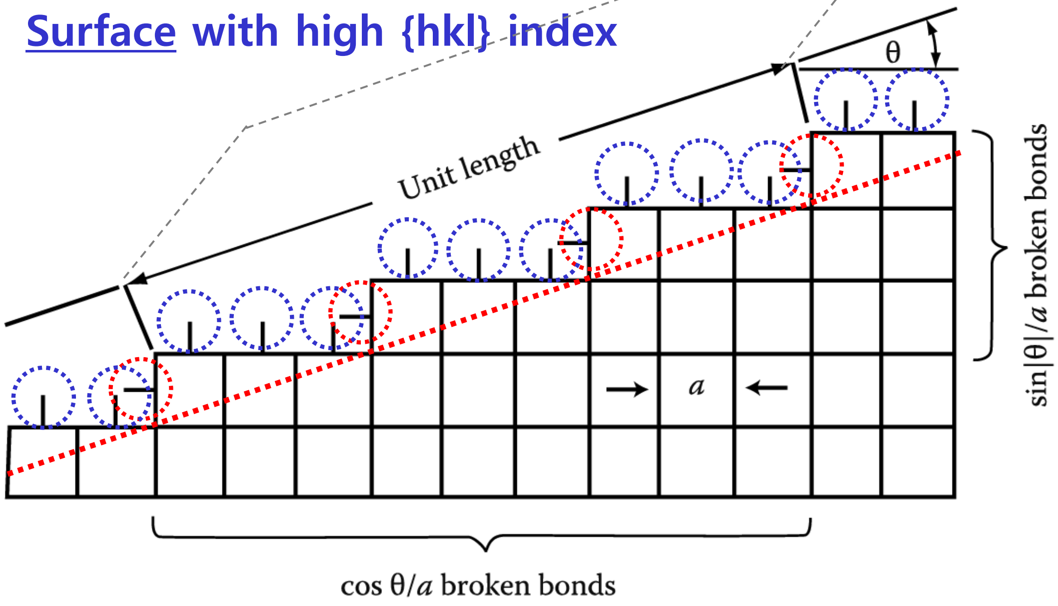
Surface energy for high or irrational {hkl} index

Closer surface packing → **smaller number of broken bond → lower surface energy**

# of broken bonds will increase through the series {111} {200} {220} → γ_{SV} will increase along the same series (if different entropy term is ignored)

A crystal plane at an angle θ to the close-packed plane will contain broken bonds in excess of the close-packed plane due to the atoms at the steps.

Surface with high {hkl} index



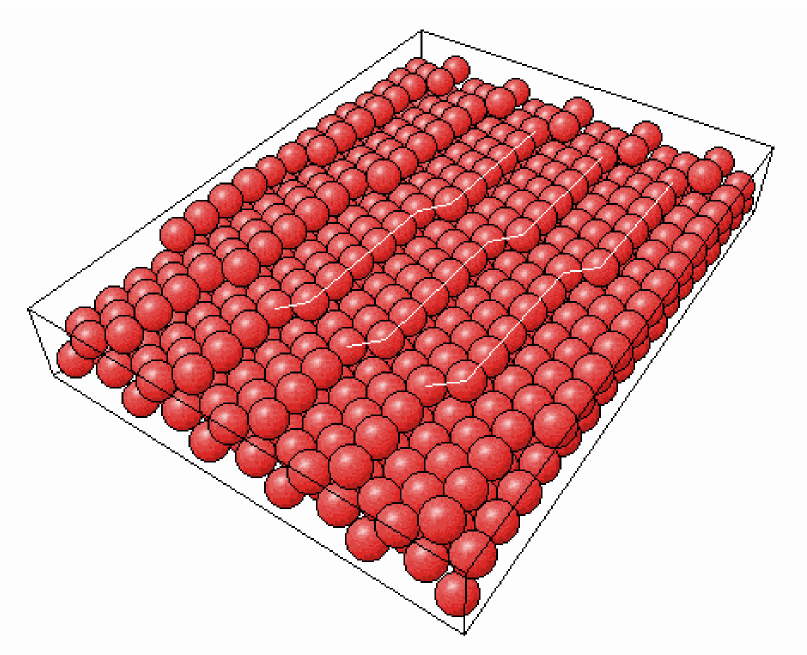


Fig. 2.2 The 'broken-bond' model for surface energy.

(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**

Surface energy for high or irrational {hkl} index

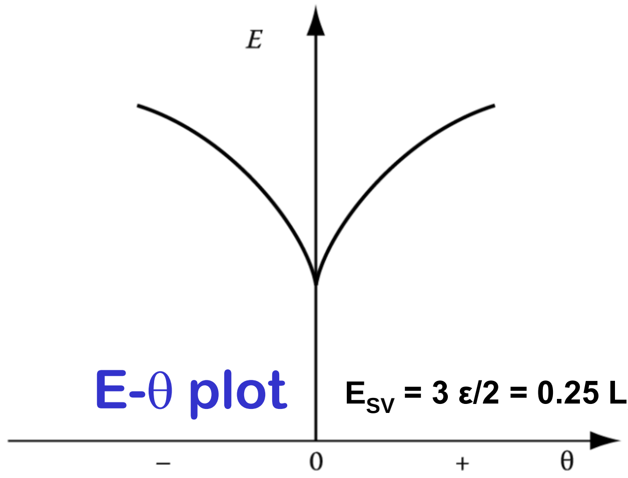
(cosθ/a)(1/a) : **broken bonds from the atoms on the steps**

(sinǀθǀ/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.**

Q: Free surface (solid/vapor interface)?

(a) E_{SV} vs γ ?

Extra energy per atom on surface　　Interfacial free energy

- 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)

(b) Equilibrium shape: Wulff surface

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

Equilibrium shape: Wulff surface

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

* 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 : $A_1\gamma_1 + A_2\gamma_2$ ….

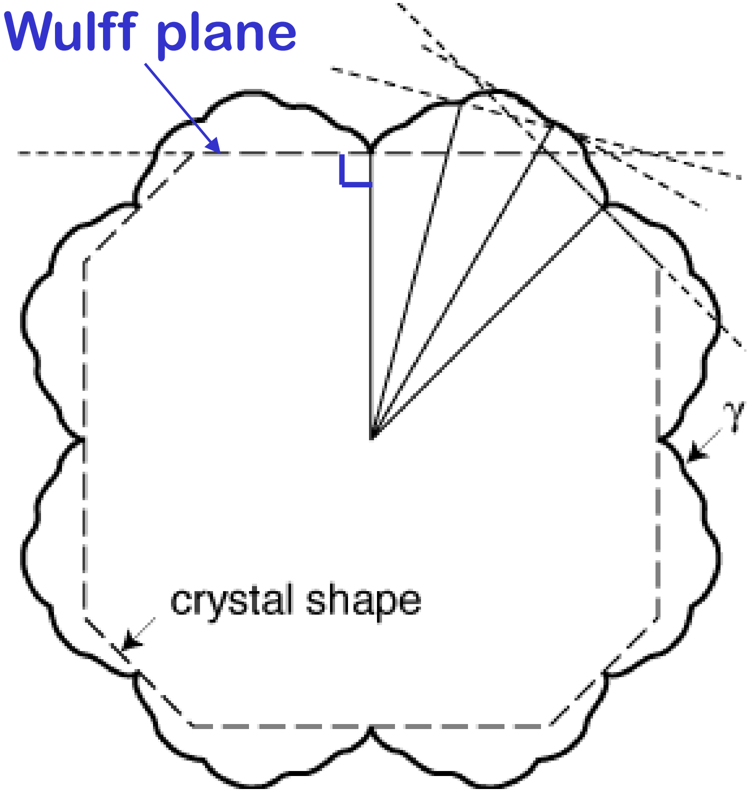
$= \sum A_i \gamma_i \rightarrow$ minimum

→ equilibrium morphology

: can predict the equilibrium shape of an isolated single crystal

How is the equilibrium shape determined?

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



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

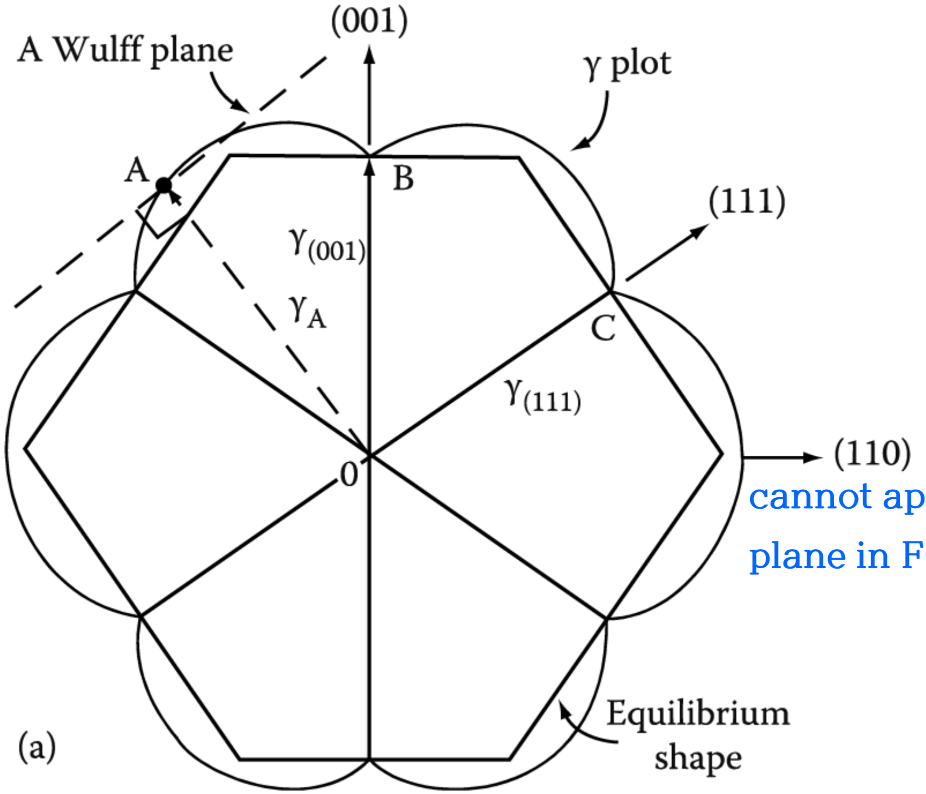
(d) Intersection of I and II

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

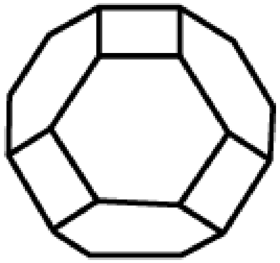
Equilibrium shape can be determined experimentally by annealing small single crystals at high temperatures in an inert atmosphere, or by annealing small voids inside a crystal.

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.

Q: Faceted interface vs. Diffusion interface

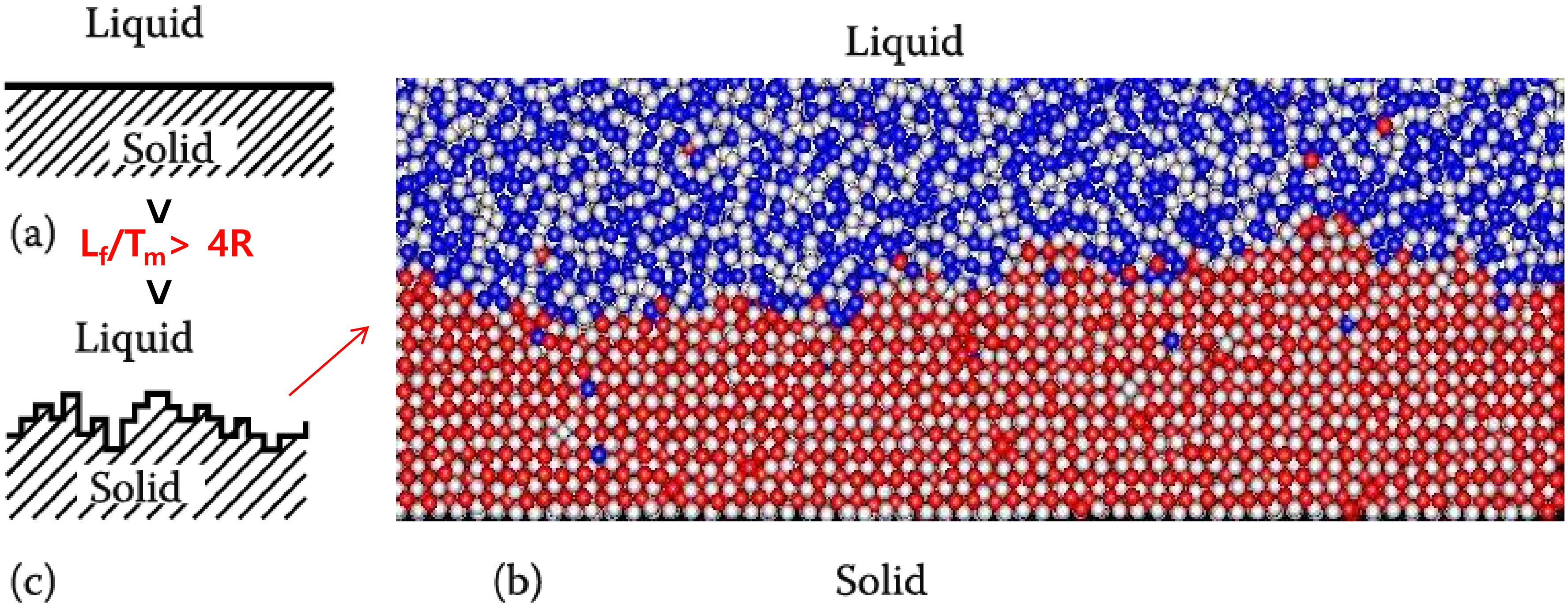
Solid /Liquid Interfaces

: consequences for the structure and energy of the interface

Faceted interface **Rather narrow transition zone** approximately one atom layer thick

Smooth ~ same as solid/vapor interfaces, i.e., atomically flat close-packed interface

: some intermetallic compounds, elements such as Si, Ge, Sb, and most non-metals



V

$L_f/T_m > 4R$

V

Fig. 3. 63 Solid/liquid interfaces: (a) atomically smooth, (b) and (c) atomically rough, or diffuse interfaces.

Diffusion interface (non-faceted) **Rather wide transition zone** over several atom layers

: most metals, L_f/T_m ~ R (gas constant) ~automatically "rough" & diffuse interface

Surface free energy ΔF_s between solid/liquid interface

$$\Delta F_s = \Delta E_0 - \Delta E_1 + T\Delta S_0 - T\Delta S_1 - P\Delta V$$

where, ΔE_0 is decrease in energy corresponding to the addition of N_A single atoms to the interface from the liquid.

ΔE_1 is the average decrease of energy of the N_A atoms due to the presence of the other atoms on the surface (2 atoms in neighboring sites would have an energy lower by L/b than if they were separated.)

ΔS_0 is the difference in entropy between the solid and the liquid.

ΔS_1 is the entropy that corresponds to the degree of randomness of the distribution of the N_A atoms on the surface.

$P\Delta V$ is the term arising from change in volume during the change in state; this term is negligible in the liquid-solid transformation.

Jackson’s approach:

Assuming “single-layer rough interface”,

$\Delta E_0 = 2L_0(\eta_0/v)N_A$, where L_0=latent heat per atom, η_0= # of nearest neighber,

v= # it would have in the interior of a crystal of the same structure

N= possible sites on the average → N_A/N = nearest neighbor sites per each atom

$E = (L_0\eta_0/v)(N_A^2/N)$, also $\Delta S_0 = (L/T_E)N_A$, since L/T_E = entropy of melting per atom.

Excess mixing Entropy

If there is no volume change or heat change,

$$w_{config} = 1 \quad \rightarrow before\_solution\_(pureA\_pureB)$$

$$w_{config} = \frac{(N_A + N_B)!}{N_A!N_B!} \rightarrow after\_solution\_(N_A, N_B)$$ ⬅ **Number of distinguishable way of atomic arrangement**

$$\Delta S^{mix} = S^{after} - S^{before} = k \ln \frac{(N_A + N_B)!}{N_A!N_B!} - k \ln 1$$

using Stirling's approximation $\ln N! \approx N \ln N - N$

$$\Delta S_1 = k \ln W = kN \ln \frac{N}{N - N_A} + kN_A \ln \frac{N - N_A}{N_A}$$

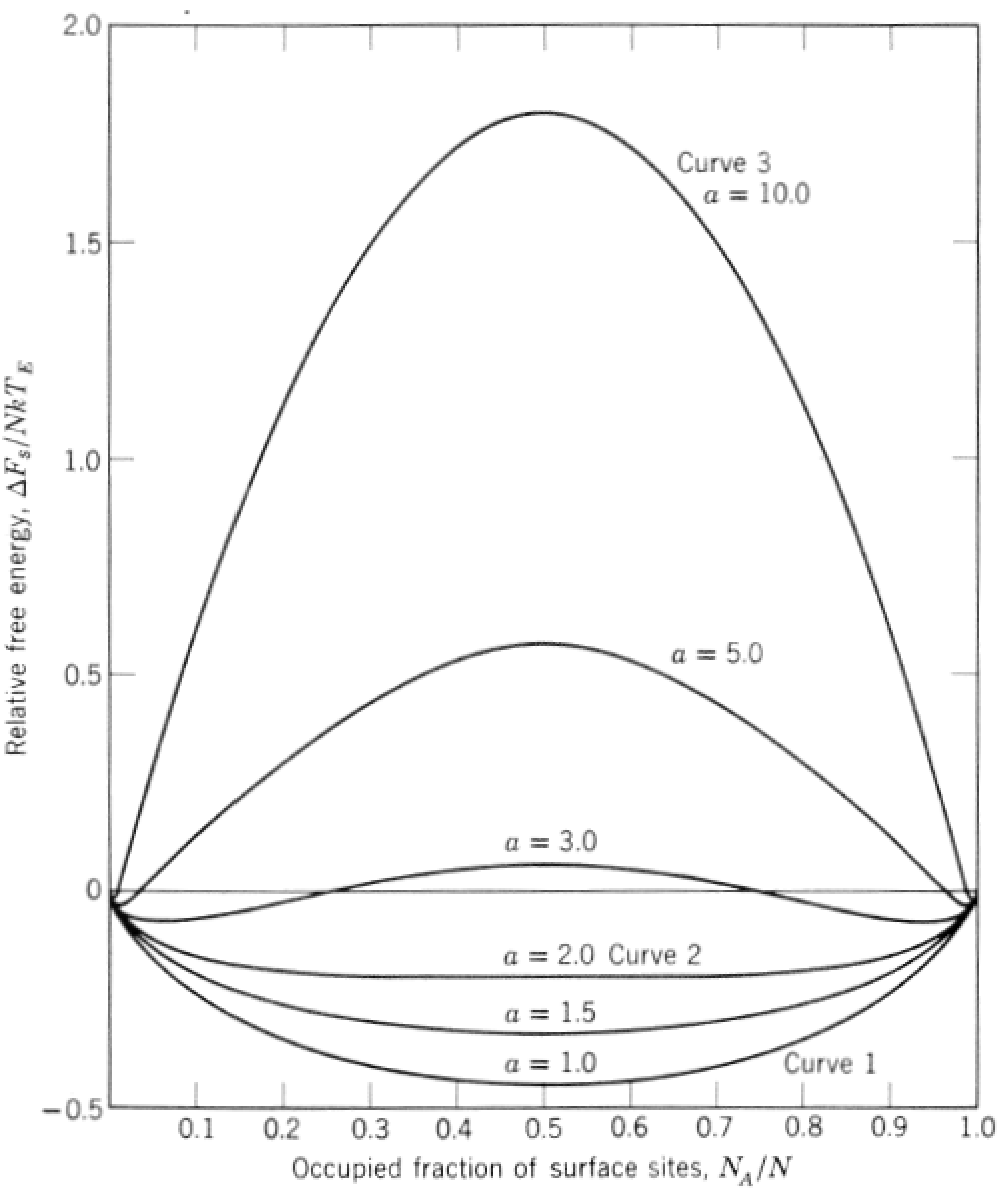
By using *L*= *L*$_0$ + k*T*$_E$ (*L*$_0$= heat of fusion, and L is the enthalpy of fusion)

Surface free energy

$$\frac{F_s}{NkT_E} = \frac{\alpha N_A(1 - N_A)}{N^2} - \ln N/(N - N_A) - \frac{N_A}{N} \ln \frac{N - N_A}{N_A}$$

where

$$\alpha = \left(\frac{L_0}{kT_E}\right)\left(\frac{\eta_1}{v}\right)$$



Variation of free energy of interface with fraction of sites filled.

(a) **Minimum of free E at $N_A/N=0.5$ for all values of α less than about 2**

→ **rough interface: stable**

→ **50 percent of the sites being filled**

→ **locally filled → multilayer**

(b) 2 minima of free E, one at very small value of N_A/N and the other for a value close to unity for all higher values

→ **very few sites are filled on a complete layer or almost all sites are filled.**

→ **smooth interface: stable**

*** Parameter α controls the structure of the equilibrium interface.**

a) L_0k/T_E~ depends on the material, the crystal structure, and on the nature of the adjoining phase

b) η_1/v~ depends on the face

L_0k/T_E ~ less than 2 for all metals, for equilibrium between melt and crystal: typically, 1.2

Since η_1/v ~ necessarily less than 0.5

α melt-crystal interface < α vaper-crystal interface

Ice: α of basal plane > 2/ but α of all other plane should be rough.

* Parameter α controls the structure of the equilibrium interface.

$$\frac{F_s}{NkT_E} + \frac{\alpha N_A(1 - N_A)}{N^2} - \ln N(N - N_A) - \frac{N_A}{N} \ln \frac{N - N_A}{N_A}$$

where

$$\alpha = \left(\frac{L_0}{kT_E}\right)\left(\frac{\eta_1}{v}\right)$$

a) L_0k/T_E~ depends on the material, the crystal structure, and on the nature of the adjoining phase

b) η_1/v~ depends on the face

v= # it would have in the interior of a crystal of the same structure

L_0k/T_E ~ less than 2 for all metals,
for equilibrium between melt and crystal:

typically, α= 1.2 since η_1/v ~ necessarily less than 0.5

α melt-crystal interface < α vaper-crystal interface

Ice: α of basal plane > 2 / but α of all other plane should be rough.

Cahn's approach for interface structure

Cahn

Interface may extend through a considerably large number of layers.

↔

Jackson

Only a single layer

Interface "degree of diffuseness of the interface"

"Step" between an atomic layer

"Sharp": incomplete superimposed layer

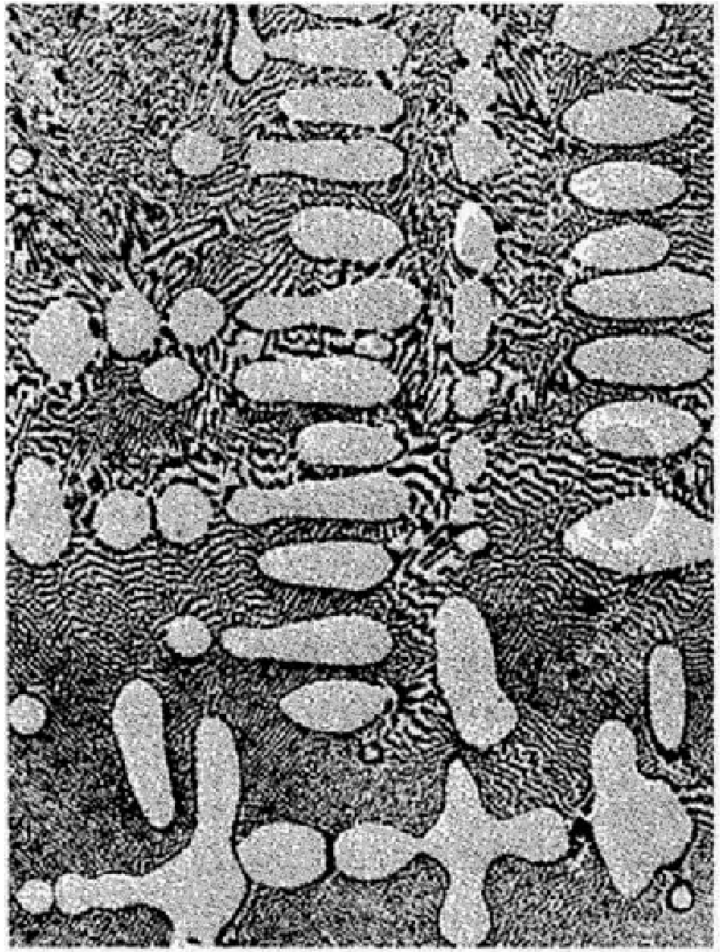
Growth → lateral propagation of step

Propagation of the interface normal to itself

Relatively low driving force ↔ Relatively high driving force

Critical driving force
depends on the diffuseness of the interface, being very large for a perfectly smooth interface, and decreasing as the roughness increases.

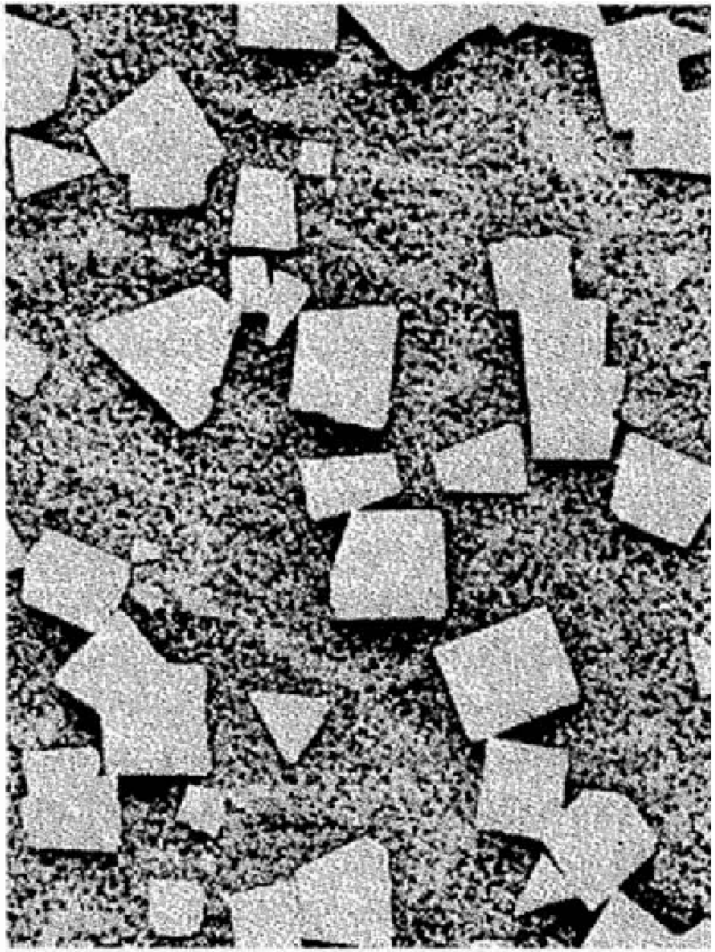
Primary Ag dendrite
in Cu-Ag eutectic matrix



(a) **Non-faceted**

- Free E ~do not vary with crystallographic orientation
- γ-plot ~ spherical

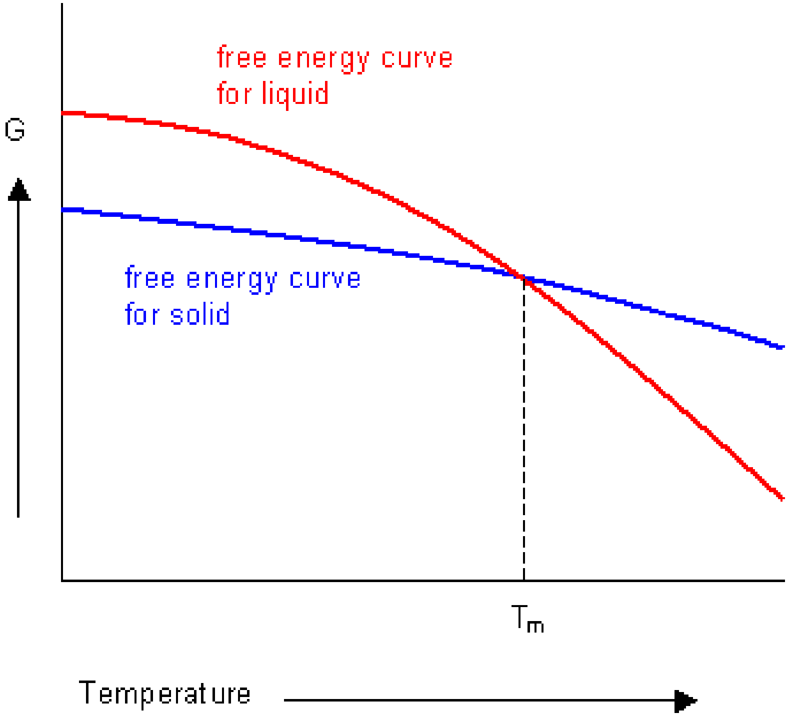
β′-SnSb intermetallic compound
in Sn(Sb) solid solution



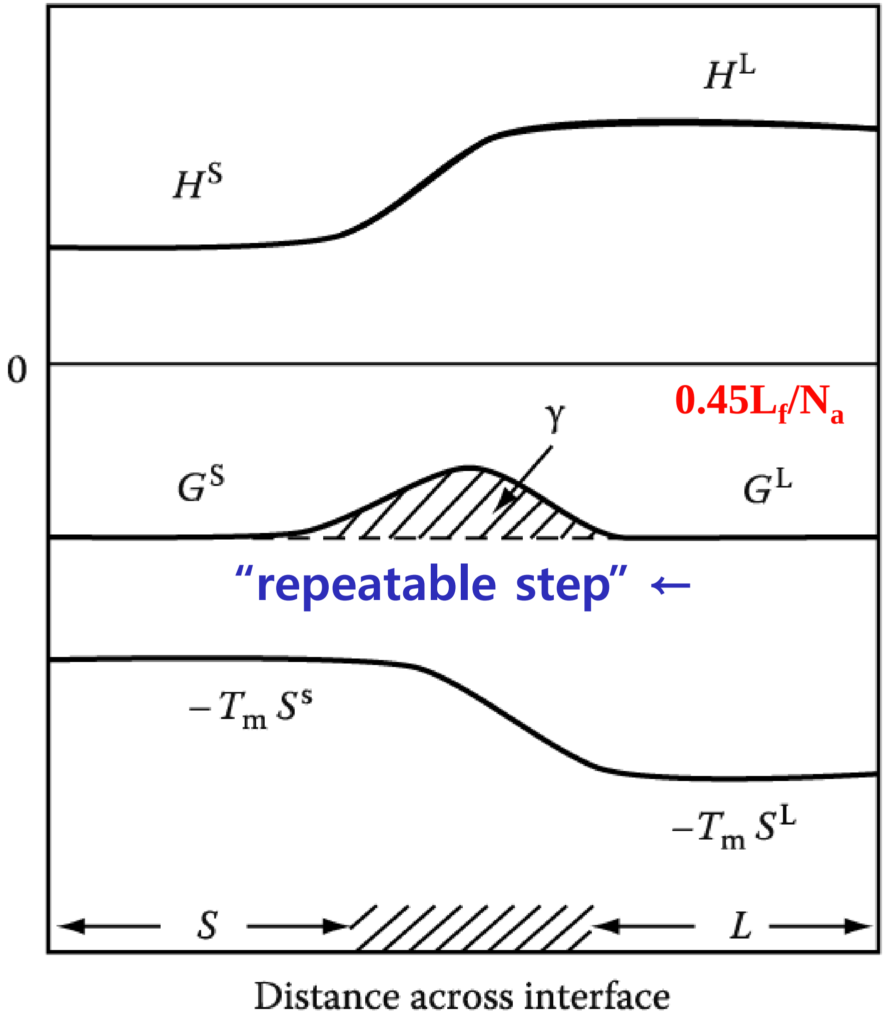
(b) **Faceted**

- Strong crystallographic effects
- Solidify with low-index close-packed facets

* Broken bond model → calculation of the E of solid/ liquid interface



at equilibrium melting temp.



$\gamma_{SL} \approx 0.45\ \gamma_b$ $(= 0.15\gamma_{SV})$
for the most metals

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

Showing the origin of the solid/ liquid interfacial energy, γ