COURSE NOTES

Materials' Defects & Disorders

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2024

Defects & Disorder in Mat. 4/1/2024.

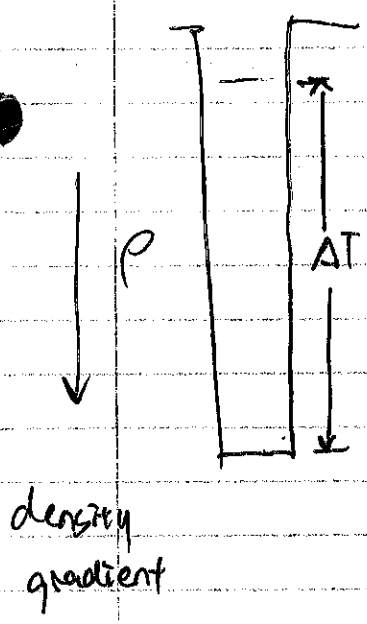
- point defects ~ new concept.

vacancies → color of salt changes

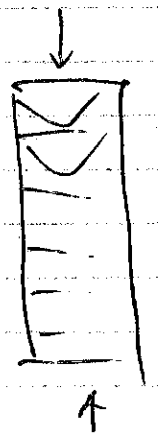
↳ thermo luminescence.

alkali halides.

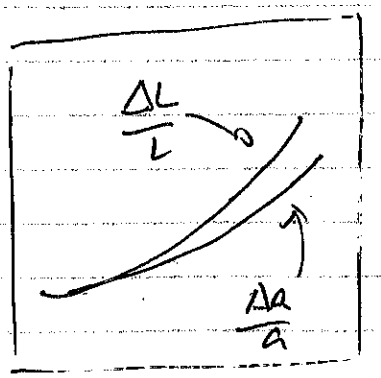
density measurement.



experiment measuring the point defect.



f(T).



↳ vacancy being created in crystals

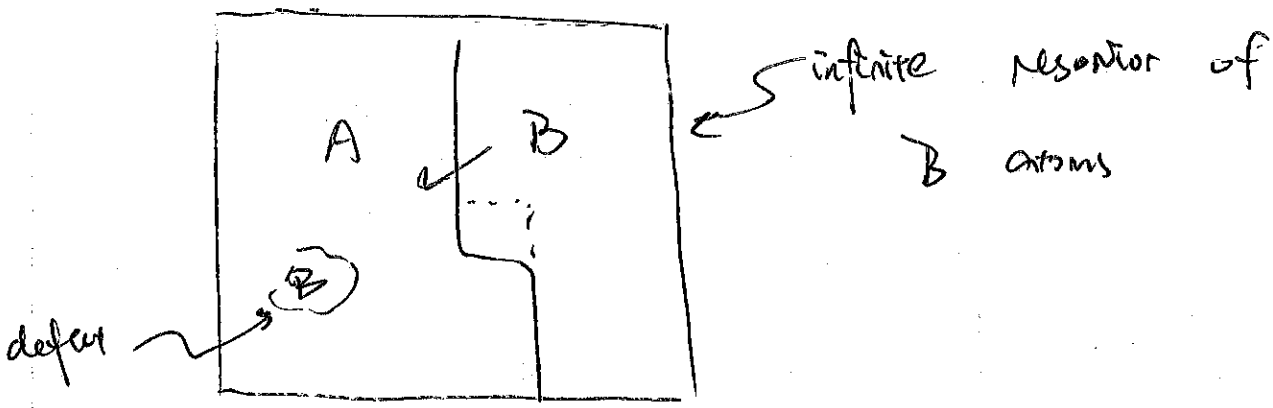
defects in metals & ionic materials

↑ charged state.

Equilibrium defects. → point defects.

Chap. 5 (Gri).

Equilibrium conc. of solutes



Fixed N_A, N_B atoms,

$$x_B = \frac{N_B}{N}, \quad x_A = \frac{N_A}{N}$$

N – total # of atoms

change of free energy:

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

ΔH – enthalpy

ΔS – entropy

$H = E + PV$. ← external pressure

$\Delta H = \Delta E + P_{ext.} \Delta V$

ΔE → change in internal energy → bond breaking, etc.

ΔV → work done against external pressure.

$\Delta E = x_B N \Delta e_f$ → formation energy of defect

↳ how many B atoms go into the A area

$\Delta e_f = \Delta e_{f\,bond} + \Delta e_{f\,strain}$

$\Delta e_{f\,bond}$ → different chemical bonds

$\Delta e_{f\,strain}$ → elastic strain energy

$\Delta e_{f\,bond}$.

coordination number

pulling A out

$$\left(\frac{Z}{2} \varepsilon_{AB} + \frac{Z}{2} \varepsilon_{AB} + \frac{Z}{2} \varepsilon_{AB} \right) - \left(Z \varepsilon_{AA} + \frac{Z}{2} \varepsilon_{BB} + \frac{Z}{2} \varepsilon_{AB} \right)$$

↑ forming the bond

↑ breaking the bond

$$= z\left(\varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}\right)$$

$$\Delta e_{\text{strain}} = \frac{\mu\,(\Delta v)}{2\pi r_0^3\left(1 + \frac{4\mu}{3B}\right)}$$

local vol mismatch

shear

atomic radius

Bulk

Pert. Δv

$$\Delta v = \chi_B N \Delta V_f$$

Δ formation

Ω_A at vol of A
Ω_B at vol of B

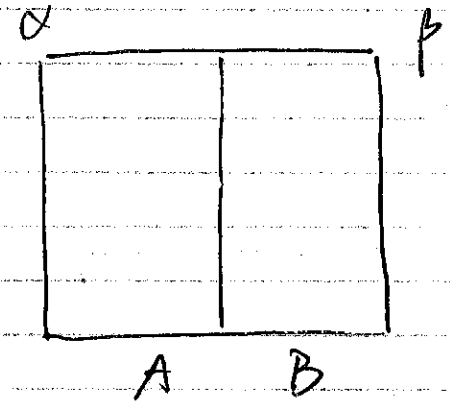
Ω_A^* at vol of A in B
Ω_B^* at vol of B in A

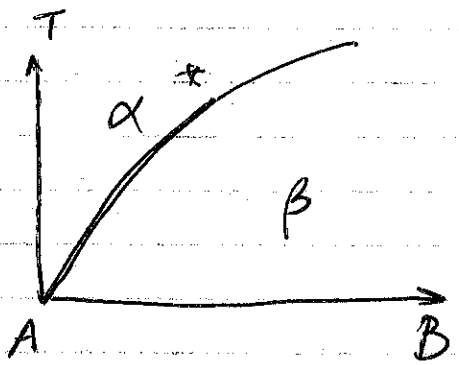
$$\Delta V_f = \Omega_B^* - \Omega_B$$

formation volume

lecture 2 4/3/2024

eql. concen. of solutes.





N_A N_B

$N = N_A + N_B$

$\chi_B = \frac{N_B}{N}$

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

$\Delta H \rightarrow \Delta E + P_{ext}\Delta V$

$\Delta E \rightarrow \Delta E_{bond} + \Delta E_{strain}$

$\Delta S = \Delta S_{config.} + \Delta S_{vibration}$

$\Delta S_{config} = -NK_B[\chi_B \ln \chi_B + (1-\chi_B)\ln(1-\chi_B)]$

↖ positive number

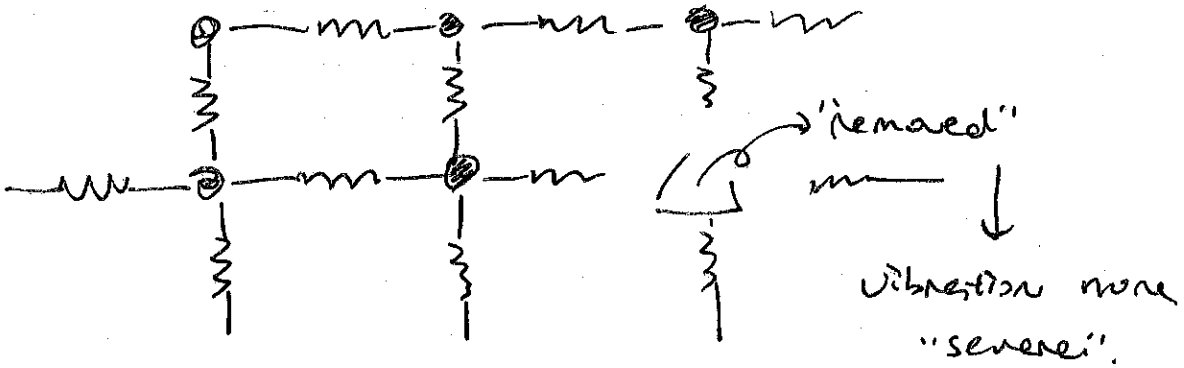
$\Delta S_{vib} = x_B N \Delta S_f$

↳ formation entropy.

ΔV: formation volume

$\Delta E_{bond} + \Delta E_{strain}$: formation energy.

in 2D. "harmonic oscillator".



the vibrational features for the surrounding atoms are different around the subs. atom.

$$\Delta G = \underbrace{x_B N (\Delta e_f + P_{ext} \Delta V_f - T \Delta S_f)}_{\text{enthalpic contribution}} + \underbrace{N k_B T (x_B \ln x_B + (1 - x_B) \ln (1 - x_B))}_{\text{entropic contribution}}$$

ΔG ↪ free energy change for having N_B atoms into A.

$$= N_B(\Delta e_f + P_{ext}\Delta V_f - T\Delta S_f)$$

$$+ k_B T\left[N_B \ln\left(\frac{N_B}{N_A+N_B}\right) + N_A \ln\left(\frac{N_A}{N_A+N_B}\right)\right]$$

find minimum.

$$\frac{\partial \Delta G}{\partial N_B} = 0 \quad = (\Delta e_f + P_{ext}\Delta V_f - T\Delta S_f)$$

$$+ k_B T \ln(x_B) = 0$$

$$x_B = \exp\left(\frac{-(\Delta e_f + P_{ext}\Delta V_f - T\Delta S_f)}{k_B T}\right)$$

~ Qi & Nix, Ch. 5.

Let 'B' be a vacancy.

$$x_V = \exp\left(\frac{\Delta S_V}{k_B}\right)\exp\left(\frac{-[\Delta e_V + P_{ext}\Delta V_f]}{k_B T}\right)$$

Δe_V = formation energy of vacancy.

[eV]

$1.6 \times 10^{-19}\,J = 1\,eV$

↪ Vacancy energy.

surface energy → γ 1 J/m²

0.3 nm

$1eV \approx 6\, a^2\, \gamma$ ← $1\ J/m^2$

ΔV_f = formation volume of vacancy.

$\Delta V_f = \Omega_B^* - \Omega_B$

$\simeq 0.5 - 0.7\, \Omega_A$

ΔS_f = formation entropy.

$\sim 2 - 8\ k_B$.

P_{ext} ← 1 atm T ← room temperature

$\chi_V(T = 300k) = 10^{-16}$

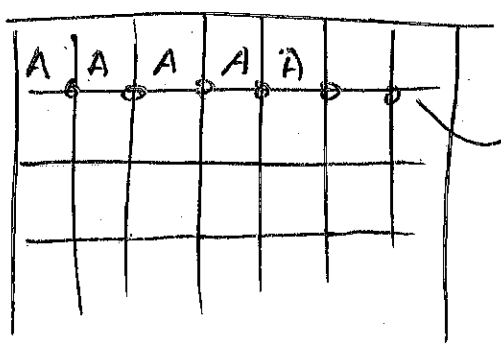
χ → vacancy calculation

10^{22} atom / cm^3

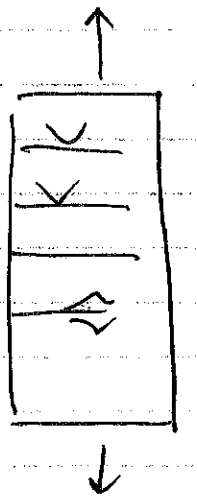
Interstitials

$$\chi_i = \frac{1}{1 + \exp\left[\frac{\Delta e_f + P_{ext}\,\Delta V_f - T\Delta S_f}{k_B T}\right]}$$

↖ FM class



↳ admissible interstitial vacancy sites.



- volume will increase

- lattice constant decrease

↑ because ele surrounding crystals will "collapse".

at a given temp.

$$\frac{\Delta V}{V} = 3\left(\frac{\Delta L}{L}\right) = \chi_v + \beta\chi_v$$

(negative "shrinking")

dilatometer to measure

addition of atoms to surface

$$3\left(\frac{\Delta a}{a}\right) = \beta\chi_v$$

X-ray deflection

$$\chi_v = 3\left(\frac{\Delta L}{L}\right) - 3\left(\frac{\Delta a}{a}\right)$$

↳ abs. value of vacancy

what's a positron?

↓

dies faster in more defected materials

→ Review.

▶ Equilibrium concentration of solutes

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

$\Delta H \approx \Delta E + P_{atm}\Delta V$.

$\Delta E = \alpha N \Delta e_f$

$\Delta e_f = \Delta e_f^{bond} + \Delta e_f^{strain}$.

$\Delta e_f^{bond} = \frac{1}{2}\sum z$

"Interaction Energy"

$\Delta e_f^{strain} = \frac{\mu(\Delta V)^2}{2\pi r_0^3\left(1+\frac{4\mu}{3B}\right)}$

$\Delta V = \chi N \Delta V_f$.

↳ $\Delta V_f = \Omega_B^* - \Omega_{B_0}$.

$\Delta S = \Delta S_{config} + \Delta S_{vib}$

$$\Delta S_{config} = -N k_B [x \ln x + (1-x)\ln(1-x)]$$

$$\Delta S_{vib} = N_v \Delta S_f = x N \Delta S_f$$

$$x = \exp\left(-\frac{\Delta g_f}{k_B T}\right)$$

$$\Delta h_f = \Delta e_f + P_{ext} \Delta v_f$$

$$\Delta g_f = \Delta h_f - T\Delta S_f$$

final derived form:

Equilibrium concentration of vacancy

$$\Delta G = N_v (\Delta e_v + P_{ext} \Delta v_v - T\Delta S_v) + k_B T \left[N_v \ln \frac{N_v}{N_A + N_v} + N_A \ln \frac{N_A}{N_A + N_v}\right]$$

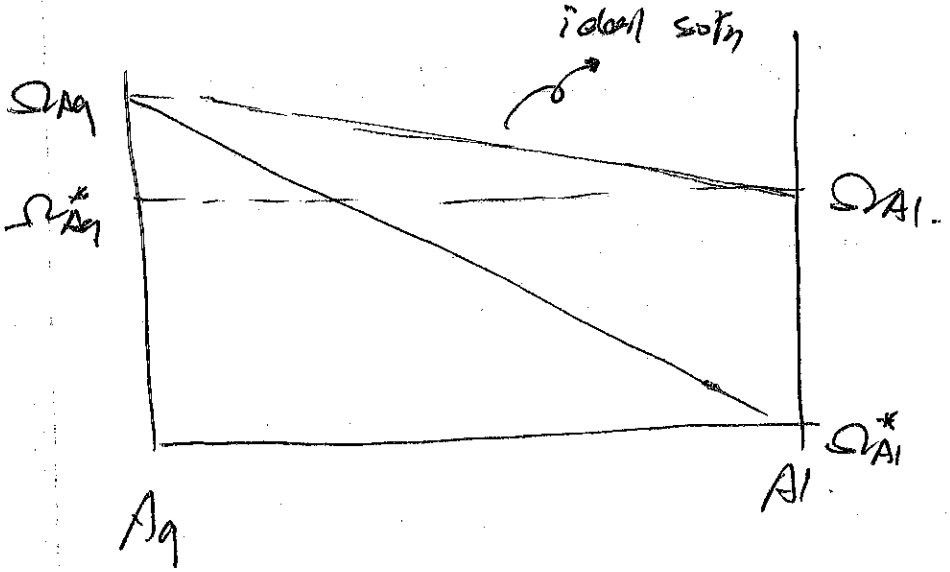
Solved equilibrium vacancy fraction.

$$x_v = \frac{N_v}{N_A + N_v} = \exp\left(-\frac{g_v}{k_B T}\right)$$

...

$$= \exp\left(\frac{\Delta S_v}{k_B}\right) \exp\left(-\frac{\Delta e_v + P_{ext} \Delta v_v}{k_B T}\right)$$

Lecture 3.



Increase pressure, will solubility change?

$$\chi_B \propto \exp\left(-\frac{P_{ext}\,\Delta V}{k_B T}\right)$$

$\Omega^*_{Al} - \Omega_{Al}$ → negative

↓

solubility increase

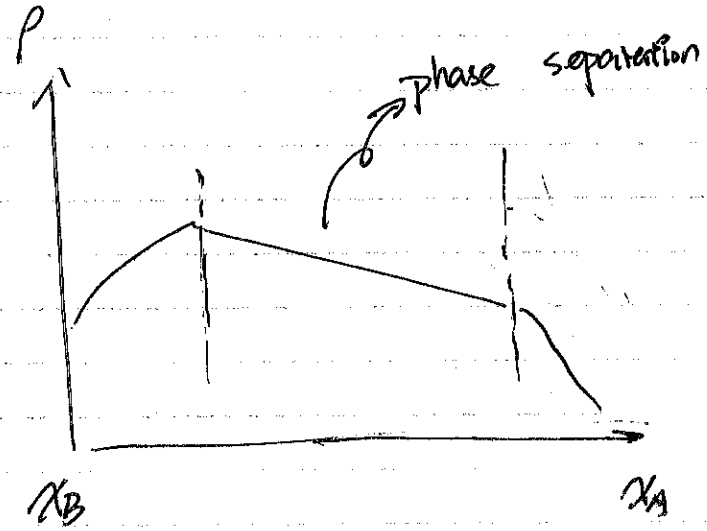
vacancies → less vacancy.

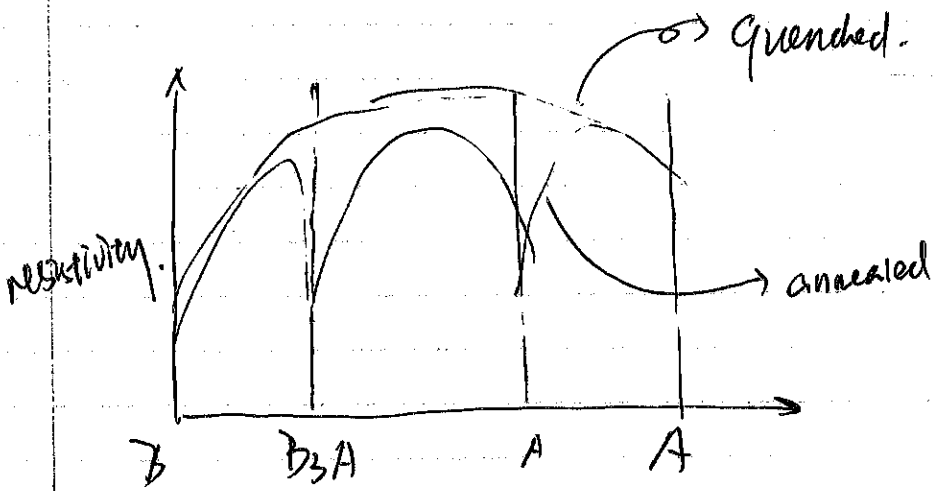
→ i.e., pressure ↑ vacancy ↓

P_{ext} $10^5\ N/m^2 \times 10^{-30}\ m^3$

$= 10^{-25}\ J \simeq 10^{-6}\ eV$

$1eV$ → bond breaking.





↳ intermetallics.

$$\varepsilon_{AB} - \left(\frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}\right) = 0$$

↳ if zero, no preference between A/B

↓

non-interacting soln.

↓

ideal soln.

χ_v^2

$\exp\left(\frac{2\Delta S_v}{k}\right) \exp\left(-\frac{2\Delta e_v}{kT}\right)$

$\exp\left(-\frac{+ 2 P_{ext} \Delta V}{kT}\right)$

Divacancies.

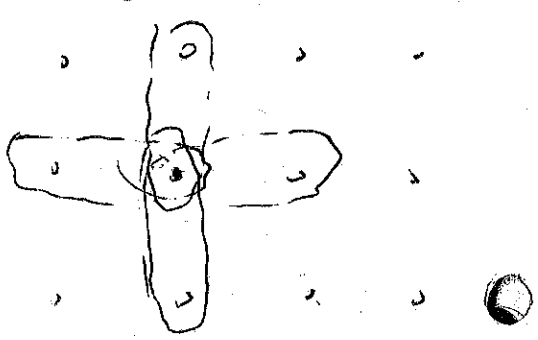
$$\chi_{1v} = \exp\left(-\frac{\Delta g_v}{k_B T}\right)$$

$$\chi_{2v} = \exp\left(-\frac{\Delta g_{2v}}{kT}\right)$$

$$\chi_{2v} = \frac{n_{2v}}{N_{2v}^{sites}}$$

coord. #

N_{sites}, z (4)



$$N_{2v}^{sites} = N z / 2$$

# of sites of crystal

$$n_{2v} = N z/2 \exp\left(\frac{\Delta S_{2v}}{k}\right) \exp\left(-\frac{\Delta e_{2v}}{kT}\right) \exp\left(-\frac{P_{ext} \Delta V_{2v}}{kT}\right)$$

Monovacancy

$\Delta V_{2v} = 2\Delta V_v$.

$\Delta S_{2v} = 2\Delta S_v$ ← negative number

$\Delta e_{2v} = 2\Delta e_v + \Delta e_{bind}$

$$n_{2v} = \frac{N z}{2} \exp\left(\frac{2\Delta S_v}{k}\right) \exp\left(\frac{-(2 e_v + \Delta e_{bind})}{kT}\right)$$

$$\exp\left(\frac{-2 P_{ext} \Delta V}{kT}\right).$$

$$n_{2V} = \frac{N_2}{2} \chi_V \exp\left(-\frac{\Delta e_{bind}}{kT}\right)$$

$$\chi_{2V} = \chi_0^2 \exp\left(-\frac{\Delta e_{bind}}{kT}\right) \rightarrow \text{negative}$$

10^{-6} ↑ 10^{-3}

$$V + V \rightleftharpoons 2V \quad K_{eq}$$

chem. molarity: $\frac{[2V]}{[V]^2} = K_{eq} = \text{const.}$

$$[2V] = [V] \times K_{eq}$$

$$G = U + PV - TS.$$

$$dG = dU + P\,dV + V\,dP - T\,dS - S\,dT.$$

$$dU = T\,dS - P\,dV.$$

$$dG = V\,dP - S\,dT.$$

n moles of ideal gas.

const T.

$$dG = V\,dP$$

(ideal gas) $PV = nRT$.

$$dG_T = nRT\, dP / P.$$

Integrate both sides:

$$\int_{G_0}^{G} dG_T = \int_{P_0}^{P} nRT \frac{dP}{P}$$

$$G - G_0 = nRT \left(\frac{P}{P_0}\right)$$

from some 0 to current state

$$\mu = \mu_0 = RT \left(\frac{P}{P_0}\right) \leftarrow \frac{dG_T}{dn}$$

μ_0: standard state

$\frac{dG_T}{dn}$: change no. of moles.

if $P_0 = 1$ atm.

$$\mu = \mu_0 + RT \ln\left(\frac{P}{P_{0=1\,atm}}\right) = \mu_0 + RT \ln(a).$$

a: activity

Lecture 4 4/10/2024

Recap: $\mu = \mu_0 + RT \ln\left(\frac{P}{P_0}\right)$ ← 1 atm.

$\mu_0 + RT \ln(a)$

"standard state".

↳ leads to defect reactions & derivations

$aA + bB \rightleftharpoons cC + dD$.

$\Delta G = c\mu_c + d\mu_d - (a\mu_a + b\mu_b)$

$\Delta G = \Delta G^\circ + RT \ln\left[\frac{a_C^c \, a_D^d}{a_A^a \, a_B^b}\right] = 0$

equilibrium const.

$\Delta G^\circ = -RT \ln K$

... defects

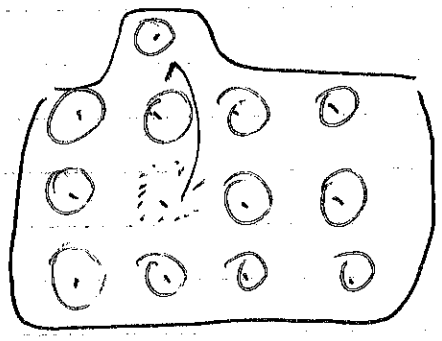
$K = \exp\left(\frac{\Delta S^\circ}{R}\right) \exp\left(\frac{-\Delta H^\circ}{RT}\right)$

Vacancy formation.

$A_A \rightleftharpoons V_A + A_A$

↓ 1950s

apply for defects



let the activity of defects in crystals be "molar site fraction". ↳ between 0 ~ 1

small ↖ a_V a_A → 0.99...

$$K = \frac{a_V a_A}{a_A} = \frac{[V]}{[A]}$$

↳ equilibrium constant.

$$\Rightarrow = \frac{\frac{[V_A]}{[A]} \cdot \frac{[A_A]}{[A]}}{\frac{[A_A]}{[A]}} = [V_A] \simeq K$$

$$[V_A] = \exp\left(\frac{\Delta S^\circ}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right)$$

ΔS°: formation entropy

ΔH: E + PV. formation enthalpy.

Explaining notation A_A.

Kroger - Vink relation.

main symbol ↳ A^{c}_{s}

c ← charge

s ← site, chemical symbol of normal occupancy of site

vacancy.

V_O

Effective charge = Real charge of the isolated defects.

– Real charge of the sites in a perfect crystal.

$Zn^{2+}\ O^{2-}$.

↳ fully ionic.

2+	2−	2+	2−	2+	= 2+
Zn	O	Zn	O	Zn	

0 − (−2).

↓

$V_O^{\cdot\cdot}$

(vacancy.

x ← 0

/ ← negative

• ← positive

Zr ion vacancy in ZrO_2 → $V_{Zr}^{''''}$

4+	2−	2−	4+	
$Zr^{\cdot}$	O	O	Zr	....

$-(+4) = -4$

lithium ion interstitial

$Li_I^{\bullet}$

electrons

e' .... free elec.

free holes. $h^{\bullet}$ > not giving us any sites

Y in ZrO_2

↑

Y_2O_3 ↗ substitute Zr

↓

Y'_{Zr} [+3] - [+4]

P in Si ... TBD

Al. Si P

P'_{Si}

✡ covalency makes this confusing

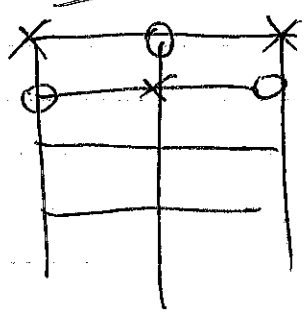
- Frenkel reaction
- Schottky reaction ~1930s

→ Schottky defect. MO.

$$M_M^{\times} + O_O^{\times} \rightleftharpoons V_M'' + V_O^{\cdot\cdot} + M_M^{\times} + O_O^{\times}$$

reactants → products

1. Mass balance
2. Site balance ← only for crystal?
3. Charge neutrality



→ Equation simplified to:

$$\text{null} \rightleftharpoons V_M'' + V_O^{\cdot\cdot} \quad (K_s \text{ eq const.})$$

$$K_s = a_{V_O^{\cdot\cdot}} \cdots a_{V_M''}$$

$$K_s = \frac{[V_O^{\cdot\cdot}]}{[O]} \cdot \frac{[V_M'']}{[M]}$$

$[O]$ → 1, $[M]$ → 1

$$K_s = [V_O^{\cdot\cdot}][V_M'']$$

↓ (1)

$$2 \times [V_O^{\cdot\cdot}] = 2 \times [V_M''] \rightarrow (2)$$

positive charges. negative charges

$$[V_O^{\cdot\cdot}] = [V_M''] = \sqrt{K_s}$$

↳ equilibrium constant.

⇓

is temperature-dependent.

$$= \exp\left(-\frac{\Delta G_s^\circ}{2RT}\right)$$

↓

came from the square.

e^-

$h^\cdot$

n p → np = const.

$[e'] = [h^\cdot]$

$$= \exp\left(\frac{-\Delta h^\cdot}{2kT}\right)$$

$$null \rightleftharpoons e' + h^\cdot$$

$$k_r[e'] = [h^\cdot]$$

$$[e'] \cdot [h^\cdot] = k$$

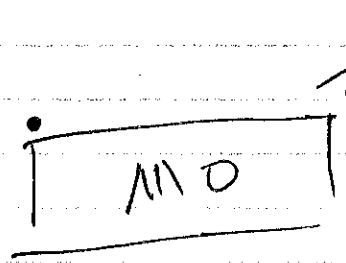
$$[e'] = [h^\cdot] = \sqrt{k}$$

"chemical reaction"

$$\frac{np}{N_c N_v} = \exp\left(-\frac{E_g}{kT}\right)$$

effective density of states

2 holes. ($+2h^{\cdot}$) — from site balance ($+V_M''$)



$\frac{1}{2}O_2(g) \rightleftharpoons O_O^{\times}$ charge element

"crystal talkin to atmosphere"

→ { mass balance ✓ / charge neu. ✓

$$K = \frac{[h^{\cdot}]^2 \frac{[V_M'']}{[M]} \cdot \frac{[O_O^{\times}]}{[O]}}{P_{O_2}^{1/2}}$$

P_{O_2} ← experimentally set partial pressure

$$2[V_M''] = 1 \times [h^{\cdot}]$$

MooMooMoo[]oo

Example: $M^{+II}O_2 \rightleftharpoons O_2$

$$O_{2(g)} \rightleftharpoons 2O_O^{\times} + V_M''' + 4h^{\cdot}$$

defn of chemical potentials.

$$\mu_i' = \left.\frac{\partial G}{\partial n_i}\right|_{\substack{T,P \\ n_{j\neq i}}}$$

↖ cannot do experiments in metals

Questions

$$dG = dU - TdS + PdV \ldots$$

$+ \mu e N$

↖ Fermi's level effect.

↖ variables that control the free energy

can change the point defect formation energy.

P_{Si}^{x} → Q2 all covalent bond ...?

↓ some equilibrium const.

↳ $P_{Si}^{\cdot} + e'$ ← anti-dope

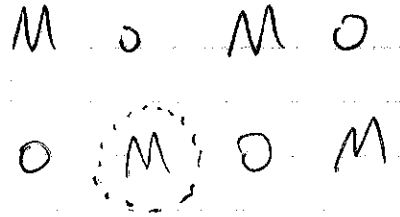
Q3: theory only for ionic bond?

4/15/2024 Lecture 5

Frenkel Defect in $M^{2+} O^{2-}$

AgBr $\quad M_M^{\times} + V_i^{\times} \rightleftharpoons M_i^{\cdot\cdot} + V_M''$

$$K_F = \frac{a_{M_i^{\cdot\cdot}} \, a_{V_M''}}{a_{M_M^{\times}} \, a_{V_i^{\times}}}$$



$$\frac{\dfrac{[M_i^{\cdot\cdot}]}{[i]=1} \; \dfrac{[V_M'']}{[M]=1}}{\dfrac{[M_M^{\times}]\approx 1}{[M]=1} \; \dfrac{[V_i^{\times}]\approx 1}{[i]=1}}$$

$$K_F = [M_i^{\cdot\cdot}][V_M''] \quad (1)$$

$$2[M_i^{\cdot\cdot}] = 2[V_M''] \quad (2)$$

Q4: why? do not agree w/ Thayer in books

Frenkel defects come in pairs

→ ZnO example

reduce O partial pressure

↳ O → go to ambient.

... create O vacancy, create electron.

↳ Q:

accelerate electron diffusion.

↳ metals with defect diffusion

metals w/ many defects.

Electrolyte oxygen: oxygen sufficient.

hydrogen make with ions can be used for diffusion,

→ lithium ones do not use point defect

↳ battery: amorphous.

→ Oxygen deficient oxide.

(think TCO, fuel cell electrolyte)

conductor

$$O_O^x + M_M^x \rightleftharpoons V_O + M_M^x + 2e' + \tfrac{1}{2} O_2(g).$$

Oxygen evolution process.

$$K_{V_O} = \frac{[V_O^{\cdot\cdot}]\, n^2 P_{O_2}^{1/2}}{[O_O^x \approx 1]}$$

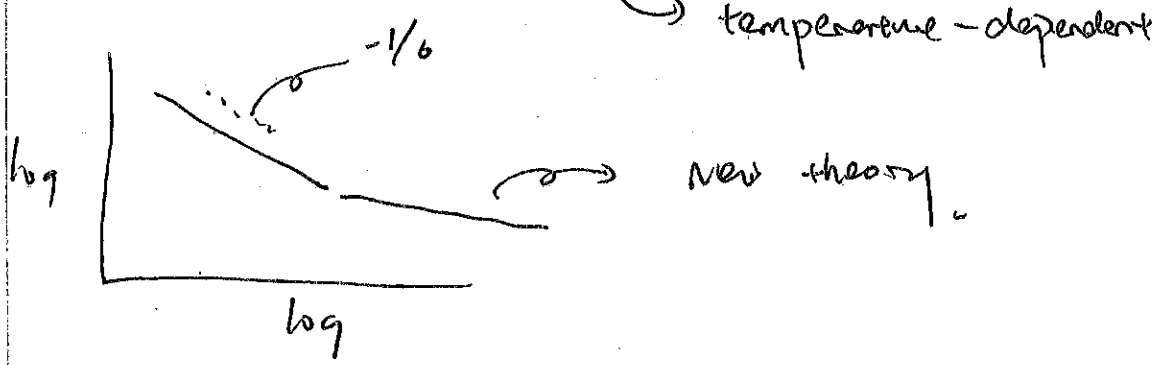
$$n = 2[V_O^{\cdot\cdot}]$$

↳ from $2e'$ on RHS.

$$\frac{n^3}{2} P_{O_2}^{1/2} = K V_O \quad (\text{const.})$$

$$n = (2K_6) P_{O_2}^{-1/6}.$$

↳ temperature-dependent



$$M_M^x + e' = M_M'$$

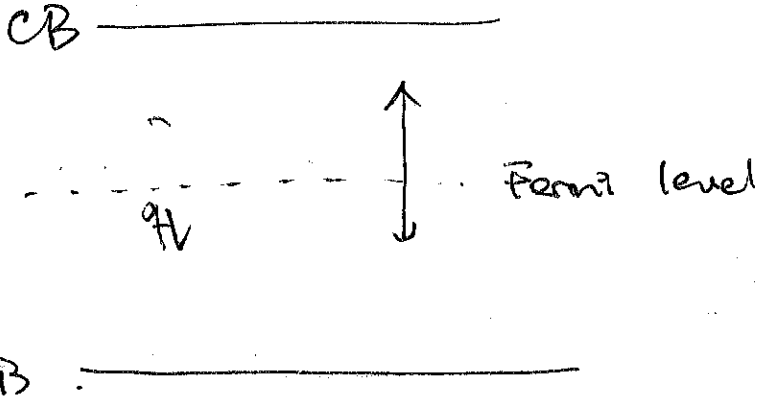
Electrons get localized

$$\rightarrow O_O^x + 2M_M^x \rightleftharpoons V_O'' + 2M_M' + \frac{1}{2}O_2(g)$$

(charging valence state)

insulator

... How to tell whether $2e^-$ on the RHS



$$O_O^x \rightleftharpoons V_O^x + \frac{1}{2}O_2(g).$$

$$K_{V_{ox}} = \frac{[V_O^x]\, P_{O_2}^{1/2}}{[O_O^x]} \quad \ldots (3)$$

if equation is possible

then $K_{V_{ox}}$ is the equilibrium const.

$$V_O^x \rightleftharpoons V_O^{\cdot} + e' \qquad (c) \rightarrow (b)$$

$$K_{VO_1} = \frac{[V_O^{\cdot}]\, n}{[V_O^x]} \quad \cdots (1)$$

we are allowed to formulate such formulae, need to define with the balanced charge.

$$V_O^{\cdot} \rightleftharpoons V_O^{\cdot\cdot} + e'$$

$$K_{VO_2} = \frac{[V_O^{\cdot\cdot}]\, n}{[V_O^{\cdot}]} \qquad (b) \rightarrow (a) \quad \cdots (1)$$

Electroneutrality.

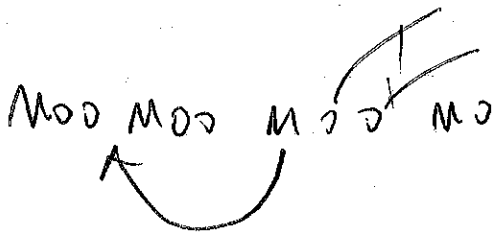
$$n = [V_O^{\cdot}] + 2[V_O^{\cdot\cdot}] \quad \cdots (4)$$

V_O^x, $V_O^{\cdot}$, $V_O^{\cdot\cdot}$, ~~O_i''~~ too few

~~n~~ Q: ... what are the four variables?

Oxygen leaves the crystal. but no oxygen vacancies created

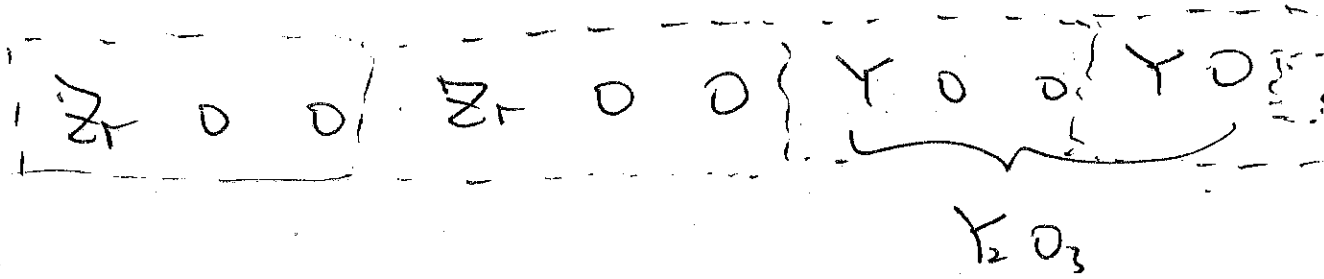
Start with an oxygen-excess crystal.



... Q: why no oxygen vacancy?

ZrO_2

Y_2O_3 in $Zr^{4+}O_2$



Next class: substitutional defect

lecture 6 6/17/2024

Tilley Sn. 7.4

Nonstoichiometric crystal MO

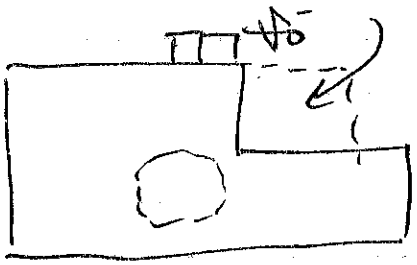
→ Assume only vacancies.

(# formation energy too high to form interstitials in metal.

V_M'' , $V_O^{\cdot\cdot}$

always present use e' and $h^{\cdot}$.

① Schottky defect equilibrium.



$\frac{1}{2} O_2(g)$

$$null \rightleftharpoons V_M'' + V_O^{\cdot\cdot}$$

$$K_S = [V_M''][V_O^{\cdot\cdot}]$$

② Electronic defect equilibrium

$$null \rightleftharpoons e' + h^{\cdot}$$

$$[e'][h^{\cdot}] = K_e$$ ← band gap for semiconductor

3. Oxidation.

$$\frac{1}{2}O_2(g) \rightleftharpoons O_O^x + V_M'' + 2h^\cdot$$

$$K_O = \frac{[V_M''][h^\cdot]^2}{P_{O_2}^{1/2}}$$

4. Reduction.

$$O_O^x \rightleftharpoons \frac{1}{2}O_2(g) + V_O^{\cdot\cdot} + 2e'$$

$$K_R = [V_O^{\cdot\cdot}][e']^2 P_{O_2}^{1/2}$$

$$\boxed{K_1 = \frac{K_S K_e^2}{K_O}}$$

→ "One of the 4 eqns is redundant!"

$2[V_O^{\cdot\cdot}] = [e']$

5. Electro-neutrality (order of mag. larger; "ignored")

$$2[V_M''] + [e'] = 2[V_O^{\cdot\cdot}] + [h^{\cdot}] \quad \cdots (*)$$

mixed ionic elec. mat.

most ionic

Brouwer diagrams

from experiments

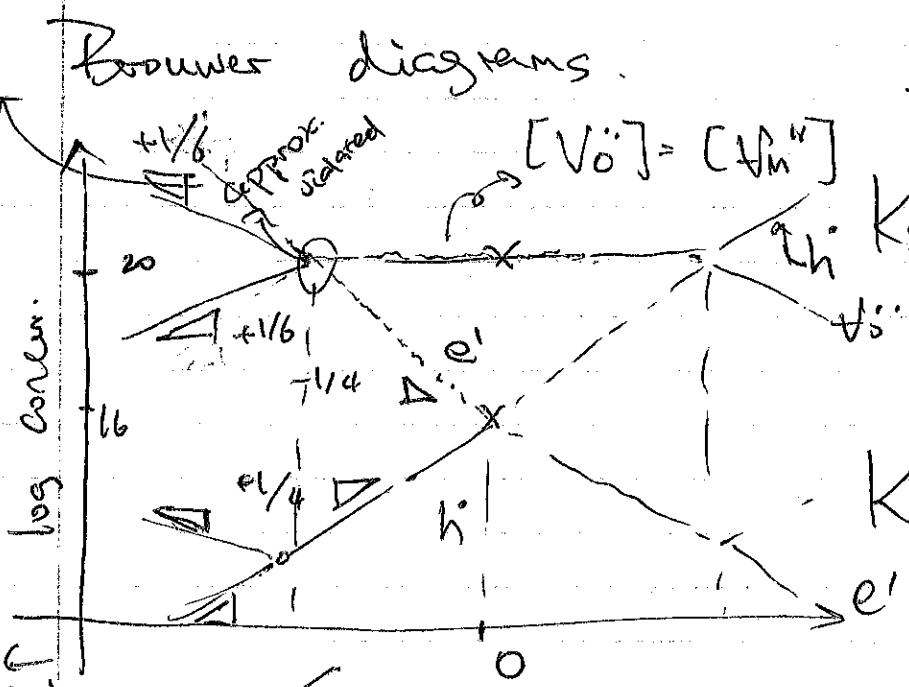
$[V_O^{\cdot\cdot}] = [V_M'']$

$K_S = [V_M''][V_O^{\cdot\cdot}]$

10^{40} defects^2/m^6

$K_e = [e'][h^{\cdot}]$

10^{32} defects^2/m^6



Material behaves conductive

at 1 atm: $M_{1.000\ldots}\ O_{1.000\ldots}$

$[V_M''] = [V_O^{\cdot\cdot}] = 10^{20}$ defects/m^3

$[e'] = [h^{\cdot}] = 10^{16}$ defects/m^3

Eqn (*): approximation:

$2[V_M''] = 2[V_O^{\cdot\cdot}]$

$[e'] = K_n^{1/2} K_S^{-1/4} P_{O_2}^{-1/4}$

$$[h^{\cdot}] = K_O^{1/2} K_S^{-1/4} P_{O_2}^{+1/4}$$

Rewrite the new electro-neutrality.

$$2[V_O^{\cdot\cdot}] = [e']$$

$$[e'] = (2K_R)^{1/3} P_{O_2}^{-1/6}$$

$$[h^{\cdot}] = \underline{\qquad} P_{O_2}^{+1/6}$$

$$[V_M''] \quad \underline{2K_S (2K_R)^{-1/3}} P_{O_2}^{+1/6}$$

Ionic doping.

Zr^{4+} Zr_1O_2 add Y^{3+} Y_2O_3

Y_{Zr}'

$$Y_2O_3 \xrightarrow{Zr O_2} 2Y_{Zr}' + 3O_O^X + V_O^{\cdot\cdot}$$

Great for electrolytes

Site balance

YSZ
ScSZ

(dopant) (host) transluscent

$2SnO_2 \xrightarrow{In_2O_3} 2Sn_{In}^{\cdot} + O_i''$

$+3O_o^x$

ITO

$InO\ In_{In}\ O_O\ Sn_{In}\ O$

$Sn_{In}\ O_O$

made under reducing conditions.

$O_i'' \rightarrow \frac{1}{2}O_{2(g)} + V_i + 2e^-$

∴ transparent conducting oxide

ITO
CdTe

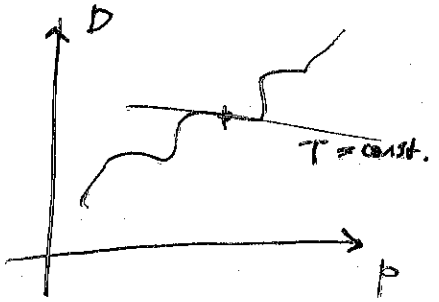
IGZO

* Mobility
* Carrier concentration

HW#1

Pb.#4

$$V = \left(\frac{\partial \Delta G_V}{\partial P}\right)_{T} \quad \sim 0.5 - 0.7$$

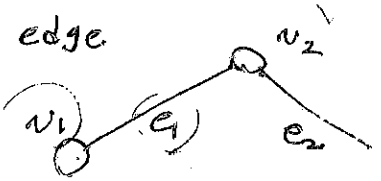


(a) $\partial D / \partial(\Delta G_V) \cdot \partial(\Delta G_V)/\partial P = \partial D/\partial P$

$\Rightarrow \dfrac{\partial D}{\partial(\Delta G_V)} \cdot V_{eff}\Big|_{T=const.} = \dfrac{\partial D}{\partial P}$

(V_{eff} (formation volume) $\parallel$ coeff. vs hyd. press.

$\partial D/\partial(\Delta G_V)$ ↓ (rate, migration, vacancy)



v (v) v

v

$r = (v) \exp(-\beta \cdot E)$

exp

$$V = \frac{P}{e^{\frac{\Delta G_V}{RT}} e^{-\frac{\Delta G_m}{RT}}}$$

$$= \frac{P}{e^{-\frac{\int V dP}{RT}} e^{-\frac{\Delta G_m}{RT}}}$$

$V \downarrow$

Lecture 7 4/22/2014.

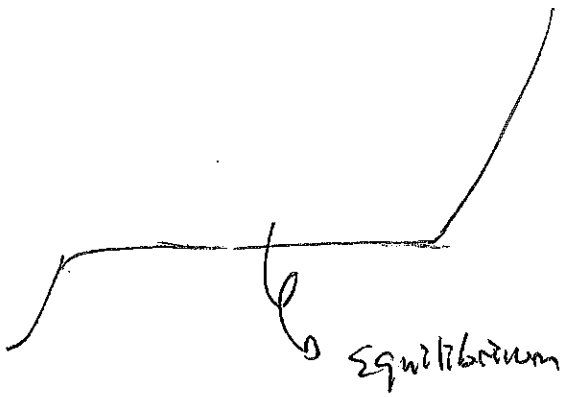
$[Ti_{Ti}^{\times}] = 4[V_O^{\cdot\cdot}]$ ← Site molar fraction

$\partial[V_O^{\cdot\cdot}]$

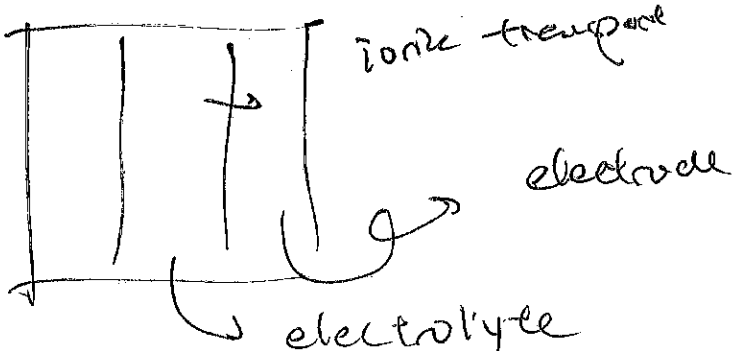
ionic "doping" by substitutional defects.

$P_{Si}^{\times} = P_{Si}^{\cdot} + e'$ ← electronic doping

$B_{Si}^{\times} = B_{Si}^{'} + h^{\cdot}$



Same number of carriers



n-type (electrons)

p-type (holes)

——— $\frac{1}{10}$" Re^- ↗

electrons cancelling out the holes

↓

compensation

$Li^{1+}Co^{3+}O_2$ we want more electrically conductive

B ← Si

make Si p-type

$LiCoO_2 \rightarrow LiMg_{0.05}Co_{0.95}O_2$

Battery materials: { NMC
LFP.

$dG = dU - TdS + PdV$ ... ③

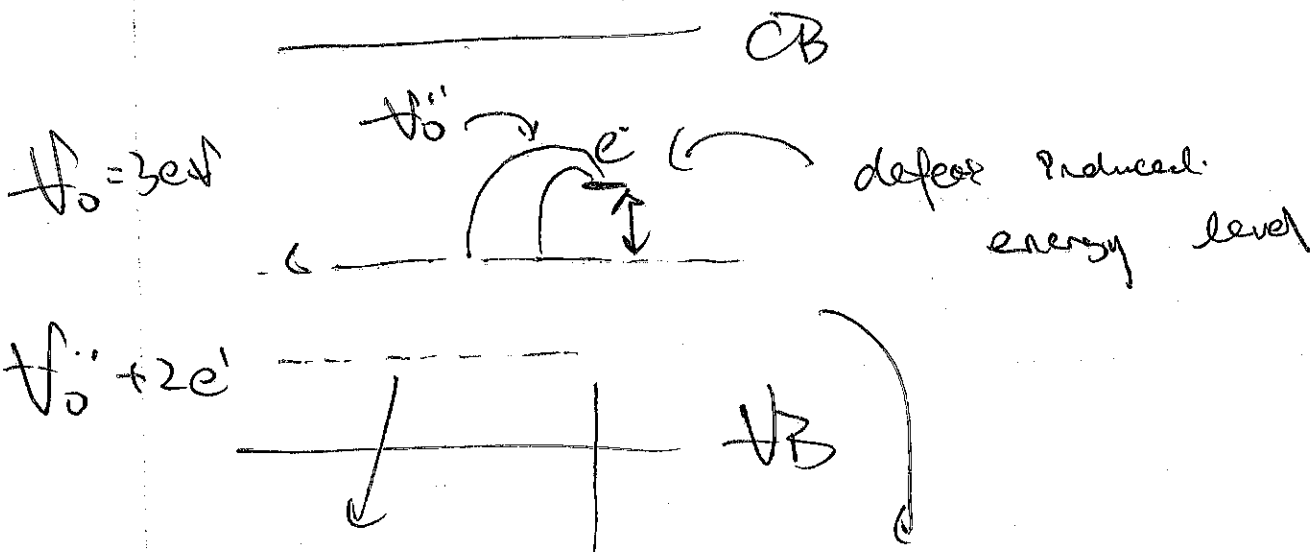
① ↗ ② ↗ $+\mu dM$ ↖ chge chem potential

$$\Delta_f E(X) = E(X_0^q) + E(bulk) - \sum_i \langle n_i \mu_i + q \varepsilon_f$$ (Fermi level)

buy & sell atoms

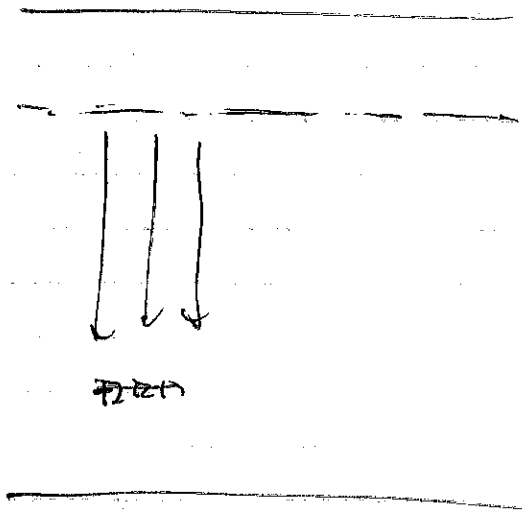
buy & sell electrons

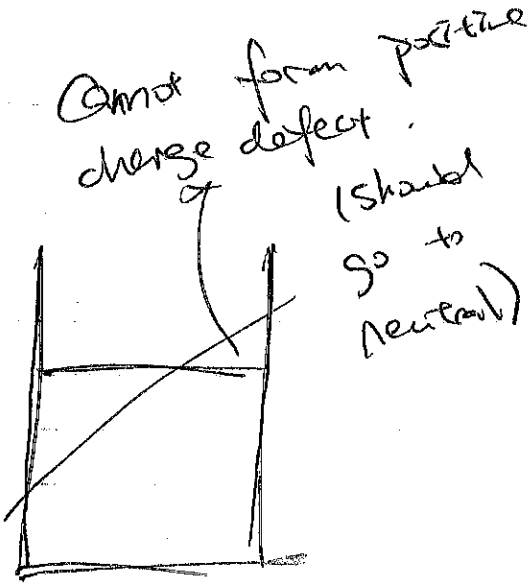
focusing on the term $q\varepsilon_f$

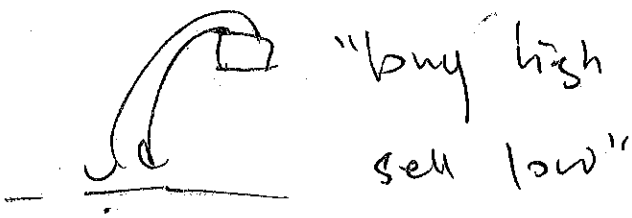


As Fermi level goes lower,

One can recover oxygen vacancy



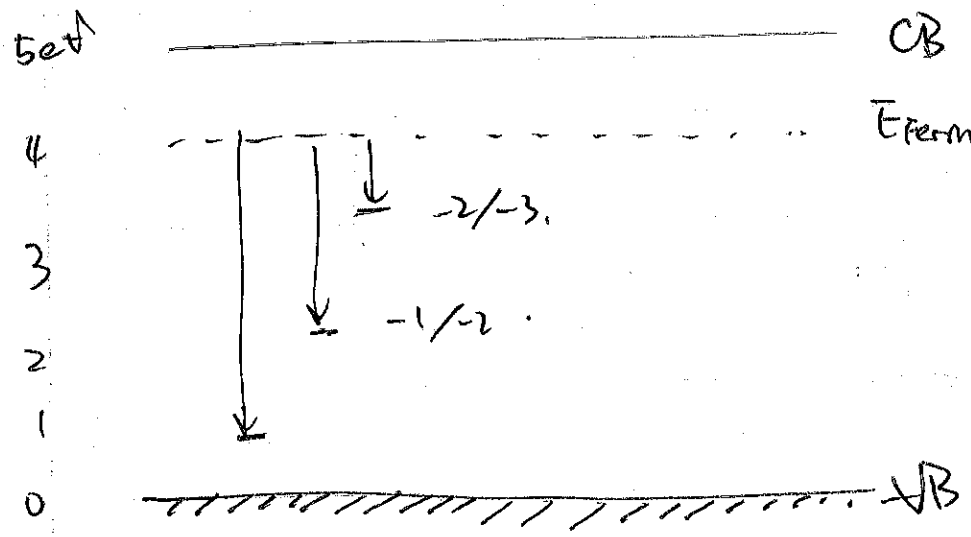


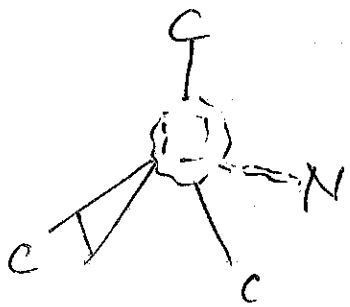


doping of semiconductors

How to set Fermi level, use doping!

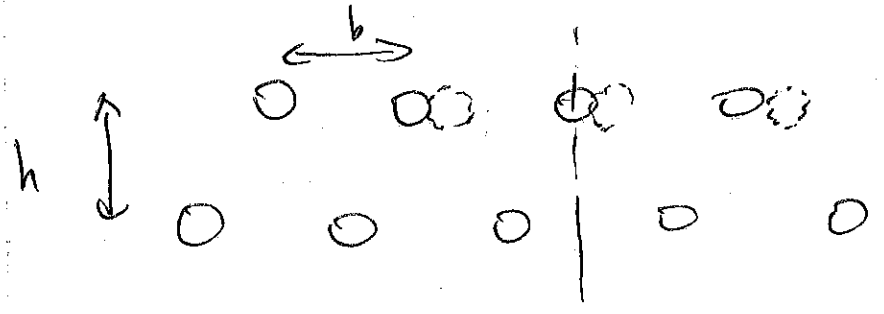
Leonne 8 4/24/2024

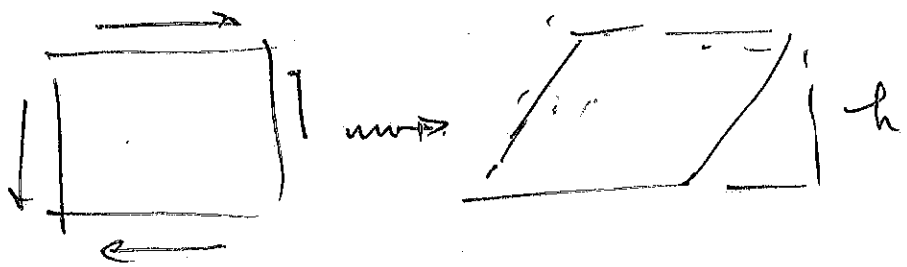




NV center

Frenkel.

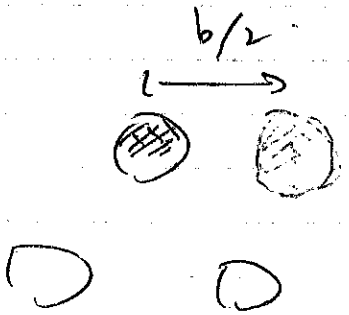


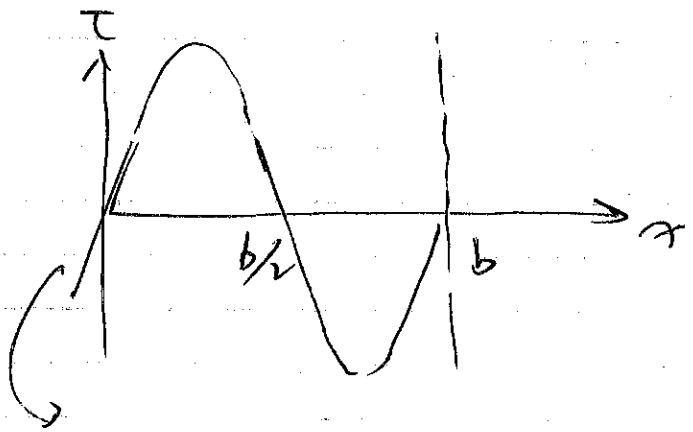


$\tau = f(x)$

→ valid for crystal

$\tau = \tau_{max} \sin\left(\frac{2\pi x}{b}\right)$.





Elastic region

$\tau = \mu \gamma$.

$\simeq \mu \frac{x}{h}$

$\tau_{max} = \frac{\mu b}{2\pi h}$ ← $\frac{\tau_{max} 2\pi x}{b}$

Valid for all.

$= \frac{\mu}{2\pi} \simeq \frac{\mu}{10}$

↑ Most shear one can apply

~ Metals

$\mu = 100$ GPa.

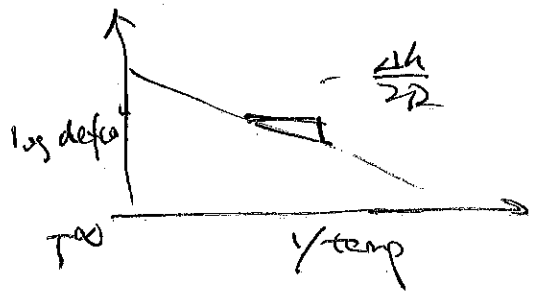
$\tau_{max} \simeq 10$ GPa → off factor 100 x

$\tau_{max, measured} = 100$ MPa

1930s : ~ 100 × off w/ theory predictions

{ Taylor
Orowan.
Polyani

Sources of dislocations.
(point defect)
- Quenching
- Crystal growth
- plastic deformation
(bending).

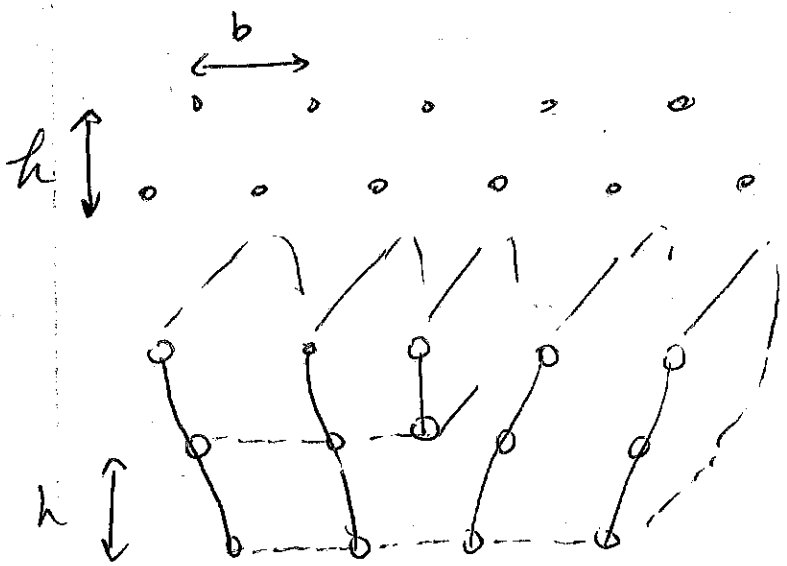


point defect
↓
dislocation loops

OH

"if we are stuck at a vacancy of 1 type, e.g. $V_O^{\cdot\cdot}$, one can always create another vacancy to balance and remove the both."

Lecture 9 6/29/2024



Shear modulus

$$\tau_{max} = \frac{\mu}{l_0}$$

crystallographic

$$\tau_{max\text{-}peierls} = \frac{2\mu}{1-\nu} \exp\left(\frac{-2\pi h}{(1-\nu)\, b}\right)$$

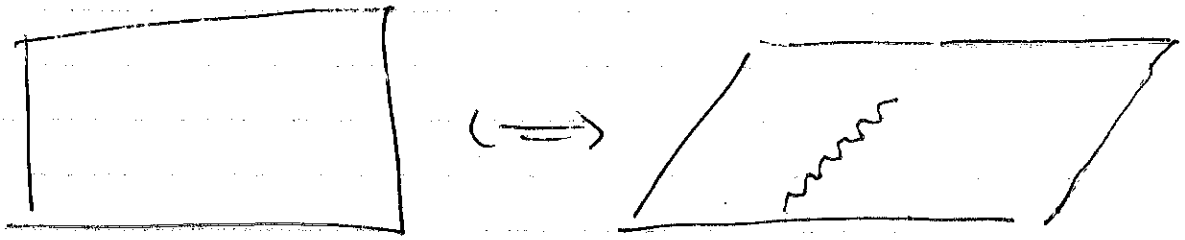
Poisson's ratio

$\vec{b}$: Burgers Vector

ξ. line direction. Sense vector

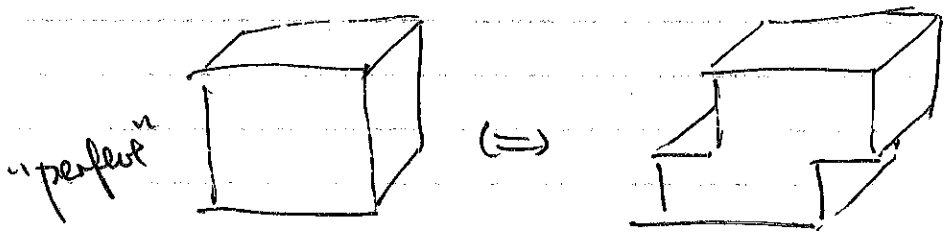
Unit vector

apply shear

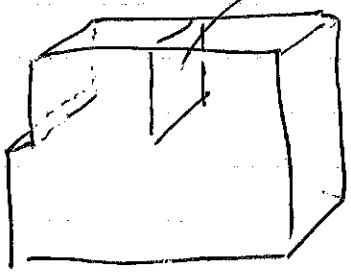


↓

Zoomed view.



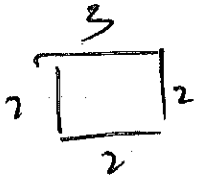
↳ intermediate → extra "half" plane

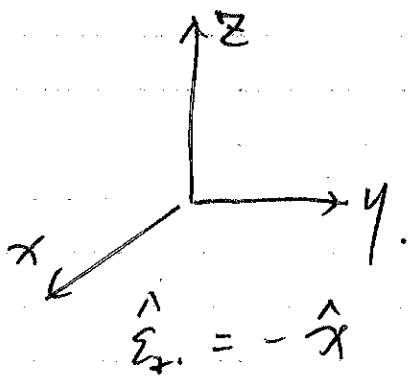


"pop off" to the other side

line direction. sense vector. unit vector

"into the plane"



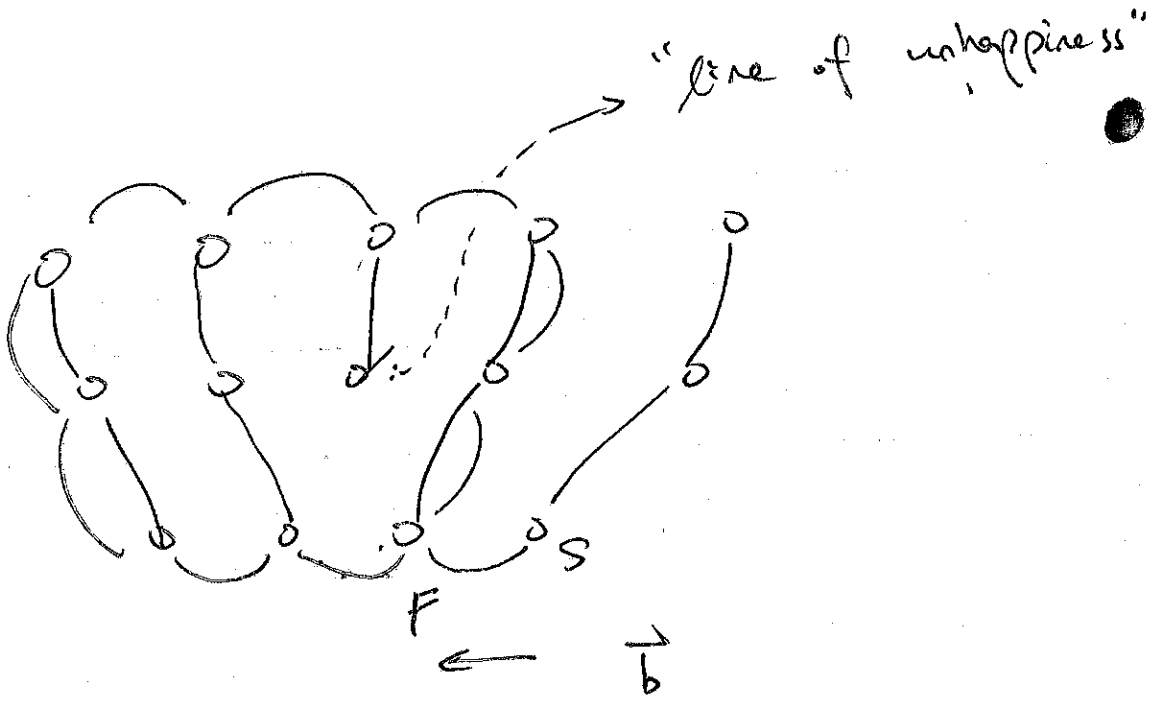


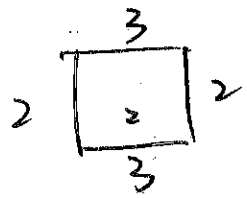
$\hat{\epsilon}_{z.} = -\hat{x}$

RH - SF

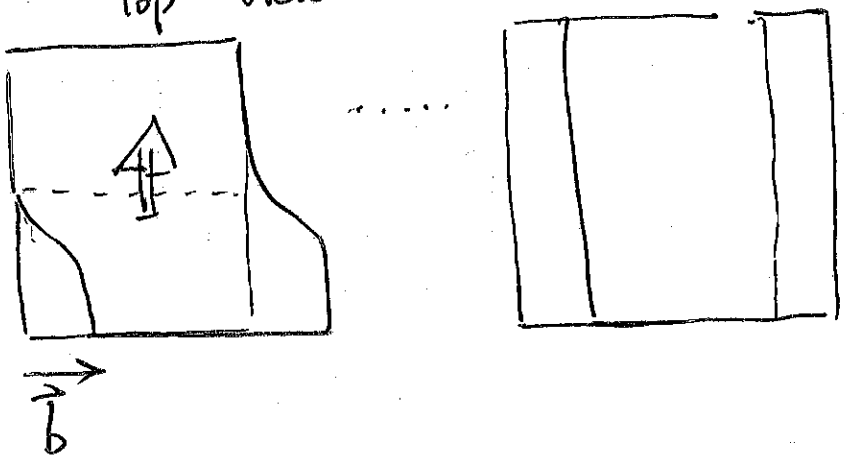
↓ ↳ finish

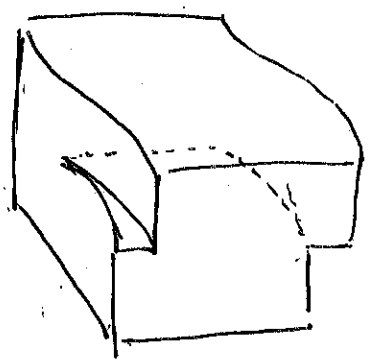
start





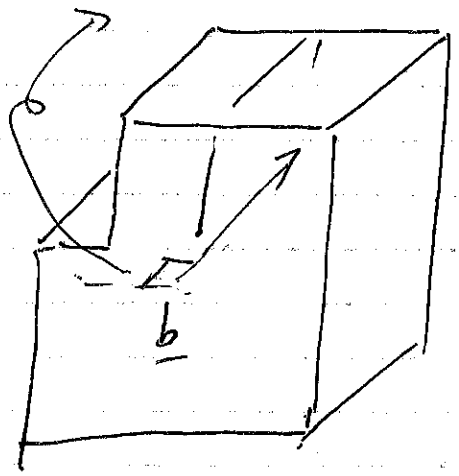
Top View.





Angle between $\vec{b}$ and $\vec{\xi}$:

90°: edge dislocation



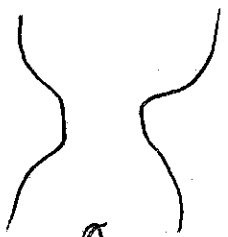
$\vec{\xi} : -\hat{x}$

$\vec{b} : +\hat{x}$

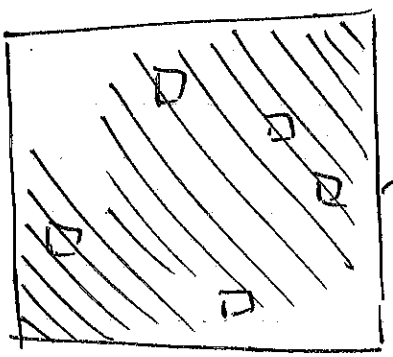
0° degree

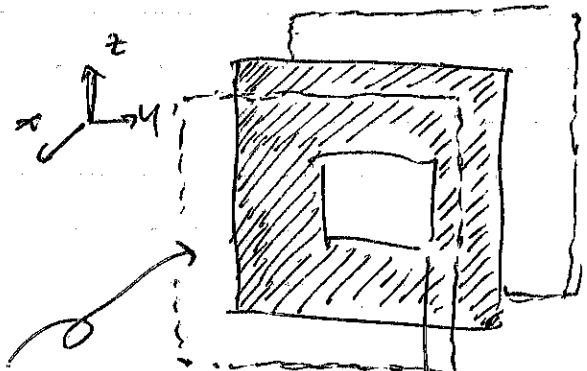
180° degree

dislocations



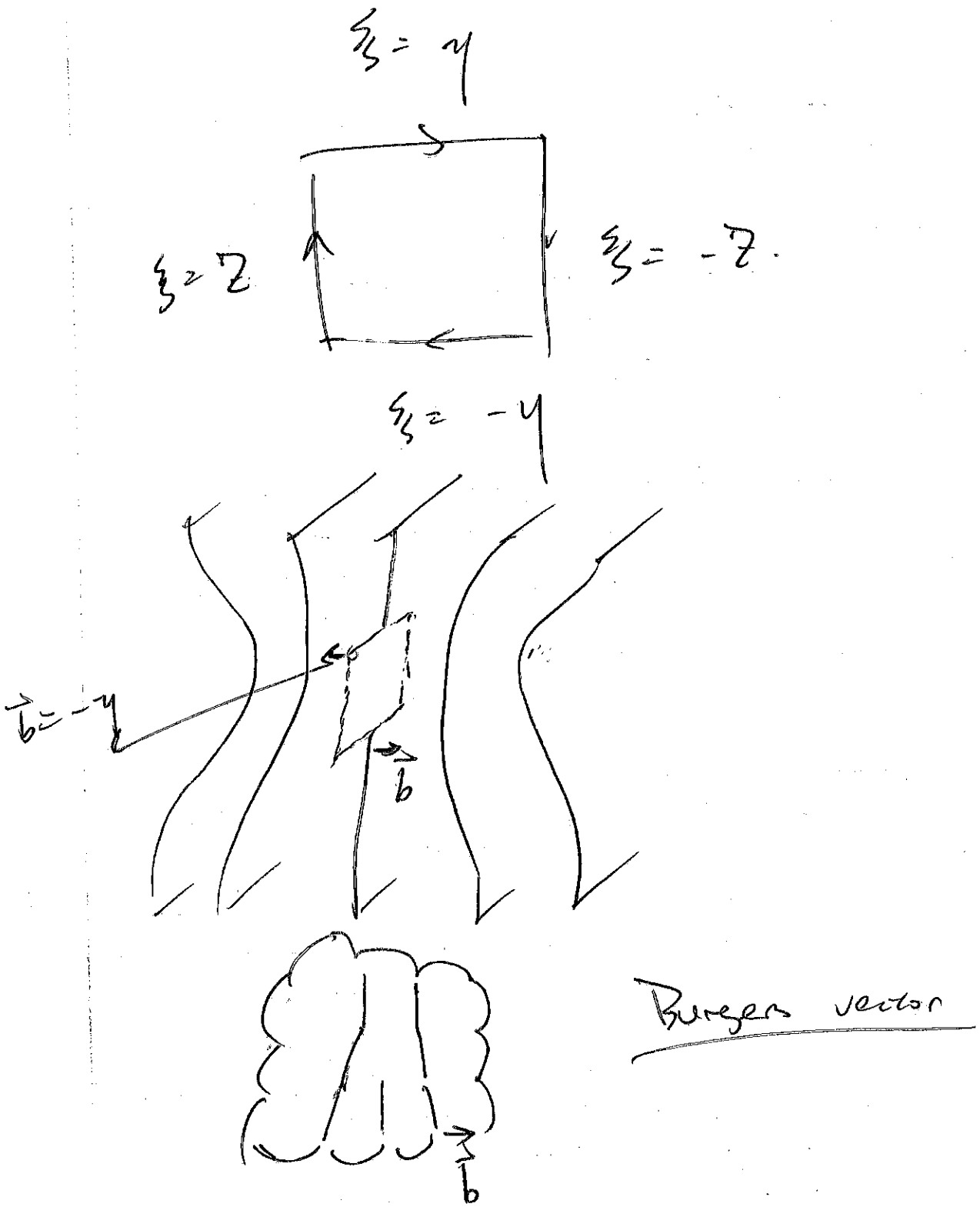
plane of atoms ...



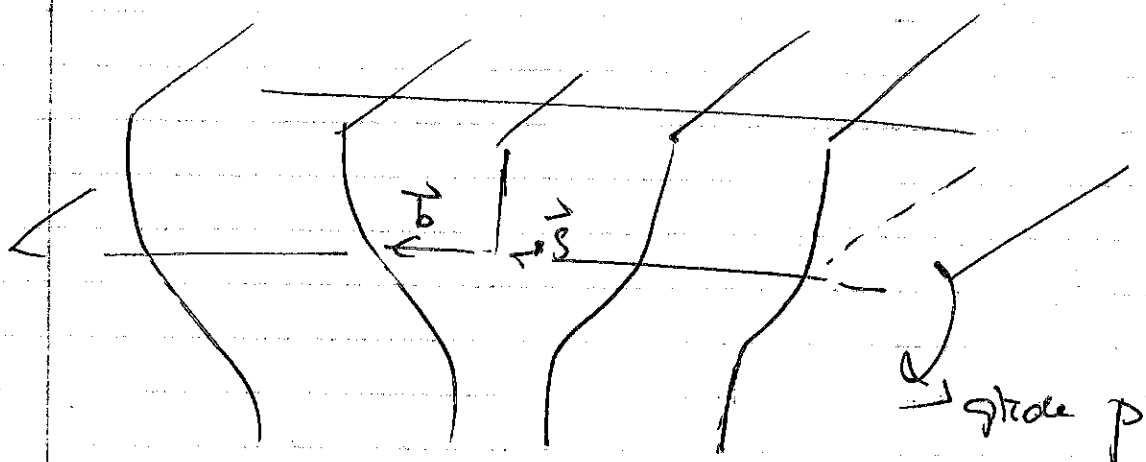


→ vacancies

bounding bar is the dislocation



Burgers vector



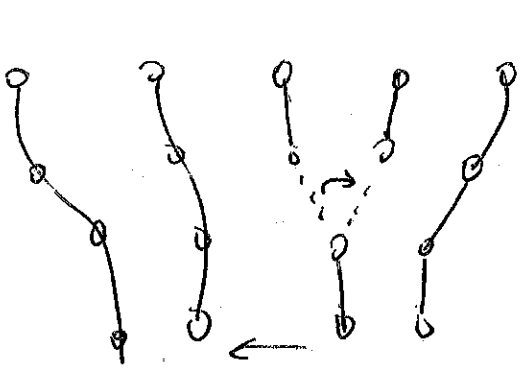
glide plane for dislocations

↳ ... breaking an unbreakable bond.

self plane.

dislocation ← put energy into system.

lecture 10 5/1/2024

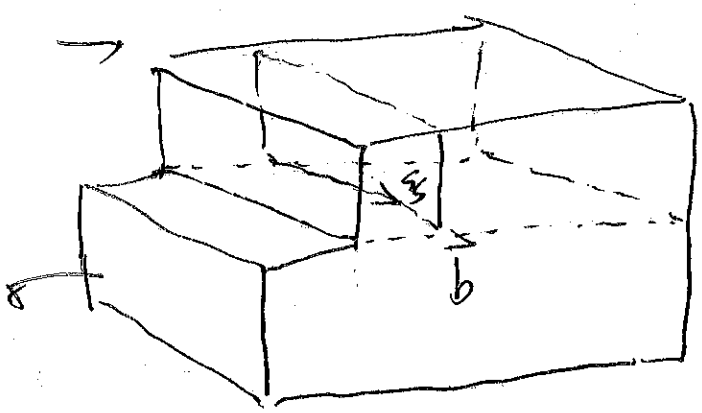


glide.

↓

consecutive motion

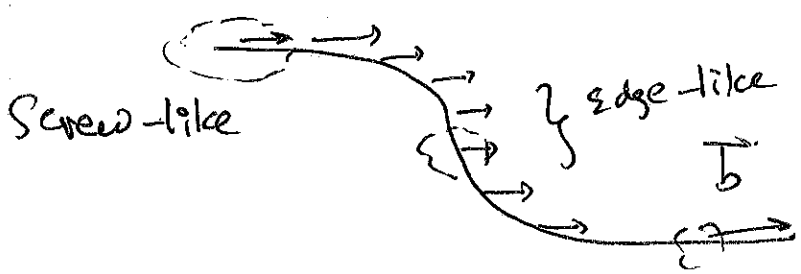
$\vec{b}$

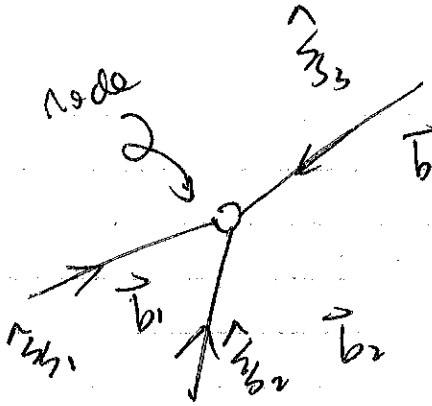


glide plane: contain $\vec{b}$ and $\hat{\xi}$

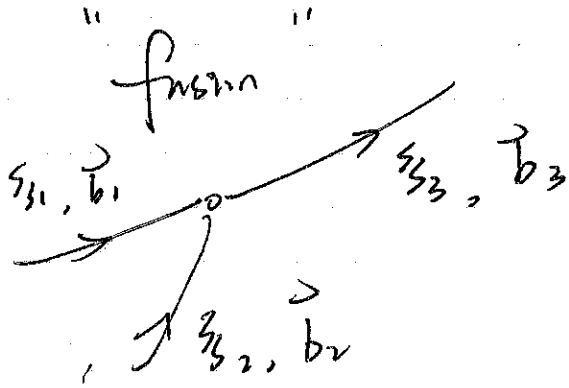
$\vec{b} \perp \hat{\xi}$ edge dislocation.

$\vec{b} \parallel \hat{\xi}$ screw dislocation

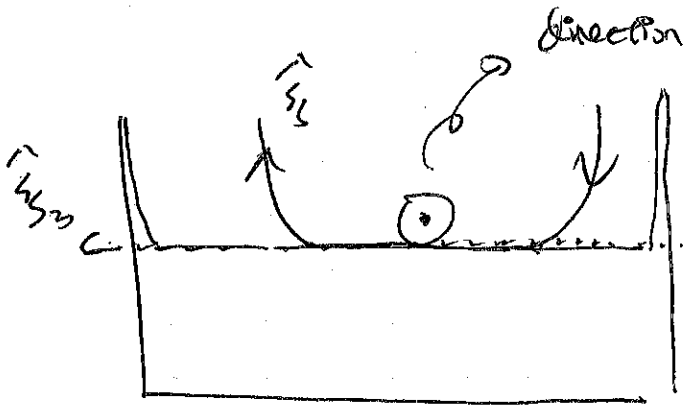


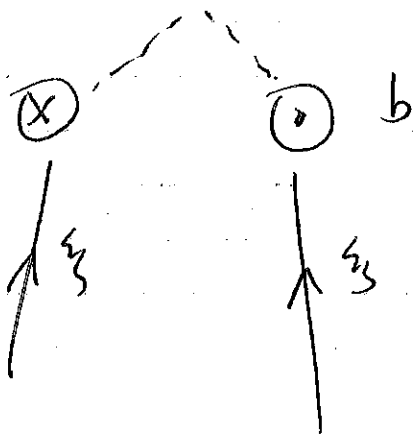


if $\hat{\xi}_3$ points toward the node, $\sum_i \vec{b}_i = 0$

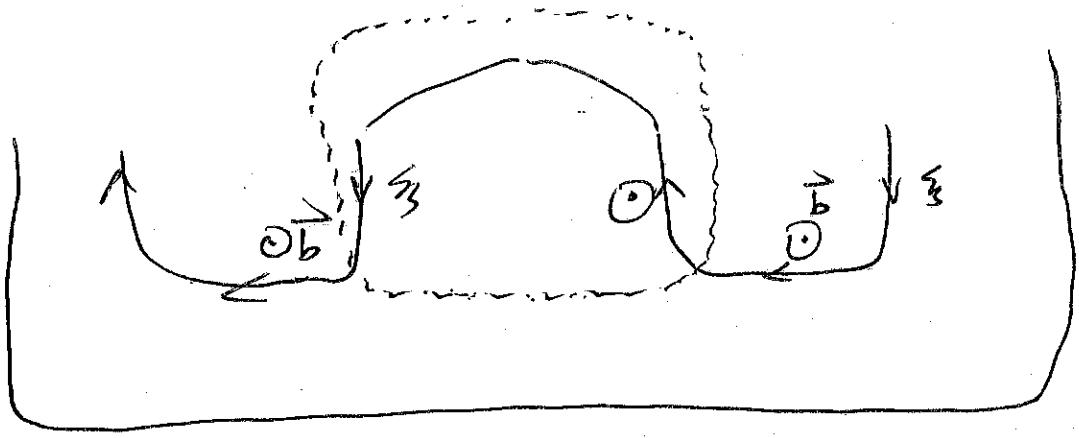


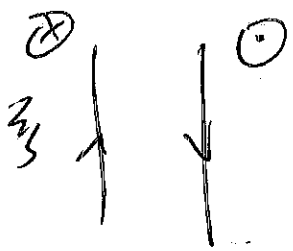
$\vec{b}_1 + \vec{b}_2 = \vec{b}_3$

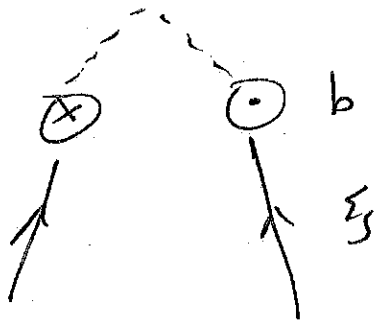


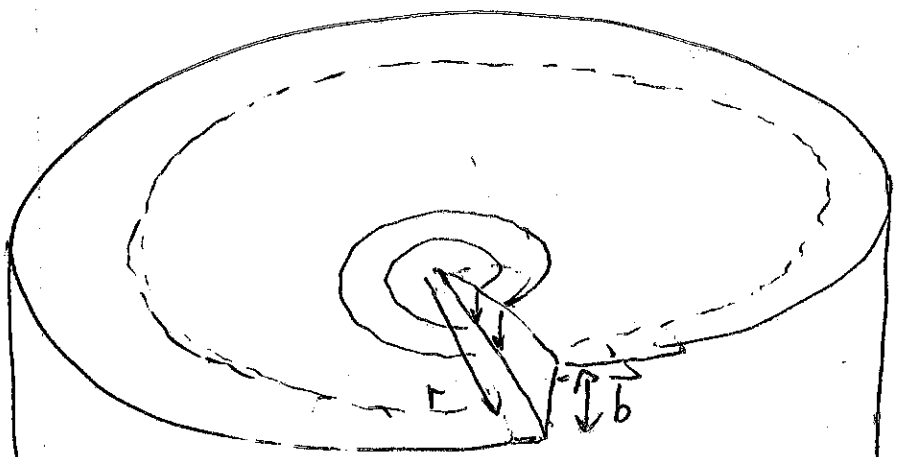


annihilation









$\gamma = \frac{b}{2\pi r}$

$2\pi r$, up by $\vec{b}$

$$u(\gamma) = \int \tau \, d\gamma$$

Strain energy per unit vol. $= \frac{1}{2} \tau \gamma$

μ → shear mod.

$$= \frac{\mu \gamma^2}{2}$$

$$= \frac{\mu b^2}{8\pi^2 r^2}$$

$$U_{screw} = \int u \, dV$$

$$U_{screw} = \text{unit length} \times \int_{r_0}^{r} \frac{\mu b^2}{8\pi^2 r^2} \, 2\pi r \, dr$$

r_0 → cut off $\propto \frac{b}{2}$

$$= \frac{\mu b^2}{4\pi} \ln\left(\frac{r}{r_0}\right)$$

r → Outer Cutoff

$\approx \mu b^2$

inner cutoff

Inter-dislocation distance.

linear elasticity not valid

$\mu = 100$ GPa.
$b = 0.3$ nm. }

$(100 \times 10^9)(0.3 \times 10^{-9})^2$

$= 10^{-8}$ J/m

Energy per plane of atoms

10^{-8} J/m $\times$ 0.3×10^{-9} m

$= 3 \times 10^{-18}$ J

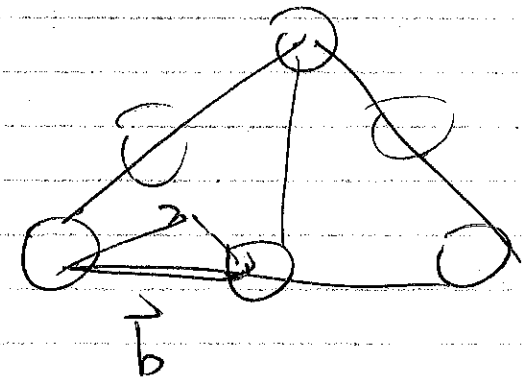
1.6×10^{-19} J = 1 eV.

≈ 5 eV / plane of atoms

20 % core

80 % elastic field

If there exists a dislocation, $\vec{b}$ will be minimized.



$\frac{a}{2}[110]$

NaCl.

FCC ← lattice

basis

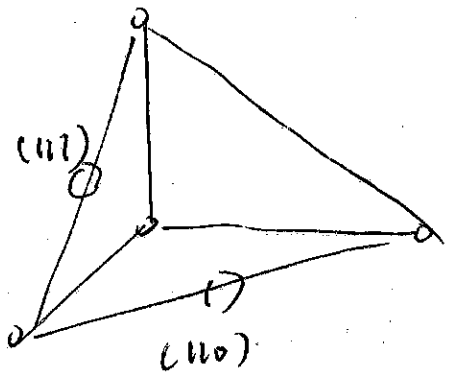
Na → Na

Na → Cl

Cl → Cl

↳ X "not allowed"

Lecture 11. Week 6 . 5/6/2024



glide plane .

containing both

$\hat{\xi}$ & $\vec{b}$

close packed plane .

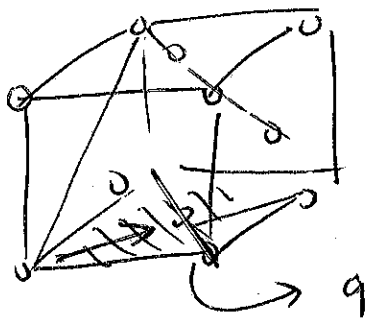
close packed plane / Burgers vector .

Slip system.

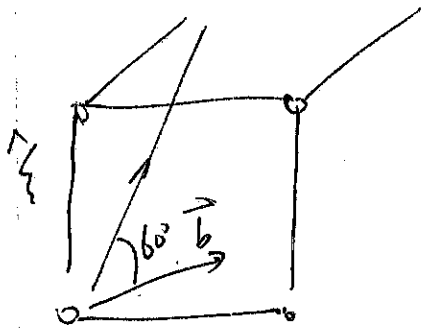
FCC. $\frac{a}{2}\langle 1\,1\,0\rangle . \{1\,1\,1\}$

$\vec{b}$ - vector

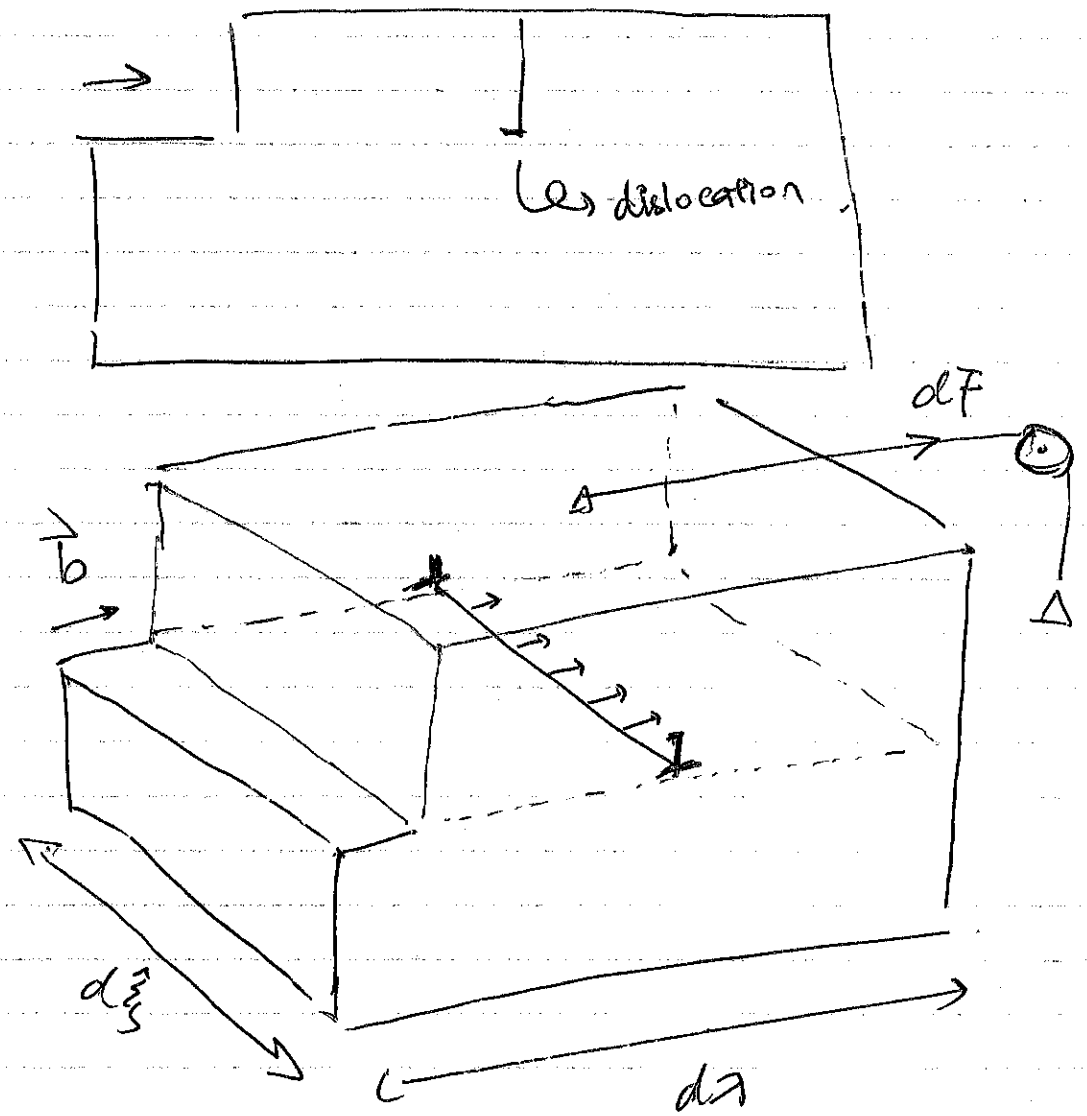
glide plane



$\langle . \rangle \{ . \}$



60° dislocation BCC



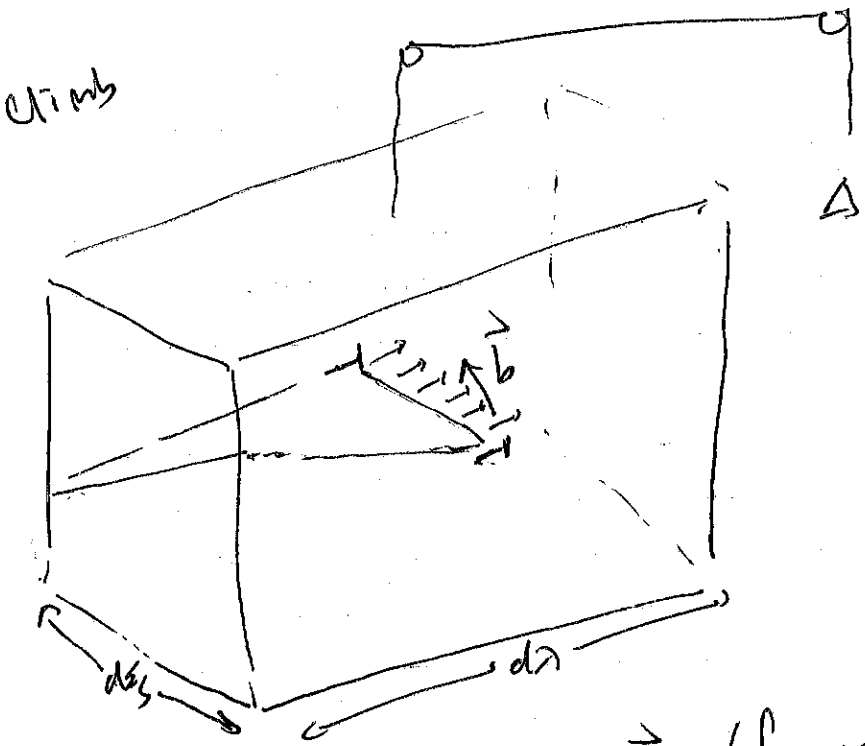
$$dF = \tau (d\xi \times d\lambda)$$

dislocation feels force / unit length. $\rightarrow f_g$

$$W = dF \times b = (f_g \times d\xi) \times d\lambda$$

$$= 2\,(d\xi \times d\lambda) \times b \quad \leftarrow \text{how much force disl. feel}$$

$$= f_g \times d\xi \times d\lambda \rightarrow f_g = \tau b$$



$$W = dF \times \vec{b} = (f_c \times d\xi) \times d\lambda$$

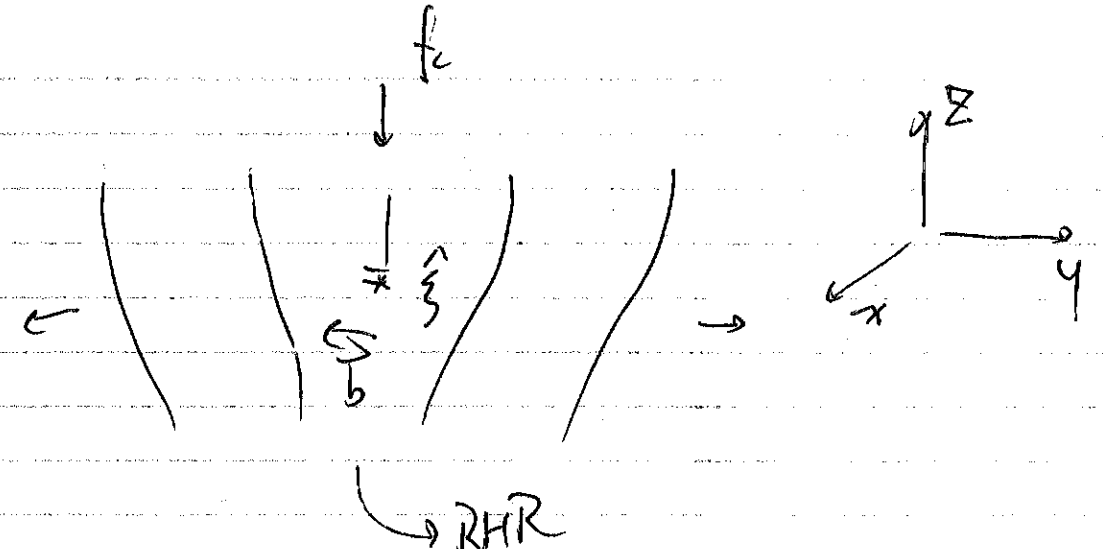
$$\sigma(d\xi \times d\lambda) \times b = f_c \times d\xi \times d\lambda$$

$$\sigma b = f_c$$

In general

$$\frac{\vec{F}}{l} = (\underline{\underline{\sigma}} \cdot \underline{b}) \times \hat{\xi}$$

↖ stress tensor



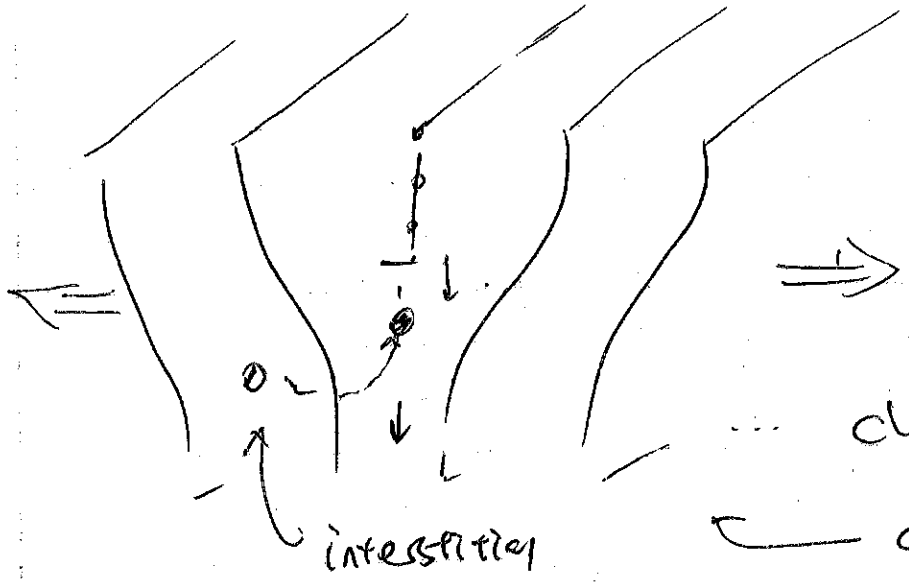
$$\hat{\xi} = \begin{bmatrix} -1 \\ 0 \\ 0 \end{bmatrix} \qquad \vec{b} = \begin{bmatrix} 0 \\ -b \\ 0 \end{bmatrix}$$

$$\underline{\underline{\sigma}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\underline{\underline{\sigma}} \cdot \underline{b} = \begin{bmatrix} 0 \\ -\sigma b \\ 0 \end{bmatrix} \times \begin{bmatrix} -1 \\ 0 \\ 0 \end{bmatrix}$$

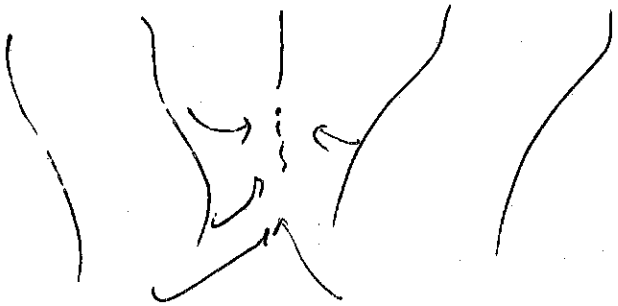
$$\begin{vmatrix} i & j & k \\ 0 & -\sigma b & 0 \\ -1 & 0 & 0 \end{vmatrix} = \underline{i}(0\cdot 0) - \underline{j}(0) + \underline{k}(-\sigma b)$$

$$= -\sigma b \cdot \underline{k}$$



" we need many point defect. to move down the glide plane.

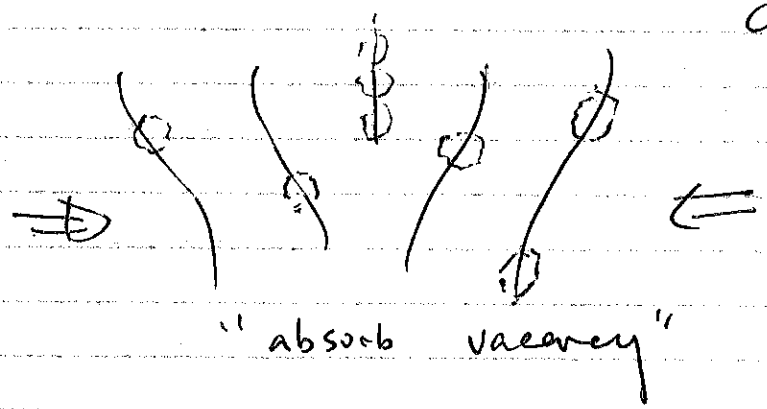
another way

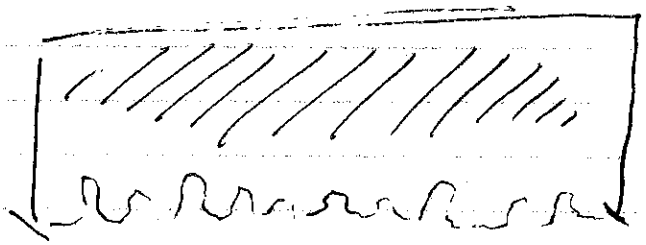


steal atoms from surround, by creating vacancies.

opposite process

climb: high temperatures

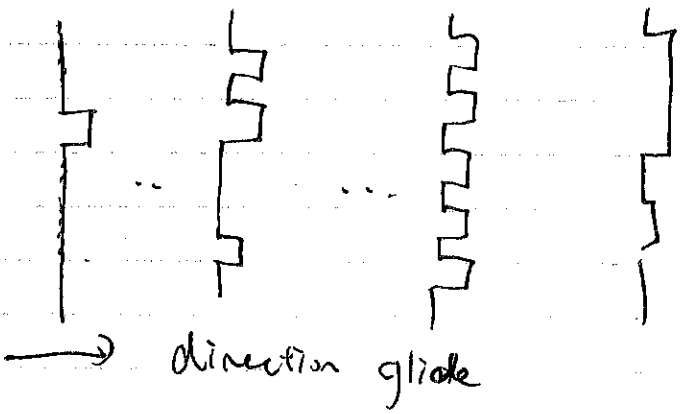


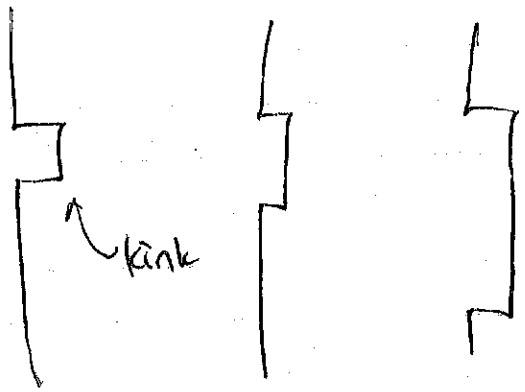


glide : low temperature.

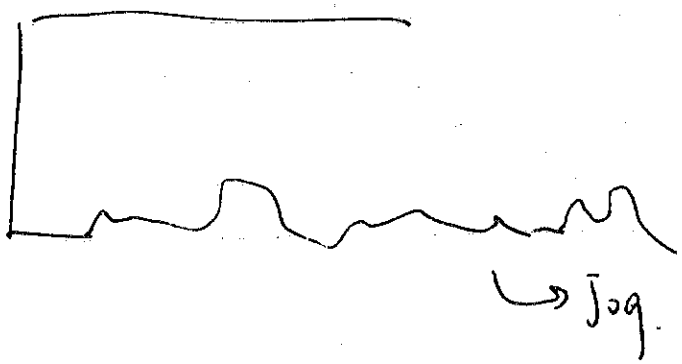
glide + climb : high temperatures.

top view dislocation





having kinks
increases entropy
of dislocation



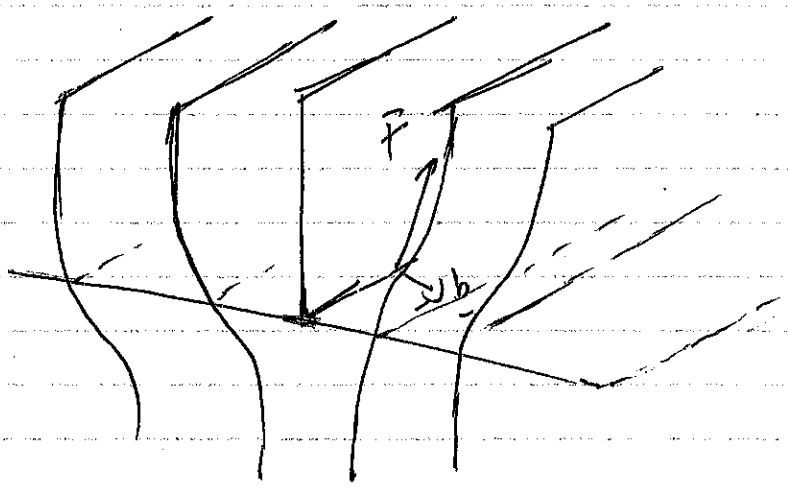
Lecture 12 5/8/2024

$$\frac{F}{l} = f = (\underline{\underline{\sigma}} \cdot \underline{b}) \times \hat{\xi}$$

Step 1

$$\begin{bmatrix} \sigma_{xx} & & \\ & \sigma_{yy} & \\ & & \sigma_{zz} \end{bmatrix} \begin{bmatrix} b_x \\ b_y \\ b_z \end{bmatrix} \rightarrow \begin{bmatrix} \quad \end{bmatrix} \times \begin{bmatrix} \quad \\ \quad \\ \quad \end{bmatrix}$$

3x3 3x1 3x1



$$\begin{bmatrix} \quad \\ \quad \\ \quad \end{bmatrix}$$

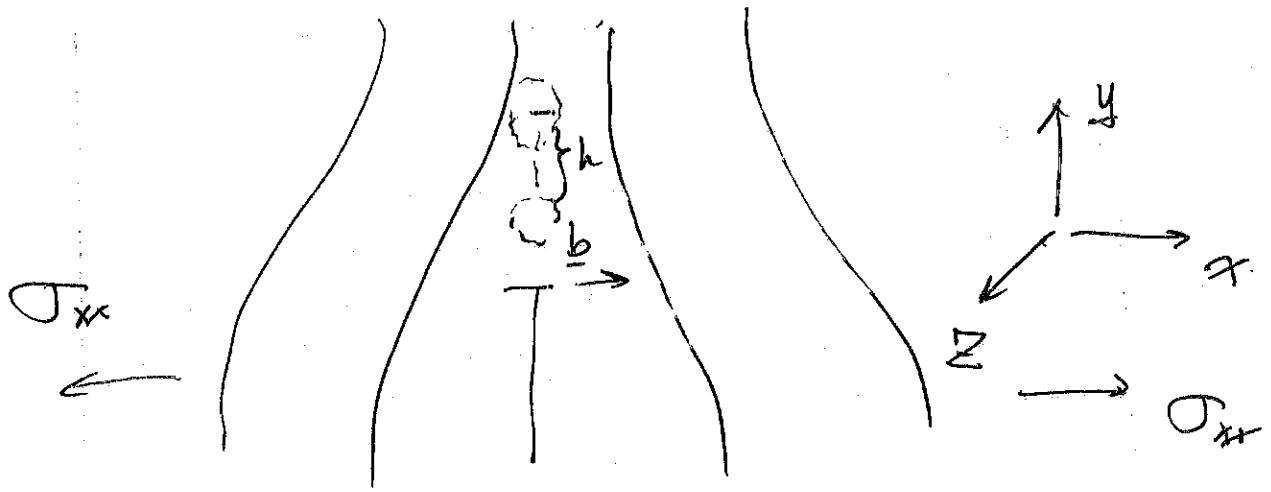
Step 2: Resolve F/l as glide & climb forces. f_c

f_g > [ ]

f_c > [ ]

f_g ↓ ×

Step 3. Judge whether it moves or not



$$\hat{\xi} = (0, 0, -1).$$

$$\underline{b} = (b_x, 0, 0)$$

$$f_c = \sigma_{xx} \cdot b \cdot \hat{j}$$

Consider dislocation moving up by h.

↳ work done.

- absorbs interstitials,
- emit vacancies.

$$\frac{d\mathcal{G}}{L} = \bar{G}(bh)/\Omega$$

$\bar{G}$: chem. pot. vacancies

Ω: atomic vol.

$Lbh \rightarrow$ volume of vacancies

$$\bar{G} = kT \ln\left(\frac{C}{C_0}\right)$$

C: actual concentration

C_0: equilibrium concentration

$$\boxed{\begin{array}{l} C > C_0 \\ C < C_0 \end{array}}$$

Assume $C > C_0$

$$F_{osmotic} = -\frac{\bar{G} b}{\Omega}$$

$$= -kT \ln\left(\frac{C}{C_0}\right) \frac{b}{\Omega}$$

$$f_{c_{total}} = \sigma_{xx} b - \frac{kT}{\Omega} \ln\left(\frac{C}{C_0}\right) b$$

$\sigma_{xx} b$: external stress

$\frac{kT}{\Omega} \ln\left(\frac{C}{C_0}\right) b$: point defect supersaturation

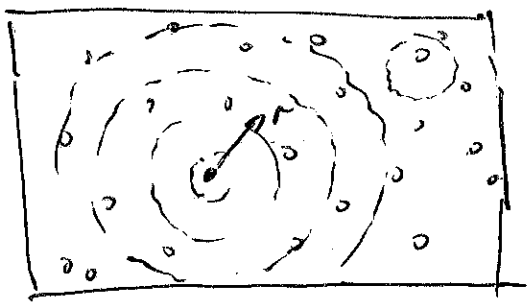
$$\sigma_p = \frac{2\mu}{1-\nu} \exp\left(\frac{-2\pi h}{(1-\nu)\, b}\right)$$

Lecture 13 5/13/2024.

Disordered Materials.

Chapter 2. & 3 of Zallen.

Density function



V, N atoms

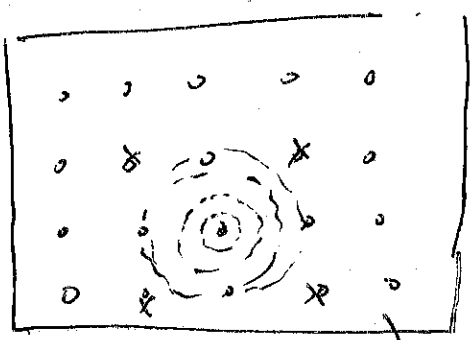
$$\rho^\circ = \frac{N}{V}$$

local density $\rho = \frac{dN}{dV}$

$$\rho(r) = g(r)\,\rho_0$$

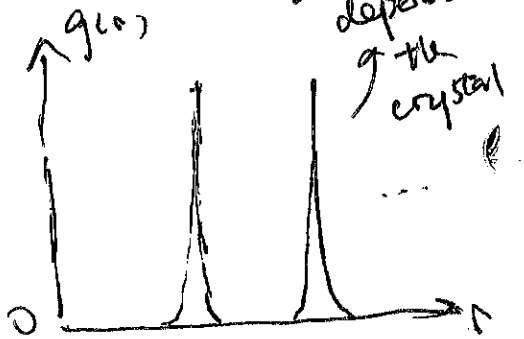
ρ_0 ← avg. density

$g(r)$ ← pair distribution function

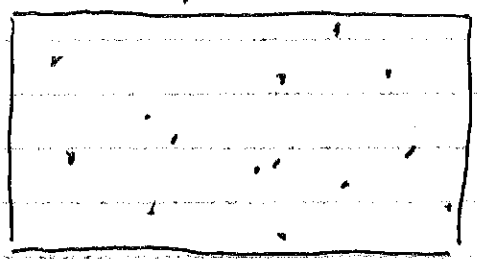


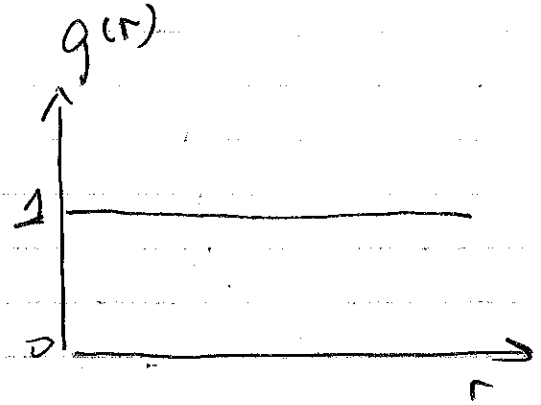
$$\therefore g(r) = \frac{\rho(r)}{\rho_0} \rightarrow \text{dimensionless}$$

a series of delta function ←

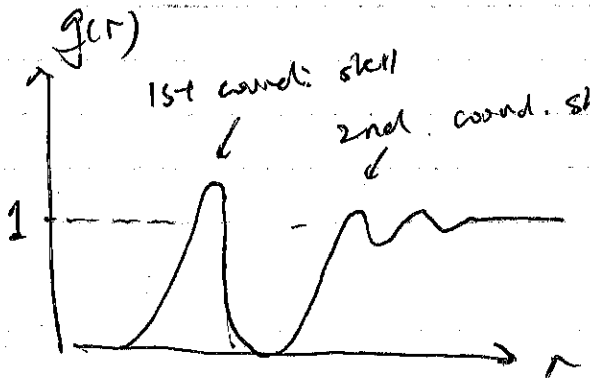


Ideal gas.





Amorphous solid



- $g(r)$ cannot be negative
- $g(r) > 1$ increased local density
- $g(r) < 1$, decreased local density

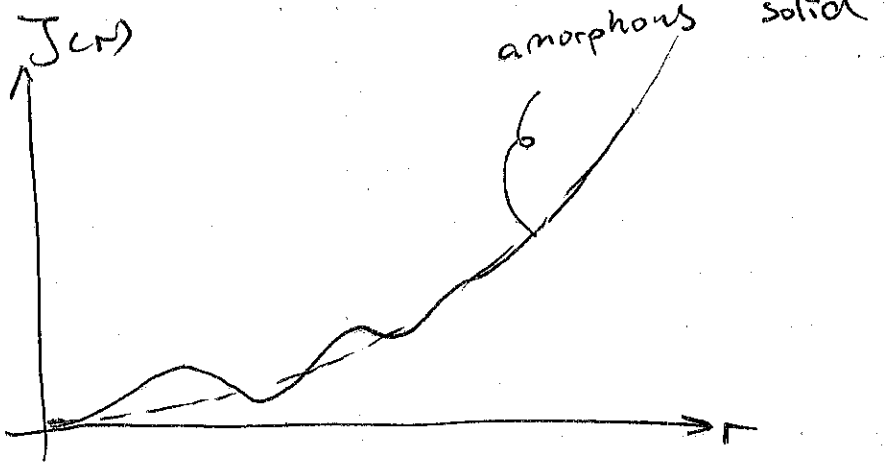
Radial distribution function

$$J(r) = 4\pi r^2 \rho(r)$$

$J(r)$: # atoms / cm

$\rho(r)$: # atoms / cm^3

$4\pi r^2 \rho(r)\, dr$ = # of atoms between r & $r + dr$



Reduced. Radial distribution function

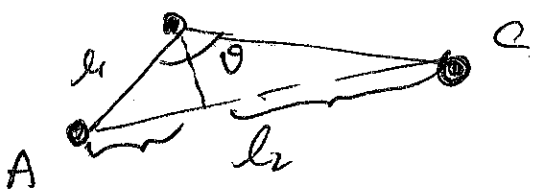
$$G(r) = \frac{J(r)}{r} - 4\pi r \rho_0$$

↳ "difference function"

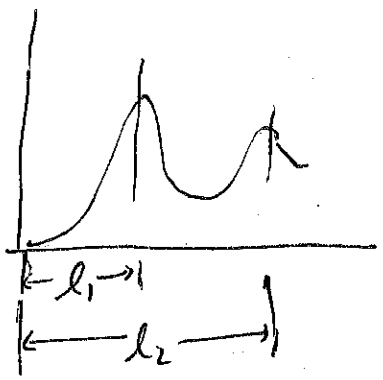
$$= 4\pi r \rho(r) - 4\pi r \rho_0$$

↑ can be experimentally measured

B



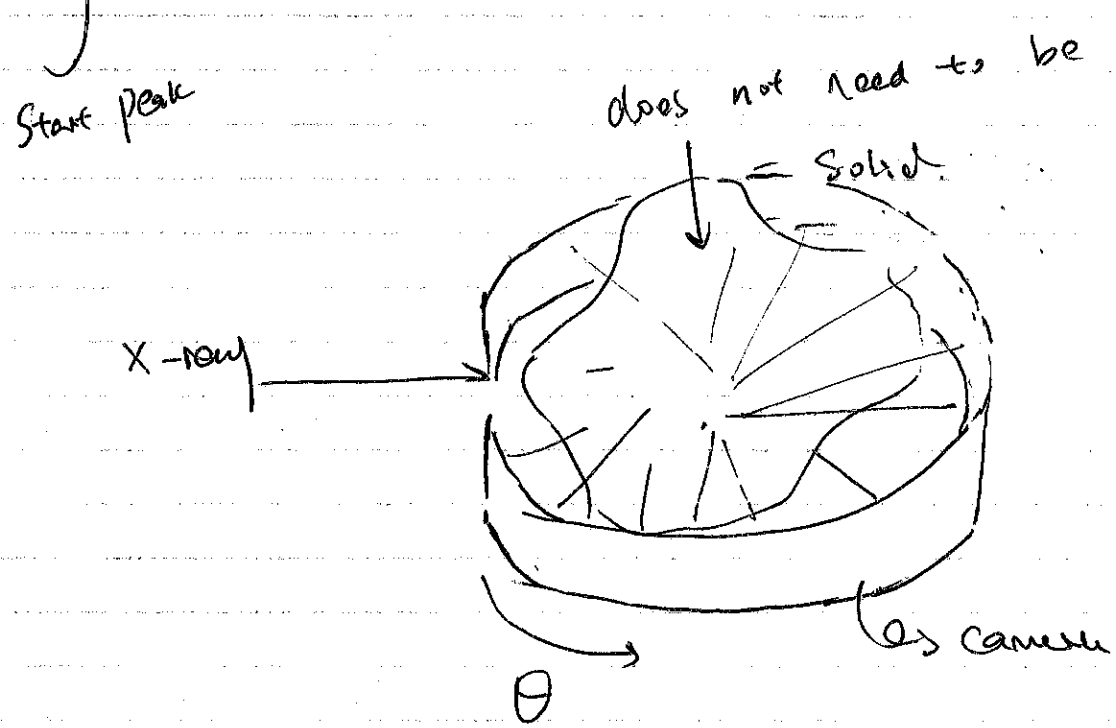
one can find the bond length & angles



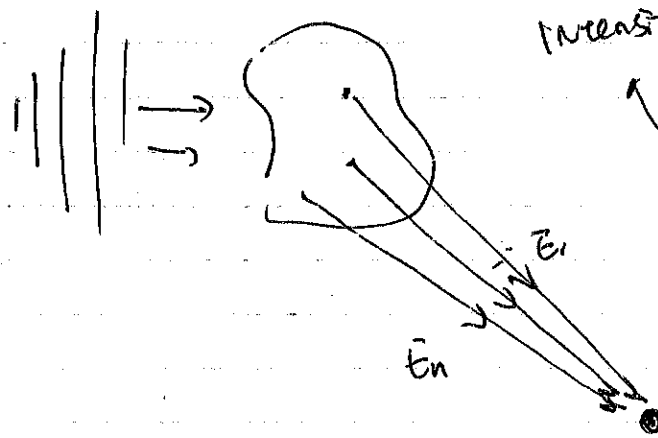
$$\rightarrow \theta = 2 \sin^{-1}\left(\frac{l_2}{2 l_1}\right)$$

Area under first peak in (coordination number)

$$\int_{\text{start peak}}^{\text{end peak}} 4\pi r^2 \rho(r)\, dr = \#\text{ of atoms}$$



angular-dependence of the scattering.



intensity.

$I = \Sigma\Sigma^*$ ← complex conjugate

$\Sigma = e^{i\omega t}$

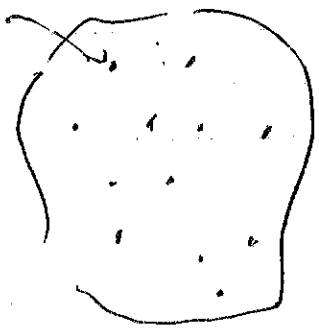
$$\left[\sum_i E_n \cos\frac{2\pi x}{\lambda} - i\sum_i E_n \sin\frac{2\pi x}{\lambda}\right]$$

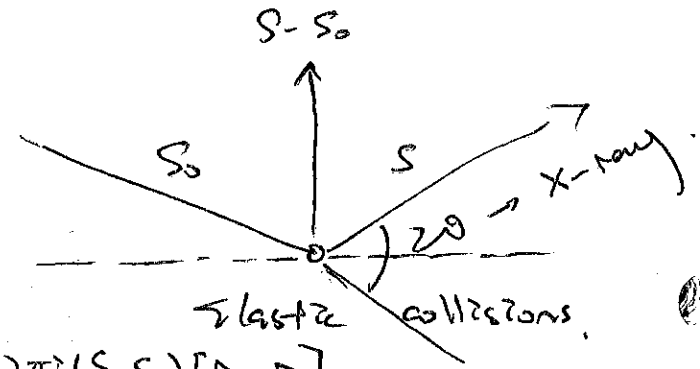
$$I = \left(\sum_{1}^{m} f_m \, e^{\frac{2\pi i}{\lambda}(s - s_0)\gamma_m}\right)\left(\sum_{1}^{n} f_n \, e^{-\frac{2\pi i}{\lambda}(s-s_0)\gamma_n}\right)$$

m ↗ ↑

atomic form factor

("atomic strength")





$$I = \sum_m \sum_n f_m f_n \, e^{2\pi i (s-s_0)[r_m - r_n]}$$

difference distance between atoms m & n

Crystal. $r_m - r_n$ ← are lattice vectors

r_1 r_2 r_3 r_4 r_5 r_6

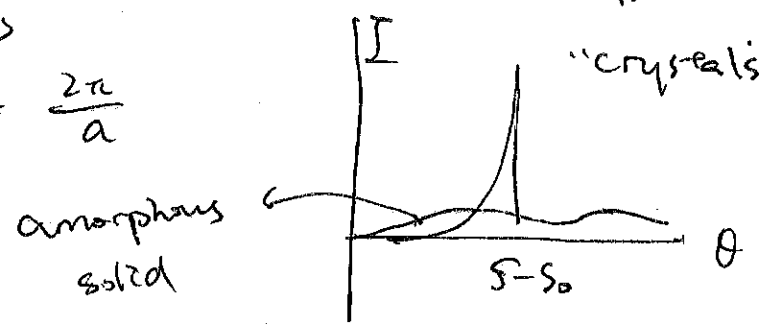
• → • • • • •

——————→

say $s - s_0 = \frac{2\pi}{a}$

XRD

"crystals"



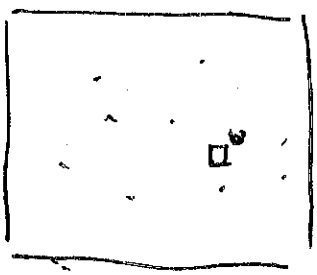
Lecture 16. 5/22/2024

Recap. density function

$$\frac{\rho(r)}{\rho_0} = g(r)$$

↑ pair distribution function

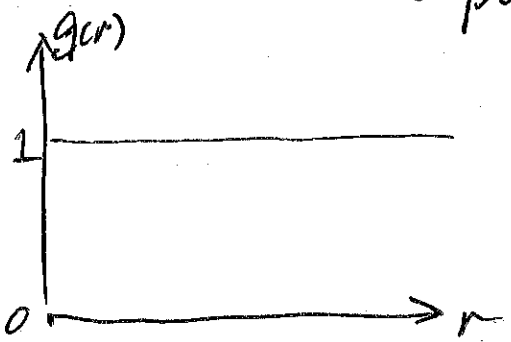
perfect / ideal gas



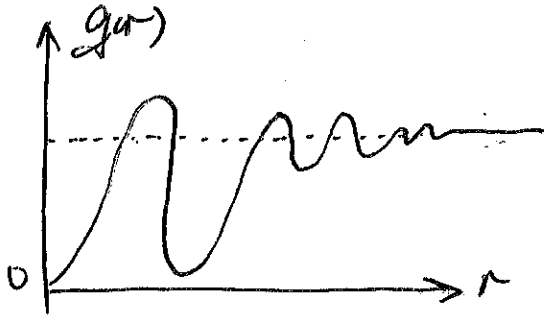
Amorphous Solid

"Position matters !!!"

because it's solid & there's bond



→ "1 means average, doesn't matter where's the atom".

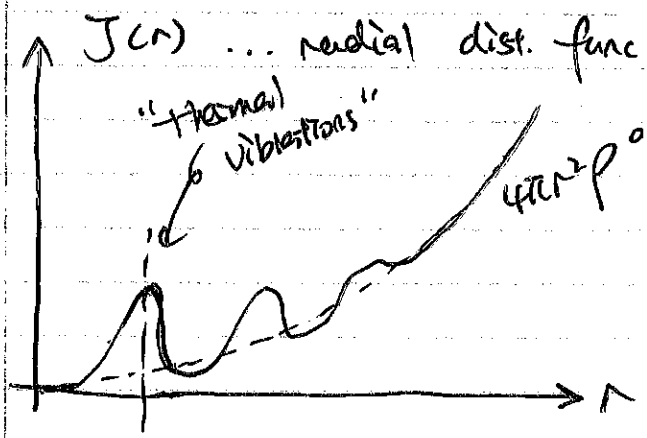


Radial dist. function.

$J(r) = 4\pi r^2 \rho(r)$. → $4\pi r^2 \rho(r)\,dr$ "avg # of atoms lying between r, $r+dr$"

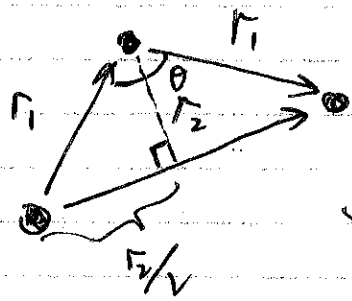
Reduced radial dist. function.

$$G(r) = \frac{J(r)}{r} - 4\pi r \rho^\circ$$



... average function for the entire solid.

Area under the first peak is coordination number.



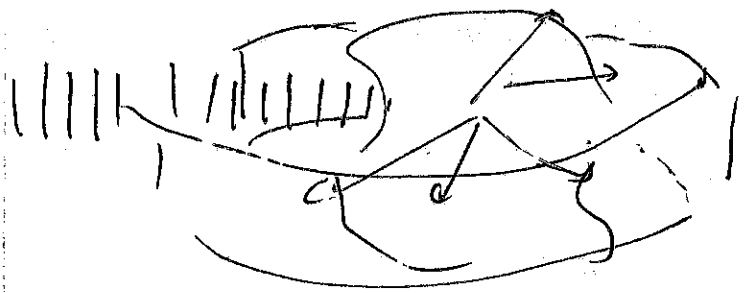
↪ representation of the sys.

Nearest neighbor should be the same.

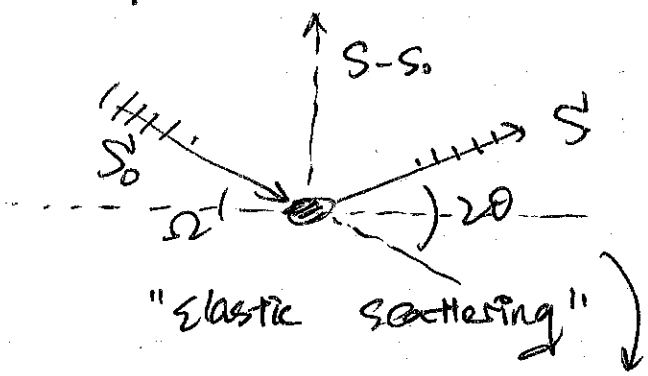
$$\sin\left(\frac{\theta}{2}\right) = \frac{\frac{r_2}{2}}{r_1} \rightarrow \theta = 2\arcsin\left(\frac{r_2}{2r_1}\right)$$

the change of $J(r)$ of crystalline vs. amorphous characterizes the bond change.

Recap for X-ray diffraction.



Total Scattering Experiments.



"Elastic scattering"

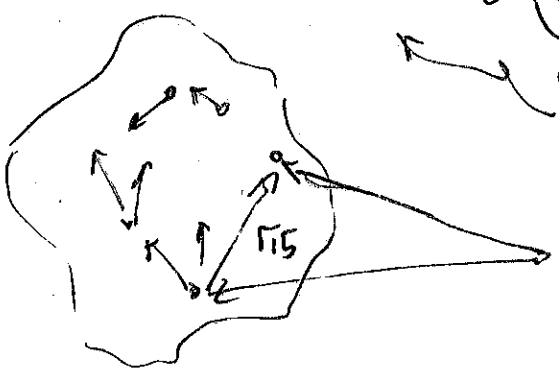
X-ray angle-shift

the intensity that the detector "sees":

$$I = \sum_m \sum_n f_m f_n e^{\frac{2\pi i}{\lambda}(S-S_0) r_{mn}}.$$

$f_m f_n$ → atomic form factors

$e^{\frac{2\pi i}{\lambda}(S-S_0) r_{mn}}$ → "Signal X-ray sees"



Interatomic Separation.

$r_{mn} = r_m - r_n$.

↖ isotropic solid

r_{mn} is isotropic (i.e., points in all 3D space)

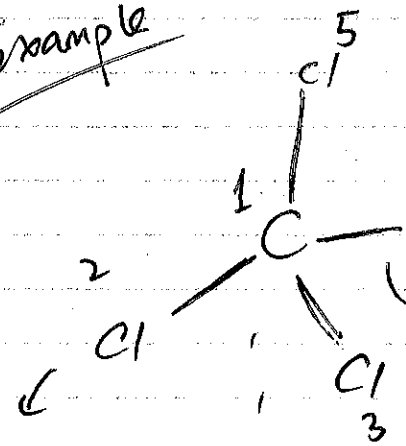
$$I = \sum_m \sum_n f_m f_n \frac{\sin(k r_{mn})}{k r_{mn}}$$

where: $k = \frac{4\pi \sin\theta}{\lambda}$

↖ wavelength of X-ray.

Example

CCl_4



↖ stay fixed.

bond lengths are the same.

$m=1$, $n=1$ → r_{C-C}.

"it is not a solid, not densely packed".

$m=1$, $n=1,2,3,4,5$

$$I = f_C \left[f_C + 4 f_{Cl} \frac{\sin(k r_{C-Cl})}{k r_{C-Cl}} \right] \leftarrow m=1$$

"1st loop" + ...

$m=2$ ↝ see "Cl" atom

$n=1, 2, 3, 4, 5$

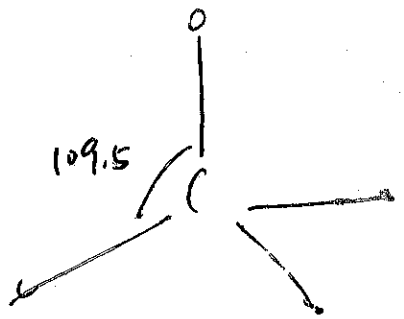
$$\cdots + 4 f_{Cl} \left[f_{Cl} + f_C \frac{\sin(k r_{C-Cl})}{k r_{C-Cl}} + 3 f_{Cl} \frac{\sin(k r_{Cl-Cl})}{k r_{Cl-Cl}} \right]$$

$n = 1, 3, 4, 5$
"all the same"

... done

k is the experimental parameter.

bond length is not known.



r_{C-Cl} ← unknown

$r_{Cl-Cl} = \sqrt{\frac{8}{3}}\, r_{C-Cl}$

↓

Angle 109.5°.

Remark: for solid, the sum will go on forever as the atoms are all "connected".

for solid, example monoatomic solid,

$$I = \sum_m f^2 + \sum_m \sum_{m \neq n} f^2 \frac{\sin(kr_{mn})}{kr_{mn}}$$

$$= \sum_m f^2 + \sum_m f^2 \int \rho(r) \frac{\sin(kr)}{kr} dV$$

↳ because it's monoatomic isotropic it doesn't matter.

$$= \sum_m f^2 + \sum_m f^2 \int_0^\infty \rho(r)\, 4\pi r^2 dr \frac{\sin(kr)}{kr}$$

$$I = \sum_m f^2 + \sum_m f^2 \int_0^\infty 4\pi r^2 \left[\rho(r) - \rho^0\right] \frac{\sin(kr)}{kr} dr$$

$$+ \sum_m f^2 \int_0^\infty 4\pi r^2 \rho^0 \frac{\sin kr}{kr} dr$$

func of r "coupled"

$$\int 4\pi r \rho^0 \frac{\sin(kr)}{k} dr = 0$$

← 'even in x"

# of atoms.

$$I = N f^2 + N f^2 \int_0^\infty 4\pi r^2 \left(\rho(r) - \rho^0\right) \frac{\sin(kr)}{kr}\, dr$$

$$k\left(\frac{I}{N} - f^2\right) = \int_0^\infty \underbrace{4\pi r \left(\rho(r) - \rho^0\right)}_{G(r)} \sin(kr)\, dr$$

i.e., reduced radial distribution func.

$$F(k) = \int_0^\infty G(r) \sin(kr)\, dr$$

$F(k)$: measured. $G(r)$: desired.

→ LHS is experimentally measured

RHS is related to the $G(r)$.

"Sanity check".

for solid. the initial slope should be $4\pi\rho_0 r$

Brief state on amorphous Solid.

Formation of amorphous solid: Splash the liquid into ultra-low temperature to avoid crystallization.

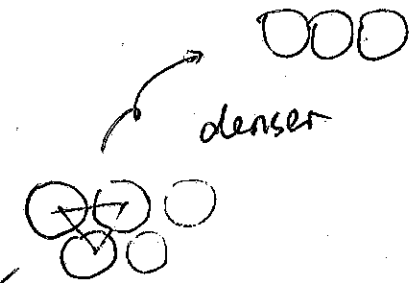
Properties: local planarity at the contact Interface.

Lecture 17 5/29/2024

2D metallic glasses

"independent of quenching rate"

with metallic bonding is non-directional

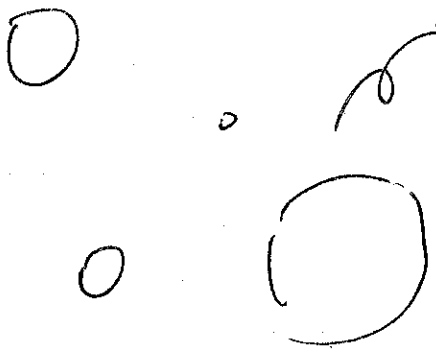


most efficient "motif" for packing

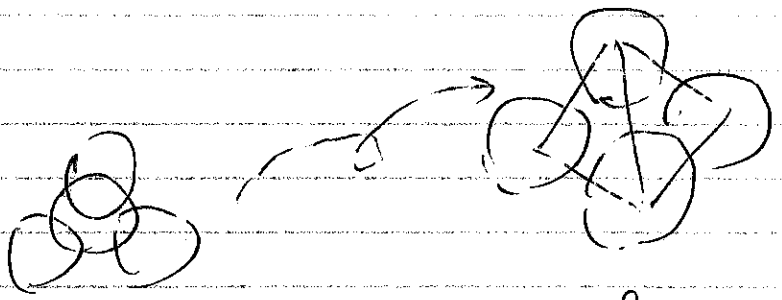
global optimum

maximize nearest neighbors

differently sized atoms

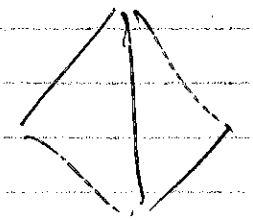


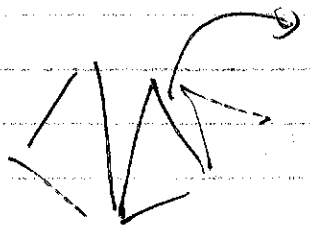
3D



more efficient way

to pack 4 atoms.



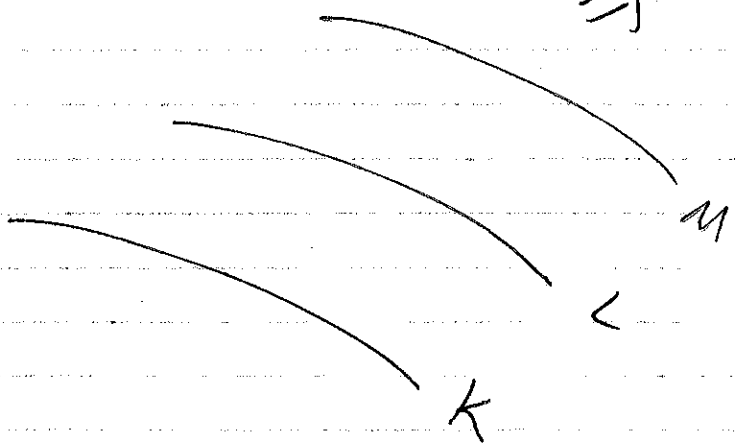


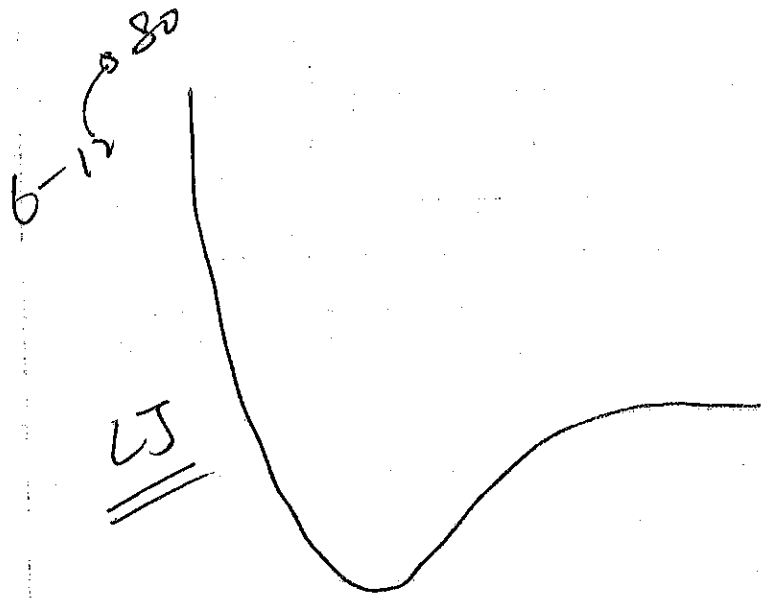
getting gaps.

from stacking tetrahedron.

f → atomic form factor

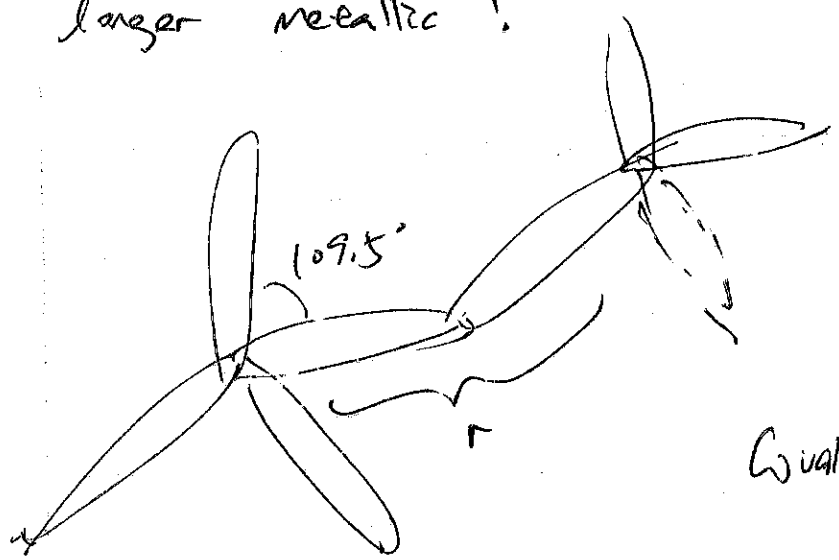
$\Rightarrow$





reproduce the RDF from experiments.

What happens when bonding is no longer metallic?



metals

DRP / RCP

Covalent → Continuous random networks.

$k\theta^2 < kx^2$

CRN

Lecture 19 6/3/2024

1. Dense random pack – metallic glass

Wigner-Seitz Cell

SRO < short-range order

MRO medium-range order

2. – Covalent : Continuous random networks

α-Si: 1. $Z=4$
2. Const. bond length.
3. No dangling bonds
4. Spreading angle: $\Delta\theta = \sim 11°$

α-SiO_2: 1. $Z_{Si}=4$, $Z_O=2$
2. Const. bond length.
3. No dangling bonds
4. $O-Si-O = 109.5°$

$\bar{\beta} = 150°$
$Si-O-Si$
$\Delta\beta = 15°$
torsion not specified

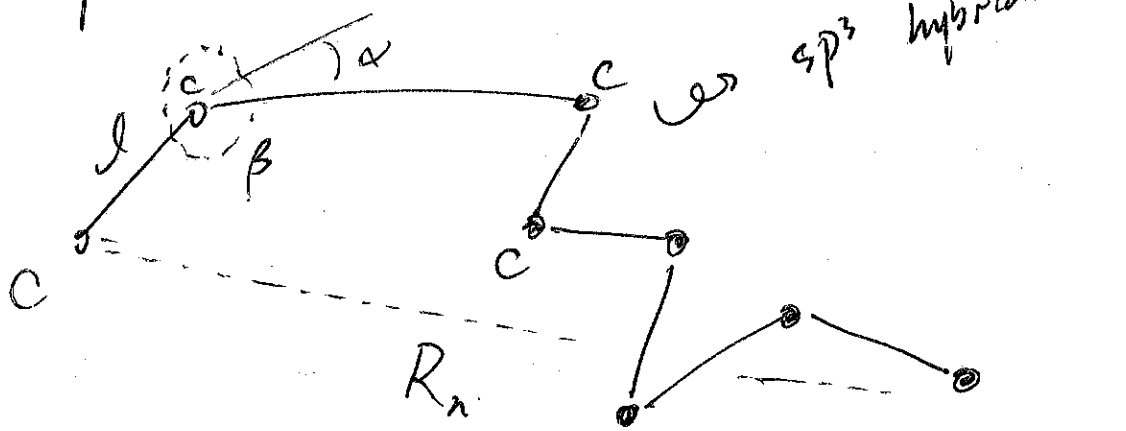
the more bonds, the tighter the network

3. random coil model (polymers)

↓

covalently bonded.

Freely joined model



↳ sp^3 hybridized

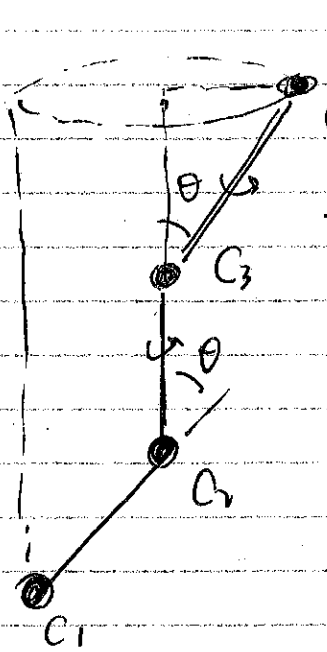
n- monomers

end-to-end separation

$$\langle R_n^2 \rangle^{1/2} = l\, n^{1/2}$$

number of monomers

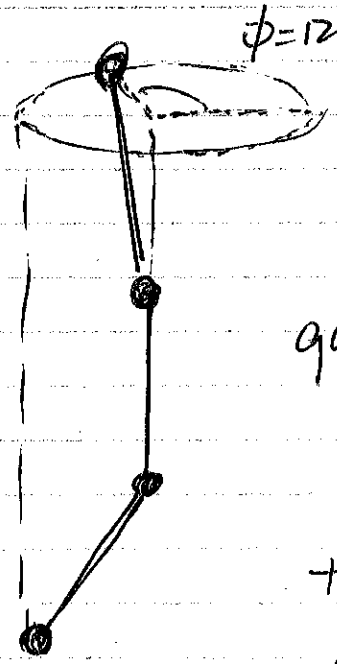
Freely rotating model



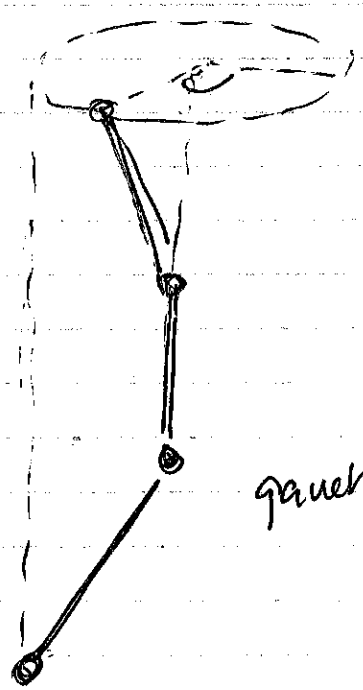
torsion angles.

θ: sp^3 hybridization.

trans distribution (state)

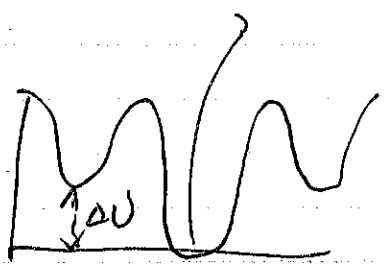


gauche +



gauche −

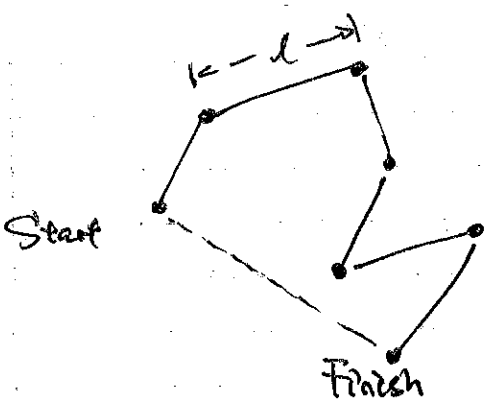
trans. state



Lecture 20. 6/5/2024.

Polymers.

Recall freely jointed Model.



n = # of monomers.

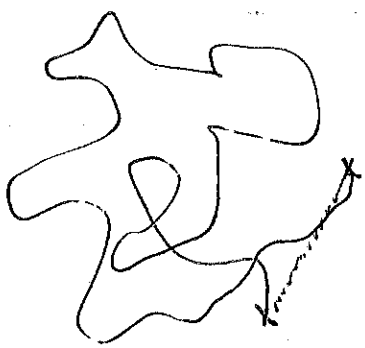
$R_n = l n^{1/2} = 60\,nm$

"end-to-end length."

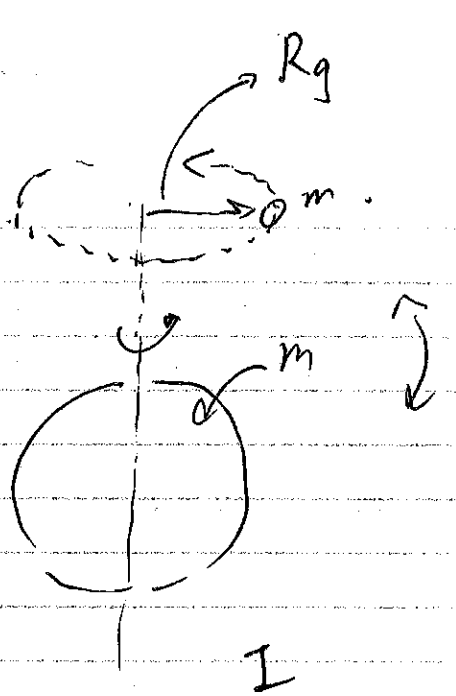
Stretched length = $l_n = 6\,\mu m$

typical val.: $l = 0.6\,nm$.

$n = 10^4$



radius of Gyration



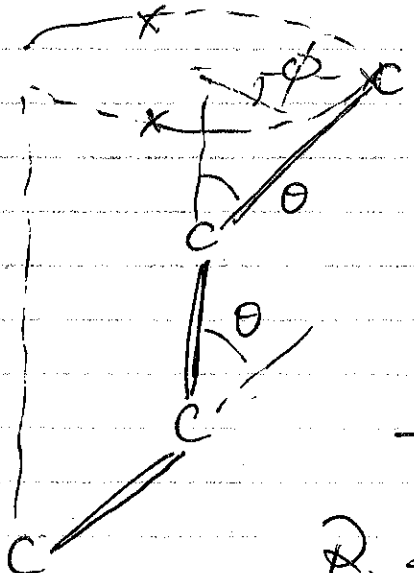
two objects have the same moments of inertia

I

- You can show $R_g = \frac{l n^{1/2}}{\sqrt{6}} = \frac{R_n}{\sqrt{6}}$

Can be experimentally obtained

Freely rotating model.



Constraint of angle

$\rightarrow$ make the polymer end-to-end distance longer.

$\rightarrow$ true for polymers.

$$R_n = C_\infty n^{1/2} l$$

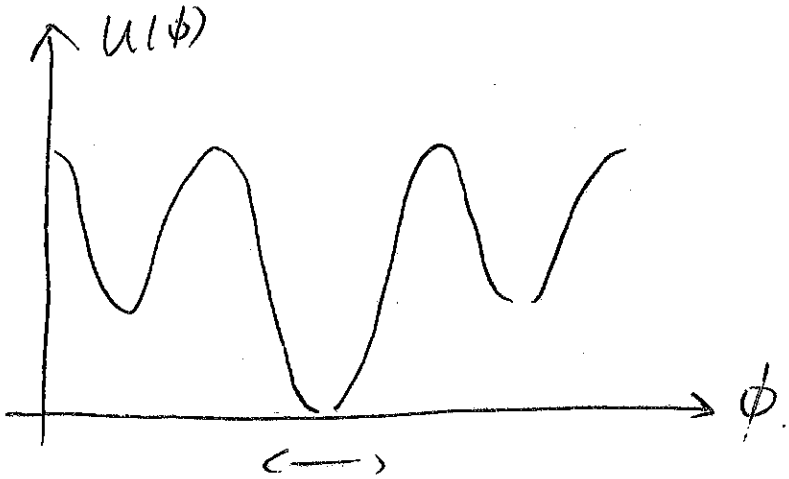
defn: $R_n^2 = C_\infty n l^2$

fixed : 109.5°

$$C_\infty = \left(\frac{1+\cos\theta}{1-\cos\theta}\right)\left(\frac{1+\langle\cos\phi\rangle}{1-\langle\cos\phi\rangle}\right)$$

ϕ is not strictly fixed

$$\langle\cos\phi\rangle = \frac{\int_0^{2\pi} \cos\phi \exp\left(\frac{-U(\phi)}{kT}\right) d\phi}{\int_0^{2\pi} \exp\left(-\frac{U(\phi)}{kT}\right) d\phi}$$



change temperature, entire energy profile shows up

$C_\infty = 5 \sim 10$ (for many polymers)

to measure large angles, use small θ.

1. dense random part (polyglass)

2. CRN (semiconductors)

3. Random coil (polymers)

Auricupride: Cu_3Au