Chapter 4

Part 1: Defects and Imperfections in Solids
Part 2: Nucleation and Growth

Defect: deviations from the ideal are called **imperfection** or **defects**

Note that even if we were able to build a perfect crystal, unless we could keep it at absolute zero (T=0K), defects would appear

Even if they didn't, **vibrations** would ensure that the crystal is not perfect

In some cases, it is desirable to have crystals as perfect as possible
- e.g., crystals for optoelectronics;

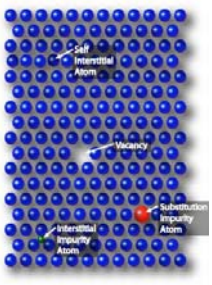
in other cases, imperfections are deliberate
- e.g., alloys of two randomly mixed metals for greater strength;
  doping of semiconductors to achieve specific electrical properties

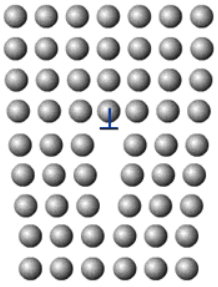
In either case **defect control** is important

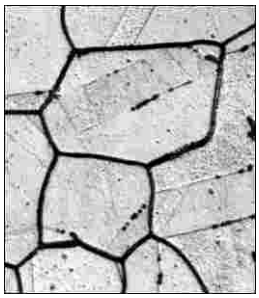
Defect Classification

Can be divided according to their geometry and shape

- 0-D or point defects
- 1-D or line defects (dislocations)
- 2-D (external surface)
- 3-D (grain boundaries, crystal twins, twists, stacking faults, voids and precipitates)



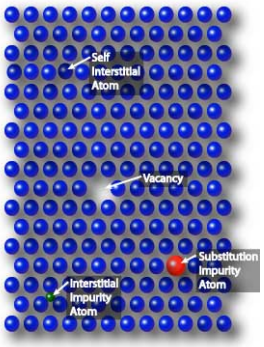




4.1 Point defect (0 D)

The simplest type of imperfection is the **point defect**

These are cases where the perfect order is only disturbed at one (or a few) lattice sites



- **Homogeneous** (all atoms are the same)

ex.: vacancy, self interstitial

- **Heterogeneous**

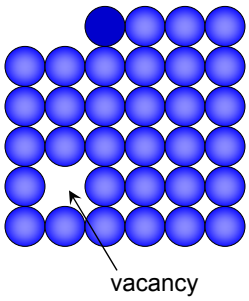
ex.: interstitial impurity atom, substitution impurity atom

4.2 Vacancies and Self-Interstitials

The simplest point defect is the **vacancy (V)** – an atom site from which an atom is missing

Vacancies are always present; their number N_V depends on temperature (T)

$$N_V = N \times e^{-\frac{E_V}{kT}}$$



N_V - # of vacancies

N - number of lattice sites

E_V – energy required to form a vacancy

k – Boltzmann constant

k = 1.38 ×10^{-23} J K^{-1}; or 8.62 ×10^{-5} eV K^{-1}

T – absolute temperature

This type of defect (along with where the atom went) is called a ***Schottky defect***

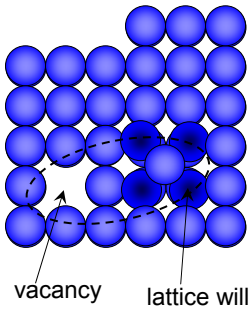
Q.: How many vacancies per cm^3 does Cu have at (a) 293K, (B) 1200K.
Assume E_v = 0.9eV/atom,
the atomic weight (A.W.) is 63.5g/mol, and that the density of Cu is 8.94g/cm^3 (@ 293K) and 8.4g/cm^3 (@1200K)
What is the probability of any given site to be vacant?

Note that by raising the temperature by a factor of 4, we have raised the number of vacancies by a factor of a trillion (10^{12})

Self-interstitial

Extra atom from the lattice site can go between lattice sites - this is called a self-interstitials

- Combination of vacancy and interstitial atom is called a ***Frenkel defect***



• Crystalline lattice must be strained for this type of defects (this raises E_v)

• There are **fewer** of these defects

• They occur more easily near **boundaries** (more room for the strain ⇒ can be not uniformly distributed)

4.3 Impurities in Solids

- there are always *some impurities* in any real material
- consider Au with purity of 99.999% (impurities - 0.001%)
  ⇒ how many atoms..?

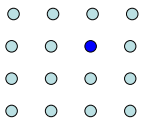
- Addition of impurities will lead to a **solid solution** (the mixture of two of more elements in the solid with random distribution ⇒ uniform properties)

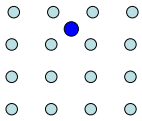
Terms: **Solvent** – the majority atom type (also called host atoms)
Solvent – the element with lower concentration

Two types of solid solution: substitutional and interstitial

Substitutional – a solid solution in which the solute atoms are replaced by solute

Interstitial – solute atoms are located in gaps between host atoms





Substitutional and Interstitial Solutions

Hume-Rothery rules:

A high concentration of solute can only occur in a **substitutional** solid solution if:

1. atoms have similar radii
2. both pure materials have same crystal structure
3. similar electronegativity (otherwise may form a compound instead)
4. solute should have higher valence

Ex.: Cu and Ni are completely mixable

R(Cu)=0.128nm, R(Ni) = 0.125nm,

both *fcc*, electronegativity 1.9 and 1.8

An **interstitial** solution can only occur for small impurity atoms

Even then there is some strain, so typically maximum concentrations are small

ex.: C in Fe (steel)

4.4 Specifications of Composition

Fractions:

1. **By mass (C_A)**

- if we have two elements, A and B, we call the mass fraction of element A:

$$C_A = \frac{m_A}{m_{total}} = \frac{m_A}{m_A + m_B} \quad \text{(as a fraction)} \quad \text{or} \quad C_A(\%) = \frac{m_A}{m_A + m_B} \times 100\%$$

$$C_B = \frac{m_B}{m_{total}} = \frac{m_A + m_B}{m_A + m_B} - \frac{m_A}{m_A + m_B} = 1 - C_A \quad \text{or } C_B(\%) = 100\% - C_A$$

2. **By mole or by # of atoms (C^I_A)**

- if the amounts of A and B are n_A and n_B (we can use either moles or # of atoms)

$$C^I_A = \frac{n_A}{n_{total}} = \frac{n_A}{n_A + n_B} \quad \text{or} \quad C^I_A(\%) = \frac{n_A}{n_A + n_B} \times 100\%$$

Conversion between mass fraction and mole fraction:

$$C^I_A = \frac{C_A \times B}{C_A B + C_B A} \quad C^I_B = \frac{C_B \times A}{C_A B + C_B A} \quad C_A = \frac{C^I_A \times A}{C^I_A A + C^I_B B} \quad C_B = \frac{C^I_B \times B}{C^I_A A + C^I_B B}$$

where A and B are atomic weights of elements A and B

Just a bit of algebra…

Q: A canadian sterling silver (50c) coin has a mass of 9.3g. Composition is 92.5% Ag, 7.5% Cu (by mass).

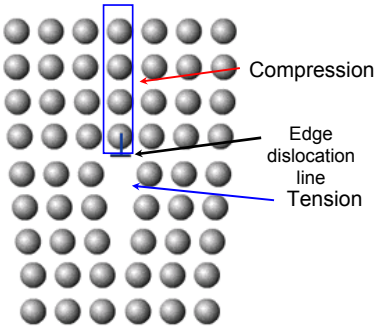
a) How much silver does it contain?

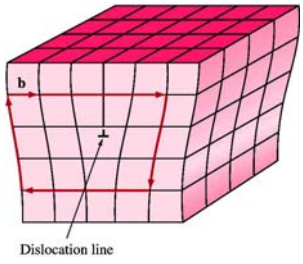
b) What (%) of the atoms are silver?

4.5 1D (Linear) defects

- 1D or linear defect - dislocations
  - edge dislocation
  - screw dislocation

- Edge dislocation (an extra partial plane of atoms)
- there will be local lattice distortion (relaxed at long distance)
- Strain fields (compression and tension)

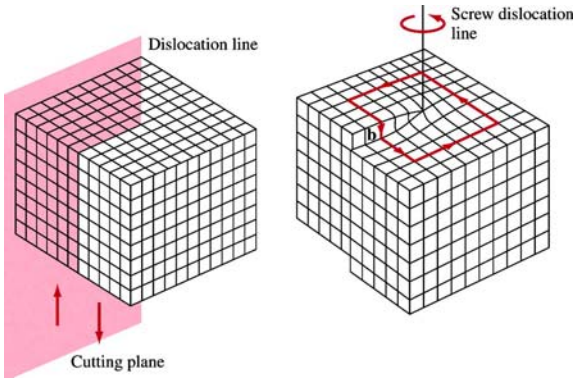




Mathematically ***slip or Burger vector*** **b** is used to characterize displacement of atoms around the dislocation

b is perpendicular to the edge-dislocation line

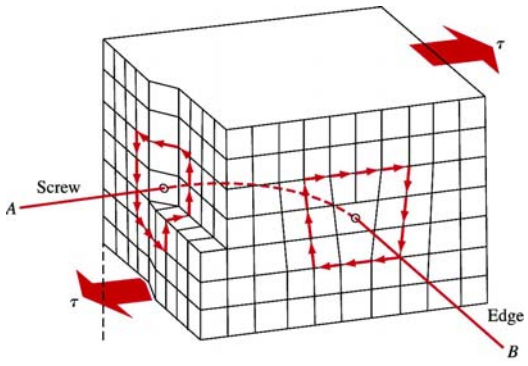
1D - Screw dislocation



By following a loop of atoms around dislocation line ⇒ end up one plane up or down

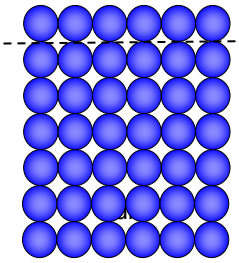
Burger vector is parallel to the screw dislocation line

Mixed edge and screw dislocations



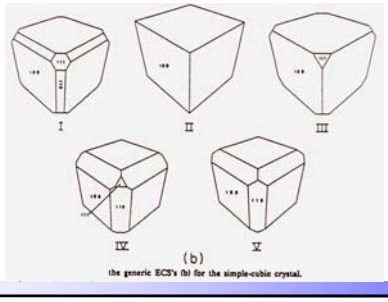
Most dislocations found in crystalline material are neither pure edge nor pure screw, but exhibit components of both types

4.6 2D - External Surface

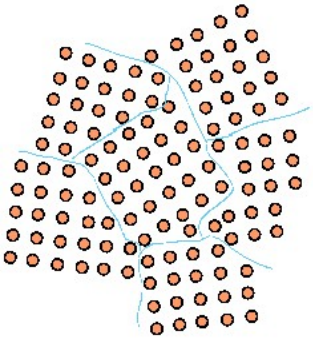


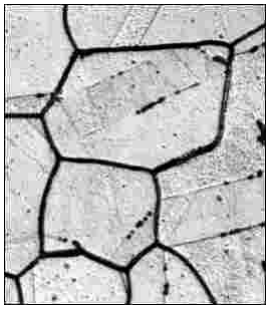
bulk

- Unsaturated bonds ⇒ surface always have an associated ēnergy (called **surface energy** – γ– or surface tension)
- In equilibrium, shape of a given amount of crystal **<u>minimizes</u>** the total **surface energy**
- *Liquids*: raindrops are spherical to have minimum surface-to-volume ration
- *Solids*: Equilibrium Crystal Shape (ECS), determined using Wulff's Theorem (more later…)



4.7 3D Defects - Grain Boundary

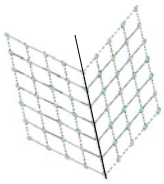




- "internal" surfaces that separate grains (crystals) of different orientation
- created in metals during solidification when crystal grow from different nuclei
- atomic packing is lower in the grain boundary compared to crystal grain, can be also partially amorphous

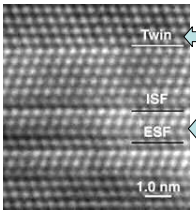
Volume defects

Crystal twins
Grain boundary is not random, but have a symmetry (ex.: mirror)





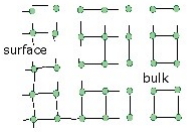
Stacking faults
fcc: …ABCABC…
…ABCABABCABC…



Crystal twin

Stacking fault

Voids the absence of a number of atoms to form internal surfaces; similar to microcracks (broken bonds at the surface)



Summary

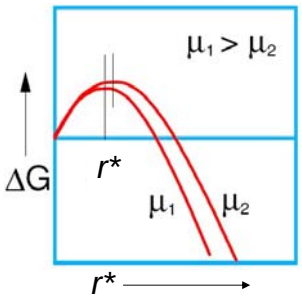
- Microscopic defects can occur in crystals
- In crystals there are:
- 0D: Point defects (vacancies, interstitials, impurities)
- 1D: Line defects (edge and screw dislocations)
- 2D: External surfaces
- 3D: Planar defects (grain boundaries, crystal twins, stacking faults, voids and precipitates)

Chapter 4b: Nucleation and Growth

• Homogeneous and heterogeneous nucleation, and energetic

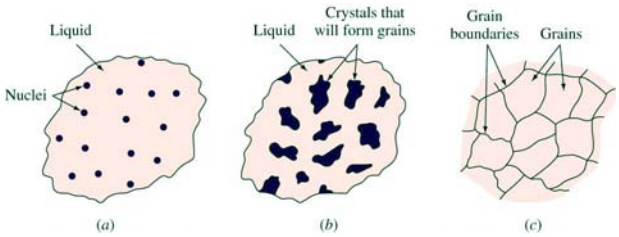
• Growth of metal crystals and formation of a grain structure

• Crystal growth in industry: polycrystalline and single crystal (pp. 133-138, posted as suppl. material on the web-site)



1. Chapter 4.1-4.2 in Smith & Hashemi
2. *Crystal growth for beginners: fundamentals of nucleation, crystal growth, and epitaxy*, by Markov I.V., World Scientific, 1995.

4.8 Solidification of Metals



Solidification of a metal or alloy can be divided into the following steps:

1. The formation of stable nuclei in the melt – nucleation
2. The growth of nuclei into crystals and formation of a grain structure

(Note that the grains are randomly oriented)

4.9 Formation of Stable Nuclei in Liquid Metal

Two main mechanisms of solid particle nucleation in liquid metal

- **Homogeneous** nucleation: the formation of very small region of a new phase (called nuclei) in a pure metal that can grow until solidification is completed

Embryo **Critical size nucleus** **Nucleus**

Nucleus size increases ⟶

- **Heterogeneous** nucleation: the formation of a nuclei of a new solid phase at the interfaces of solid impurities.

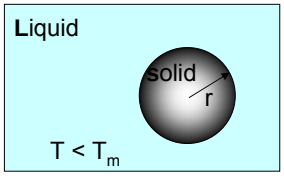
These impurities lower the critical size at a particular T of a stable nuclei

Metal	Freezing Temp.		Heat of fusion (J/cm^3)	Surface energy ($\times 10^7$, J/cm^2)	Maximum undercooling observed (ΔT [K])
	°C	K			
Pb	327	600	280	33.3	**80**
Cu	1083	1356	1826	177	**236**
Pt	1772	2045	2160	240	**332**

Homogeneous Nucleation

- Even if $T < T_m$ (T_m – the equilibrium phase coexistence temperature or melting point), it may not occur immediately
- Driving energy for the liquid-to-solid transformation is the difference in the volume free energy $\Delta\mu$ of the **liquid (L)** and that of the **solid (S)**

V, μ_L ⟹ V, μ_S



Consider a spherical solid "droplet" surrounded by an undercooled melt

- if $T < T_m$, where T_m – the equilibrium phase coexistence temperature (or melting point); thus $\mu_S < \mu_L$

- but there is also an energy associated with the interface (or surface energy, *specific surface free energy* - γ)

Compared to the *homogeneous liquid phase*, the presence of the sphere droplet changes the free energy (ΔG) by:

$$\Delta G_{total} = \frac{4}{3}\frac{\Pi r^3}{\nu}\Delta\mu + 4\Pi r^2\gamma$$

$$\Delta\mu = \mu_S - \mu_L$$

The surface area of a sphere of radius r is $A = 4\,\Pi\,r^2$

A sphere enclosed volume is

$$V = \frac{4}{3}\frac{\Pi r^3}{\nu}$$

Free-energy change *vs* radius of nucleus

$$\Delta G_{total} = \frac{4}{3}\frac{\Pi r^3}{\nu}\Delta\mu + 4\Pi r^2\gamma$$

ΔG_{total} – total free-energy change

r – radius of embryo or nucleus

$\Delta\mu$ – volume free energy

γ - specific surface free energy

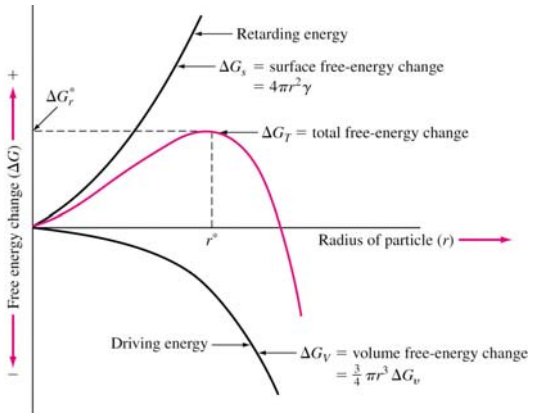
Two components: (i) volume free-energy change (ΔG_V or $\Delta\mu$) and (ii) surface free-energy change (ΔG_S)

$$\Delta\mu = \mu_S - \mu_L < 0;$$

$$\mu_S < \mu_L$$

(i) is negative,

(ii) ΔG_S is positive



r* - critical radius

-if r < r*, droplet can shrink or dissolve

-if r > r*, droplet grows

Critical radius, r*

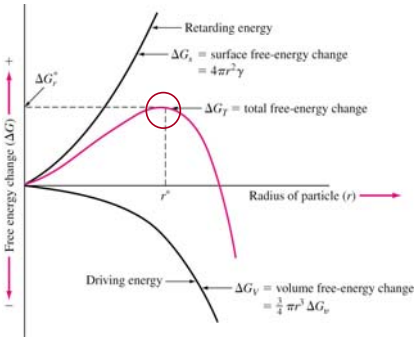
We can find the value of the critical radius by setting:

$$r^* = -\frac{2\gamma \times v}{\Delta\mu}$$

Growth cannot proceed until a droplet with radius at least as large as r* forms

The energy of this critical nucleus relatively to the liquid phase is:

$$\Delta G^* = \frac{16\Pi\gamma^3 v^2}{(\Delta\mu)^2}$$



The probability of this happening by chance is

$$P_{nucleation} \propto e^{-\frac{\Delta G^*}{kT}} = e^{-\frac{16\Pi}{3}\frac{\gamma^3 v^2}{kT(\Delta\mu)^2}}$$

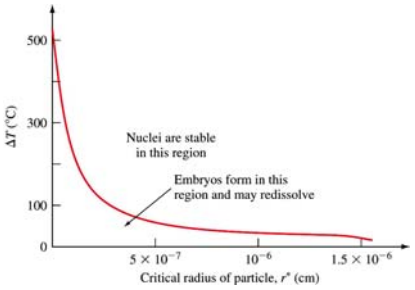
r* *vs* undercooling temperature (ΔT)

How big is the critical nucleus? And what determines it's size?

$$r^* = -\frac{2\gamma v}{\Delta\mu}$$

• The greater the degree of ***undercooling*** ΔT(= T - T_m), the greater the change in the volume free energy Δμ (ΔG_V)

• γ (ΔG_s) - no changes as a function of T



Critical radius of Cu nuclei vs degree of undercooling

• at $T \rightarrow T_m$; $\Delta T \rightarrow 0$; $r^* \rightarrow \infty$

• at $T << T_m$; $r^* \rightarrow 0$

The critical-sized nucleus is related to the amount of ΔT by:

$$r^* = 2\gamma T_m / \Delta H_f \Delta T$$

where r^* - critical radius of nucleus; γ– – surface free energy; ΔH_f - heat of fusion; ΔT – amount of undercooling at which nucleus is formed

Q.: (a) Calculate the critical radius (in cm and in nm) of a homogeneous nucleus that forms when pure liquid Cu solidifies. Consider two cases: ΔT(undercooling) = 0.2 T_m , and (ii) ΔT(undercooling) = 0.02T_m. Use data from Table 4.1 (T_m=1083°C; γ = 177×10^{-7}J/cm^3, ΔH_f = 1826J/cm^3)

(b) For each case calculate the number of atoms in the critical-sized nucleus at both T.

4.10 Heterogeneous Nucleation

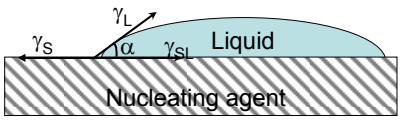
Heterogeneous nucleation: the formation of a nuclei of a new solid phase on the surface of its container, insoluble impurities, and other structural material

that **lower the critical free energy** required to form a stable nucleus

$$r^* = -\frac{2\gamma \times v}{\Delta\mu}$$

Requirements: (a) The solid nucleating agent (impurity or container) must be **wetted** by the liquid metal (similar to wetting process by liquid)

(b) liquid should solidify easily on the nucleating agent

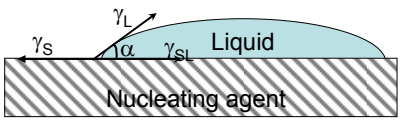


Equilibrium shape and wetting angle of the solid on a nucleating agent

Wetting - low contact angle (α)

γ is lower for heterogeneous nucleation → the total free-energy change is lower → → r* is smaller

Contact Angle



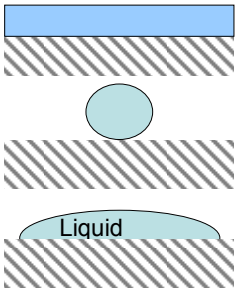
Equilibrium shape and wetting angle of the solid on a nucleating agent

γ_L , γ_S– surface free energy of liquid (solid)

γ_{SL} – interface energy

Surface tension exerts force along surface at line of intersection

At equilibrium: $\gamma_L \cos\alpha = \gamma_S - \gamma_{SL}$ (Young's eq.)



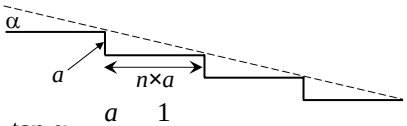
$\gamma_S > (\gamma_{SL} + \gamma_L)$ complete wetting

$\gamma_{SL} > (\gamma_S + \gamma_L)$ no wetting, $\alpha > 90^o$

$-\gamma_L < (\gamma_S + \gamma_{SL}) < \gamma$ wetting

Anisotropy of surface free energy, γ

Consider stepped or (vicinal) surface of 2D solid:



$$\tan\alpha \sim \frac{a}{na} = \frac{1}{n}$$

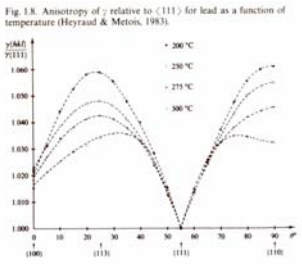
$$\gamma(\alpha) = \gamma(0) + \frac{\beta}{a}|\alpha|$$

Starting from plane, addition of each step adds energy

Define β – energy per step

$$\frac{steps}{unit_cell} = \frac{1}{na} = \frac{\tan\alpha}{a} \approx \frac{\alpha}{a}$$

$\gamma(\alpha)$ has discontinuous derivative at $\alpha = 0$; i.e., there is a *cusp*

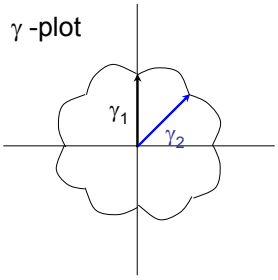


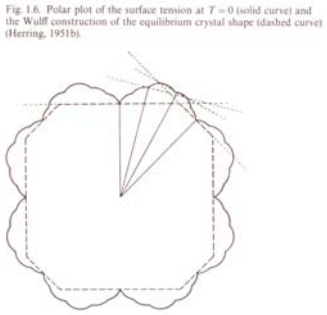
A *cusp* exists at every direction corresponding to a rational Miller index (i.e., low index plane, for example: (100), (111), (110)

Anisotropy of the γ -plot

- A plot of surface tension has many "cusps"

γ -plot





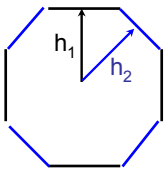
Crystal will seek an equilibrium crystal shape (ECS) determined by minimum surface e free energy at constant volume

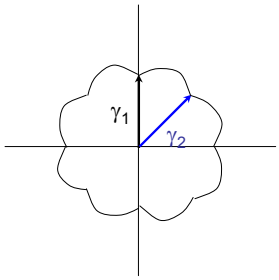
Use **Wulff's Theorem** to determine ECS

Wulff's theorem

- For a crystal at equilibrium, there exists a point in the interior such that its perpendicular distance h_i from the i^{th} face is proportional to γ_i

2D ECS





$$\frac{\gamma_1}{h_1} = \frac{\gamma_2}{h_2} = \ldots$$

Procedure:

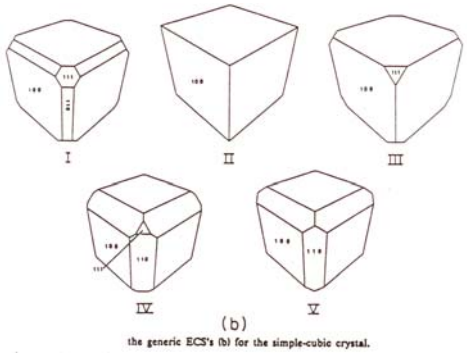
1. given $\gamma(n)$, draw a set of vectors from a common origin with length hi proportional to γ_i, and with directions normal to plane in question
2. construct planes perpendicular to each vector
3. find the geometric figure having the smallest size with non-intersecting planes
4. this is the **ECS** (in practice - in 3D)

ECS

•In equilibrium, shape of a given amount of crystal **minimizes** the total **surface energy**

• ***For Liquids***: spherical shape

• ***For Solids***: Equilibrium Crystal Shape (ECS) has facets



(b)

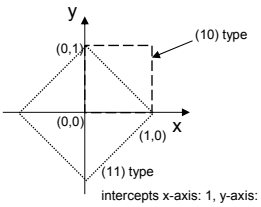
the generic ECS's (b) for the simple-cubic crystal.

Example of ECS for a 2D crystal

$\oint \gamma dl =$ minimum for constant area

Suppose γ-plot has only two types of cusps: (10) and (11)

γ_{10} = 250 ergs/cm; γ_{11} = 225 ergs/cm

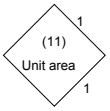




If only (10) type edges:

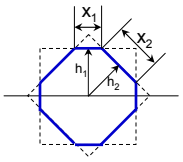
$E = 4 \times 1cm \times 250erg/cm = 1000erg$

If only (11) type edges:



$E = 4 \times 1cm \times 225erg/cm = 900erg$

Need to find minimum energy configuration:



$E_{\min} = 4 \times x_1 cm \times 225erg/cm + 4 \times x_2 cm \times 250erg/cm = 900erg$

for shape (shown in blue) given by Wulff's construction:

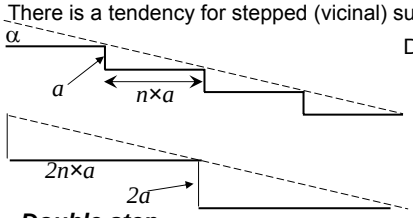
$$\frac{250}{h_1} = \frac{225}{h_2}$$

$x_1 = 0.27; x_2 = 0.513; E_{\min} = 4 \times 0.27 \times 225 + 4 \times 0.513 \times 250 = 756$

Consequences for planar surfaces

- There is a tendency for stepped (vicinal) surface to form facets by step bunching

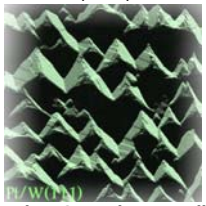
Driving force → minimize edge energy



Double step

- Impurity-induced faceting: adsorb impurities (oxygen, metallic films)

e.g. bcc W(111) → Pt/W{011} and {112}



T.E.Madey, C.-H.Nien, K.Pelhos, *Surf. Sci. 438 (1999)191-206*

O/Ir(210) → Ir{311} and Ir (110) facets

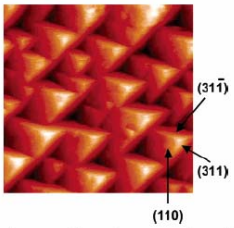
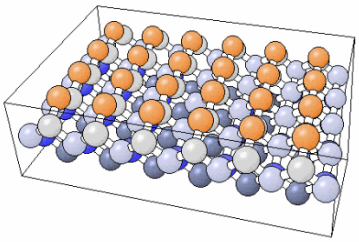


Figure 1. Scanning tunneling microscope (STM) image (100 nm × 100 nm) from oxygen-covered faceted Ir(210) showing the morphology of three-sided pyramidal facets. Faceting is induced by flashing Ir(210) in O_2 (5×10^{-8} Torr) to $T > 1700$ K and subsequent cooling in O_2 to 300 K.

Si(001): minimization of bonds

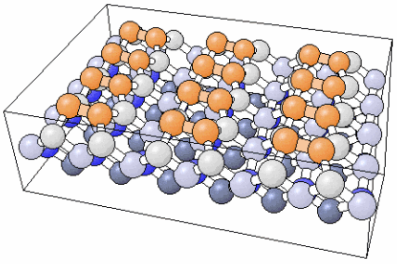
Unreconstructed Si(100)-(1x1) surface

The Si atoms of the topmost layer are highlighted in orange



Reconstructed Si(100)-(2x1) surface

The Si atoms of the topmost layer form a covalent bond with an adjacent surface atom are thus drawn together as pairs; they are said to form "*dimers*".



Chapter 4

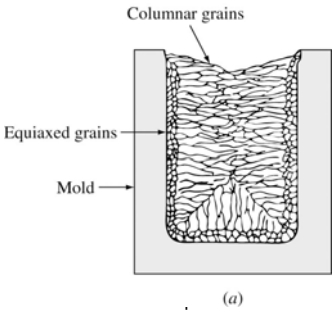
4.11 Growth and formation of a grain structure

When solidification of the metal is finally completed, the crystals (**grains**) join together in different orientation and form crystal boundaries (**grain boundaries**)

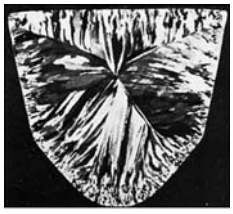
Such solidified metal containing many crystals is said to be **polycrystalline**

# of nucleation sites → different grain structure (e.g.: fewer nucleation sites produces a coarse, large grain structure)

1. Equiaxed grains
2. Columnar grains



(a)



(b)

Summary

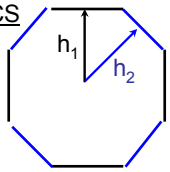
- Homogeneous nucleation, driving energies, and critical nucleus radius

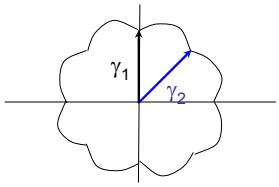
$$\Delta G_{total} = \frac{4}{3}\frac{\Pi r^3}{\nu}\Delta\mu + 4\Pi r^2\gamma \qquad r^* = -\frac{2\gamma\nu}{\Delta\mu}$$

- Heterogeneous nucleation, growth on the surface, Wulffs theorem

(**For a crystal at equilibrium, there exists a point in the interior such that its perpendicular distance h_i from the i^{th} face is proportional to γ_i**)

2D ECS





$$\frac{\gamma_1}{h_1} = \frac{\gamma_2}{h_2} = \ldots$$

- Growth of metal crystals and formation of a grain structure

Problems:

4.1 Calculate the radius of the largest interstitial void in the BCC α iron lattice. The atomic radius of the iron atom in this lattice is 0.124 nm, and the largest interstitial voids occur at the (¼, ½, 0); (½, ¾, 0); (¾, ½, 0); (½, ¼, 0), etc., type positions.

4.2 Using the data in the table below, predict the relative degree of solid solubility of the following elements in aluminum: (a) Cu (b) Mn (c) Mg (d) Zn (e) Si. Use the scale very high, 70-100%; high, 30-70%; moderate, 10-30%, low, 1-10%; and very low, <1%.

4.3 Calculate the size (radius) of the critically sized nucleus for pure platinum when homogeneous nucleation takes place.

4.4 Calculate the number of atoms in a critically sized nucleus for the homogeneous nucleation of pure iron.

4.5 During solidification, how does the degree of undercooling affect the critical nucleus size? Assume homogeneous nucleation.

Element	Atom radius (nm)	Crystal structure	Electro-negativity	Valence
Aluminum	0.143	FCC	1.5	+3
Copper	0.128	FCC	1.8	+2
Manganese	0.112	Cubic	1.6	+2, +3, +6, +7
Magnesium	0.160	HCP	1.3	+2
Zinc	0.133	HCP	1.7	+2
Silicon	0.117	Diamond cubic	1.8	+4