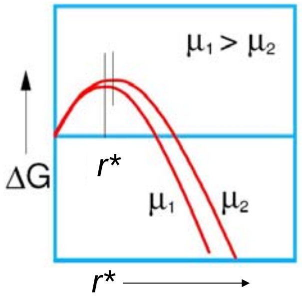
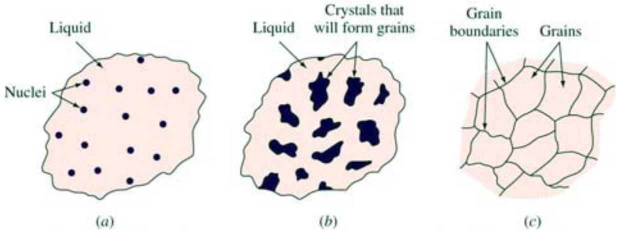
Chapter 4b: Nucleation and Growth

- 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)



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



(a) (b) (c)

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 →

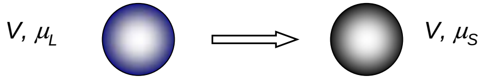
- **Heterogeneous** nucleation: the formation of a nuclei of a new solid phase at the interfaces of solid impurities.

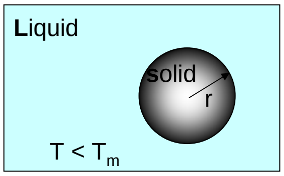
These impurities lower the critical size at a particular T of a stable nuclei

Metal	Freezing Temp.		Heat of fusion (J/cm^3)	Surface energy ($\times 10^7$, J/cm^2)	Maximum undercooling observed (ΔT [K])
	^{o}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)**





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:

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

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

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

A sphere enclosed volume is

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

Free-energy change *vs* radius of nucleus

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

ΔG_{total} – total free-energy change

r – radius of embryo or nucleus

Δμ – volume free energy

γ - specific surface free energy

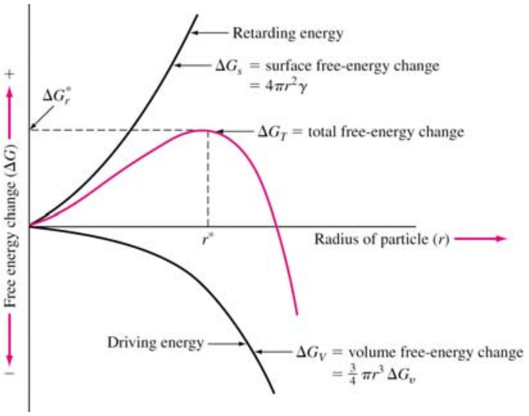
Two components: (i) volume free-energy change (ΔG_V or $\Delta\mu$) and (ii) surface free-energy change (ΔG_S)

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

$$\mu_S < \mu_L$$

(i) is negative,

(ii) ΔG_S is positive



r* - critical radius
-if r < r*, droplet can shrink or dissolve
-if r > r*, droplet grows

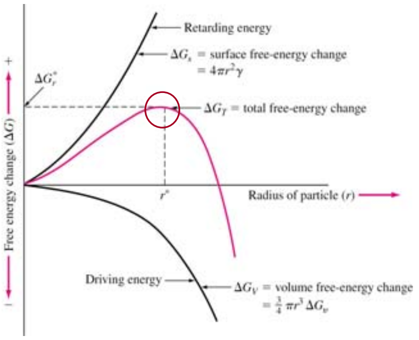
Critical radius, r*

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

$$\frac{\partial \Delta G_T}{\partial r} = 0 = \frac{\partial}{\partial r}\left(\frac{4}{3}\frac{\Pi r^3}{v}\Delta\mu + 4\Pi r^2\gamma\right) = \frac{4}{3}3\frac{\Pi r^2}{v}\Delta\mu + 4\times 2\Pi r\gamma \quad \text{when } r = r^*$$

$$\frac{4\Pi r^2\Delta\mu}{v} = -8\Pi r\gamma$$

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



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

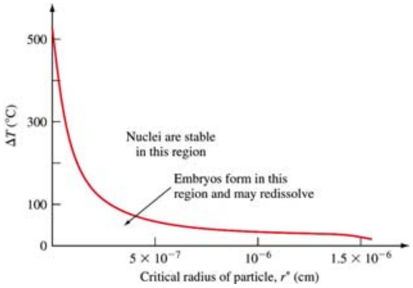
$$P_{nucleation} \propto e^{-\frac{\Delta G^*}{kT}} = e^{-\frac{16\Pi}{3}\frac{\gamma^3 v^2}{kT(\Delta\mu)^2}}$$

r* *vs* undercooling temperature (ΔT)

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

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

- 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→T_m; ΔT → 0; r* → ∞
- at T<<T_m; r* → 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

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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^{o}C; $\gamma = 177\times10^{-7}$J/cm^3, ΔH_f = 1826J/cm^3)

(b) For both undercooling conditions calculate the number of atoms in the critical-sized nucleus

4.10 Heterogeneous Nucleation

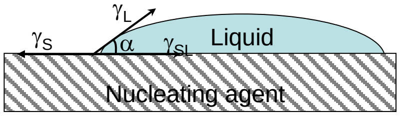
Heterogeneous nucleation: the formation of a nuclei of a new solid phase on the surface of its container, insoluble impurities, and other structural material

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

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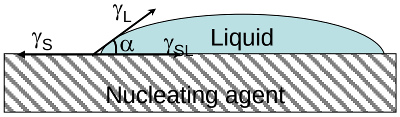
Contact Angle



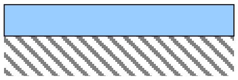
Equilibrium shape and wetting angle of the solid on a nucleating agent

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

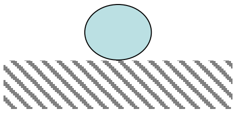
γ_{SL} – interface energy

Surface tension exerts force along surface at line of intersection

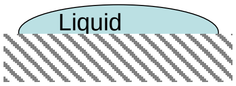
At equilibrium: $\gamma_L \cos\alpha = \gamma_S - \gamma_{SL}$ (Young's eq.)



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



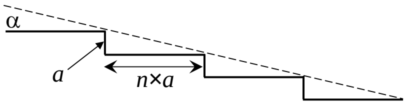
$\gamma_{SL} > (\gamma_S + \gamma_L)$ no wetting, $\alpha > 90^o$



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

Anisotropy of surface free energy, γ

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



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

Starting from plane, addition of each step adds energy

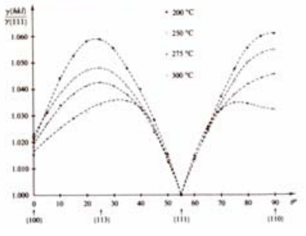
Define β – energy per step

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

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

γ (α) has discontinuous derivative at α = 0; i.e., there is a *cusp*

Fig. 1.8. Anisotropy of γ relative to ⟨111⟩ for lead as a function of temperature (Heyraud & Metois, 1983).



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”

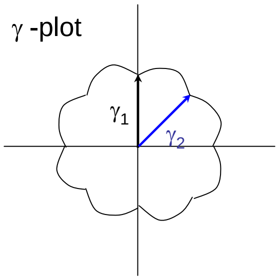
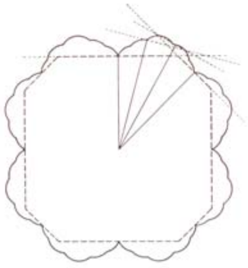


Fig. 1.6. Polar plot of the surface tension at $T = 0$ (solid curve) and the Wulff construction of the equilibrium crystal shape (dashed curve) (Herring, 1951b).



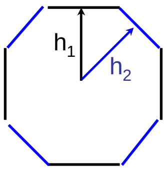
Crystal will seek an equilibrium crystal shape (ECS) determined by minimum surface e free energy at constant volume

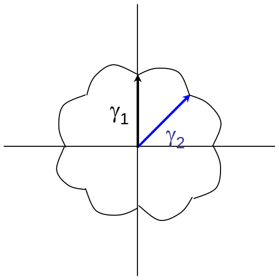
Use **Wulff’s Theorem** to determine ECS

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





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

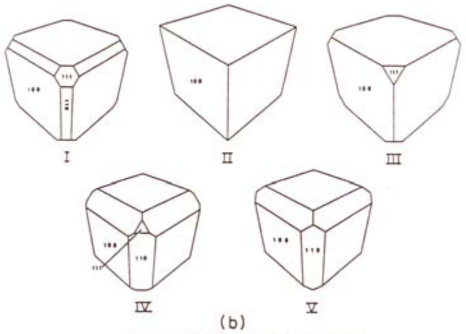
Procedure:

1. given $\gamma(n)$, draw a set of vectors from a common origin with length hi proportional to γi, 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 **<u>minimizes</u>** 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 <u>constant area</u>

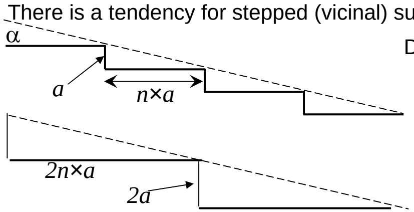
Suppose γ-plot has only two types of cusps: (10) and (11)

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

Consequences for planar surfaces

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

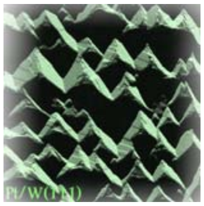
Driving force → minimize edge energy



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

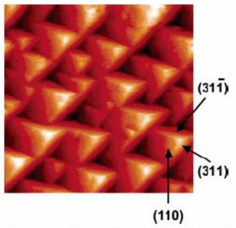


Figure 1. Scanning tunneling microscope (STM) image (100 nm × 100 nm) from oxygen-covered faceted Ir(210) showing the morphology of three-sided pyramidal facets. Faceting is induced by flashing Ir(210) in O_2 (5×10^{-8} Torr) to $T >$ 1700 K and subsequent cooling in O_2 to 300 K.

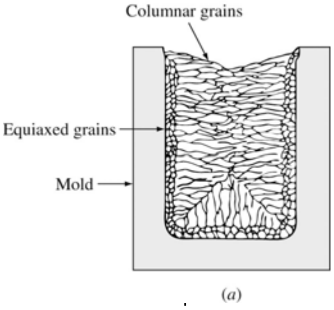
4.11 Growth and formation of a grain structure

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

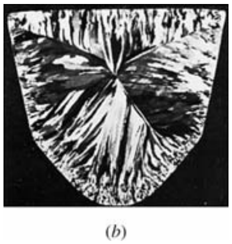
Such solidified metal containing many crystals is said to be **polycrystalline**

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

1. Equiaxed grains
2. Columnar grains



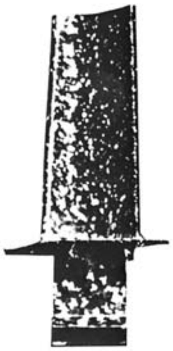
(*a*)



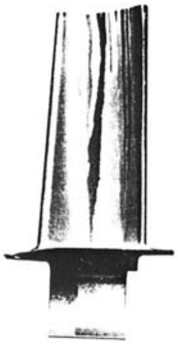
(*b*)

4.12 Industrial Growth Processes

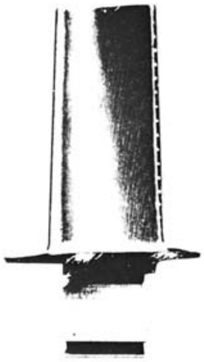
- Metals and alloys are cast into various shapes
- Different growth processes for polycrystalline and single-crystal metals



(*a*)
Polycrystal
equiaxed



(*b*)
Polycrystal
columnar



(*c*)
Single
crystal