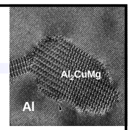
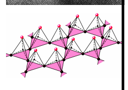
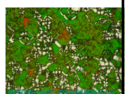
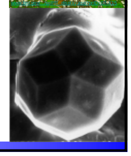
Lecture 2

Complex Structures







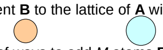


References:
1. Marder, Chapter 5
2. Kittel, Chapters 17 and 21, p.48
3. Ashcroft and Mermin, Chapter 19
4. Kaxiras, Chapters 12-13

2.1 Alloys

Thermodynamic considerations: entropy favors mixing!!!

Adding element **B** to the lattice of **A** with energy penalty ε > 0



The number of ways to add *M* atoms **B** to a lattice of *N* atoms **A** (N >>M)

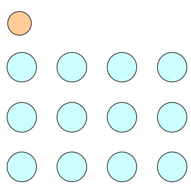
$$\binom{N}{M} = \frac{N!}{M!(N-M)!} \approx \frac{N^M}{M!}$$

$$\text{Concentration} \quad c = \frac{M}{N}$$

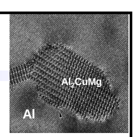
$$S = k_B \ln\left(\frac{N^M}{M!}\right) \approx -k_B N(c \ln c - c)$$

$$G = \mathrm{E} - TS = N(c\varepsilon + k_B Tc \ln c - k_B Tc)$$

$$\text{G(c) has minimum at } c = e^{-\frac{e}{k_B T}}$$



2.1.1 Phase Diagrams



A **phase** in a material is a region that differ in its microstructure and or composition from another region
- homogeneous in crystal structure and atomic arrangement
- have same chemical **and** physical properties throughout
- have a definite **interface** and able to be mechanically separated from its surroundings

A **phase diagrams** is a type of graph used to show the *equilibrium* conditions between the thermodynamically-distinct phases; or to show what phases are present in the material system at various T, p, and compositions
- "equilibrium" is important: phase diagrams are determined by using slow cooling conditions ⇒ no information about kinetics

Degree of freedom (or variance) F is *the number* of variables (T, p, and composition) that can be changed independently without changing the phases of the system

Gibbs Phase Rule

Gibbs' phase rule describes the possible # of **degrees of freedom (*F*)** in a **closed system** at **equilibrium**, in terms of the number of separate **phases (*P*)** and the number of **chemical components (*C*)** in the system (derived from thermodynamic principles by Josiah W. Gibbs in the 1870s)

$\boxed{F + P = C + 2}$

F is # of degrees of freedom or variance

P is # of phases

C is # of components

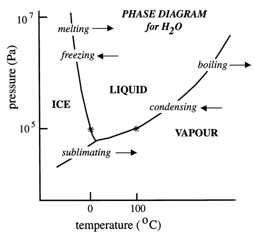
Component is the minimum # of species necessary to define the composition of the system

<u>H_2O</u>   C=1

(i) P=1, F=2;

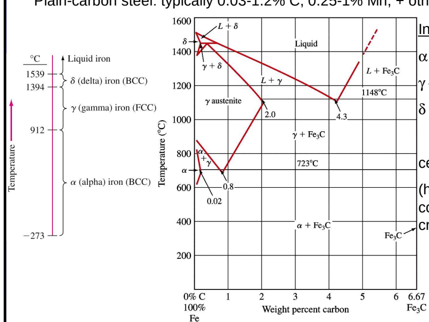
(ii) P=2, F=1;

(iii) P=3, F=0



The Fe-C System

Plain-carbon steel: typically 0.03-1.2% C, 0.25-1% Mn, + other minor impurities



<u>Interstitial s. s. solutions</u>

α ferrite – Fe (0.02%C)

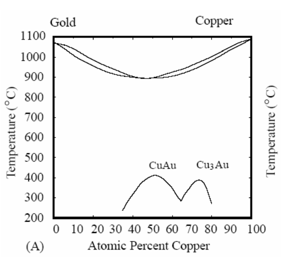
γ – austenite Fe (2.08%C)

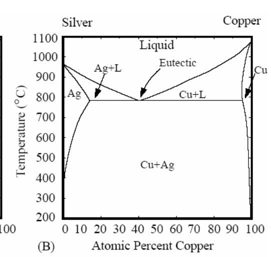
δ - ferrite (0.09% C)

cementite - Fe_3C

(hard and brittle compound, different crystal structure)

Example Phase Diagrams

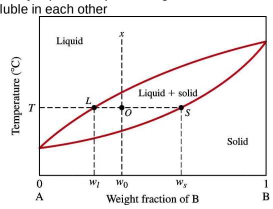




The Lever Rule

The weight percentages of the phases in any 2 phase region can be calculated by using the **lever rule**

Consider the binary equilibrium phase diagram of elements A and B that are completely soluble in each other



C_o

Mass fraction of B

Let *x* be the alloy composition of interest, its weight (mass) fraction of B (in A) is w_o (C_o)

Let *T* be the temperature of interest ⇒ at T alloy *x* consists of a mixture of liquid (with w_L (C_L) - mass fraction of B in liquid) and solid (with w_S (C_S) - mass fraction of B in solid phase)

Lever Rule (cont.)

First: recognize that the sum of the weight fractions of the liquid and solid phases =1

$$X_L + X_S = 1$$

$$\text{or } X_L = 1 - X_S \quad \text{and} \quad X_S = 1 - X_l$$

Considering the weight balance of B in the alloy as a whole and the sum of B in the two phases:

Grams of B in 2-phase mixture = grams of B in liquid phase + grams of B in solid phase

$$w_o = X_L w_L + X_S w_S$$

$$\text{combined with } X_L = 1 - X_S \quad \Rightarrow w_o = (1 - X_S) w_L + X_S w_S = w_L - X_S w_L + X_S w_S$$

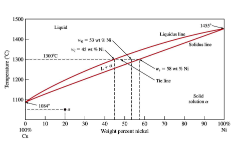
$$\text{rearranging: } X_S (w_S - w_L) = w_o - w_L$$

$$\text{Weight fraction of solid phase: } X_S = \frac{w_o - w_L}{w_S - w_L}$$

similarly...

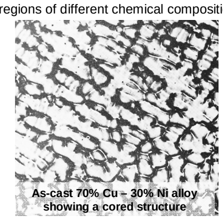
$$\text{Weight fraction of liquid phase: } X_L = \frac{w_s - w_o}{w_S - w_L}$$

Nonequilibrium Solidification of Alloys



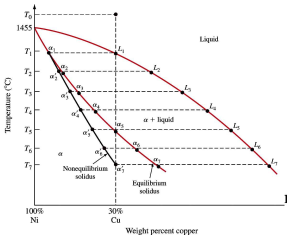
⇐ constructed by using very slow cooling conditions

Atomic diffusion is slow in solid state; as-cast microstructures show “core structures” caused by regions of different chemical composition

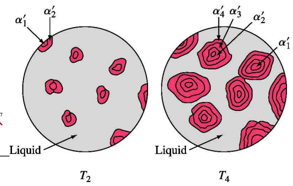


As-cast 70% Cu – 30% Ni alloy showing a cored structure

Nonequilibrium Solidus



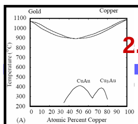
Solidification of a 70% Ni-30%Cu alloy
Fig. 8.9, Smith



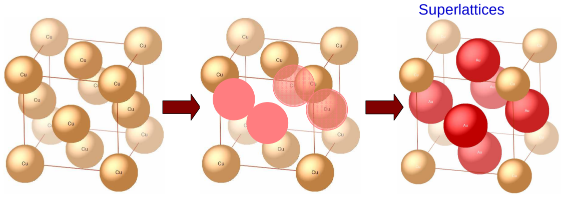
Schematic microstructures at T2 and T4
Fig.8.10, Smith

- each core structure will have composition gradient α_1-α_7
- additional **homogenization** step is often required (annealing $<T_7$)

2.1.2 Solid St. Solutions and Superlattices



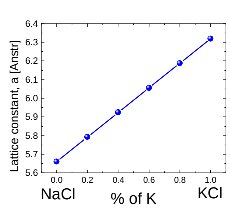
Interstitial Alloys
(Hume-Rothery rules)
vs
Superlattices



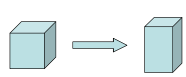
Cu : Au = 3 : 1 and Cu : Au = 1 : 1 compositions can be stabilized
Extra peaks in X-ray diffraction!

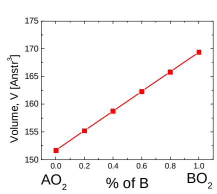
Vegard's law

Vegard's law is an approximate empirical rule
States that a linear relation exists (T = const) between the crystal lattice constant of substitutional compound (alloy) and the concentration of the constituent elements



$NaCl \Rightarrow Na_{1-x}K_xCl \Rightarrow KCl$





Order - disorder transformations

Dashed lines on phase diagram
$\Rightarrow$ ordered and disordered states of the alloy (e.g., Cu-Zn system)

T = 0K – absolute order (=1)

At T = T_c – disappearance of the long range order (or both long and short range order)

Ordered structure:

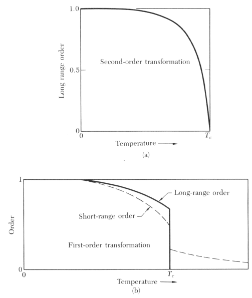
All reflections will occur

$S(hkl) = f_{Cu} + f_{Zn} e^{-i\pi(h+k+l)}; f_{Cu} \neq f_{Zn}$

Disordered:

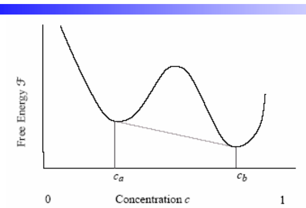
Some superstructure line vanish

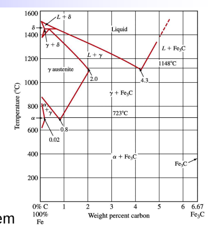
$S(hkl) = \langle f \rangle + \langle f \rangle e^{-i\pi(h+k+l)}$



A) Long-range order for AB (second order transformation)
B) Long- and short range order of AB_3 (first order transformation)

2.1.3 Phase Separation





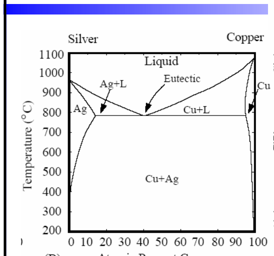
Phase separation lowers the free energy of a system

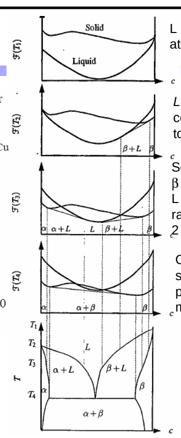
$$F_{PhS} = f \cdot F(c_a) + (1-f) \cdot F(c_b)$$

$$f = \frac{c - c_b}{c_a - c_b}$$

$$F_{PhS} = \frac{c - c_b}{c_a - c_b} \cdot F(c_a) + \frac{c_a - c}{c_a - c_b} \cdot F(c_b)$$

Phase Separation





L is of lower free energy at all *c* than the solid

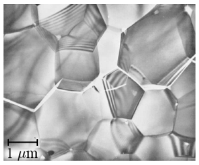
L is lower to the left, but coexists with solid β towards the right

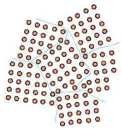
Solid α is stable for low *c*, β is stable for high c, L is stable for a small range in the middle, 2 coexistence regions

Only solid phases are stable: these can be pure α, pure β, or mixtures of the two

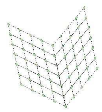
Grain Boundaries

Grain and grain boundaries





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

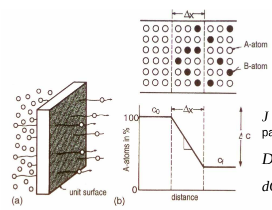


- "internal" surfaces that separate grains (crystals) of different orientation
- created in metals during solidification when crystal grow from different nuclei
- atomic packing is lower in the grain boundary compared to crystal grain, can be also partially amorphous

Dynamics of Phase Separation

Consider diffusion of solute atoms (b) in solid state solution (AB) in direction x between two parallel atomic planes (separated by Δx)

- if there is **no changes with time** in C_B at these planes – such diffusion condition is called **steady-state diffusion**



For a steady-state diffusion, **flux (flow)**, J, of atoms is:

$$\boxed{J = -D\frac{dC}{dx}}$$

J – flux of atoms, atoms/(m^2 s): the number of particles which pass through a unit area in a unit of time;

D – diffusivity or diffusion coefficient, m^2/s

dC/dx – concentration gradient, atoms/m^4

Recall: Solvent – the majority atom type (or host atoms): **Solute** – the element with lower concentration
Substitutional – a solid solution in which the solute atoms are replaced by solute
Interstitial – solute atoms are located in gaps between host atoms

Fick's first law of diffusion

$$\boxed{J = -D\frac{dC}{dx}}$$

For steady-state diffusion condition (**no change in the system with time**), the net flow of atoms is equal to the diffusivity D times the diffusion gradient dC/dx

$$J\left(\frac{atoms}{m^2 s}\right) = -D\left(\frac{m^2}{s}\right)\frac{dC}{dx}\left(\frac{atoms}{m^3}\times\frac{1}{m}\right)$$

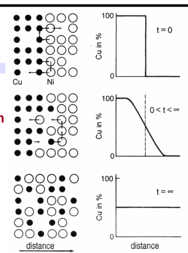
'-' sign: flux direction is from the higher to the lower concentration; i.e. it is the opposite to the concentration gradient

Solute	Solvent (host structure)	Diffusivity (m^2/s) 500°C (930°F)	1000°C (1830°F)
1. Carbon	FCC iron	(5×10^{-15})*	3×10^{-11}
2. Carbon	BCC iron	10^{-12}	(2×10^{-9})
3. Iron	FCC iron	(2×10^{-23})	2×10^{-16}
4. Iron	BCC iron	10^{-20}	(3×10^{-14})
5. Nickel	FCC iron	10^{-23}	2×10^{-16}
6. Manganese	FCC iron	(3×10^{-24})	10^{-16}
7. Zinc	Copper	4×10^{-18}	5×10^{-13}
8. Copper	Aluminum	4×10^{-14}	10^{-10} M†
9. Copper	Copper	10^{-18}	2×10^{-13}
10. Silver	Silver (crystal)	10^{-17}	10^{-12} M
11. Silver	Silver (grain boundary)	10^{-11}	
12. Carbon	HCP titanium	3×10^{-16}	(2×10^{-11})

Diffusivity D depends on:

1. Diffusion mechanism
2. Temperature of diffusion
3. Type of crystal structure (bcc > fcc)
4. Crystal imperfections
5. Concentration of diffusing species

Non-Steady-State Diffusion



Change in concentration in 2 semi-infinite rods of Cu and Ni caused by diffusion, From G. Gottstein "Physical Foundations of Material Science"

In practice the **concentration** of solute atoms at any point in the material changes **with time** – **non-steady-state diffusion**

For non-steady-state condition, diffusion coefficient, D - NOT dependent on time:

Second Fick's law of diffusion: $\boxed{\frac{dC_x}{dt} = \frac{d}{dx}\left(D\frac{dC_x}{dx}\right)}$

If $D \neq D(x)$, in 1D case: $\boxed{\frac{dC_x}{dt} = D\frac{\partial^2 C}{\partial x^2}}$ The rate of compositional change is equal to the diffusivity times the rate of the change of the concentration gradient

In 3D case: $\boxed{\frac{dC_x}{dt} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right)}$

Non-Steady-State Diffusion (continued)

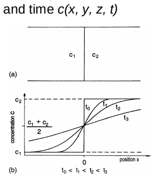
With specific initial or boundary conditions this partial differential equations can be solved to give the concentration as function of spatial position and time *c(x, y, z, t)*

Let us consider two rods with different concentrations c_1 and c_2 which are joined at x=0 and both are so long that mathematically they can be considered as infinitely long

The concentration profile at t = 0 is discontinuous at x = 0:

$x < 0$, $c = c_1$; $x < 0$, $c = c_2$

We can obtain solution of: $\boxed{\frac{dC_x}{dt} = D\frac{\partial^2 C}{\partial x^2}}$



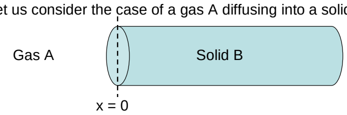
$$c(x,t) - c_1 = \frac{c_2 - c_1}{\sqrt{\pi}} \int_{-\infty}^{\frac{x}{2\sqrt{Dt}}} e^{-\xi^2} d\xi = \frac{c_2 - c_1}{2}\left(1 + erf\left(\frac{x}{2\sqrt{Dt}}\right)\right)$$

where $erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\xi^2} d\xi$, is known as the error function

$$z = \frac{x}{2\sqrt{Dt}}$$

Gas diffusion into a solid

Let us consider the case of a gas A diffusing into a solid B



$$\frac{C_s - C_x}{C_S - C_o} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

C_S – surf. C of element in gas diffusing into the surface

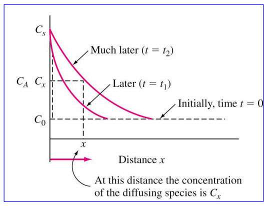
C_o – initial uniform concentration of element in solid

x - distance from surface

D – diffusivity of diffusing solute element

t – time

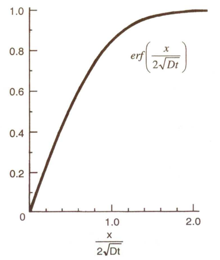
erf – mathematical function called **error function**



Error function

Curve of the error function *erf (z)* for

$$z = \frac{x}{2\sqrt{Dt}}$$



z	erf z	z	erf z	z	erf z	z	erf z
0	0	0.40	0.4284	0.85	0.7707	1.6	0.9763
0.025	0.0282	0.45	0.4755	0.90	0.7970	1.7	0.9838
0.05	0.0564	0.50	0.5205	0.95	0.8209	1.8	0.9891
0.10	0.1125	0.55	0.5633	1.0	0.8427	1.9	0.9928
0.15	0.1680	0.60	0.6039	1.1	0.8802	2.0	0.9953
0.20	0.2227	0.65	0.6420	1.2	0.9103	2.2	0.9981
0.25	0.2763	0.70	0.6778	1.3	0.9340	2.4	0.9993
0.30	0.3286	0.75	0.7112	1.4	0.9523	2.6	0.9998
0.35	0.3794	0.80	0.7421	1.5	0.9661	2.8	0.9999

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Q: Consider the gas carburizing of a gear of *1018* steel (C 0.18 wt %) at 927℃. Calculate the time necessary to increase the C content to 0.35 wt % at 0.40 mm below the surface of the gear. Assume the C content at the surface to be 1.15 wt % and that the nominal C content of the steel gear before carburizing is 0.18 wt %. *D* (*C* in γ iron) at 927℃ = 1.28 × 10^{-11} m^2/s

$$\frac{C_s - C_x}{C_s - C_o} = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

where: $C_s = 1.15\%$ $\quad C_o = 0.18\%$ $\quad C_x = 0.35\%$

$x = 0.40 \text{ mm} = 4\times10^{-4} \text{ m}$ $\quad D_{927°C} = 1.28\times10^{-11} \text{ m}^2/\text{s}$

Substituting $$\frac{1.15-0.35}{1.15-0.18} = \text{erf}\left[\frac{4\times10^{-4}\text{ m}}{2\sqrt{(1.28\times10^{-11}\text{ m}^2/\text{s})t}}\right]$$

$$0.8247 = \text{erf}\left[\frac{55.90}{\sqrt{t}}\right] = \text{erf}\, z$$

Interpolating from Table 5.3,

erf z	z
0.8209	0.95
0.8247	x
0.8427	1.0

$$\frac{0.8247-0.8209}{0.8427-0.8209} = \frac{x-0.95}{1.0-0.95} \quad x = 0.959$$

Thus,

$$z = \frac{55.90}{\sqrt{t}} = 0.959$$

$t = 3397.7$ s = **56.6 min.**

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Correlation Functions and Order Parameters

Liquid Phase ⇔ Solid Phase

Order Parameter – function designed to

- vanish when the desired form of order is absent
- rise from zero as soon as order is present

$$n_2(\vec{r}_1, \vec{r}_2, t) = \left\langle \sum_{l \neq l'} \delta(\vec{r}_1 - \vec{R}_l(0))\delta(\vec{r}_2 - \vec{R}_{l'}(t)) \right\rangle$$

$$S(\vec{q}) \equiv \frac{I}{NI_{atom}} =$$

$$= \frac{1}{N}\sum_{l,l'} \left\langle e^{i\vec{q}(\vec{R}_l - \vec{R}_{l'})} \right\rangle = 1 + \frac{1}{N}\int d\vec{r}_1 d\vec{r}_2 n_2(\vec{r}_1, \vec{r}_2, 0) e^{i\vec{q}(\vec{r}_1 - \vec{r}_2)}$$

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2.2 Liquids: Long- and Short-Range Order

- Long-range order in crystals:

$$O_{\vec{K}} = \frac{V}{N^2} n_2(\vec{K})$$

- Short-range order in liquids:

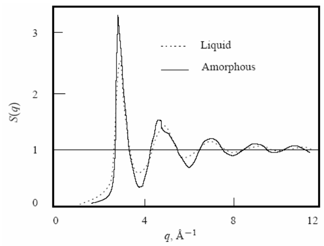
$$g(r) = \frac{n_2(r)}{n^2}$$

Also Kittel, pp. 522-530

$$S(\vec{q}) = 1 + n\int g(r)e^{i\vec{q}\vec{r}}d\vec{r} = 1 + n\int (g(r)-1)e^{i\vec{q}\vec{r}}d\vec{r} + n\int e^{i\vec{q}\vec{r}}d\vec{r} \approx$$
$$\approx 1 + n\int (g(r)-1)e^{i\vec{q}\vec{r}}d\vec{r}$$

Static structure factor, S(q)

Structure factor for liquid and amorphous nickel



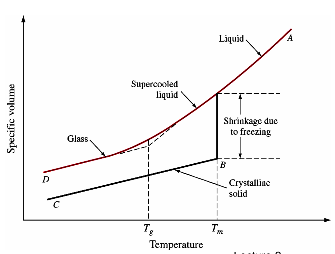
$$z = n\int_0^{\text{first peak}} 4\pi r^2 g(r)dr$$

Area under the first peak gives the average number of ***N.N*** or ***coordination number***

2.3 Glasses - Definition

Glass: an product of high temperature treatment (fusion) that has been cooled to a rigid condition without crystallization

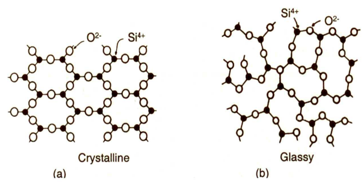
Solidification behavior of a glass will be intrinsically different compared to the crystalline solid



Glass liquid becomes more viscous as T ⇓

Transforms from soft plastic state to rigid brittle glassy state in narrow ΔT

Lower Coordination Number



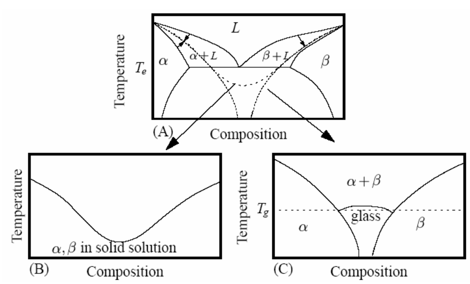
The strong dependency of the bonding on crystallographic direction for covalent compounds result in a barrier to a formation of a crystalline structure

Strictly periodic arrangements cannot be easily established during solidification, and only chain molecules are formed

Glass Properties vs cooling rate

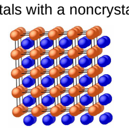
$$\rho \propto \exp\left[\frac{C}{T-T_o}\right]$$

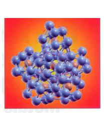
empirical relationship - Vogel Fulcher law



Bulk Metallic Glasses (BMG)

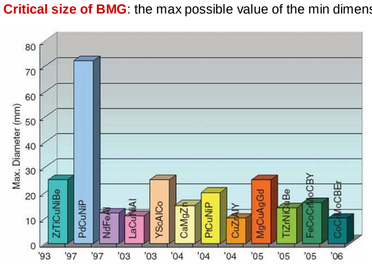
Metals with a noncrystalline structure (also called glassy metals)





No pure metals and few metallic alloys are natural glass-formers

Critical size of BMG: the max possible value of the min dimension



MRS bulletin, August 2007, P.611

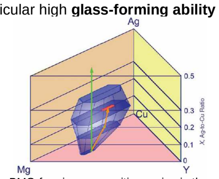
Initial idea: extremely fast quenching (10^5 K/s)

Challenging…

Thermodynamic and kinetic factors

Some alloy compositions may exhibit particular high **glass-forming ability**

BMG are more likely to have :
- 3-5 components
- with large atomic mismatch
- composition close to eutectic
- be densely packed



BMG-forming composition region in the Mg-(Cu,Ag)-Y system. Within the blue region, the critical diameter of the glasses exceeds 8 mm

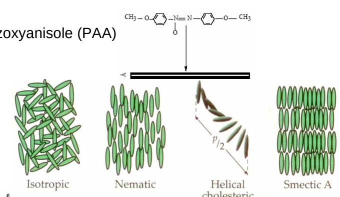
- low enthalpy and entropy ⇒ low thermodynamic driving force for crystallization
- low atomic mobility associated with viscosity
- viscosity is high and relatively weak T dependent

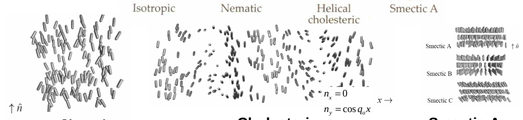
2.4 Liquid Crystals

Intermediate in order between *liquids* and *crystals*

Orientation is constant over large range; mechanical properties of liquid

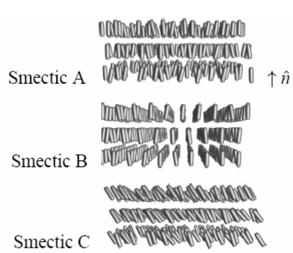
Example: p-azoxyanisole (PAA)





Nematic **Cholesteric** **Smectic A**

Smectics



Long-range orientation order

plus

Long range position order **<u>in 1D</u>**

Liquid Crystal Order Parameter:

$$\mathrm{O} \propto \int n_1(\vec{r}_1, \theta_1)(3\cos^2\theta_1 - 1)dr_1 d\theta_1$$

2.5 Polymers

$$n[CH_2 = CH_2] \xrightarrow{heat, pressure, catalyst} -[CH_2 - CH_2]_n -$$

Ethylene monomer — Polyethylene polymer

n – degree of polymerization (DP); also the number of subunits (mers) in the polymer, mers/mol

- polymer chains typically arranged at random
- some constraints: bond angle, hindrance of side groups
- Result is size (e.g., end-to-end length) << chain length

$$L = N\, d \sin \Theta$$

$$\langle R \rangle = d \sqrt{N}$$

- the tangling of chains and sticking of side groups determines the strength of polymer and ability to stretch

Ideal Radius of Gyration

Radius of gyration ***R***: sqrt of distance from one end of polymer to another

$$\mathcal{P}_{N+1}(\vec{R}) = \int d\vec{R}' \mathcal{P}_N(\vec{R}') \mathcal{P}_1(\vec{R} - \vec{R}')$$

$$\Rightarrow \quad \mathcal{P}_{N+1}(\vec{k}) = \mathcal{P}_N(\vec{k}) \mathcal{P}_1(\vec{k})$$

$$\Rightarrow \quad \mathcal{P}_N(\vec{k}) = [\mathcal{P}_1(\vec{k})]^N.$$

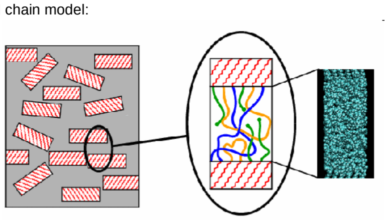
$$\int d\vec{R} \qquad \mathcal{P}_1(\vec{R}) = 1 \Rightarrow \mathcal{P}_1(\vec{k} = 0) = 1.$$

- Polymer behaves like an ideal spring
- Spring constant that rises in proportion to temperature, falls in proportion to the molecular weight $R^2 \propto N$

Structure of Partially Crystalline Polymers

The longest dimension of crystalline regions in polycrystralline polymeric materials is usually ~5-50nm ⇒ much less compared to the fully extended length

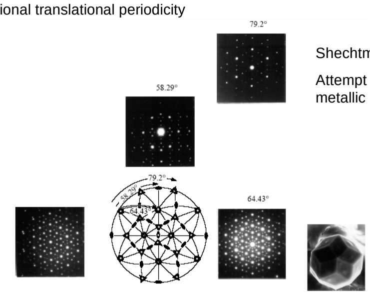
- Folded chain model:



2.5 Quasicrystals

Five- and ten-fold symmetry is impossible… and yet

Quasicrystals are materials with perfect long-range order, but with no three-dimensional translational periodicity

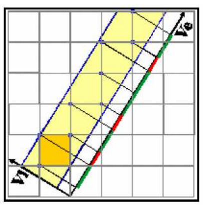


Shechtman (1984)

Attempt to prepare metallic glass Al_{86} Mn_{14}

http://jcrystal.com/steffenweber/

1D Quasicrystals



Fibonacci numbers are the numbers in the following sequence:

0, 1, 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, 144…

$x_n = n + (\tau - 1)\,\mathrm{int}\,(n/\tau)$

Two segments of different lengths (L-long and S-short)

The distance between successive points is either

$$\tau, \tau = 1 + \frac{1}{\tau} = \frac{\sqrt{5}+1}{2} = 1.618..., \text{or } 1$$

Deflation rule:

Replace τ with sequence "τ, 1"

Replace every 1 with τ ⇒ τ1 τ τ1…

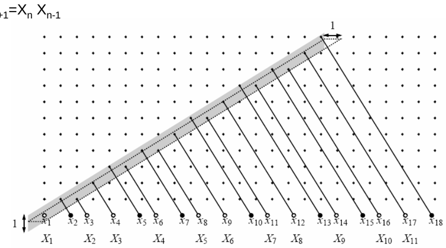
τ1 τ τ1 τ1 τ…

One can generate longer chains!!!

1D Quasicrystals

$X_{-1} = \tau$; $X_0 = \tau\ 1$; $X_1 = \tau\ 1\ \tau$; $X_2 = \tau 1\ \tau\ \tau 1$

$X_{n+1} = X_n\, X_{n-1}$



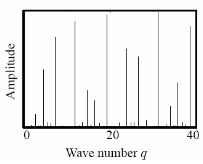
$$x_m = m + \sum_n n\,\theta\left(n - \frac{m}{\tau} + 1\right)\theta\,\frac{\left(\frac{m}{\tau} - n\right)}{\tau};$$

where $\theta = 1$ if $x > 0$ (Heaviside step function)

Scattering from 1D Quasicrystal

The peaks are at: $q = \dfrac{2\pi\left(\dfrac{m'}{\tau} - n'\right)}{\tau^{-2}+1}$ (see Marder, pp.119-120)

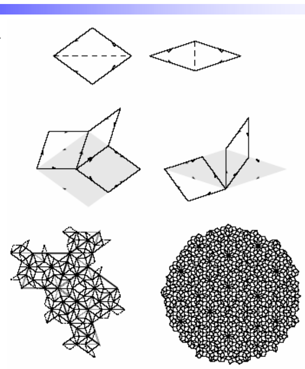
Square amplitude is proportional to:



$$\sin^2\left(\pi\left[\frac{m'\tau - n'}{\tau+\tau^{-1}}\right]\right) \Big/ \left(\frac{q}{\tau - 2\pi m'}\right)^2$$

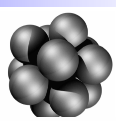
Two-Dimensional Quasicrystals

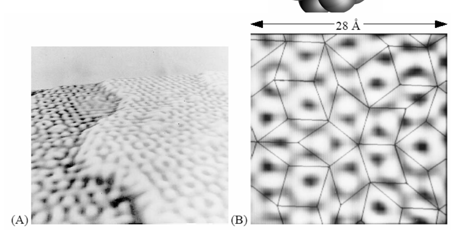
Penrose, Gardner



Physical reasons for quasicrystals

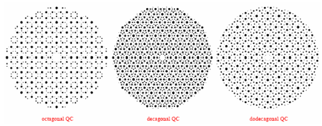
Al_6Li_3Cu is real equilibrium quasicrystals





Experimental Techniques for QC

- **Selected area electron diffraction**: obtain reciprocal space information (symmetry, point group)



- **High resolution transmission electron microscopy** (HRTEM): real structure information
- **X-ray diffraction techniques** Laue, Precession, *quantitative measurement:* Powder diffractometer,
- **Neutron diffraction:** obtain partial structure factors to assist structure refinement