

* Discussion of regular solids so far...

- ① electrostatic interactions and entropic effects drive solidification
- ② atomic trends and bonding scenarios
- ③ the first-order transition and its nucleation
- ④ growing and refining large single crystals

Alloys

* simplest deviation from perfect regularity is contamination by a small concentration of impurity atoms

→ thermodynamics tells us that a small quantity of impurities is always soluble in a crystal in equilibrium at temp $T > 0$

→ e.g. small amount of carbon atoms in an otherwise pure crystal of iron:

- energy penalty ϵ for each C-Fe substitution

- M carbon atoms in N iron atoms can be substituted

$$\binom{N}{M} = \frac{N!}{M!(N-M)!} \text{ ways}$$

- via Stirling's approx, $\log n! = n(\log n - 1)$, this leads to an entropy

$$k_B \log \binom{N}{M} \approx -k_B N c (\log c - 1) \text{ where } c = \frac{M}{N}$$

- free energy of the admixture is

$$\begin{aligned} F &= E - TS = ME - T k_B \log \binom{N}{m} \\ &= Nc\varepsilon + T k_B Nc (\log c - 1) \\ &= N [c\varepsilon + k_B T c \log c - k_B T c] \end{aligned}$$

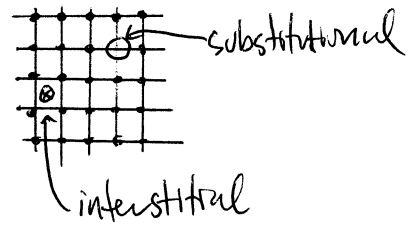
which has an optimal concentration value

$$c \sim e^{-\varepsilon/k_B T} \quad (\text{via } \frac{\partial F}{\partial c} = 0)$$

* As a consequence, no solid elements ~~occur~~ occur in pure form. They tend to contain impurities at the 1% level. (But we can purify via zone refining.)

→ impurities may be substitutional (e.g. Zinc in copper)

or interstitial (typically hydrogen, boron, carbon, or nitrogen)



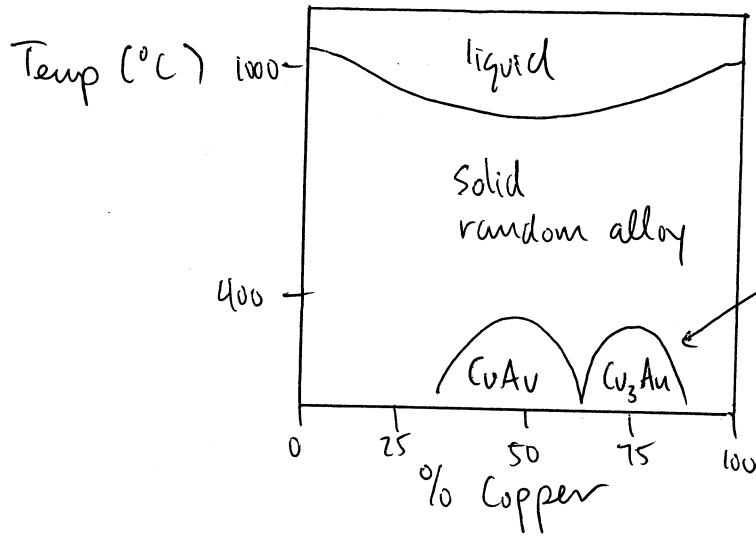
→ in some special cases, two components can be continuously admixed in any concentration

e.g. AuAg, AuPd, ~~etc~~ NiMn, CuPt, and CuNi

all have fcc groundstate and similar lattice constants

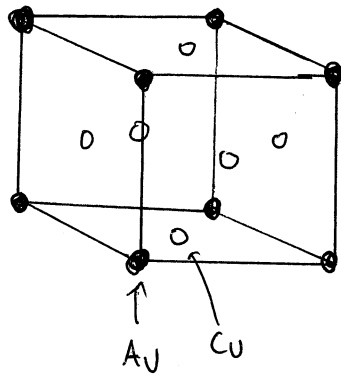
→ more generally, the atoms undergo structural transitions as a function of concentration and temperature

* one possible outcome is the formation of superlattices



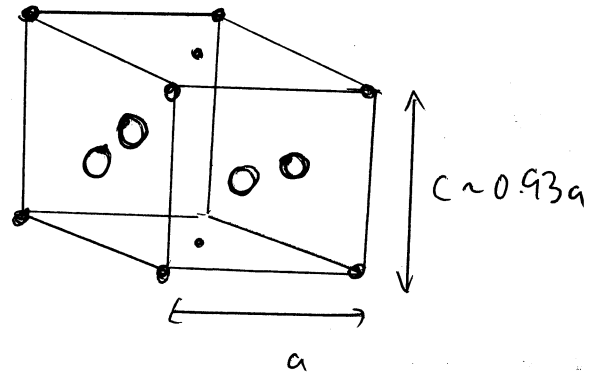
new diffraction peaks appear; new intermetallic crystalline compound forms

3:1



fully interpenetrating superlattice

1:1



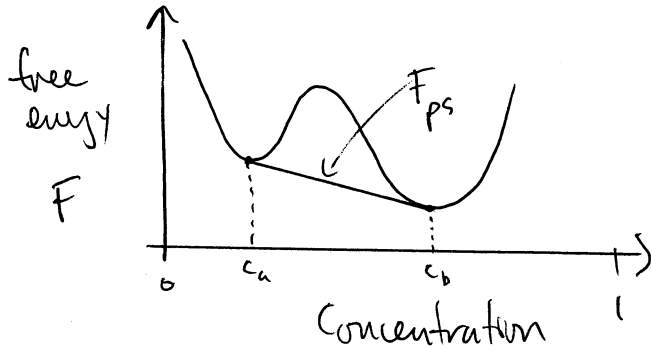
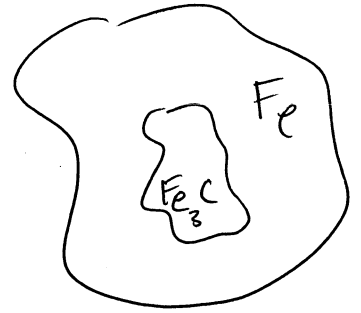
layered structure

- the superlattice only appears if the system is annealed (i.e. cooled very slowly from the liquid state)
- quenched systems (i.e. those that have been rapidly cooled remain disordered)

* another outcome is phase separation

→ e.g. Fe and Fe₃C are each stable materials

→ form in physically separated regions so as to minimize the total free energy



$$F_{ps} = f F(c_a) + (1-f) F(c_b)$$

↑
fraction of concentration c_a

$$\Rightarrow \text{total } c = f c_a + (1-f) c_b$$

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

→ Hence $F_{ps} = \frac{c - c_b}{c_a - c_b} F(c_b) + \frac{c_a - c}{c_a - c_b} F(c_a)$ gives rise to the geometrical construction shown above

→ Basic dynamics are slow and diffusive

$$\vec{j} = -D \vec{\nabla} f$$

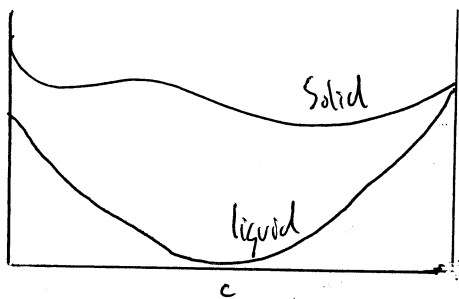


droplet grows

as \sqrt{t}

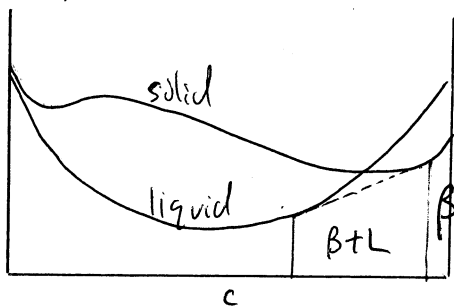
shape depends on sign of surface tension

$F(T_1)$

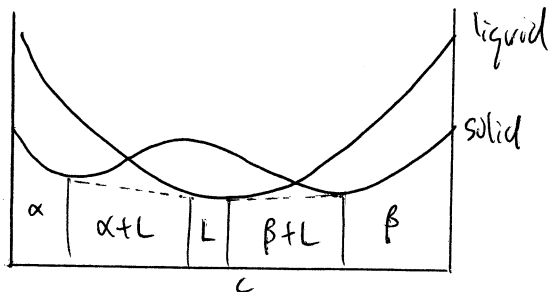


$$T_1 > T_2 > T_3 > T_4$$

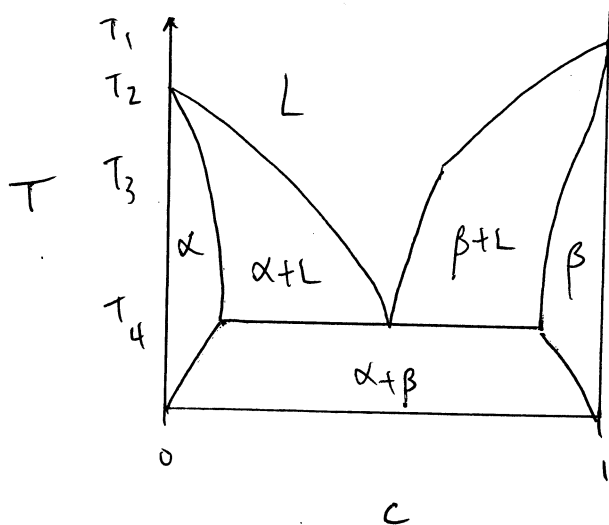
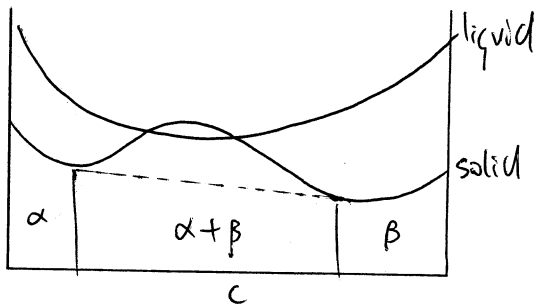
$F(T_2)$



$F(T_3)$



$F(T_4)$



Glasses

- * liquids have mobile atoms and are generally ergodic (sample all of the $q-p$ phase space over the time-scale of observation)
- * glasses tend to look like a liquid locked into place
 - no movement on observable time scales
 - has none of the regularity of a crystalline solid
 - still a mysterious phase of matter
- * very likely related to metastability and "jammed" dynamics

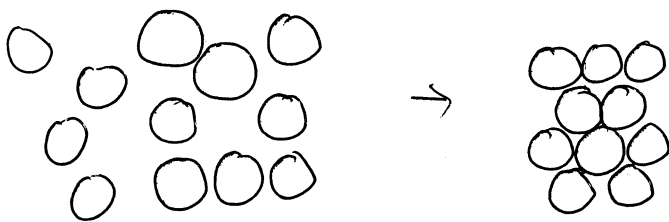


(complicated energy landscape)

→ not clear if a glassy state can ever be a true ground state

→ it may be that any collection of atoms can form a glass if quenched rapidly enough

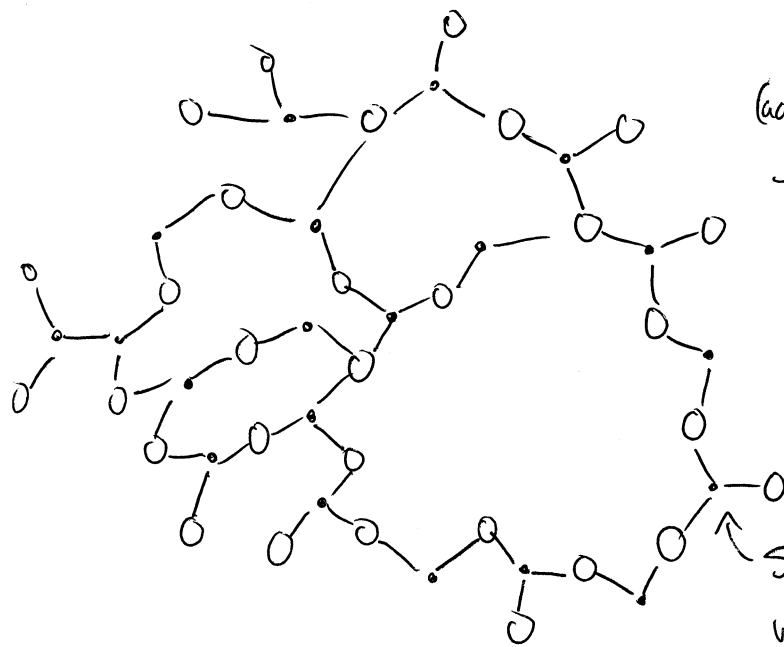
- * computer simulations of hard sphere systems suggest that these would form glasses if cooled rapidly enough



recovering the crystalline configuration requires global rearrangements of the atoms!
dynamics are frozen

* Strong glasses have a random network quality

→ e.g. SiO_2 , where Si wants to bond with four neighbouring oxygens



(additional bonds out of the plane to fill 3D)

Si not too stiff with respect to bond angle

→ guide heuristic: suppose there are ideally b bonds per atom in a system with N atoms. We need to determine the optimal length of $\frac{Nb}{2}$ bonds and $N \binom{b}{2} = \frac{N b!}{2! (b-2)!} = N(2b-3)$ bond angles.

Set

$$\begin{array}{ccc} 3N & = & N(2b-3) + \frac{Nb}{2} \\ \uparrow & & \underbrace{\hspace{10em}} \\ \text{degrees} & & \text{total number of} \\ \text{of freedom} & & \text{mechanical constraints} \end{array}$$

⇒ average coordination $b = \frac{12}{5} \doteq 2.4$
(far from close packing)

Incommensurate structures

* structures that are neither random nor periodic

→ quasiperiodic

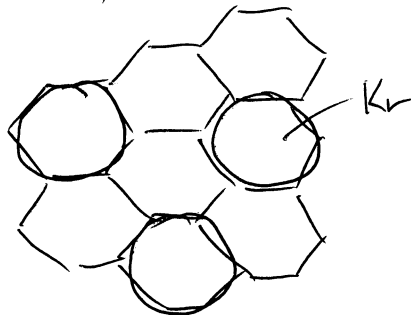
→ spatial modulations with relatively irrational periods

→ e.g. noble gas (He, Xe, Kr, ...) atoms adsorbed on the surface of graphite (carbon honeycomb)

- adatoms adhere to the surface and are confined to the 2D plane

- Lennard-Jones (6-12) potential favours a triangular lattice with a preferred separation that is different from the lattice constant a_s of the underlying substrate

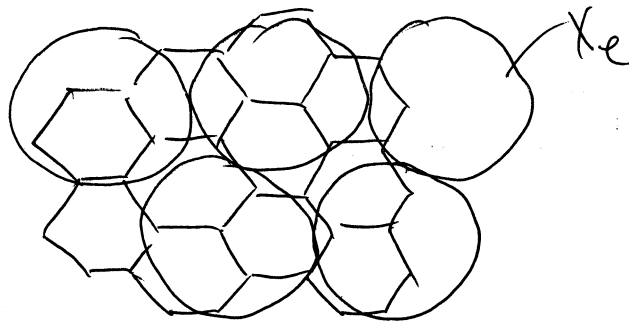
- if potential of the periodic substrate is strong, adatoms form a lattice that is commensurate with the substrate (i.e. corresponding to an integer number of unit cells)



$$a = \sqrt{3} a_s$$

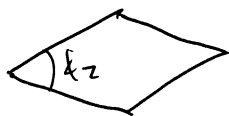
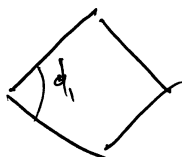
$\sqrt{3} \times \sqrt{3}$ 120°
structure

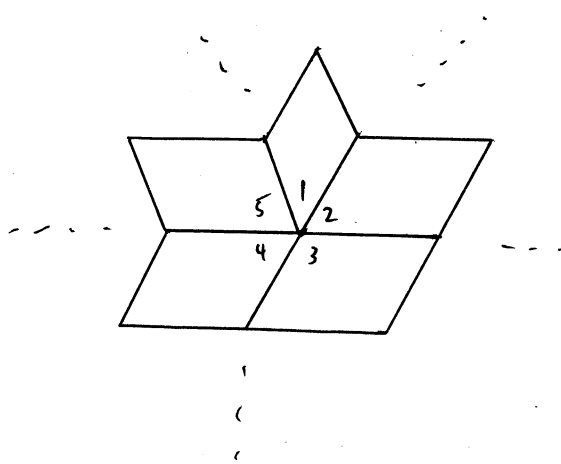
- opposite limit, potential has only a weak effect on the adatom lattice; in an incommensurate pattern, the substrate unit cells per adatom unit cell tends to infinity



Quasicrystals

- * space-filling pattern of several different repeat units but no long range pattern
- * first evidence in quenched $Al_{75}Mn_{25}$
 - expected to form a metallic glass
 - instead, x-ray diffraction revealed a 5-fold symmetry (crystallographically impossible)
- * Penrose construction
 - can't fill 2D space with pentagons (squares and hexagons work)
 - use two different repeating tiles ("fat" and "thin") with angles $\phi_1 = \frac{2\pi}{5}$ and $\phi_2 = \frac{2\pi}{10}$ but same edge length

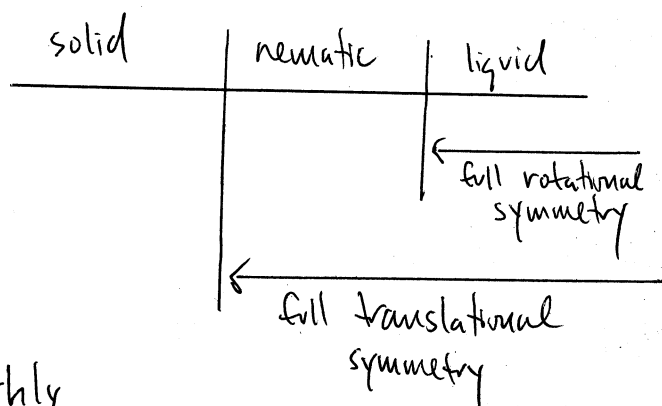
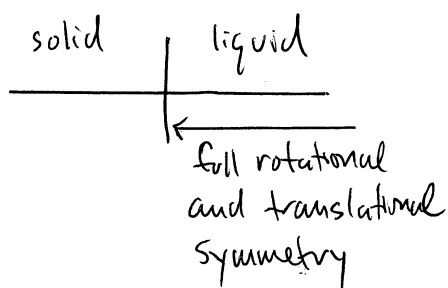




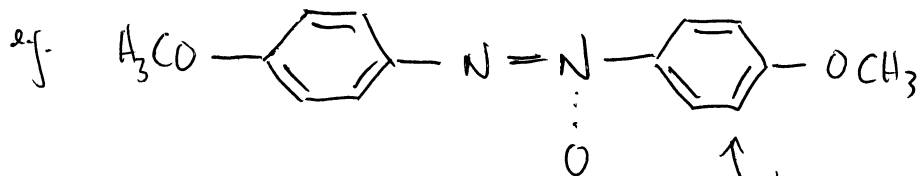
→ forms many locally 5-fold coordinated points

Liquid crystals

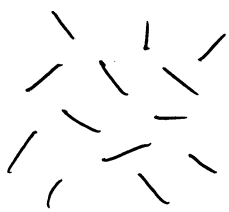
* intermediate phases between homogeneous, isotropic liquids and crystalline solids



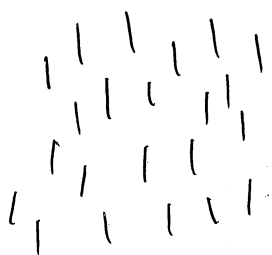
→ orientational order in highly anisotropic molecules (hard ellipsoids)



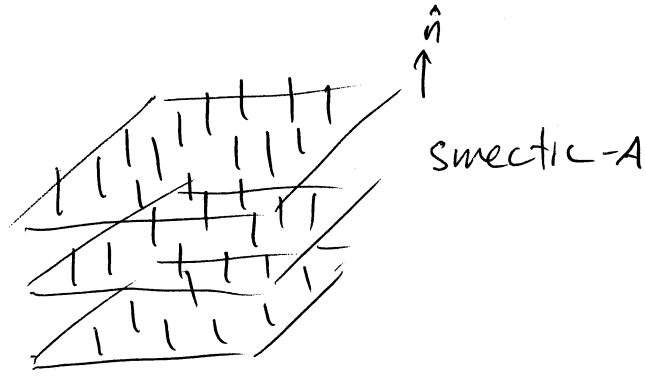
↑ typically contain benzene rings that provide rigidity



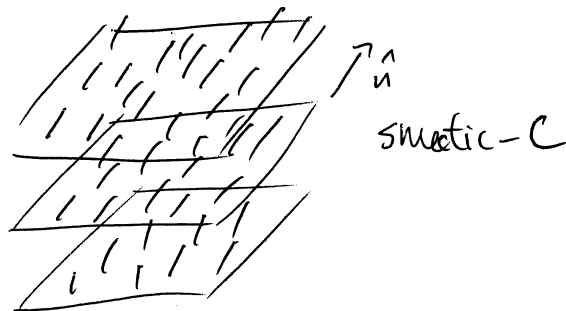
isotropic



\hat{n} "director"
nematic



smectic-A



smectic-C

* director invariant under 180° rotation ; preferred axis
but not a vector order parameter

→ general order parameter

$$Q_{\alpha\beta} = \epsilon_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \sum_r \epsilon_{\alpha\beta}$$

↑ any tensor property (eg. dielectric constant)
↑ phase transition evident from spectrum of eigenvalues

→ orientation symmetry breaking can be determined from
~~thermodynamic limit only~~ (thermodynamic limit only)

$$Q = \int d^3r d\theta n(\vec{r}, \theta) \frac{1}{2} (3 \cos^2 \theta - 1)$$

↑ number density at \vec{r} pointing
at angle θ

→ better to think in terms of angle-angle correlation functions