* 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 ΔE for each C→Fe substitution
   - N 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

\[
\log_2 \binom{N}{M} = -k_B N \log(C/c - 1) \text{ where } C = \frac{M}{N}
\]
- free energy of the admixture is

\[ F = E - TS = ME - T k_B \log \left( \frac{N}{M} \right) \]

\[ = NCE + T k_B NC (\log C - 1) \]

\[ = N \left[ CE + k_B T c (\log c - 1) \right] \]

which has an optimal concentration value

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

* As a consequence, no solid elements 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, NiMn, CuPt, and CuNi:
  all have the same ground state 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.

→ 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 forming physically separated regions so as to minimize the total free energy.

![Graph](image)

\[ F_{ps} = fF(c_a) + (1-f)F(c_b) \]

\[ f = \frac{c - c_b}{c_a - c_b} \]

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

- Basic dynamics are slow and diffusive.

\[ \dot{j} = -D \nabla f \]

- Droplet grows as \( \sqrt{t} \)
- Shape depends on sign of surface tension.
$T_1 > T_2 > T_3 > T_4$
Glasses

* Liquids have mobile atoms and are generally ergodic (sample all of the q-p phase space over the true 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
  → Not clear if a glassy state can even 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

  ![Diagram of atoms forming a crystalline configuration]

  Recovery of the crystalline configuration requires global rearrangements of the atoms; dynamics are frozen
Strong glasses have a random network quality
- e.g. $\text{SiO}_2$, where Si wants to bond with few neighbouring oxygens

\[
\text{Si-O-Si} \quad \text{(additional bonds out of the plane to fill 3D)}
\]

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 $N(b) = \frac{Nb!}{2!(b-2)!} = N(2b-3)$ bond angles.

Set

\[
3N = \frac{N(2b-3) + Nb}{2}
\]

\[
\text{degrees of freedom} \quad \text{total number of mechanical constraints}
\]

\[
\Rightarrow \text{average coordination } b = \frac{12}{5} \approx 2.4
\]

(far from close packing)
Incommensurate structures

* structures that are neither random nor periodic
  - quasi-periodic
  - 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 favors 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)

\[ \sqrt{3} \times \sqrt{3} R \, 30^\circ \] Structure

\[ a = \sqrt{3} a_s \]
- 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$_{86}$ Mn$_{14}$
  → 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

\[ \diamondsuit \quad \square \]
Liquid crystals

* Intermediate phases between homogeneous, isotropic liquids and crystalline solids

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→ orientational order in highly anisotropic molecules (hard ellipsoids)

2f. $\text{A}_2\text{CO} \quad \text{N} = \text{N} \quad \text{OCH}_3$

↑ Typically contain benzene rings that provide rigidity
* director invariant under 180° rotation; preferred axis but not a vector order parameter

→ general order parameter

\[ \omega_{\alpha \beta} = \xi_{\alpha \beta} - \frac{1}{3} \delta_{\alpha \beta} \xi \]

→ any tensor property (e.g. dielectric constant)

phase transition evident from spectrum of eigenvalues

→ orientation symmetry breaking can be determined from

(thermodynamic limit only)

\[ \Theta = \int d^3 r \ d\theta \ n(\alpha, \theta) \frac{1}{2} (3 \cos^2 \theta - 1) \]

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