MATRL 218/CHEM 227: Class II — Classification of materials as amorphous and crystalline, and the structural hierarchy in a polycrystalline material

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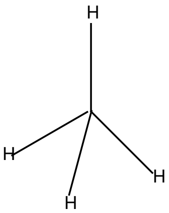
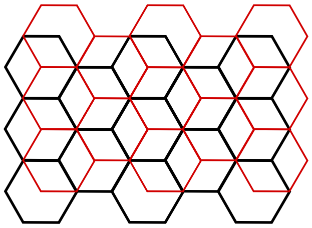
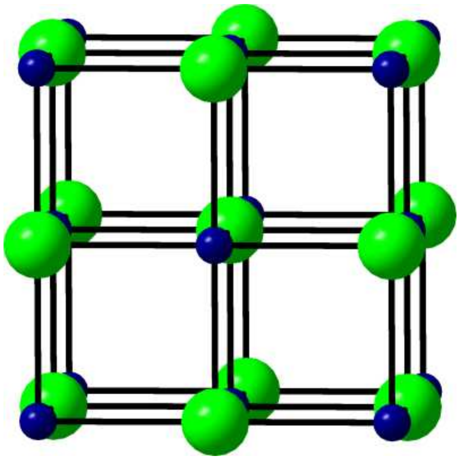
- Molecules *vs.* extended solids:
  - Molecules are finite and have a distinct identity whether solid, liquid or gas (*eg.* the methane molecule)
  - Extended solids are defined by the *phase*. When they melt or vaporize, they are no longer the same material (*eg.* graphite)

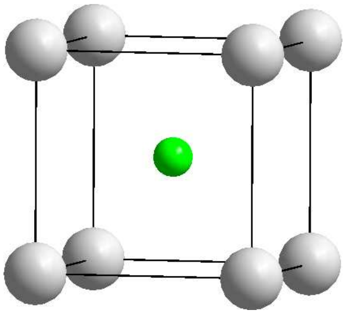




The methane molecule (left) and a portion of a graphite crystal (right). In the graphite crystal, two sheets are displayed. The actual crystal has, effectively, an infinite number of sheets stacked one upon another, and the sheets in addition, extend infinitely in the plane.

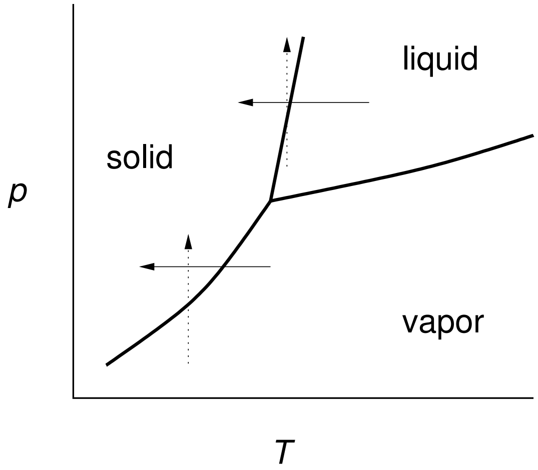
- Extended solids (whether crystalline or amorphous) can be classsified according to their bonding – whether it is directional (as in graphite or diamond) or not (as in most inorganic materials that we shall discuss in this course). A caveat: Many solids (for example, silicate glasses and minerals) are somewhere in-between. Solids with directional bonding typically have atoms with low coordination numbers (CN = number of neighbors). Polymers are extended, directional solids, in 1D.
- Examples of non-directional solids — NaCl (left) and CsCl (right):





Under pressure, NaCl in the NaCl structure transforms to the CsCl structure, going from CN = 6 to CN = 8 — non-directional solids are not terribly particular about CN.

- The formation of a crystalline solid — One can either cool across vapor-solid or liquid-solid coexistence curves (solid arrows), or one can crush (dotted arrows) across them:

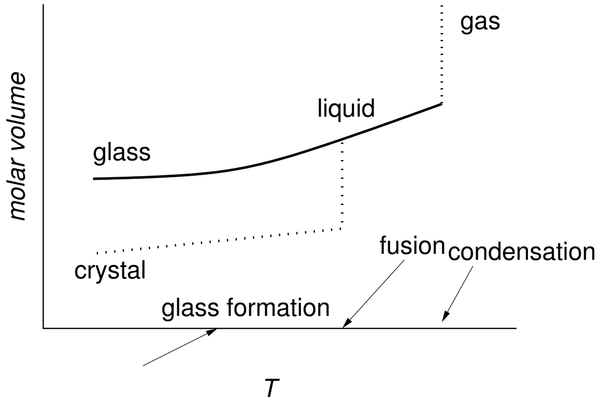


In all cases, the phase transition is strongly *first-order* and is characterized by symmetry breaking. Remember that gases and liquids have higher symmetry than do crystals, characterized by the ability of the atoms to translate continuously. This is lost in the crystal.

- In crystals, atoms are ordered at the microscopic level. This microscopic order manifests at a macroscopic level — as sharp edges, and regular and constant angles between faces of a crystal. The external morphology of crystals allowed 19th century crystallographers to guess the nature of atomic ordering in simple crystals (in NaCl, for example) well before the advent of X-rays.

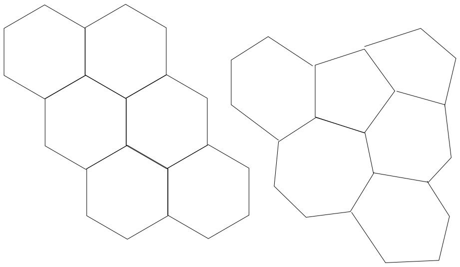
- The work of Alder and Wainright on hard sphere computer simulations demonstrated that purely repulsive interactions are sufficient for crystals to form (the *Alder transition*). The formation of crystals is entropy stabilized. See the note: Insights into phase transition kinetics from colloid science, V. J. Anderson and H. N. W. Lekkerkerker, *Nature* **416** (2002) 811-815 (DOI).

- The formation of a glass cannot be described using an equilibrium phase diagram. Glasses form when a liquid is cooled sufficiently rapidly that crystallization is avoided:



Please also see Allen and Thomas, The Structure of Materials (MIT Press).

- A liquid can therefore solidify in two ways:
  - discontinuously, into a crystal
  - continuously, into a glass



Schematic arrangements of atoms in a planar crystal (left) and glass (right). Note that the coordination numbers of the atoms (CN = 3) remains the same.

- The tendency to form glasses (see D. R. Nelson and F. Spaepen, *Polytetrahedral Order in Condensed Matter*, an article in the series *Solid State Physics* (Academic Press, San Diego) **42** (1989) 1-90.
  - In 2D, close packing of 3 discs results in triangles. Triangles can tile the plane – two dimensions are not frustrated !
  - In 3D, close packing of 3 spheres gives a triangle. The fourth sphere gives a tetrahedron. Tetrahedra cannot be used to tile 3D space[1] – three dimensional space is frustrated, and glasses form easily.
- Glass formers are of two kinds:
  - Systems with low coordination numbers (such as planar borates and tetrahedral silicates) that form network glasses – this is the continuous random network model. Look at the handout.
  - Systems with high coordination number (such as metals) that are unable to find the potential energy minumum corresponding to the crystal. Such glasses were first found in Au:Si alloys. See Spaepen and Nelson to find out more.
- The hierarchy of structure in a polycrystalline material:
  - Atoms come together in a crystal, the basic builiding block being the unit cell (1)
  - Many unit cells make the crystal (2)
  - Depending on how the unit cells are put together, the crystal's habit can change (3)
  - The polycrystalline material comprises of many crystals separated by *grain boundaries* (4)
  - Crystals can themselves have defects (5)

turn

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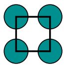
[1] Just as pentagons cannot tile a flat surface



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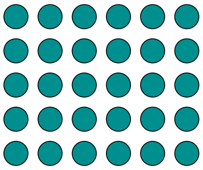

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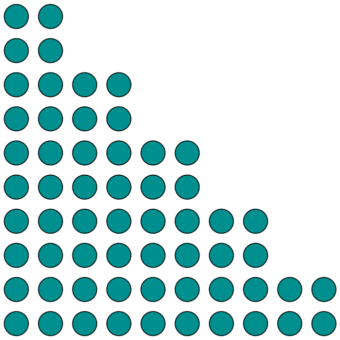

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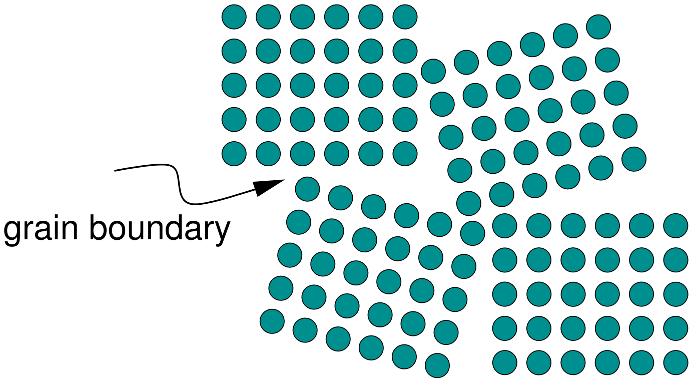

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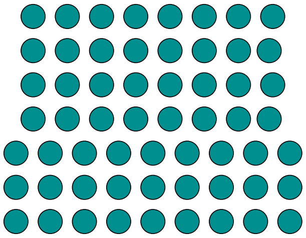

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