Physics 489 S 04 Lecture 7
Cohesion of Solids (Ashcroft and Mermin, chapters 19, 20)

1. Cohesion due to attractive interaction - balanced by repulsion at equilibrium
   E_{coh} = cohesive energy relative to separated atoms
   Equilibrium: $V(dE/dV) = 3a(dE/da) = 0$
   Bulk Modulus: $B = V(d^2E/dV^2) \equiv 1/K$, K = compressibility

2. Repulsion: Pauli exclusion principle - increase of Kinetic energy
   Very strong repulsion between cores for all atoms except H
   Sometimes modelled by inverse power law R^{-12}

3. Attraction:

Rare Gas	van der Waals force	Close packed FCC, HCP
Ionic	Coulomb force	Close packed in shells
Metallic	Free electron gas	Close packed
Covalent	Directional bonds	Open lattice, eg Diamond, ZnS
Molecular*	van der Waals force	Depends on shape of molecule
Molecular*	Hydrogen bonds	complex, eg water

   *Treated only cursorily in this course

4. Van der Waals interaction.
   Spherical atom has quantum fluctuations, generating an electric dipole.
   Induced field at second atom $\propto R^{-3}$, so energy $\propto R^{-6}$
   Lennard-Jones "6-12" potential for molecular interaction.
   $U = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$
   Minimize U: gives interatomic separation $R = 1.09\sigma$ for FCC.
   Excellent agreement with experimental R for rare gases.

5. Ionic crystals.
   "Ionic radius" good to 2% for alkali halides.
   Large $U_{Coulomb}$ term overcomes ionization potentials.
   Madelung sum, $\alpha = 1.7476$ for NaCl, 1.7627 or CsCl.
   Energy per ion pair, $u(r) = -\alpha e^2/r + C/r^m$, is 90% due to first term.

6. Metallic bonding.
   Repulsion due to kinetic energy of electron gas, $u_{kin} = (3/5)E_F \propto r_S^{-2}$
   Attraction due to Coulomb terms $\propto r_S^{-1}$. Quantitatively rather bad.

7. Covalent bonding.
   Unfilled states in free atom, especially p-states, available for pairing.
   Degenerate states give multiple bonds, hence stronger crystals.
   Mixing of orbitals, e.g. sp^n, allows more overlap, lower energy.
   Choice of structure determined by directions of bonds, not close packing.

8. Under pressure all solids tend toward closer packing.
   Relevant in geophysics, planetary physics.