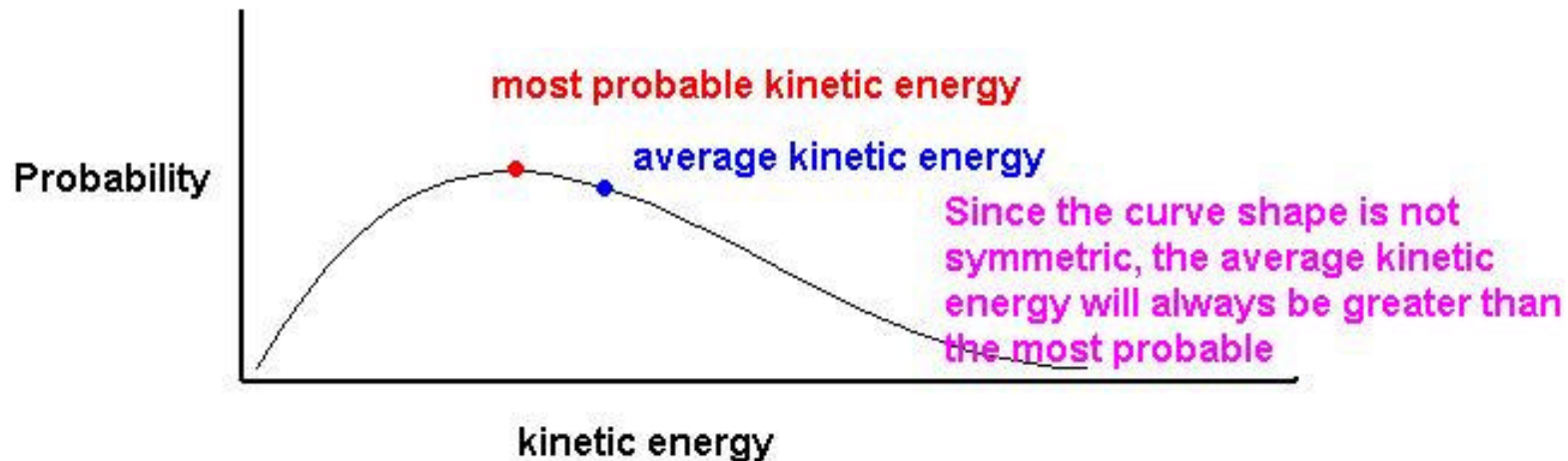


General Info

- Exams will be returned at the end
- New homework posted-due next Tues

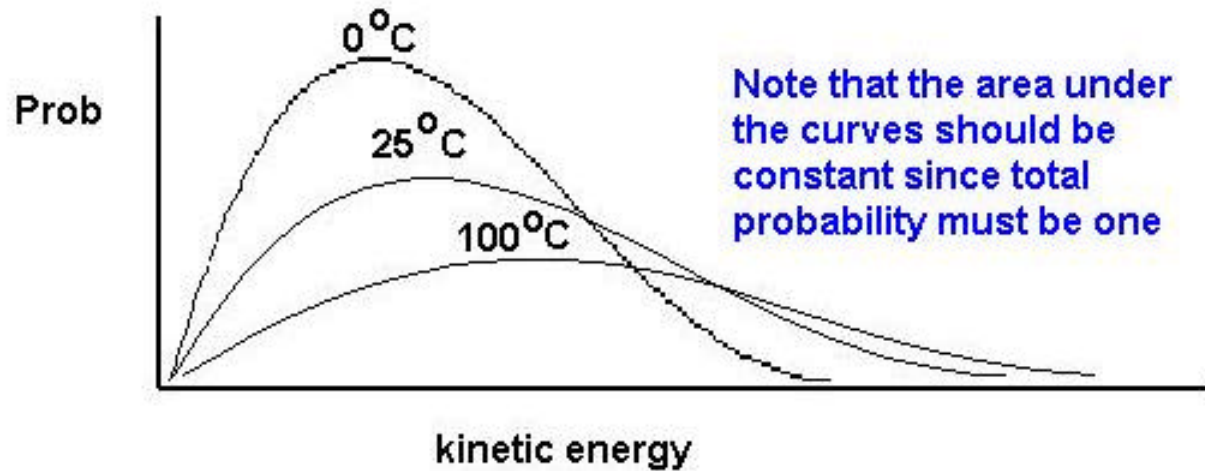
A closer look at energies

- The Boltzmann Distribution represents the actual distribution of energies in a population of “molecules”



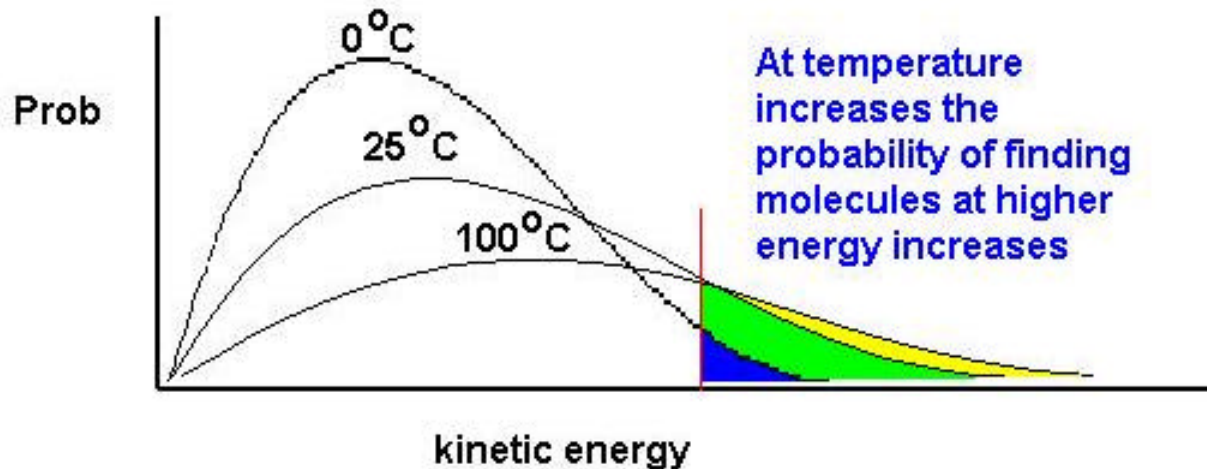
Changing T

- Changing Temperature redistributes the energies accordingly



Threshold Energy

- If a certain minimum energy is needed for a process to proceed, only those “molecules” with at least that energy will proceed. As the temp increases, the process will speed up as a higher proportion of molecules can proceed.



What's this entropy thing?

- Since we skipped the intro to entropy and the first law, a little catching up is in order.
- Entropy is a measure of probability. It is not a measure of disorder or randomness which are, in actuality, value judgments. A better term would be to consider the number of possible alternatives for two states. For example, you might say that pool balls in a rack are more ordered before than after the break. (If you don't know what "in the rack" and "after the break" mean, you need to get out more.) Is that true? Is a new deck of cards more ordered before the first shuffle? What about after the first shuffle vs after the second.
- Entropy favors the state with the highest number of options.

The condensed phases-solids and liquids

- Lack of compressibility-components are in close contact
- Since they interact (unlike gases):
 - Properties depend on the identity of the material so it is part of the state definition
 - The nature of the intercomponent force is critical
- There are two ways of stating this:
 - Because they are in a condensed phase, they interact strongly
 - Because they interact strongly, they are in a condensed phase

The Intercomponent Forces

These forces are characteristic of pure, single component systems (these and others may also be present in mixtures). In order of energy:

- 1. Ion-ion: very strong, present in ionic solids and represented by the lattice energy. Compounds are generally high melting point solids**
- 2. Covalent bond: network solids (C as diamond or graphite, SiO₂, etc.**
- 3. Metal bonding: most easily described as metals immersed in a “sea of electrons”**
- 4. Hydrogen bonding: H bonded to N,O,F,Cl (S,Br,I)**
- 5. Dipole-dipole: permanent molecular polarity resulting from polar bonds (diff. in electronegativities)**
- 6. Van der Waals: induced, temporary polarity**

In the simplest sense, whether or not a material will be in a condensed phase is a question of the comparison of the kinetic energy due to T and the attractive forces between species. Not surprisingly, 1,2,3 above all lead to solids (except Hg), whereas 4-6 may be any one of the three phases)

Predicting phases at RT

- The generic question is: Will it be a room temperature solid, liquid or gas (and explain why)?
- Considerations:
 - Nature and extent of intercomponent forces
 - If the material is molecular (how do you know?) . What type of forces are present and what is its 3-D structure and its overall size(this is particularly important for van der Waals forces).
 - Gases and solids are usually easily identified-why?
 - Liquids-not obviously a solid or gas=>perchance it's a liquid.

Heat terms-fusion, vaporization and sublimation

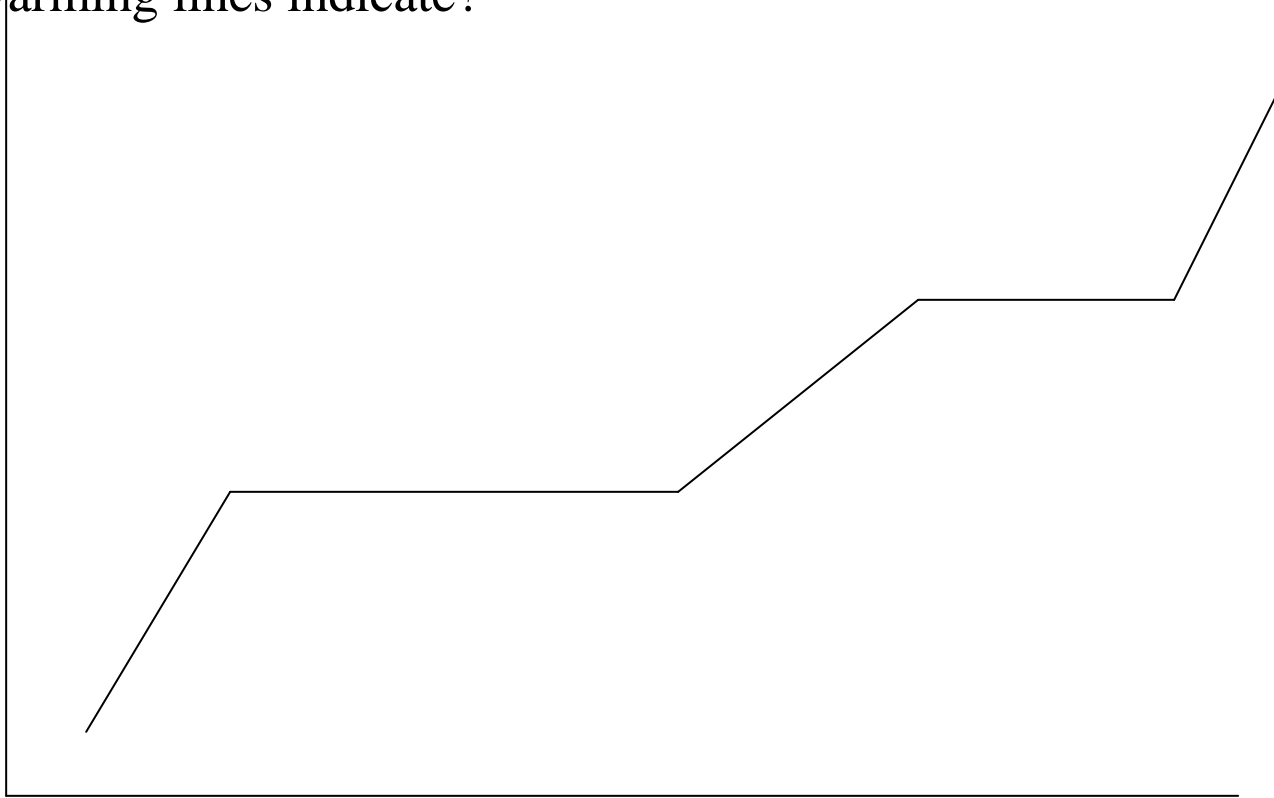
- Definitions:
 - Solid to liquid-fusion $\Delta H_{\text{fus}} > 0$
 - Liquid to solid-freezing $\Delta H_{\text{freez}} = - \Delta H_{\text{fus}}$
 - Liquid to gas-vaporization $\Delta H_{\text{vap}} > 0$
 - Gas to liquid-condensation $\Delta H_{\text{cond}} = - \Delta H_{\text{vap}}$
 - Solid to gas-sublimation $\Delta H_{\text{sub}} > 0$
 - Gas to solid-deposition $\Delta H_{\text{dep}} = - \Delta H_{\text{sub}}$
- These are all temperature constant processes and are sometimes called latent heats. Standard conditions require a $P=1.00\text{atm}$
- How is ΔH_{sub} related to other quantities?

Sample Calculations

- How many KJ of heat are required to melt 35.6g of ice if its molar heat of fusion is 6.01KJ/mol.
- How is the above different from the question: What is q for the melting of 35.6g of ice?
- A cube of ice with a mass of 14.5g is dropped into 120g of water(l) at 87°. What is the resulting temperature?

Heating and Cooling Curves

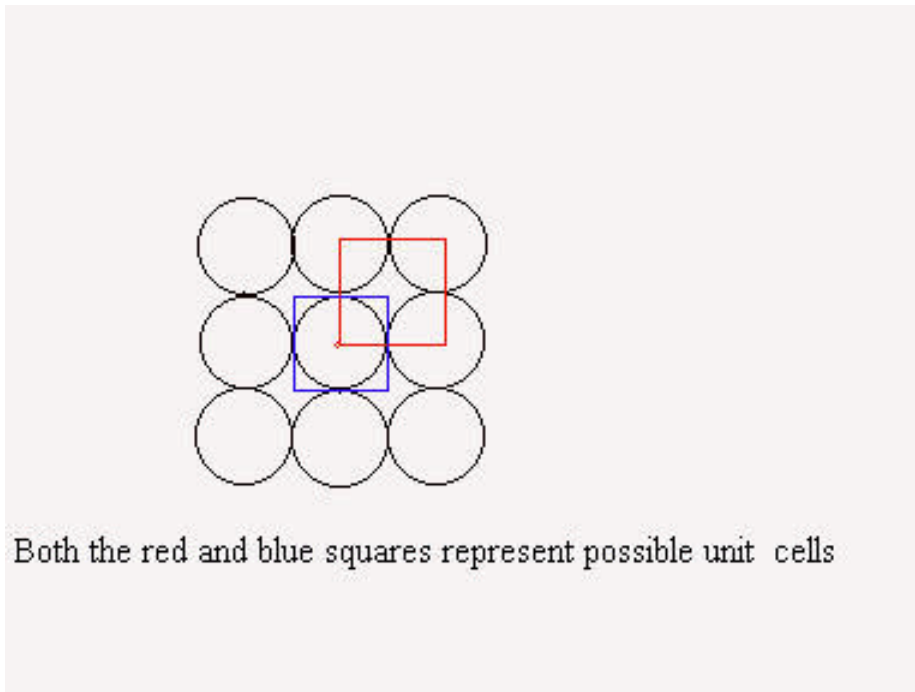
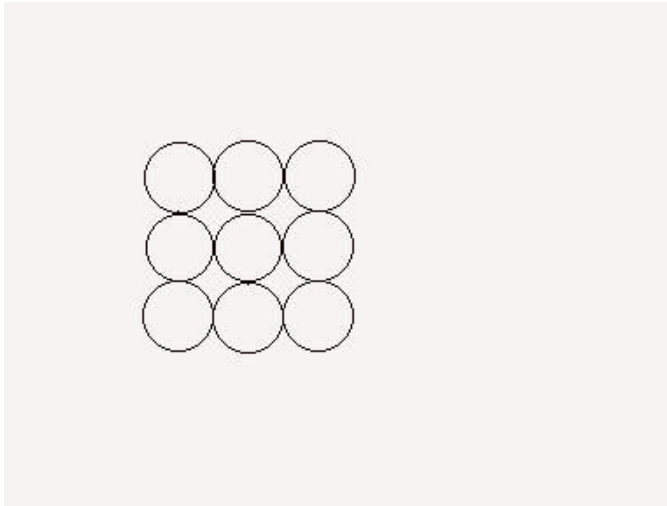
- solid warming, melting, liquid warming, boiling, gas warming. If the input of heat is constant, what do the differences in slopes of the warming lines indicate?



Structures of solids and liquids

- To what extent can a liquid be described as having structure?
- Solids can be either quite random or extremely regular.
- Solids which can be described in terms of a microscopic unit (the unit cell) which is arranged in a regular, repeating 3D array are termed crystalline.
- The unit cell must have the properties that the bulk structure can be assembled by combining unit cells without leaving any void area. For example, unit cells cannot have five sides. Why not? A given crystal can have many units cells. One normally chooses the smallest one as “the unit cell”

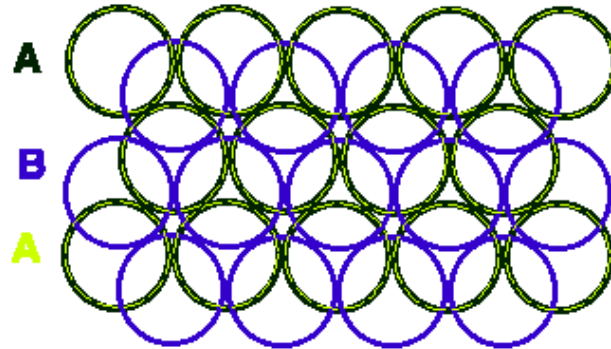
Packing and the unit cell



Both the red and blue squares represent possible unit cells

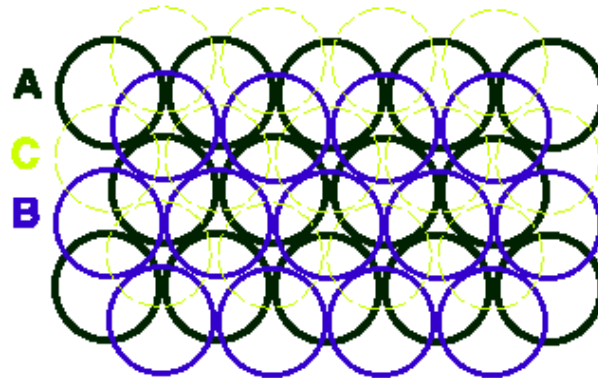
Close Packing

3 Layers

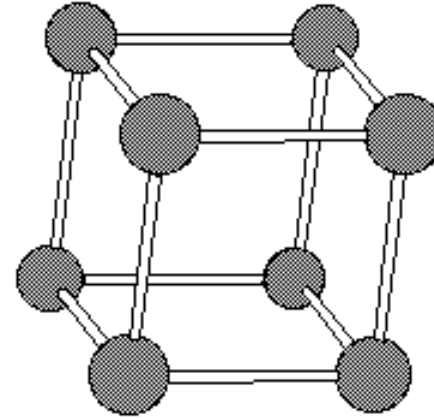
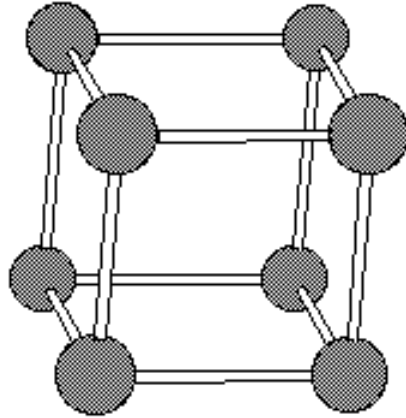


ABA Hexagonal Close-Packing (HCP)

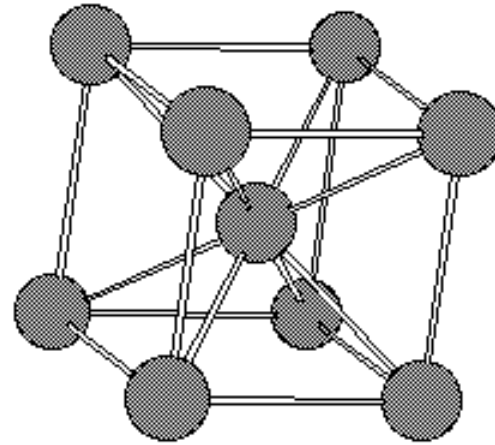
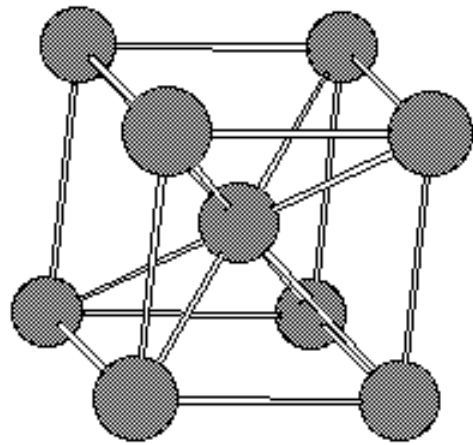
ABC Cubic Close-Packing (CCP)



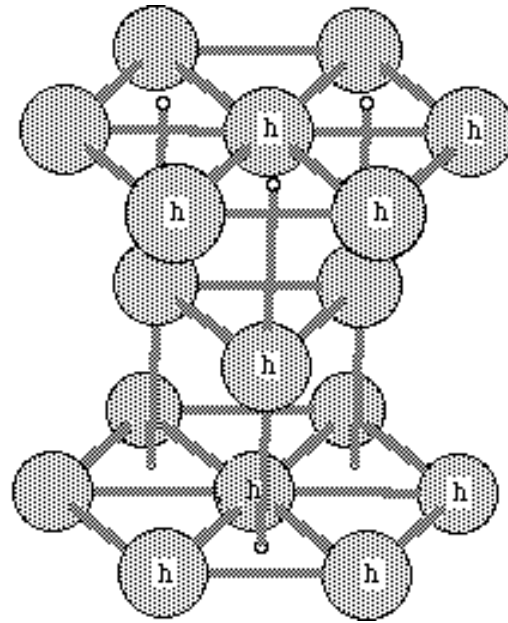
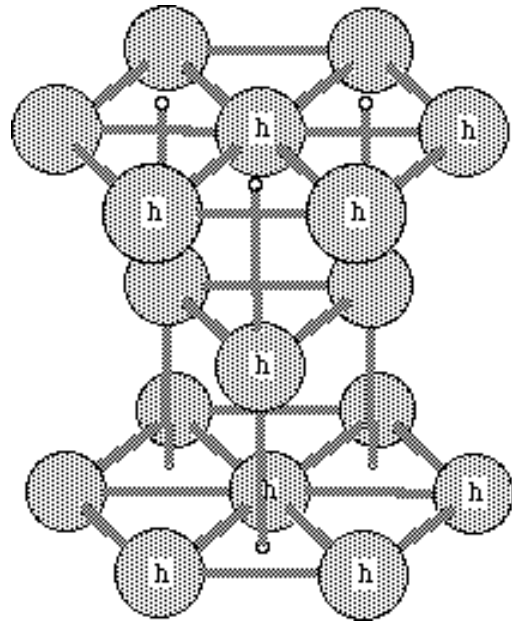
Simple Cubic



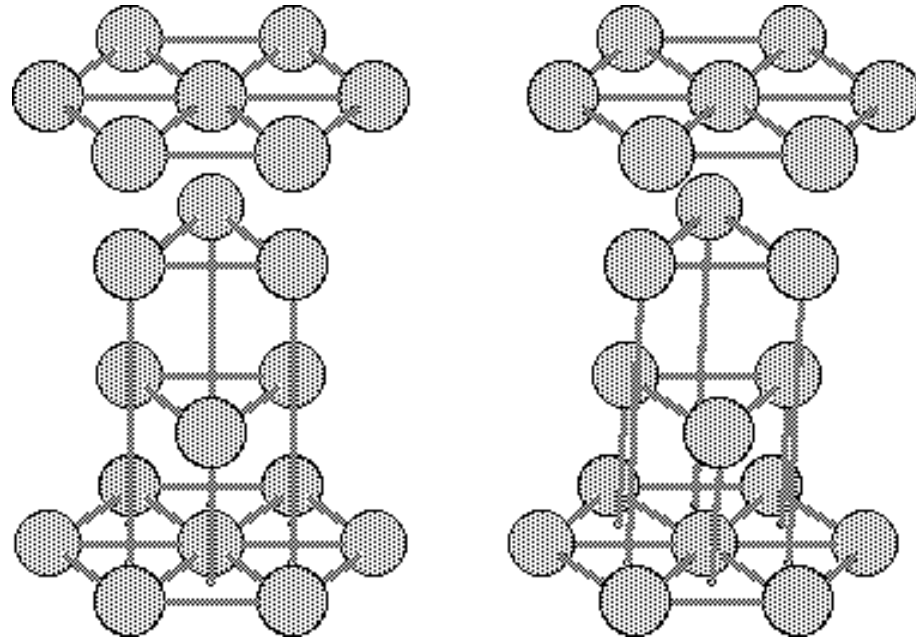
Body centered



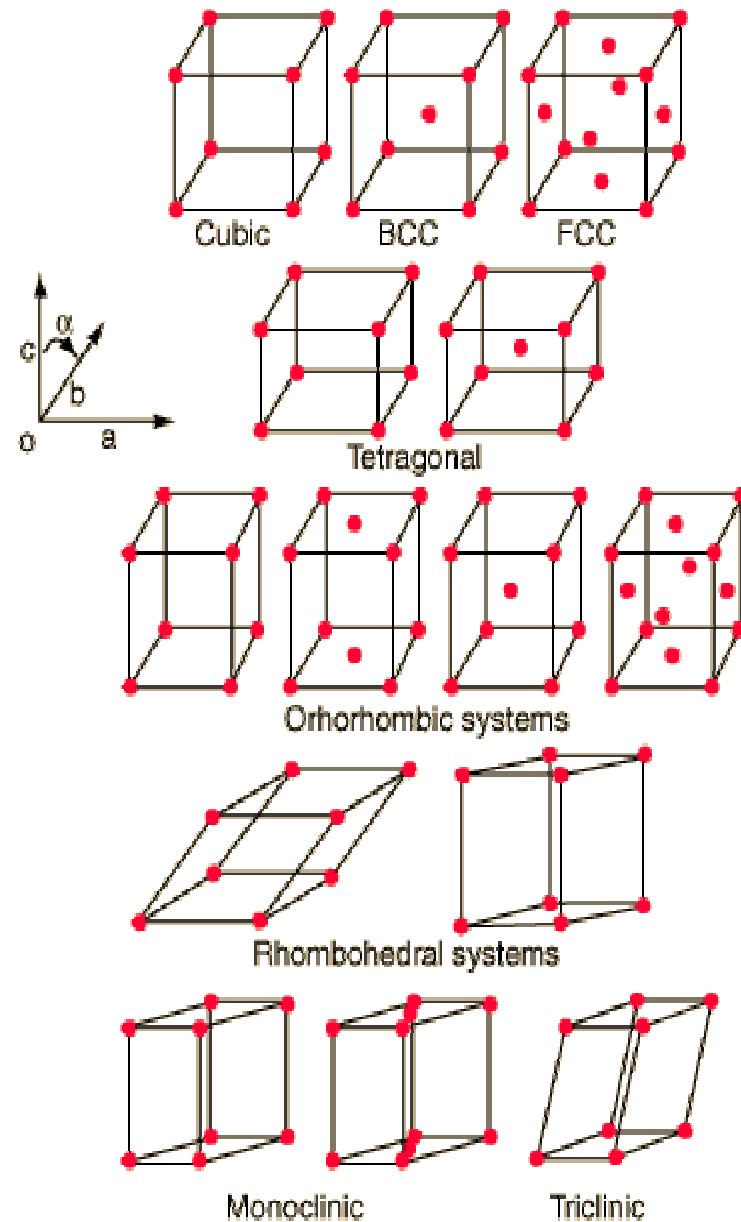
hcp



ccp



Bravais Lattices



Packing and densities

- One should be able to see that the solid density of a pure element, since atoms can be approximated as spheres, is a function of three factors:
 - The mass of the atom (or the gaw at the mole level)
 - The size of the atom (atomic radius, r)
 - The packing arrangement of the atoms in solid structure
- Qualitatively-how should these be related? Present an equation for density by placing the above in correct relative geometric positions,
 - $d=$

The Actual Equations

- $d \propto (\text{number of atoms in the unit cell}) * M_{\text{atom}} / r^3$
- If one looks at the cubic packings: simple cubic, body centered cubic and close packed (hcp or ccp), several things become apparent:
 1. For each of these, the number of atoms per unit cell is constant.
 2. The volume of the cube will be a function of the geometry and the atomic radius and can be written $V = C * r^3$
 3. The above two can be combined to yield a constant for each structure type and the general formula written as:

$$d = \text{Constant} * M_{\text{atom}} / r^3$$

If M is in gm and r is in cm, this will give a “normal” density.
Otherwise (for instance, M in amu and r in picometers),
some conversions are needed.

For the three structures, the constants are:

simple cubic: 0.1250

bodycentered: 0.1624

hcp or ccp: 0.1768