3.012 Problem Set 1 **3.012**
Issued: 09/10/04 **Fall 2004**
Due: 09/15/04

Graded problems:

1. A simple ionic structure type, with which almost everyone is familiar, is that assumed by rocksalt, NaCl. The unit cell of the structure has the shape of a cube. If a Cl^- ion is placed at one corner of the cube, other Cl^- ions will be positioned at all other corners and also at the center of each of the faces, an arrangement referred to as "face centered cubic." The Na^+ ions then assume positions at the midpoint of every cube edge and also at the center of the cube.

    a. Which ions are in contact in this structure type?

    b. If it is possible to assign a value of an ionic "size" to Na^+ and Cl^- (it is!), specified by radii R_{Na+} and R_{Cl-}, what would be the value of the length of the edge of the cube in terms of these radii?

2. There is an unoccupied interstitial site in the rocksalt structure at locations with coordinates (measured as fractions of the cell edge) such as 1/4 1/4 1/4.

    a. How many nearest-neighbor ions surround this site?.

    b. How many sites of this sort are contained within one unit cell?

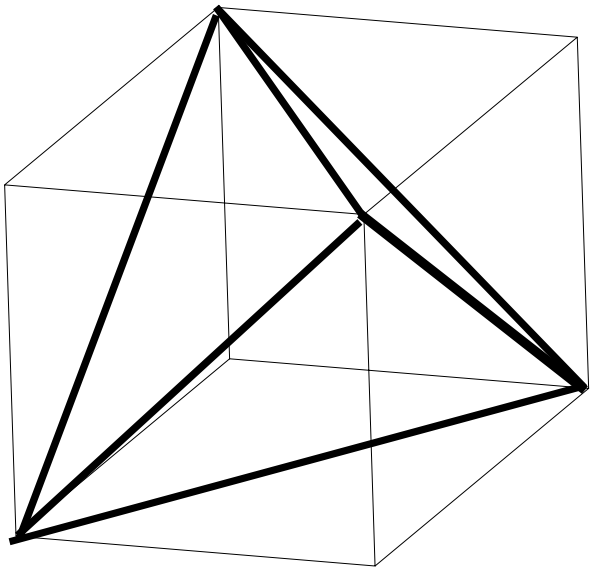
    c. What is the maximum radius of a sphere (in terms of R_{Na+} and R_{Cl-}) that could just fit into this site without producing any distortion of the structure?

3. The arrangement of neighboring atoms or ions about a central species is called a "coordination polyhedron." It is useful to view structures in terms of the way in which these polyhedra are linked together- through sharing of corners, edges, or faces.

    Let's consider tetrahedral coordination: four coordinating spheres of radius R_B surrounding and in contact with a center sphere of radius R_A. Can the central sphere, **A**, ever become large enough relative to **B** that the tetrahedra could not be linked by sharing faces, simply because sphere A pokes out of the face of the tetrahedron? If so, compute the radius ration R_A/R_B for which this would occur.

    Hint: The geometry of a tetrahedron is most readily treated in terms of a cartesian coordinate system. Construct a cube which has the reference axes *x*, *y* , and *z* along its

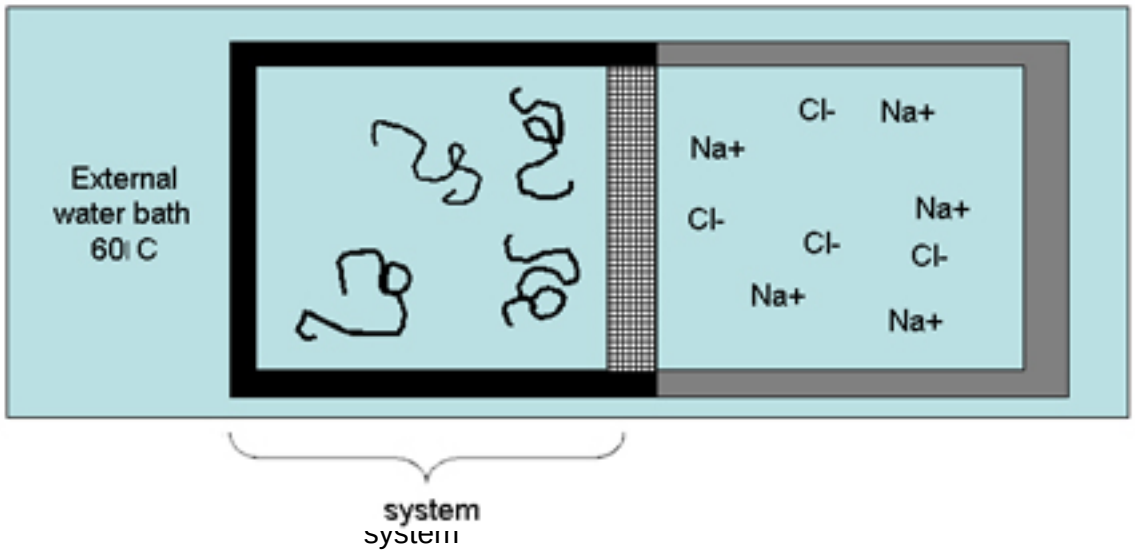
edges. The tetrahedron may be defined relative to this reference system by connecting two corners along a face diagonal of the top of the cube and two corners along the opposing face diagonal at the bottom of the cube. Connect the ends of these lines with four diagonals in the remaining four faces of the cube and –voila!- you have a tetrahedron inscribed in a cube.



4. Thermodynamics does not make predictions about the rate at which changes of state will happen in systems, and this fact makes it often very difficult to **prove** that a system is in equilibrium. Explain this statement in 1-2 sentences.

5. For each statement below, identify the type of thermodynamic system and process involved. State the assumptions you make to clarify your choices.

   (a) Our system is an aqueous polymer solution in a sealed chamber kept in contact with a water bath at a temperature of 60°C (see sketch below). One wall of the chamber is a membrane that has pores large enough for water molecules and salt ions to pass but too small to permit passage of the polymer molecules. The membrane is placed in contact with a second chamber that contains a sodium chloride solution and the system is allowed to equilibrate with the second chamber.



   (b) A metal foam is mechanically compressed by a constant applied force in a chamber open to the atmosphere at a constant temperature.

   (c) A chemical reaction is carried out in a sealed dewar vessel which is thermally insulated from the surroundings. (A dewar is a flask which has an inner chamber separated from its outer jacket by an evacuated space).

   (d) A polymer solution in a rigid glass test tube capped by a rubber stopper is heated from 20°C to 80°C by placing the test tube in a thermostated water bath.

6. **Identifying phases and components**. For each system described below, identify the phases and components present.

   (a) A beaker contains a mixture of salt water (sodium chloride in water) and ice cubes.

   (b) A sample is comprised of Pb and Sn, and has two types of crystals: crystals with composition (18 wt% Sn/82 wt% Pb) and crystals with composition (95 wt% Sn/5 wt% Pb).

   (c) You have a sample of solid linear polyethylene, which is semicrystalline: it contains regions where the linear polymer chains have folded on themselves to form crystallites surrounded by amorphous regions- regions lacking crystalline order where the chains follow random walk trajectories- as illustrated below.