Environmental Physics for Freshman Geography Students

Professor David Faiman. Lecture 9. v.3.5   (December 30, 2003)

1. Solids

We have already seen some examples of how the forces among electrons are responsible for the chemical reactions between atoms. These forces also determine the *average* distance between atoms or molecules in bulk matter, and their relative orientations. I have emphasized the word "average" here because the molecules are not stationary in a solid: They actually vibrate very rapidly about their average positions. I shall say more about this vibration later but, for the present, let us concentrate on the average positions of the molecules.

In the first lecture we encountered the fact that crystals contain regular arrays of atoms spaced typically about 0.5 nm apart. Now, depending upon the specific atoms in question (and external conditions such as temperature and pressure), their geometrical arrangement within a crystal will take one form or another from among a relatively small number of possibilities. Four examples of so-called *unit cells* for crystals are shown in **Fig. 1**. You will notice that each of these cubic unit cells is slightly different from the others.
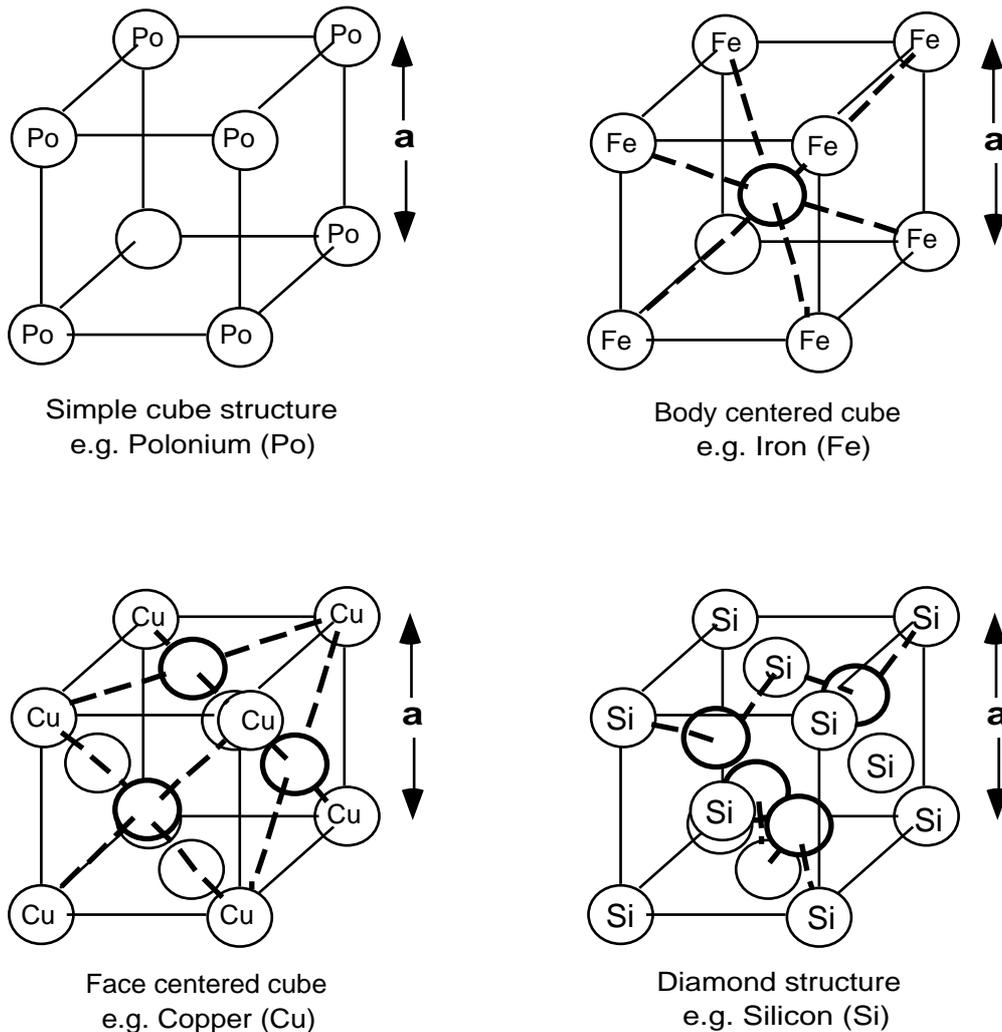

Simple cube structure
e.g. Polonium (Po)

Body centered cube
e.g. Iron (Fe)

Face centered cube
e.g. Copper (Cu)

Diamond structure
e.g. Silicon (Si)

Figure 1: Four examples of possible cubic arrangement of atoms in solids

In the case of the element polonium (Po is element number 84 in Mendeleev's Periodic Table of the elements) the atoms occupy the corners of an empty cube of side **a** (**a** is called the *lattice constant*). This structure is called *simple cubic* and abbreviated *sc*. The upper left diagram in **Fig. 1** shows a unit cell of solid polonium.

Atoms of iron (Fe is element number 26 in Mendeleev's Table) also arrange themselves at the corners of a cube but there is an extra atom in the center of the cube. This structure is therefore called *body-centered cubic*, or *bcc*. The upper right diagram in **Fig. 1** shows a unit cell of solid iron.

Atoms of copper (Cu is element number 29 in Mendeleev's Table) arrange themselves at each corner of a cube and also at the center of each of its faces. Therefore this structure, not surprisingly, is called *face-centered cubic* or *fcc*. The lower left diagram in **Fig. 1** shows a unit cell of solid copper.

Finally, silicon (Si is element number 14 in Mendeleev's Table) atoms arrange themselves in an fcc structure but, in addition, there are 4 extra atoms completely within the cube. This structure - you will probably not guess - is called *diamond structure* or *ds* (because the carbon atoms that make up diamonds take this same crystalline form). The lower right diagram in **Fig. 1** shows a unit cell of solid silicon.

There are also a number of other crystalline shapes, which are not cubic. For example, aluminum crystallizes with a *hexagonal* shaped unit cell, but I shall not discuss these more complicated structures because they require more than a single lattice constant to specify their geometry. I would, however, like to emphasize that *all* minerals crystallize into one of a relatively small number of possible crystal shapes, which relate many of their physical properties to the underlying atomic structure. The following section will illustrate one example.

2. Density of Crystals

An important practical feature of unit cells is that we may consider a real crystal of, say, a few cm in size, as being made up of a large number of unit cells replicated some 10^8 times in each direction. In such a crystal, a corner atom in any given unit cell is actually shared by the 8 unit cells that meet each other at that atom. Similarly, a face-centered atom in a given unit cell is shared by that cell and the adjacent unit cell: i.e. by 2 unit cells. Finally, a completely enclosed atom in a body-centered unit cell belongs only to the unit cell in which it sits.

Thus, a unit cell of a bcc material such as iron actually contains, on average, only two atoms: one atom in the center and 1/8 of an atom at each of its 8 corners.

We may now perform the following simple calculation:

Let the mass of a single atom be m. Then the mass of a bcc unit cell is:

$$M = 2m \qquad (9.1)$$

Since the lattice constant is a, the volume of a bcc unit cell is:

$$V = a^3 \qquad (9.2)$$

Therefore, the density ρ of a bcc unit cell is:

$$\rho = M/V = 2m/a^3 \qquad\qquad (9.3)$$

At this stage, just to check that you have understood the argument, you may like to deduce the corresponding expression for the densities of unit cells of type sc, fcc and ds. The results will be useful in the exercises below.

Now we can measure the density of iron by dividing the mass of a piece of the material by its volume (obtained, for example by immersing it in a fluid). The result is 7.86 g cm^{-3}, or in SI units: 7,860 kg m^{-3}.

On the other hand, from our knowledge of atoms, we can calculate the mass of a unit cell of iron since it contains 2 iron atoms, each of which has an atomic mass of A = 55.8, i.e. the mass of each iron atom is 55.8 times heavier than a hydrogen atom (which, as we have seen, weighs 1.67 x 10^{-27} kg). This knowledge therefore enables us to calculate the average distance between the iron atoms!

Re-writing eq. (9.3) as:

$$a^3 = 2m/\rho \qquad\qquad (9.4)$$

and inserting numbers, we have:

$a^3 = 2 \times 55.8 \times 1.67 \times 10^{-27}$ kg / 7,860 kg m^{-3} $= 23.7 \times 10^{-30}$ m^3

Hence, by taking the cube-root, a = 2.87 x 10^{-10} m = 0.287 nm, which is the desired answer. That is to say, we have used the physical density of iron, some information from chemistry, and our knowledge of its crystalline structure to calculate the distance between neighboring atoms in the crystal!

Now let us look at what assumptions have gone into deducing this result. First, there is the assumption that solid materials in general, and iron in particular, are made of atoms.

Secondly we have assumed that we know the crystalline structure of iron. This can also be determined experimentally, by scattering X-rays or neutrons from a sample of iron and studying the resulting patterns made on photographic film. In fact, by this technique, one can independently measure the 0.287 nm spacing between iron atoms.

Finally, we made use of some atomic properties of iron atoms which were determined by chemists about 100 years ago, i.e. how many times heavier than hydrogen is an atom of iron and how heavy is a hydrogen atom.

From a detailed knowledge of the forces between atoms, physicists are able to calculate what kind of crystal structures should occur in nature and, also, many of their physical properties (in addition to the density). For example, carbon crystallizes both as a diamond structure - which enables its extreme hardness to be understood - and, also, in the form of graphite. We have not discussed the graphite structure here but its geometrical form allows us to

understand why carbon in this crystalline form acts as a lubricant. An exciting "new" form of carbon was discovered in recent years, when it was realized that the same inter-atomic forces that can produce diamond and graphite can also produce a giant molecule of 60 atoms arranged like the surface of a soccer-ball. This material was named Buckminsterfullerene after the American architect, Buckminster Fuller, who suggested this kind of structure for making large, rigid, dome-shaped buildings.

3. Thermal Energy and Temperature

I'd now like to return to my earlier remark that the geometrical arrays in crystal unit cells represent only the *average* position of the vibrating atoms. The vibrations are caused by the kinetic energy of the atoms. This energy can be increased by providing heat from outside, or decreased by removing heat (via a refrigerator).

As we cool a crystal the atomic vibrations become smaller and smaller, until ultimately, we could think of the atoms as being completely motionless. At that stage it would not be possible to extract any further energy from them, as they would have none to give. Correspondingly, it would not be possible to reduce their temperature any further. Their temperature at that stage would thus truly be *absolute zero.* This temperature turns out to be -273.15 $^{\circ}$C on the *Celsius scale*. It is also denoted 0 K on the so-called *Kelvin scale* - which is just like the Celsius scale except shifted by 273.15 degrees.

If we move in the other direction - by adding energy, i.e., by heating the crystal, the atomic vibrations will become more and more violent. At a certain stage of heating, the amplitude of the atomic vibrations will be larger than the average distance between the atoms. When this happens, the crystal will lose its shape - the solid will become a liquid!

If we continue heating the liquid, some of the molecules will jump right out and never return. At this stage the liquid has boiled and become a vapor!

Again, depending upon the specific atoms and their interatomic forces, the solid, liquid and vapor phases of their existence will occur at different temperatures and pressures. For example, among the halogens, at room temperature: iodine (I) is solid; bromine (Br) is liquid; and chlorine is a gas. If we heat them they all become gases: If we cool them they all become solids.

3.1 Specific Heat (*Chom Seguli*)

The *specific heat* of a material is defined as the *rate of change with temperature of its energy per unit mass*. In the case of liquid water, the specific heat C = 4.19 kJ kg^{-1} K^{-1}. For example, if we wish to know how much energy is required to heat the contents of a 120 liter tank of water from 20^{0}C to 60°C, the answer is:

120 kg x 40 K x 4.19 kJ kg^{-1} K^{-1} = 20.112 MJ (= 5.59 kWh) (9.5)

3.2 Latent Heat of Fusion (*Chom Kamus shel Hituch*)

Ice, the solid form of water, has a specific heat of C = 2.10 kJ kg^{-1} K^{-1}. This means, for example, that we would need to add 2.1 kJ of energy in order to heat a 1 kg block of ice from a temperature of -3 ^{0}C to -2 ^{0}C; another 2.1 kJ to raise its temperature to -1 ^{0}C and yet another

2.1 kJ of energy to raise the temperature of the ice to 0 ^{0}C. At this stage something different happens. If we add another 2.1 kJ of energy, the temperature of the ice will remain at 0 ^{0}C and nothing will seem to have happened. But as we continue to add more energy to the ice block, something is actually happening to the molecules inside. The kinetic energy we are supplying to them is allowing them to break loose from the rigid crystalline structure within which they were frozen. Gradually, as we add more energy, the ice melts. After we have added 334 kJ we find that the 1 kg block of ice has completely melted, and we are left with 1 kg of liquid water, still at a temperature of 0 ^{0}C. From then onwards, as we continue to add heat energy, we shall find that each additional 4.19 kJ of energy will raise the water temperature by 1 ^{0}C. The energy needed to melt a sold, L_f = 334 kJ kg^{-1} in the case of ice, is called its *latent heat of fusion*.

3.3 Latent Heat of Vaporization (*Chom Kamus shel Iduy*)

A corresponding phenomenon occurs when a liquid is on the point of boiling: It requires *extra* energy to enable the molecules to leave the liquid - i.e. for the liquid to convert to a gas. In the case of water, this *latent heat of vaporization*, as it is called, amounts to L_v = 2260 kJ kg^{-1}. Thus, 4.19 kJ of energy will suffice to raise 1 kg of liquid water from a temperature of 99 ^{0}C to 100 ^{0}C, but the water will remain in its liquid phase, without increasing in temperature, until we have added an extra 2260 kJ of energy. At that point, all of the water will have converted to steam. Incidentally, if the 1 kg of steam were not lost but collected in a vessel at atmospheric pressure, we would find that each further 1.95 kJ of energy would raise its temperature by 1 ^{0}C, because the specific heat of water vapor at atmospheric pressure is C = 1.95 kJ kg^{-1} K^{-1}.

Problem set 9: (solids and liquids)

1. Obtain the corresponding values for the lattice constants of polonium (atomic weight = 209, density = 9,400 kg m^{-3}), copper (atomic weight = 63.5, density = 8,933 kg m^{-3}) and silicon (atomic weight = 28, density = 2,329 kg m^{-3}).

2. Use the information given in section 3 of this lecture to calculate how much energy is required in order to convert 0.5 kg of ice at -15 ^{0}C into steam at +115 ^{0}C.