## VIII. INTERATOMIC POTENTIAL

8-1 THE CHARGE DENSITY AND INTERATOMIC POTENTIALS

In the last chapter we saw that the electron density is responsible for holding atoms together. In other words, it is the density that creates a potential between the atoms, which as Feynman said, "attracts [atoms] when they are a little distance apart, but repels [them] upon being squeezed into one another." What Feynman is describing is the interatomic potential. Depending on the exact electron density, this potential can take on different forms, but they all share the same general features as shown in Figure 1. Each of these potentials represents some real molecule held together by bonds that we describe as ionic, covalent, etc., and each has a different set of properties.
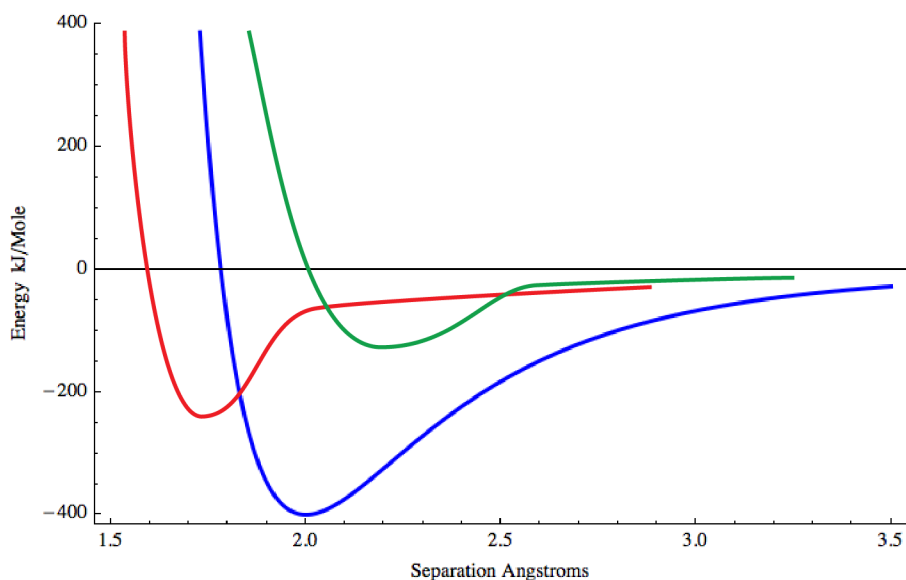


FIG. 1: Every electron distribution will give rise to a different interatomic potential and hence different properties.

At present there is a good deal of research directed toward determine the potential that will result from a particular charge density, and the properties that result from that potential. We will come back to this extremely interesting area of research in a subsequent chapter. For now, however, we want to focus on the properties that can be extracted from the interatomic potential.

We are aided in this exploration by noting that real interatomic potentials of the type

picture in Figure 1 can be approximated with a simple algebraic equation of the form:

$$V(r) = \frac{A}{r^m} - \frac{B}{r^n} \tag{1}$$

where $A$, $B$, $m$, and $n$ are adjustable parameters that depend on the electron distribution and can be varied to give a potential that fairly accurately reproduces the potential of a real of atoms. We will use to study a common engineering phenomenon–fracture of a brittle material. We are going to calculate the "theoretical" work of fracture.

8-2 THE WORK OF BRITTLE FRACTURE

We will begin by creating a structure made from atoms interacting through an idealized interatomic potential: a rod with a square cross section of 1 cm on a side and 10 cm long. This rod is made from long strings of bound atoms running along the length of the rod. In cross section these strings are arranged on a square lattice 5 Å apart. The atoms interact through an interatomic potential of the form:

$$V_m(r) = 51200 \left( \frac{32}{r^{12}} - \frac{1}{r^6} \right) \tag{2}$$

where $r$ is the distance between bound atoms measured in Å and $V_m$ is in units of kJ/mole. Graphically the potential has the form shown below.
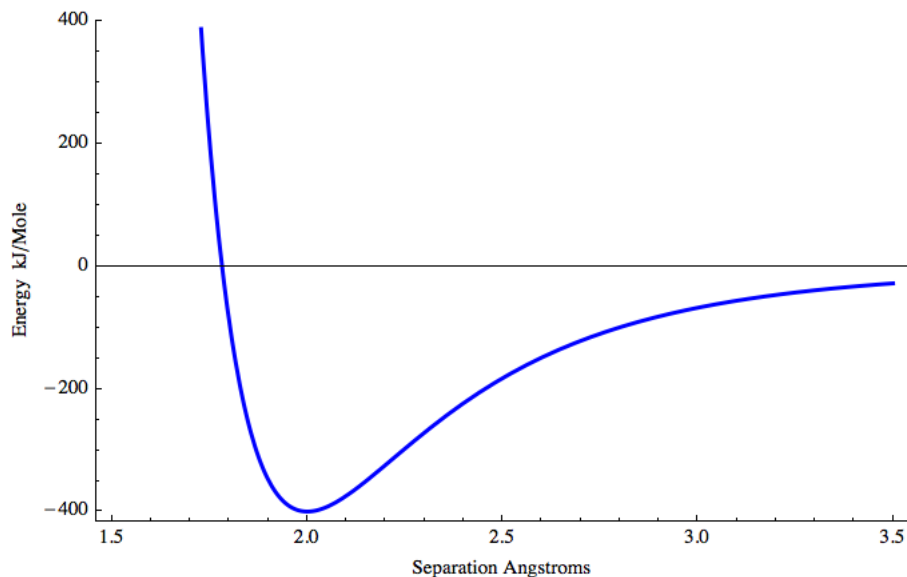


FIG. 2: The potential energy between pairs of atoms bound by the potential given in Equation 1.

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We will need several bits of information that can be extracted from the potential. The first is the force versus displacement function, that is the amount of force that must be exerted to change the distance between the atoms and correspondingly stretch or compress the rod. This is an easy matter as we know that this force, $F_m(r)$, is given by the derivative of the potential in the direction of the applied force, i.e. (You should verify this calculation)

$$F_m(r) = \frac{-\partial V_m(r)}{\partial r} = 51200 \left( \frac{384}{r^{13}} - \frac{6}{r^7} \right) \tag{3}$$

The units on $F_m(r)$ are kJ/mole/Å (verify that these are units of force).

It is useful to superimpose the plots of $V_m(r)$ and $F_m(r)$, as this will allow us to understand qualitatively how the energy of bound atoms changes as we imagine pulling them apart or pushing them together.
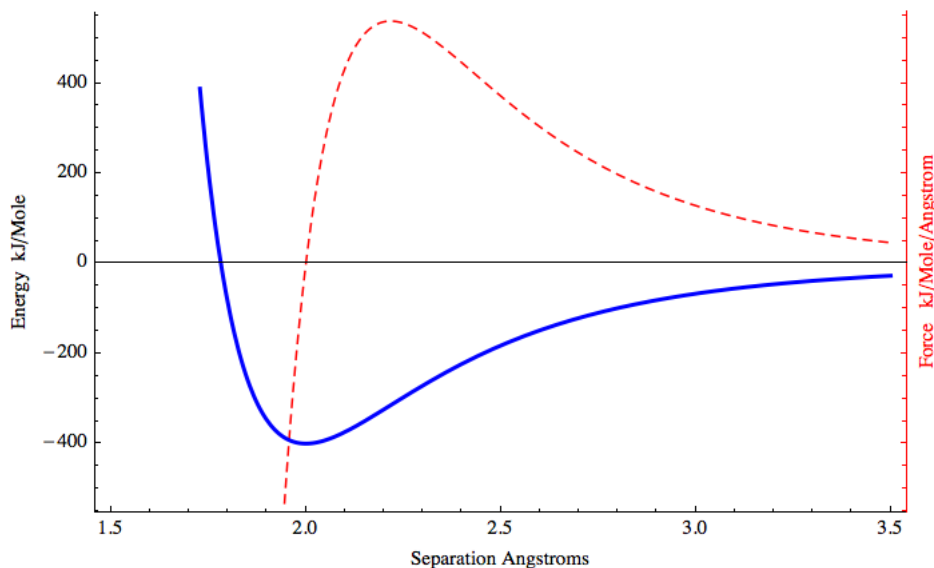


FIG. 3: The blue curve is the potential energy as a function of separation (Equation 1) and the dashed red curve is the force versus separation curve (Equation 2).

First and foremost, we note that the point at which no force is required to maintain a particular separation corresponds to the minimum of $V_m(r)$. (Can you explain why this is the case using both mathematical and physical arguments?) This point is the equilibrium separation of our atoms along the strings–a distance often denoted as $r_0$. We can quickly find this separation by setting Equation 2 equal to zero and solving for $r$. You should do this and verify that $r_0 = 2$ Å.

When the atoms are separated by 2 Å they are at the lowest possible energy and we would like to know what this energy is. To find it all we need do is set $r = 2$ in Equation 1 giving $V_m(2) = -400$ kJ/mole. So a pair of atoms separated by 2 Å will have an energy of -400 kJ/mole. But as we can see from Figure 1, when they are separated by just a few more Å, their energy is very close to zero. In order to separate these atoms we will have to add 400 kJ/mole to the system in the form of mechanical work (force acting through a distance). The work required to rearrange the atoms is called the bond energy or the work of separation. For any potential, it is given simply as $V_m(\infty) - V_m(r_0)$. (It is also given by $\int_{r_0}^{\infty} F_m(r)\, dr$, can you explain why?) So the bond energy between our atoms is 400 kJ/mole.

Returning now to Figure 2. Note that to push the atoms closer together than 2 Å requires a negative (compressive) force and to hold them at distances greater than 2 Å requires a positive (tensile) force. Further, there is a maximum force that we can apply to separate these atoms. Let's find the magnitude of this force and the interatomic separation at which it occurs.

The interatomic separation at the maximum force will correspond to the value of $r$ at the point of inflection of $V_m(r)$ (explain why this is the case). We find this point by setting the second derivative of $V_m(r)$ with respect to $r$ equal to zero and solving for $r$. As a first step we find the stiffness function, $C_m(r)$, i.e.

$$C_m(r) = \frac{\partial^2 V_m(r)}{\partial r^2} = 51200 \left( \frac{4992}{r^{14}} - \frac{42}{r^8} \right) \tag{4}$$

Setting $C_m(r)$ equal to zero and solving for $r$ gives $r_{F_{max}} \approx 2.217$ Å. To get the the magnitude of the force at this point simply evaluate Equation 2 for $r = 2.217$ which gives, $F_m(2.217) = F_{max} = 538$ kJ/mole/Å.

These are strange units so let's convert them to more traditional units of force, Newtons (kg m/s$^2$) which gives us $8.93 \times 10^{-9}$ N/bond. This is equivalent to the force of gravity acting on an object with a mass of about a microgram. In other words, if we could hang a microgram mass from one of these bonds, it would stretch the bond from 2 to 2.217 Å.

But how much energy is stored in the bond as it is stretched to this point? This is given by taking the difference between the potentials at $r = r_0$ and $r = r_{F_{max}}$, that is $V_m(r_{F_{max}}) - V_m(r_0) = -314.8 + 400 = 85.2$ kJ/mole. With these bond parameters it is an easy matter to calculate the macroscopic properties of our 10×1×1 cm rod.
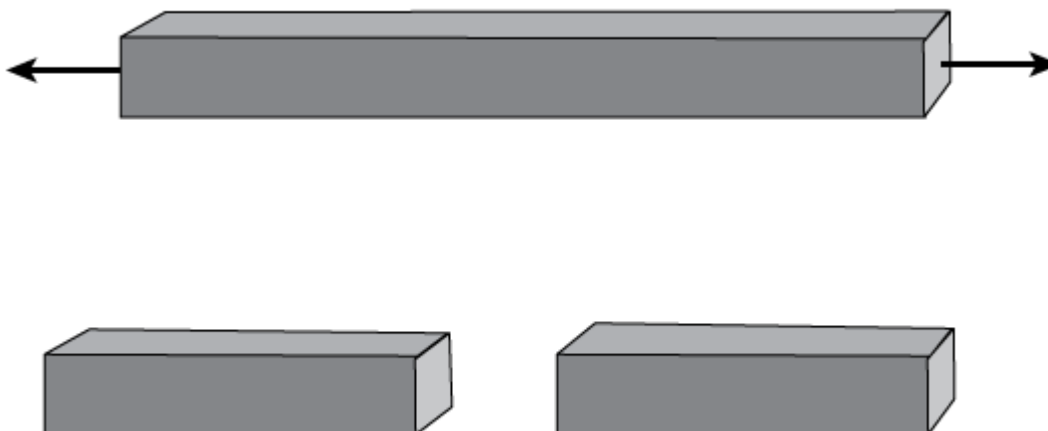
FIG. 4: Imagine pulling on the rod until it breaks. The work of fracture is given only by the energy needed to rearrange the atoms of the rod

First let's calculate the work of fracture, that is the amount of energy needed to separate the rod into two pieces as in the folowing picture.

Recall that the work of a process is nothing more than the energy used to change the structure and rearrange the atoms. In this case the change in structure amounts to creating two new surfaces. The matter that has been rearranged is the electrons in the bonds that held the two sides of the bar together. The energy necessary to break these bonds is given by the number of bonds × the bond energy. Thus we need the number of bonds broken to calculate the work of fracture.

As the strings of atoms are 5 Å apart and an Å is equivalent to $10^{-10}$ m, along a length of one meter there will be $1/(5 \times 10^{-10}) = 2 \times 10^9$ strings and along a cm there will $2 \times 10^7$ strings. Obviously, $(2 \times 10^7)^2$ or $4 \times 10^{14}$ strings will run through the 1 cm$^2$ cross section of the rod, which is the same number of bonds that will be broken in separating the two halves of the rod. Hence, the work of fracture is: $400 \times (4 \times 10^{14}) = 1.6 \times 10^{17}$ kJ/(mole of bars) $= 2.65 \times 10^{-4}$ J/bar (verify the arithmetic). This is a tiny amount of work. It is roughly the work done in lifting 1 gram 3 cm. How is it possible that this is all the energy necessary to fracture the rod?

Remember there is another component of energy associated with any process and that is heat. Let's see how much heat might be generated in fracturing the bar. For this we have to imagine the whole process leading up to the fracture, so assume that our bar is
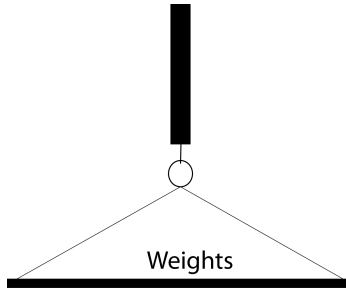
FIG. 5: Our imagined experimental setup to measure the energy to stretch the rod to its breaking point.

suspended from a very rigid structure on one end and supporting a platform to which we can add weights on the other end. All of our connections from the bar will be made with infinitely strong and unstretchable materials.

As we add weights, the atoms in the strings will move apart until the restoring force between them just balances the force of the weights. This will continue as more weight is added until the bonds reach their maximum restoring force, add more weight and the force of the weight will exceed the restoring force of the bonds and the material will break, the force at this point is a measure of the rod's "ultimate strength."

We can calculate the ultimate strength of the rod much as was done in calculating the fracture energy. We will multiply $F_{max}$ for one bond by the number of bonds in the cross section of the rod: $(8.93 \times 10^{-9}$ N/bond$) \times (4 \times 10^{14}$ bonds$) = 3.57 \times 10^{6}$ N. The force due to 1 kg on the Earth's surface is 9.80 N so our rod could support a load of 364,286 kg before breaking.

Typically, ultimate strength is reported for a standardized cross section of 1 m$^2$ giving units of N/m$^2$ called Pascals and denoted Pa. In these standardized units our bar has a "tensile strength" of $3.37 \times 10^{10}$ Pa. The tensile strength of the very strongest steel is right around $5 \times 10^{9}$ Pa and the strongest known materials, carbon nanotubes, are predicted to have a tensile strength of $6 \times 10^{10}$ Pa. Considering everything, our model is not too bad, though our numbers are probably a little high for reasons that will become evident.

Now let's calculated the energy needed to stretch the rod to the breaking point. Again this is an easy matter. We have already calculated the energy needed to stretch a bond to $r_{F_{max}}$ to be 85.2 kJ/mole. Multiply this by the number of stretched bonds and we have the answer.

The number of stretched bonds will be the total number of bond in the rod. There are

$4 \times 10^{14}$ strings of atoms running through the rod and the bonds in each string are 2 Å long. Hence every 10 cm string will contain $5 \times 10^8$ bonds. Giving us $2 \times 10^{23}$ bonds in the rod. And the energy need to stretch the rod to its breaking point is 28.3 kJ

This is remarkable, of the energy put into the rod through the stretching process a negligible amount went to work, the remainder had to go to heat or to some process that we have yet to identify.