

VI. ENERGY PROFILES AND BARRIERS

6-1 ENERGY PROFILES

In the previous chapter we saw that the interatomic potential determined how stuff responds to mechanical loading. We also made a rather remarkable discovery that for most things, actual and theoretical strength differ by an order of magnitude. You should now be able to explain why the glass rod from one of our early labs broke so easily when lightly scored. However, you will note that the other phenomena we observed in that lab, such as metallic deformation (bending) and work hardening cannot be simply explained in terms of an interatomic potential. Something is missing. What?

We have noted that atoms and molecules often respond to a process by changing their potential energy—water molecules increase their potential as they transform from ice to liquid. This transformation is analogous to the macroscopic occurrences of everyday life in which the potential energy of an object changes—for example a person climbing or descending a hill, a book moved from the floor to a bookshelf, a pair of magnets pulled apart, or the unrolling of scotch tape. The potential energy change for these processes can be determined by knowing the potential energy of the object in its initial and final state. But in addition to this energy difference, we are frequently interested in the path or route taken to get to the final state. Those of you who ski, bike, rock climb, or hike know that relating your weekend adventures in terms of where you started and ended is less interesting than how you got there. Did you get from the top to the bottom of the ski hill via *Widow Maker* or *Mary's Little Lamb*?

The path of a process is often represented with a *reaction progress diagram* or *process energy profile*, which plots the potential energy of a molecule at each point along its path. For example, Figure 6-1 shows a hypothetical process profile for hikers ascending Zion Mountain to the **M**. Consider two paths up the mountain. Hiker 1 ascends straight up the mountain (red route),

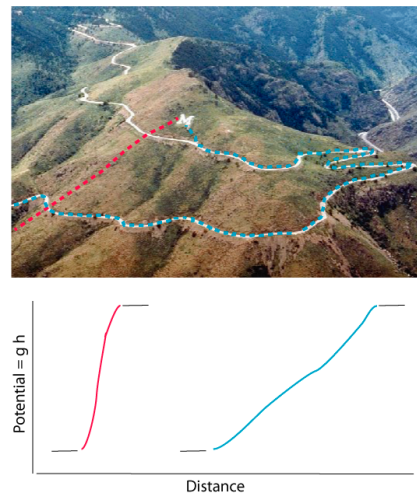


Fig. 6-1

while the Hiker 2 follows the paved road (blue route). The process profiles for each hiker are shown at the bottom of the figure. The vertical axis gives the hiker's potential energy per unit mass, while the horizontal axis gives the distances the hikers travel; the horizontal axis is known as the process coordinate (chemists call it the reaction coordinate). Per unit mass, the total work expended by both hikers (the change in gravitational potential energy) is the same. (*Where does the expended energy go?*).

However, they experience quite different hikes. Assuming each hiker covers the same distance per step, then Hiker 1 experiences a greater potential energy increase with each step but will take fewer steps to get to the **M** compared to Hiker 2. Let's make this a bit more mathematical. We will denote the process coordinate by x , making the potential a function of x , denoted $V(x)$. Now the change in potential per step is $\Delta V(x) / \Delta x$, where Δx is the length of a step. We recognize this as the slope of the energy profile. Denote this quantity with an F , that is $F(x) = \Delta V(x) / \Delta x$, which requires $F(x) \Delta x = \Delta V(x)$. F has units of force and so F is the force that must be applied through the distance Δx to yield the potential energy change of ΔV . Hiker 1 exerts greater force with each step than Hiker 2.

We can generalize this argument by noting that $F(x) = dV/dx$, where V can be any potential—strong, weak, gravitational, or electromagnetic. **Force is nothing more than the “effort” needed to change an objects potential energy, which is given by the slope of the energy profile.**

6-2 ENERGY BARRIERS

You may be thinking that when doing the **M**-climb you did not notice having to exert a force to avoid sliding down the mountain, but that is because there is something going on that we have not yet considered. To figure out what we overlooked, lets perform a thought experiment in which you have to roll a 50 kg hard rubber ball up the road to the **M**. Consider what would happen if you

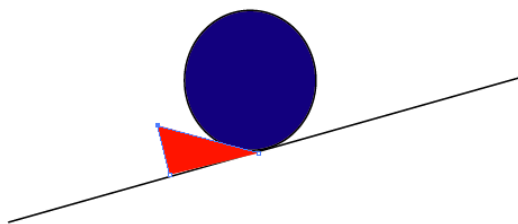


Fig. 6-2 The Blue ball can be prevented from rolling down the hill by changing the steepness of the road bed, in this case using the wedge to create a local region where the road appears to be flat and hence there is no force pushing the ball down the slope.

removed your hands even for an instant: the ball would begin to roll back down the hill. To prevent this, you must constantly exert force on the ball. I don't know about you, but if I had to roll this ball the mile or so to the **M**, I would need to rest along the way. In anticipation, I would bring with me a wooden wedge as shown in Figure 4.2. Now when I needed to rest, I would just shove the wedge under the ball. This wedge changes the apparent steepness of the road. The ball is at rest because the road is now apparently flat and the force acting to push the ball down the hill has vanished. The wedge introduces an *energy barrier* to the reaction profile. If you did not bring a wedge with you, in order to rest you would need to find a place where the natural terrain was flat over preferably a little concave some small distance; there are a few such places on the way to the **M**. Whether natural or artificial, each of these spots will be characterized by a potential energy barrier.

In general, there are two kinds of process profiles, as shown in Figure 6-3: those with barriers and those without. We take particular note of the barrier energy, which is sometimes called the *activation energy* or *activation barrier*. In addition to the barrier energy, where this barrier occurs along the reaction profile is also important. Does it occur closer to the beginning or end of the profile? Also of importance is the potential energy difference between the initial and final atomic arrangements; again, this is related to the total amount of work done on or by a molecule as a result of the structural change.

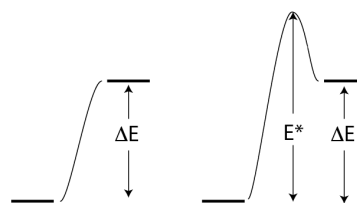


Fig. 6-3 The two general types of process profiles. On the left is a barrier free profile and on the right is an energy profile with a barrier. Of particular interest is the height of the barrier, E^* , and the potential energy difference between the initial and final atomic arrangements, ΔE .

6-3 EXAMPLES

Let's start with an example from a previous chapter: the conversion of liquid water to solid ice (freezing). The potential energy of liquid molecules is higher than that of molecules in solid ice, as represented in Figure 6-4, where the potential energy is shown decreasing when going from liquid to solid. This situation is much like the potential energy drop experienced by a ball rolling down the **M**-hill due to gravity. (*So what force is pulling these water molecules "downhill" to their lower potential energy*)

When water freezes, the potential energy decreases. Where does that “lost” potential energy go? The 1st Law of Thermodynamics tells us that it’s not lost but converted to kinetic energy. Consider the back of your freezer. How does it feel – hot or cold? If you put your hand back there, be careful: it gets hot. Some of that heat comes from liquid water molecules changing structure to form solid ice; as they transform from liquid to solid, their lost potential energy is converted to kinetic energy — molecular motion we call “heat”.

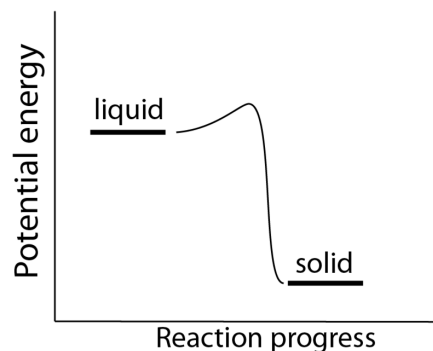


Fig. 6-4 The reaction profile of a water molecule “reacting” with ice to grow the ice crystal.

Next, let’s look at the energy barrier in this process, also shown in Figure 6-4. It is very small, meaning it doesn’t take much of an energy “kick” to get water molecules to freeze into ice. Thus, we rarely notice that there is a little bit of extra energy needed to get the liquid water to *start* freezing.¹ And remember: once it gets going it releases energy, overall.

So far, we have concentrated on thermal processes - those where energy is added or removed in the form of heat. However, there are other ways to add energy to a system. One of the more common is by displacing atoms with an applied force, which we call *mechanical energy*. Lifting a steel girder into a building frame, pushing on something, stretching a rubber band, or opening a soda can with a pull tab are all examples of mechanical energy in action.

¹ We typically don’t observe the energy barrier for water freezing – because it’s so small. If you get water cold enough, it apparently starts to freeze instantly, and energy is released. But there is one place you might be able to observe this small barrier in action – you can try it yourself, or look for videos online. Take an unopened, unwrinkled, clear plastic bottle of soda, and place it in a very stable location that’s just below 0 °C. The top shelf of a fridge in a dorm-sized fridge-freezer combo is a good choice. Let it sit a few hours, but don’t let your roommate bump it. If you’re lucky, the liquid water will cool to a sub-zero temperature, but it *will not freeze*. That’s right: it is now liquid water, below the freezing point of water. It is *supercooled*. The second you pick up the bottle - or maybe not until you open it - the water molecules will have enough of an energy kick to surmount that barrier and freeze into their solid structure! The whole bottle freezes at once – typically leaving some trapped liquid, and giving you a nice soda slushy.

Say we need to take a two-ton steel girder and lift it 3 meters in the air, fixing it horizontally to support the 2nd story of a new building (Figure 6-5). All the vertical supports are already in place; we just need to lift and secure our girder alongside them. We get a crane and lift the girder into place, thereby raising its gravitational potential energy. Now we let it go, right? No! as it would just crash to the ground. What did we forget? Oh yes, to bolt into place? Let's try again...lift the beam, secure it with some bolts. Let it go...much better.



Fig. 6-5

In the absence of the bolts, the process of the girder falling to the ground is barrier-less transition, as in Figure 6-6 (a). The bolts introduce an energy barrier to the process of the girder falling, as shown in Figure 6-6(b). In this case it is a large barrier - strong bolts, secured deep into the girder. Before that girder can fall again, enough energy would have to be absorbed to

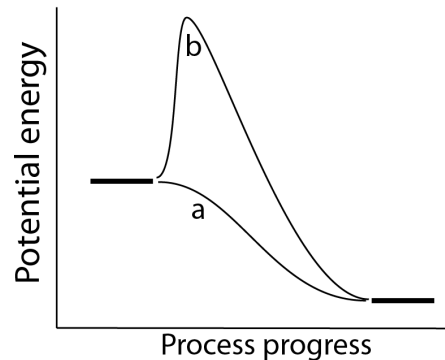


Fig. 6-6 The process progress for an unbolted girder (curve a) and a bolted girder (curve b). The state on the left is the energy of the girder 3 m above the ground while that on the right is the energy of the girder on the ground.

break all those bolts at once.

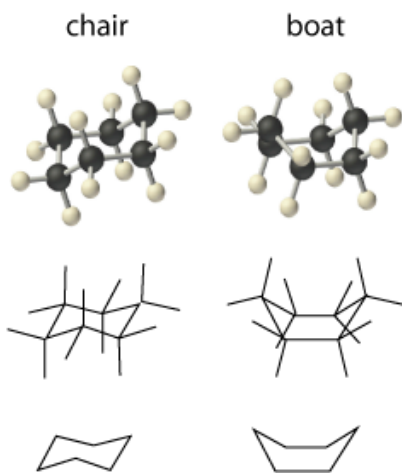


Fig. 6-7 Different representations of the chair and boat conformations of cyclohexane.

For our final example, let's go back to the molecular level: consider the energy of the transition between the two different shapes (conformations) of cyclohexane, shown in Figure 6-7. The two different shapes are called the "chair" conformation (left) and "boat" conformation (right). The energy profile for converting between these two conformations is depicted in Figure 6-8, where we see that the "chair" shape of the molecule is at a lower potential energy than the "boat" shape.

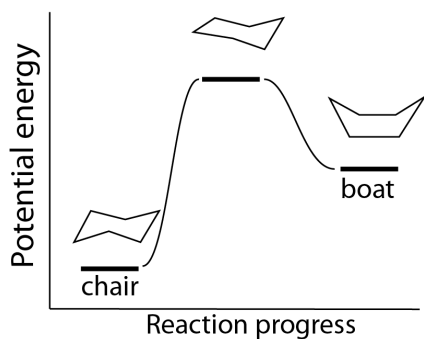


Fig. 6-8 The reaction profile as cyclohexane converts between its chair and boat forms by passing through a high energy unstable intermediate structure

Without an energy input, a molecule in the chair shape will stay that way. However, energy input can come through collisions with other molecules, which can transfer enough energy to bump a molecule up to the energy barrier. (Of course, at the same time the other molecule in the collision lost kinetic energy.) Recall heat is just internal kinetic energy – atoms and molecules are bumping into each other. At higher temperatures collisions are more frequent and more energetic.

Meaning that the probability of getting over the barrier gets better at higher temperatures.

If the collisions are just right, the atoms shift into the funky structure shown at the top of Figure 6-8, which we call the *transition state*. The potential energy of this structure determines the height the energy barrier. Once the atoms make it there, the electromagnetic forces push and pull them into the boat shape (and a few will just fall back into the same old chair shape). When they snap into their new boat configuration, they release potential energy, which is converted once again into heat (jiggling atoms) – However there is a net loss of kinetic energy as one does not get back as much as was expended pushing the molecule over the barrier. However, total energy is conserved as the lost kinetic energy is now stored as potential energy of in the “boat” conformation²

As you can see from the examples, *energy cannot be stored in barrier-less transitions*. Once the force involved in a process is removed, the atomic rearrangements revert back to their original state. Without a barrier, as soon as you stop pushing on the ball it will roll back down the hill. If you don't bolt that girder in place, it will fall to the ground. *Controlling the energy barrier is essential to storing energy in a structure.*

² The chair-boat interconversion of cyclohexane represents an important turning point in chemistry. It was discovered back in the 1960s and was one of the first experiments where scientists were able to measure the height of an energy barrier for a molecular-level process. In so doing, they opened up new avenues for controlling the properties of materials and paved the way for today's molecular engineers.

6-4 PROBLEMS FOR THE CURIOUS

- 1) We have talked in class about the strong nuclear force, which is many times stronger than the electromagnetic force. You may have also worked a challenge problem in which you found that there was a huge potential lowering associated with bringing neutrons and protons of lighter atoms together to form iron. Obviously since we don't see all of the stuff of our world spontaneously fusing to form iron, while giving off energy many times larger than a hydrogen bomb, there must be a barrier preventing this process. Research this topic and:
 - a. Describe the source of this barrier.
 - b. Explain the conditions that allow this barrier to be overcome.