

IV. ENERGY DISTRIBUTIONS

4-1 THE SECOND LAW OF THERMODYNAMICS

Though some might consider the first law a minor consideration to the science of engineering design, it is really quite remarkable. Let's see just how remarkable by summarizing everything we have discussed about the science of engineering design in Figure 4.1.

As before, we see that all process must involve the addition (or removal) of energy to a structure. Now however, we recognize that that energy can do only one of two things: it can change

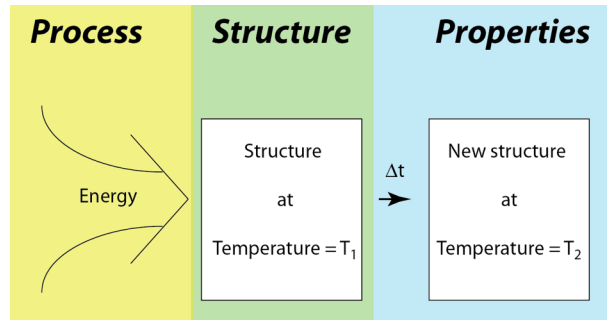


Fig. 4-1

the motion of the atoms in the structure, adding heat and thus changing its temperature; or it can do work, changing the positions and hence the potential energy of the structure's atoms. **The properties we observe depend only on the change in motion and position of the atoms. Everything we observe is a reflection of the way energy interacts with atoms.**

Of the many questions dealing with energy-atom interactions, one of the most basic concerns the way energy is distributed through a structure. By way of example, let's consider a very simple monoatomic gas system, say 10^{22} argon atoms in a rigid container held at 20° C. The atoms in the container are moving around, colliding with each other, bouncing off the walls—the system appears very chaotic.

The first law tells us that the sum of the atomic kinetic energies will be a constant, but it says nothing about the way that energy is distributed. We can imagine an infinite number of ways to spread the energy among the atoms: we could give all the energy to just one atom; we could pick out two atoms and give each one half the system's energy; or we could give every atom the exact same energy. In each case the total energy is the same—no violation of the first law here. So how is the energy distributed among our systems atoms? In answering this question, we need to be clear as to what is meant by the term “distributed.”

Let's imagine that by some means we were able to instantaneously tabulate the x-component of translational velocities for every molecule in the system. That is, at some instant in time, we find that molecule 1 is moving in the x direction at 100 m/sec, molecule 2 is moving in the x direction at -50 m/sec, etc. (Can you

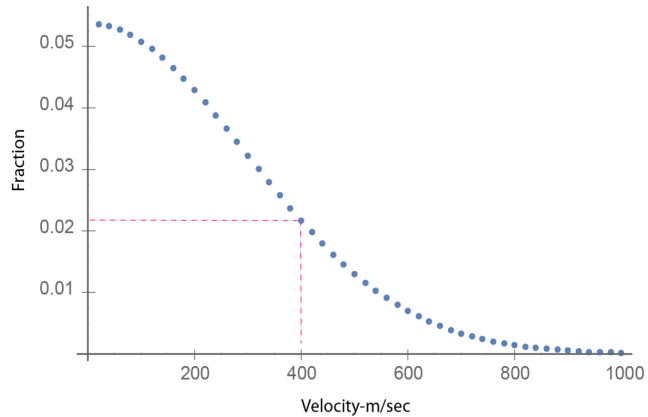


Fig. 4-2

explain why the average x-component of velocity must be zero?). We then collect all the data together and determine the number of argon atoms with an x-component of speed (speed is just the magnitude of the velocity) in some small interval, say the number with speeds ≥ 0 and < 20 m/sec, ≥ 20 and < 40 m/sec, ..., ≥ 980 and < 1000 m/sec, etc. We then divide these numbers by the total number of molecules in the system to get the fraction of molecules with x-components of speeds falling in a narrow range. The resultant graph would look something like Figure 4-2.

This data indicates that a little more than 5% of the Ar atoms have speeds in the x-direction between 0 and 20 m/sec; 2.1% have x-components of speed between 380 and 400 m/sec; and about 0.1 % have x-speeds between 700 and 720 m/sec.

If a month later we once again measure the distribution of atomic velocities, we would get identical results—and a month later, and a month later, and at any time in the future. As long as the container is held at 20° C, the velocity distributions will be identical.

Armed with this information we might be tempted to repeat the experiment with another gas, say neon. Once again, we would get a distribution of velocities that does not change with time. This distribution would be similar to that of Figure 4-2, but not identical.

Not to be dissuaded, we could easily convert our velocity distributions into kinetic energy distributions (*How would you do this?*). The resulting distribution for Ar would look like Figure 4-3. And the kinetic energy distribution for Ne would be identical—and for N₂ and O₂ and water vapor and SF₆ and for any mixture of gases, the kinetic energy distribution is always the same. The mathematical form of this distribution is known to be,

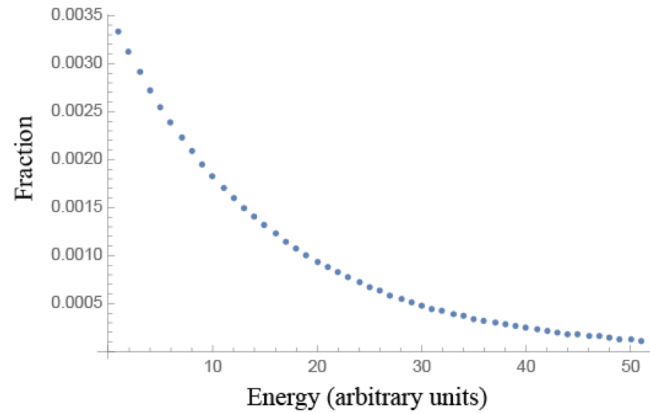


Fig 4-3

$$f(\epsilon) = A e^{-\frac{\epsilon}{kT}} \quad (1)$$

where $f(\epsilon)$ is the fraction of molecules with energy ϵ , A is a proportionality constant, k is Boltzmann's constant¹ and T is the absolute temperature. In our example the distribution depends on kinetic energy, i.e., $\epsilon = \frac{m v^2}{2}$ where m is the mass of moving atoms. However, the equation also applies to other forms of energy such as vibrations and rotations. Thermal energy in any form is distributed in accordance with Equation (1). This important discovery is credited to Ludwig Boltzmann; and Equation (1) is called the Boltzmann factor. We will use this equation repeatedly in the upcoming weeks, so it is worth committing to memory or storing it somewhere handy.

Equation (1) is one of many equivalent statement of the second law of thermodynamics. Nature is telling us that there is a preferred or best way to distribute energy through a structure. Nature is not telling us that we cannot store energy in a way

¹ You have seen Boltzmann's constant in the ideal gas law — $PV = nRT$, because $R = k * \mathcal{A}$, where \mathcal{A} is Avogadro's number. When ϵ in Equation (1) is reported as the energy per molecule, then one uses k . When ϵ is reported as the energy per mole of molecules, then one uses R in place of k .

that does not conform with Equation (1), but if we do, this less than optimum distribution will not last forever unless we tend to it constantly.

By way of illustration, imagine a thought experiment involving a frictionless billiard table (billiard tables do not have pockets) with perfectly elastic balls and side rails. We place 15 balls at one end of the table and then proceed to “break” them with the cue ball. The energy imparted to this system of balls is initially the kinetic energy of the cue ball, which immediately before and after the break is not distributed through all sixteen balls on the table in accordance with Equation (1). However, if we wait, eventually the energy distribution and consequently the motion of the balls will tend to that preferred by Nature (Equation (1)). **And once attained, this distribution will persist unless we interfere.**

We can imagine a more complex billiard table with small valleys and peaks spread across its surface. Each ball’s total energy—the ϵ of Equation (1)—will be given by the sum of its potential and kinetic energy. As balls proceed on their endless frictionless travels about the table they will undergo collisions, decelerate as they climb the small peaks and accelerate as they fall down the mountains and into the valleys. The first law tells us that the total energy of all the balls will remain constant, and the second law tells us that after some period, that energy will be distributed among the balls in accordance with the Boltzmann equation. There will be some fraction of the balls with sufficient energy to climb the peaks and some without enough to escape the valleys where they may be trapped until hit by another ball. Everything that may happen on this table is contained in Equation (1)—the second law of thermodynamics.

4-2 PROBABILITIES

There is another way to think about Equation (1) which is sometimes useful. Imagine instead of measuring the fraction of atoms or molecules with a particular energy, we are interested in following a single molecule, for a long period of time. Through collisions and such, its energy is changing. So, we might, for example, once a second for three hours measure this molecule’s total energy and ask, “What is the probability of observing this molecule with a total energy of ϵ_o ?” We can use Equation (1),

$$p(\epsilon_o) = A e^{-\frac{\epsilon_o}{kT}} \quad (2)$$

Using this formula, we can do an interesting thought experiment. Consider, as we have done before, that on a pleasant day where the temperature is 25° C an apple falls three meters from a tree to the ground. The apple's kinetic energy is transferred as heat through the atomic motions of the atoms in the air, apple, and earth. Now there is nothing that stops this energy from redistributing itself back into the apple and causing it to jump back up into the tree. Let's figure out how probable this is.

We will use Equation (2). For this problem $A = \frac{1}{kT}$. (*Can you determine why this must be the case?*). Knowing that $k = 1.388065 \times 10^{-23}$ J/K and assuming that the apple's mass is 0.25 Kg, and that the temperature is 298 K, then with a little bit of manipulation we discover that the probability of observing the apple leap into the tree is one in 10 to the 7.75839×10^{20} .

To put this number in perspective, the energy of the apple is changing with every collision between it and the molecules around it. These collisions occur with frequencies no greater than a few every femtosecond (10^{-15} sec). So we might expect to see the apple leap into the air after $10^{7.75839 \times 10^{20}}$ measurement made 1 femtosecond apart, i.e., after $\frac{10^{7.75839 \times 10^{20}}}{10^{15}} = 10^{7.75839 \times 10^{20} - 15} \approx 10^{7.75839 \times 10^{20}}$ seconds.

The age of the universe is 4.24466×10^{17} seconds. So, if we hope to see that apple leap back into the tree, we will need to observe the apple on the order of 10^{20} times the lifetime of our universe. It is likely that worms will eat the apple before we see it jump into the tree.

4-3 ENERGY BARRIERS AND CHEMICAL EQUILIBRIUM

While apples may never jump 3 meters into the air, atoms and molecules frequently jump over energy barriers to move from a structure of one potential energy to a structure of greater potential energy. We are able to change the fraction of molecules and atoms with enough energy to make these jumps by changing the system's temperature. When the temperature is increased, the number of atoms with sufficient energy to jump these barriers and adopt a new structure increases.

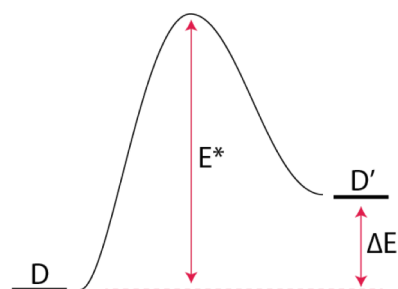


Fig 4-4

As the simplest possible example assume that a molecule can be in one of two structures (shapes), D or D' . To transform from one structure to the other, the molecule must go over an *energy barrier*, as represented in Figure 4-4 depicting the energy of the molecule (vertical axis) as it changes shape along the horizontal axis.

The Boltzman equation tells us that there is some probability that a molecule in structure D will have enough thermal energy to get over the energy barrier and in fact the probability of going from D to D' is,

$$p(D \text{ to } D') = A e^{-\frac{E^*}{kT}}. \quad (3)$$

Now, imagine all of these D molecules jiggling around and sometimes having enough energy to transform to D' . The rate at which this transformation occurs will be proportional to the number of D molecules, N_D , times the probability of transforming to D' , which we can write as,

$$R(D \text{ to } D') = N_D p(D \text{ to } D') = N_D A e^{-\frac{E^*}{kT}} \quad (4)$$

Just as D molecules are transforming to D' , D' molecules are transforming to D . The probability that such a transformation will occur is determined by the height of the barrier confronting the D' molecules, which is $E^* - \Delta E$, and the probability of transforming from D' to D is,

$$p(D' \text{ to } D) = A e^{-\frac{(E^* - \Delta E)}{kT}}. \quad (5)$$

and the rate for this transformation is given as,

$$R(D' \text{ to } D) = N_{D'} p(D' \text{ to } D) = N_{D'} A e^{-\frac{(E^* - \Delta E)}{kT}}. \quad (6)$$

We might ask, "As these molecules transforming back and forth between their two different structures, do they come to an equilibrium where the numbers of D and D' molecules are not changing?" Such a condition would be realized when the rate of transforming from D to D' is equal to rate of transformation from D' to D . Setting Equations (4) and (6) equal and solving for $N_{D'}/N_D$ gives,

$$\frac{N_{D'}}{N_D} = \frac{A e^{-\frac{E^*}{kT}}}{A e^{-\frac{(E^* - \Delta E)}{kT}}} = e^{-\frac{E^*}{kT} + \frac{(E^* - \Delta E)}{kT}} = e^{-\frac{\Delta E}{kT}} \quad (7)$$

Equation (7) is quite remarkable. It tells us that ratio of the number of molecules (or the concentrations) in each of the two structures is a temperature dependent constant that

depends only on the difference in energy between the two forms and not on the barrier between them. This constant is called an equilibrium constant denoted K_{eq} . At equilibrium, not only is thermal energy distributed in accordance with the Boltzmann equation but so is the potential energy and hence the total energy.

Equation (7) is a special case of a more general expression that can be derived from the Boltzmann equation (though the algebra is a little long), which states for a general chemical reaction, say one represented by the chemical equation,



where a , b , c , and d are stoichiometric coefficients and A, B, C, and D are reactant and product molecules. For this reaction, the equilibrium concentrations of reactants and products will be such that,

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = K_{eq}(T) \quad (8)$$

The magnitude of the temperature dependent equilibrium constant depends on the energy difference between the reactant and product molecules.

It may be hard to believe that Equation (8) is a reflection of the fact that Nature prefers energy be distributed in accordance with the Boltzmann equation, but this is the case. However, there are ways, at least temporarily, to produce energy distributions that do not conform to Equation (2). As an example, again consider Figure 4-4. Imagine we have a system at high temperatures in which D and D' are in equilibrium. If the temperature is very high, there will be nearly as many D as D' molecules (Can you explain why using Equation (7)?). If we rapidly cool the system, the probabilities for transformations between the two structures will decrease. If the barrier is sufficiently high and the temperature to which the system is cooled is sufficiently low, the fraction of molecules with enough energy to jump over the barrier in either direction becomes very small, essentially vanishing. In effect, the molecules are trapped in the high temperature equilibrium distribution.

Such systems are called metastable, in that, if we wait long enough, Nature will return the system to the Boltzmann energy distribution. All engineered structures are metastable. The key here is the time it takes for Nature to have its way and distribute energy as it

prefers. Our task is to manipulate energy barriers to make engineered structures last as long as needed to meet their performance goals.

During the next several lab periods you will have an opportunity to explore metastable structures and their properties.

4-4 PROBLEMS FOR THE CURIOUS

- 1) Equation (4) related the equilibrium constant to a ratio between the number of D and D' molecules. Explain why the result would be the same if we took the ratio of concentrations (number of atoms or moles per unit volume) of D to D'.
- 2) For the system described by Figure 4-4,
 - a. At very low temperatures what will be the ratio $N_{D'}/N_D$?
 - b. What will be the ratio $N_{D'}/N_D$ at very high temperatures?
 - c. Is it possible for $N_{D'}/N_D$ to be greater than one?
- 3) Consider a reaction of the form $A \rightleftharpoons 2B$.
 - a. Write an expression giving the equilibrium constant for this reaction.
 - b. Assume the equilibrium concentration of A is much greater than the concentration of B, i.e., $[A] \gg [B]$. What does this imply about the relative potential energy difference between A and B?
- 4) Explain why it is possible to produce metastable structures where the potential energy of the molecules in the system do not conform to the Boltzmann distribution, but we can't produce systems where the kinetic energy (thermal energy) of the molecules does not conform to the Boltzmann distribution.

INTERLUDE: THE FIRST MOLECULAR ENGINEER

MAXWELL'S DEMON

We have all observed that in the absence of a process that converts potential energy to kinetic energy, an object does not heat up of its own accord. To do so would violate the law of conservation of energy. But energy conservation does not prevent one part of an object from getting hotter while the remainder cools. Yet we do not observe such behavior. The reason is that this is yet another consequence of the second law of thermodynamics, which asserts that the spontaneous heating of one part of an object at the expense of another is impossible.

Pondering this law, the great physicist James Clerk Maxwell imagined, “... *a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributes are as essentially finite as our own, would be able to do what is impossible to us. For we have seen that molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform. Now let us suppose that such a vessel is divided into two portions, A and B, by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from A to B, and only the slower molecules to pass from B to A. He will thus, without expenditure of work, raise the temperature of B and lower that of A, in contradiction to the second law of thermodynamics.*” *(Did you understand that? This will help. Do a search on “Maxwell’s Demon Game” you will get several hits. Play the game for a bit. Now go back and reread what Maxwell wrote—does it make more sense now?)*

The being of Maxwell’s imagination became Maxwell’s demon and took on a life of its own, far removed from simply opening and closing a hole. Scientist have imagined what Maxwell’s demon would see during some atomic process. And artists have given form to Maxwell’s demon, a few examples are shown here.



Richard Einhorn composed four pieces for the electric violin named Maxwell's Demon #1, #2, #3, and #4. The innovative Ulysses Dove choreographed a series of modern ballets to these pieces. (View one of these (~4 min) as performed by the Red Angels of the New York City ballet.

Low quality but better dancers: <https://www.youtube.com/watch?v=c7W8jwsYz6A>
 Higher video quality: <https://www.youtube.com/watch?v=g7Tcl4PIDng>)

Last semester, after watching the ballet, I began to wonder what motivates Maxwell's demon. Does s/he just enjoy screwing around with the second law of thermodynamics or is there something more. What gives Maxwell's demon pleasure? Of course the answer is in Bronowski, Maxwell's demon takes pleasure in getting better at those things s/he can do. And what s/he does is manipulate atoms to produce structures. To have purpose Maxwell's demon must discover all of the structure-property relationships that govern molecules and materials. Maxwell's demon aspires to be a molecular engineer and is our class mascot.

For the remainder of the semester, and hopefully beyond that, imagine that you too are like Maxwell's demon and can dance among the atoms. What would you see?