Idea 4: Entropy and Probability - The Limits of Power

Mike Lee October 9, 1999

October 9, 1999

Contents

1 Preamble: Energy Powers Mechanics

Entropy is a little more abstract than most of what we have studied thus far. It was something that Aristotle never heard of and most eight-year-olds never heard of. But, it is as real as energy, as common and every day as heat, and there are fundamental laws which govern it.

To understand entropy, the science of thermodynamics had to mature for a century or so.

We need a few concepts and ideas from thermodynamics and we will start with that in our first section.

2 Language of Thermodynamics

Words

System: Any well defined and physically delineated set of objects or matter.

Closed System: A system is closed if it is cut off from the rest of the universe. Closed means isolated in the physical sense of not touching or being in thermal contact. Put more simply, an isolated system is completely out of touch with the rest of the universe.

Open System: A system which is somehow connected to or somehow feels the influence of the rest of the universe.

2.1 Examples

Of course, our open and closed systems are idealizations. Just as Galileo had to idealize when he dropped the balls from the Leaning Tower of Pisa so that he could make his discoveries of the fundamental laws of mechanics, scientists have had to idealize open and closed systems to discover and describe the fundamental laws of thermodynamics.

Open System: Just heating a cup of water makes the water an open system. if heat flows into a system, it is open. It could be the cup has a hole in it and leaks, which would make it open in a more classic sense too. It could be that water evaporates or that you are shaking it. Any influence is enough to make it open.

Closed System: If we took our cup of water and poured it into a Styrofoam cup and covered it with an insulating cap and placed it in a location where there were no vibrations, we would be making it a practically closed system - closed as well as we could manage anyway. For experiments which didn't take too long or were not sensitive to slight amounts of heat transfer, this would be close enough to an idea closed system. For scientific work, we might want to spend a few more bucks and get an insulated and vibration free box to hold the cup in.

Closed System: When talking about things that are not too sensitive to heat, such as the motion of our planets in the solar system, we can consider them closed if they are mechanically isolated. For studying the motion of the planets, it is a mechanical system that is closed. All the planets influence each other, but they are far enough away from the stars and the solar winds are weak enough that the solar system can be considered a closed system for such purposes. In this case, mechanical energy, KE+PE, is conserved.

3 First Law of Thermodynamics

Even in our previous (third) idea, we understood that work was a way of giving something energy and it took energy to do work.

3.1 Work and Energy

Example: System=spring.

Work done on a system can increase its energy.

If you compress a spring, some work (force times distance) is done by you. The spring, in turn, gains potential energy. Such a spring is NOT a closed system because outside influences (you) have change it. The change of interest here is not the shape so much as the fact that it has more energy after that influence.

Example: System=spring.

Work done by a system can decrease its energy.

If you take the compressed spring and place it against an object (like a ball) and let the spring expand, the spring exerts a force and moves the ball, so the spring does work on the ball. The ball acquires some kinetic energy equal to the amount of potential energy lost by the spring. By doing work, the system of the spring lost energy.

We observe that the work done **by** a system decreases its energy by an amount equal to its work. Conversely, work done **on** a system increases its energy.

3.2 Heat and Energy

Heat added to or taken from a system changes its energy.

Example: System=spring plus engine.

We clearly saw that a steam engine an do work. If we consider the engine connected to a spring as the system, then we put heat into the engine plus spring, the spring can be compressed to store energy. We produced heat to run the engine and got work out of it. The work was transformed into potential energy of the spring. (We must include in the "engine" the water and steam and collect the left over steam at the end to be technically correct. More on this later.)

Example: System=Bimetalic strip

We demonstrated how a bimetallic strip changes shape as it is heated. The strip itself (like the bimetallic strip in your thermostat at home) is a springy material. When heated, if it is not allowed to move, there is a force exerted by the strip trying to allow it to bend. This force could then be released to do work. The hot strip is then a spring really and a spring that ca do work, so it has some potential energy. This system illustrates how heat from outside the strip (system) can be converted to potential energy inside the strip (system).

We observe that the heat applied to a system increases its energy by an amount equal to its work. Conversely, work done **on** a system decreases its energy.

3.3 Statement of the First Law of Thermodynamics

The first law of thermodynamics is nothing but a fancy way of saying energy is conserved. That was our basic conclusion from Idea 3, but we are being more formal and abstract now. We will need to be to get the idea of entropy straight and it is best to start being abstract with something we are familiar with like energy.

We can state the First law several different, but equivalent, ways.

1. The total energy of a closed system never changes.

2. The energy change of an open system can be completely accounted for by the energy flow and work done.

The second of our statements is perhaps best for us most of the time. If the second statement is correct, then the first statement follows as a natural consequence and visa versa.

If we have two systems with energy content U1 and U2 and they are enclosed in a box to make them isolated (closed), then any energy lost by system 1 (decreasing U1) will exactly be equal to the amount of energy gained by system 2 (increasing U2).

System 1 and system 2 are open, but together (1+2) makes a closed system.

4 State of a System

Systems have certain very general characteristics that one can use to predict their behavior. We need to define some more words to identify those characteristics.

Equilibrium: An isolated (closed) system is said to be in thermodynamic equilibrium if it does not change in time.

Thermodynamic parameter:

To tell if a system changes, you can determine if its parameters changed. Examples of Thermodynamic Parameters that we have already encountered are:

volume, pressure, total mass, chemical composition, energy.

The parameters of a system are those global characteristics which describe its state. We say that the state of an equilibrium system is totally described by its thermodynamic parameters.

5 Ideal Gas

Thermodynamics started off as a study of the relationships between parameters of equilibrium systems. It is still that, but this study is what heralded the discovery of the three fundamental laws of thermodynamics.

One of the simplest systems to study was plain old air. Air is a gas and, it was later discovered, obeyed certain laws that all gasses obeyed. In fact, if some small deviations are ignored and you do the kind of idealization that Galileo did in ignoring friction, one can discover *ideal gas laws.* These laws, while important, are no exactly like the laws of mechanics or the laws of nature for energy conservation. The idea gas laws are not followed by real gasses, But they are pretty close and so we have now established the idealization of a physical system as a concept here and called that idealization the "ideal gas".

The initial experiments were done with air and then other common gasses - now called noble gasses (helium, neon, argon, krypton). These studies did allow true fundamental laws of nature to be discovered. Two are essential to our current study of thermodynamics.

5.1 Boyle's Law: Absolute Pressure

Pressure and vacuum have been a topic of discussion for a long time. The simple properties of pressure are well understood. If you have a gas and you want to compress it to a smaller volume, you have to exert pressure. If you measure that pressure and volume, you get a very nice relationship. To compress a gas like air to half its natural volume, you have to exert a pressure of about 14.7 pounds per square inch. We write that as 14.7lb./in^2. The air in the tires of a car are compress with a pressure of about twice that, $32 - 24 \text{lbs./in}^2$. Since this is more than double the amount that it takes to compress air to half its volume, you might think that the air has been compressed by more than half again and it occupies less than one forth its original volume. If we let the air out of a time and measure the "natural" volume, we would discover that it did not expand to four times its volume. The reason is that we are neglecting "atmospheric pressure" when we read a pressure gauge like those used for tires.

Humans (and most other life on Earth) live at the bottom of a blanket of air that is miles thick. While air is pretty light stuff, if you had a tube that was a square inch in area and five miles high and you filled it with air, that tube would have a mass of air in it that weighs more than ten pounds. More accurately, we can say that above every square inch on Earth is a quantity of air that weighs about 14.7 pounds.

If you set your gas gauge so it reads 14.7 normally, then measure the pressure and volume of gas as it is compressed or expanded, you discover that the product of the pressure and the volume remains constant. That's what Boyle discovered. He showed that if temperature is held constant and one if careful about leaks and measure pressure starting at 14.7 pounds for

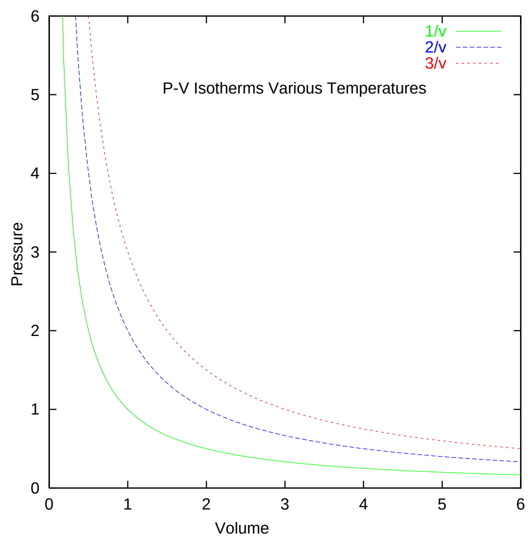

Figure 1: Absolute Pressure - Volume relations at Constant Temperature

normal atmospheric pressure, then

$$PV = \text{Constant}\,.$$

The constant was different for different amounts of gas, but was simply proportional to the amount of gas. If we take "N" to be the number of units of gas, then the constant in

$$\frac{PV}{N} = \text{Constant}\,,$$

was the same for all gasses at a given temperature. Examples of the pressure-volume relation for different amounts of gas are shown in Fig. 1.

The constant changed with temperature too, but Boyle does not get credit for figuring that out. That's Charles' law and we will study that next in Sec. 5.2.

In summary, Boyle's law shows us that there is such a thing as absolute pressure. We mean there is a definite way to determine pressure starting from zero. Zero pressure is a vacuum.

5.2 Charles' Law: Absolute Temperature

Charles' law helps us understand something a little more dramatic than absolute pressure. If the idea of emptiness (pure vacuum) was hard for people to get, then the idea of absolute temperature was even more difficult. We have nothing in our everyday experience that says that there is any lower bound to temperature. We might imagine that if we kept a perfect refrigerator running and running the temperature would just get lower and lower. Well, it doesn't. There is an absolute minimum of temperature and we first see how that came about when we look at Charles' law.

We all know that if things get cold, then shrink. Gasses are an even better example of that. heated gas expands and cooled gas contracts. The exact relationship can be studied with something a simple as air, but it works for all gasses.

If you raise or lower the temperate of a fixed amount of air at fixed pressure the volume increase and decreases linearly with temperature. If you change gasses so pure nitrogen or helium, the same thing happens. Examples of the volume-temperature relation for different amounts of gas are shown in Fig. 2.

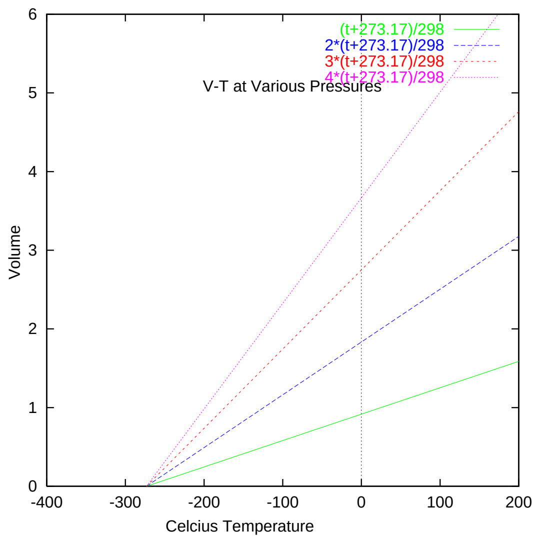

Figure 2: Volume Changes with Temperature

What we learn from Fig. 2 is that if you plot the volume of a gas against temperature, it looks like a straight line for all gasses. The slope of the line changes depending on the amount and pressure of the gas, but it is always straight. (There is a caveat to be explained about the differences between "ideal" gases and "real" gases in Sec. 5.3.)

The really important thing about the studies of Charles was that the lines that he drew always pointed to the same place on the temperature scale where the volume of the gas was predicted to go to zero. We have measures this temperature very carefully since then and it is -273.16 degrees Celsius. (In Fahrenheit, that's 523 **below zero**!) So, naturally, we ask ourselves, what happens when you get to this temperature? Do things disappear? Or, what if you cold go below this temperature? Would things have a negative volume? Does negative volume even make sense?

What we concluded form all these experiments was that there was a very lowest possible temperature. In fact, all temperatures can be measure from that very lowest temperature. Scientists discovered that if we did measure temperature starting at -273.16, only called that temperature 0 degrees, then equations with temperature were a lot simpler. Since we can't go below that temperature, we say we have discovered an absolute temperature scale. In other words, *Mother Nature* starts temperature at that point as a beginning. Temperature scales were invented with 0 as Mother nature's starting point. The most well known is the on that uses the same scale as Celsius except renumbers all the degrees. It is called the Kelvin temperature scale and we say we measure temperature in *degrees Kelvin*. (Kelvin was a physicist who studied thermodynamics.) For instance, ice freezes at 0^oC and 273^oK. Similarly, water boils at 100^oC and 373^oK. Room temperature (70^oF) is 21^oC and 294^oK.

5.3 Ideal Gas Law versus Real Gasses

.

5.4 Other laws of related interest

6 Heat Engines

6.1 Heat and Energy

7 Exam Review

1. For a closed (isolated) system,

   the sum of all forms of energy remains constant

2. For a system to which work and heat is added (but which does no work and gives off no energy),

   the total energy change of the system is equal to the increase in internal energy.

3. For a system to which work and heat is added and which also does work and gives off energy,

   the change in internal energy of the system is the energy and work put in minus the energy lost and work done.

4. Caloric Theory is wrong

   (a) Heat is not a substance.

   (b) Temperature is not a measure of the amount of heat or caloric.

   (c) Heat is not contained in the spaces between particles of a substance.

5. Temperature is a measure of the motion of atoms and molecules.

   Molecules have kinetic energy

   $$KE = \frac{1}{2}mv^2 \, .$$

   The average KE of an atom or molecule is proportional to temperature

   $$KE = \frac{3}{2}kT \, .$$

6. Latent Heat is the energy (as heat) that must be added to a material to cause it to change phase.

   For example changing ice to water or water to steam.

   The Heat energy is used to overcome forces between atoms and molecules and move them into states with higher potential energy. Work, supplied by the heat source, is done against the molecular forces. Because the temperature is normally held constant during a phase change like melting or boiling, all the heat energy goes into potential energy of atoms and molecules.

7. Things to Know about the Carnot Engine

   (a) A Carnot engine is also sometimes called an *ideal engine*.

   (b) A Carnot engine has the maximum theoretical efficiency allowed by the laws of nature.

   (c) A Carnot engine is an idealization. All real engines are less efficient.

   (d) A Carnot engine in **not** 100% efficient.

   (e) A Carnot engine , and all other heat engines, must have a hot and cold reservoir to operate.

   (f) A heat engine (even an idea one) must always give up some heat energy in each cycle to a cold reservoir.

   (g) Only the theoretical Carnot engine operating with the cold reservoir at zero temperature could be theoretically 100% efficient.

   (h) A Carnot engine does not create any entropy.

   (i) The area enclosed by the P-V curves for an engine is equal to the work done by the engine.