A Brief Introduction to Thermodynamics

Craig Michaud

11-15-2005

What is Thermodynamics?

- The branch of physics that studies the effects of temperature on physical systems at the macroscopic scale.
- The study of the relationship between heat, work, and other forms of energy.
- The science that describes what is possible and what is impossible during energy conversion processes.
- Describes the "direction" of a process.

-All of these things accurately describe thermodynamics.

-In general, though, we can say that thermodynamics is the study of energy conversion, most typically through terms of heat and work.

A (very) Brief History

- Thermodynamics has its beginnings in the study of engines, particularly steam engines.
- The word “thermodynamics” was coined by Lord Kelvin in 1849.
- Rudolf Clausius came up with the term “entropy” in 1850.
- James Maxwell formulated the *Statistical Mechanical* branch of thermodynamics in 1871.
- Ludwig Boltzmann precisely connected entropy and molecular motion in 1875.

-Thermo really starts with the coming of the Industrial Revolution in the 17th Century.

-The first steam engines were very, very inefficient, converting perhaps 2% of their fuel into useful work.

-He coined it in a paper on the efficiency of steam engines.

-Clausius also defined enthalpy, but that’s not relevant here.

-Maxwell had some help from Clausius; I will use statiscal mechanics in this lecture as it gives a good intuition into thermo without tons of math.

-Boltzmann’s formulation of entropy is perhaps the easiest formulation to understand, hence my use of it to discuss entropy.

-After this, we get into the 20th Century, where thermodynamics becomes one of the most fundamental and pervasive of the modern sciences.

The Laws

- <u>The Zeroth Law</u>
  - If two systems are each in *thermal equilibrium* with a third system, then they must be in thermal equilibrium with each other; that is, thermal equilibrium is transitive.
  - If Temp(A) = Temp(B) and Temp(B) = Temp(C) then Temp(A) = Temp(C)

Thermodynamic Equilibrium:

If an object with a higher temperature comes into contact with an object at a lower temperature, it will transfer heat to the lower temperature object. The objects will approach the same temperature, and barring further temperature loss to, or gain from, other objects, they will maintain a single constant temperature.

The Laws (cont.)

- <u>The First Law</u>
  - The first law is a consequence of conservation of energy and requires that a system may exchange energy with its surroundings strictly by heat flow or work.
  - We can thus state the first law as:
    - $\Delta E = \Delta Q - \Delta W$

(delta)E is the change in energy

(delta)Q is the change in heat

(delta)W is the change in work

Law Conservation of Energy:

This law states that the total energy of an isolated system remains constant regardless of changes within the system. Another way of stating this is that energy is a quantity that can be converted from one form to another, but cannot be created or destroyed.

Isolated System:

In thermodynamics, it is a system that does not interact with its surroundings in any way. The internal energy and mass of such a system are conserved.

Heat:

Heat is a measure of the amount of energy TRANSFERRED from one body to another because of the temperature difference between said bodies. Note that heat is NOT energy that is possessed by a body; physically, there is no heat IN a body. Energy that a body possesses due to its temperature is called internal thermal energy.

Work:

Work is the amount of energy transferred to or from a body or system as a result of forces acting upon the body, causing displacement of the body or parts of it. More specifically, the work done by a particular force is the product of the displacement of the body and the component of the force in the direction of the displacement. A force acting upon a body that undergoes no displacement does NO work on that body.

The Laws (cont.)

- <u>The Second Law</u>
  - The second law states that all work processes tend towards greater entropy over time. Another way of saying this is that the total entropy of an isolated system can never decrease.

-There's not that much on this slide, but there's a good reason: I intend to cover entropy entirely separately.

-2 reasons:

1. There's A LOT to say about entropy; if I talked about it now, by the time we got the third law, you will have long since zoned out.

2. Entropy is a very important topic, and is central not only to thermodymanics, but also to the entirety of modern science.

The Laws (cont.)

- The Third Law
  - The third law states that as temperature goes to zero, the entropy S of a system approaches some constant S_0. In simplest terms, the entropy of a pure substance at absolute zero is zero.

-Actually, only pure, perfectly crystalline structures will have zero entropy at absolute zero.

-All other substances will enter a degenerative ground state in which all the particles have the same minimum possible energy.

-(This is due to the Heisenberg Uncertainty principle).

Entropy

- Entropy is a measure of the amount of disorder in a system.
- What exactly is "disorder" though?
- We will use Boltzmann's formulation and say that entropy, S, is given by:
  - $S = k \ln \Omega$
- Where k is Boltzmann's constant and Ω is the number of microstates.

-Boltzmann's constant is a physical constant relating temperature to energy and has units of joules/Kelvin.

-Entropy also has these units, as ln has no units and (omega) is simply an integer.

-We can think of these "microstates" as the amount of disorder in the system.

Entropy (cont.)

- Entropy is a measure of the number of the possible microscopic states (microstates) of a system in thermodynamic equilibrium that are consistent with its macroscopic thermodynamic properties (its macrostate)
- A *microstate* is a description of the positions and momenta of all the atoms that make up the system.
- A *macrostate* is a description of the macroscopic properties of the system (total energy, volume, pressure, temperature, etc.)
- This begs the question...

-All the physical properties of a system can be determined from its microstate.

3 things to remember:

1. Defining a microstate requires an impractically huge amount of numbers, hence why macrostates are considered.
2. A macrostate is only defined for systems in equilibrium; if the system is in flux, even a macroscopic description would require more variables to take into account the changes at each moment the system is in flux. This, of course, quickly becomes impractical for even small systems.
3. For any given macrostate, there will be a massive number of microstates that are consistent with it.

-This is a reasonable assertion since what we consider to be an "ordered" system would have relatively few possible configurations (microstates) compared to a "disordered" system which would have many.

Entropy (cont.)

- …Just how do we determine the number of microstates?
- In classical statistical mechanics, the number of microstates is uncountably infinite, since the properties of classical systems are continuous.
- In quantum statistical mechanics, Ω is taken to be the number of energy eigenstates that are consistent with the system's thermodynamic properties.

-Before the discovery of quantum mechanics, this was an intractable problem in physics, since there was no way of even beginning to determine the number of microstates.

-As such, our current of understanding of entropy is relatively new.

Entropy and Energy

- So far, we have only discussed entropy in terms of the possible particle configuations of a system.
- These configuations are achieved by the motions of the particles, and these motions are the direct result of the energy in the system.
- How do we connect energy and entropy?
- Well, let's use an analogy…

Entropy and Energy

- Consider a gas in a high-pressure container. Is the entropy high or low?
- We then release the gas into a lower-pressure space. What does the gas do? What happens to the gas' entropy?
- This holds for energy, too: the energy of any given system will tend to distribute itself evenly throughout the system. Thus, systems in which the energy is evenly distributed will have the highest entropy

-Based on what we know about what entropy is, we would say the entropy of the gas is low, as the motion of its molecules is restricted and the number of possible microstates is therefore small. When it is released into a lower-pressure environment, it will expand to evenly fill the entire space, and we would say that the gas now has a higher entropy, as its molecules have far greater freedom of movement and there are more possible microstates.

Entropy and Energy

- Examples of Entropy Increasing
  - Heat flowing from a high-temperature body to a low-temperature body.
  - Adding heat to a substance.
- We now have another definition of entropy: *entropy is a measure of the dispersal of energy in a system.*

-Heat flowing from high-temp to low-temp increases entropy because the energy is becoming more spread out.

-Add heat to a substance increases entropy because heat Is energy, and the more energy in a system, the more ways that it can be distributed.

-Note that as energy becomes more dispersed, it becomes less "useful;" that is, it can no longer be used to do work. Consider a pile of ashes that comes from burning a piece of wood. Initially, the wood has low entropy (the energy in the wood is highly concentrated). Upon burning, that energy is released into the environment as heat and light, leaving only ashes. The energy has become more dispersed in the system, meaning that the ashes can't be burned again. They can do no more useful work.

Did Anyone See That?…

- An apparent contradiction in the second and third laws:
  - The second law states that entropy can *never* decrease, but the third law says that as the temperature drops to absolute zero, so does the entropy.
- Not a problem: remember, the second law applies only to *isolated systems*.
- Taking into account the only truly isolated system, the second law states: *the total entropy of the UNIVERSE cannot decrease*.
- So, it can decrease somewhere, as long as there is an increase somewhere else.
- Consider the formation of ice.

-There is only one known isolated system: the Universe.

-An example would be the formation of ice: ice does have a lower entropy that liquid water. But, in the process of lowering entropy, heat is transferred from the warmer water to the colder surroundings. Thus, even though the water's entropy is decreasing, the entropy of the surrounding environment is increasing.

-In all, the total entropy of the universe hasn't decreased, so there is no contradiction. Thermodynamics holds strong, thanks to the law of conservation of energy.

Works Cited

- "A Glossary of Frequently Misused or Misunderstood Physics Terms and Concepts." - http://spider.ipac.caltech.edu/staff/jarrett/LiU/resource/misused_glossary.html

- "Thermodynamics -- from Eric Weisstein's World of Physics" - http://scienceworld.wolfram.com/physics/topics/Thermodynamics.html

- "Thermodynamics" - http://en.wikipedia.org/wiki/Thermodynamics

- "Entropy" - http://en.wikipedia.org/wiki/Entropy