The Second Law of Thermodynamics & the Arrow of Time

Objectives:

- Give you a sense of what the second law of thermodynamics really says about how nature works: What restrictions does it impose on processes that can occur in nature?

- Illustrate the law with specific, everyday examples and experiences it ties together and unifies: How do we see this underlying principle expressed in operation in our common experiences with the world?

- Explore a few ideas about the underlying foundations of the law: Why do we think it's true, beyond just the observational fact that it has worked so far? What do these ideas have to say about how we see ourselves in relation to the rest of the world (e.g. our experience that time has a direction)?

- Provide a common background of concepts for everyone to participate in the discussion/questions.

The second law is considered one of the most fundamental and well-established principles of physics…

"The law that entropy always increases—the second law of thermodynamics—holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations—then so much the worse for Maxwell's equations. If it is found to be contradicted by observation—well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation."

– A. S. Eddington (1929)

…but what is the basis for this confidence, and what does the second law really even *say* about nature?

Context: Review of Energy & the First Law of Thermo.

• The **first law of thermodynamics** (law of conservation of energy) puts a sweeping restriction on how things are allowed to happen in nature (& thus on our ability to manipulate things to achieve outcomes we'd like):

> Energy is like the currency in nature's accounting: Every process or configuration of a system has a number, called its energy, that can be calculated and assigned to that state of the system. That amount of energy must be made available from somewhere in order for the process to occur.
>
> The first law says that the total amount of energy stays the same (energy is conserved), even as the arrangement of things changes, so the energy *added* to one part of a system to make something happen must be *lost* from somewhere else.
>
> (For more details on this, the first lecture is at www.scienceintegration.org/Education/Previous/Lecture1/essay1.html)

• So if we want to know whether a given state of things we'd like to achieve is possible, the first law tells us that we must look to see if there is a source of the energy needed to achieve that state (e.g. how much food must we eat to climb a mountain of a certain height?)

But experience tells us this is not the whole story about energy…

Why we need a *second* law of thermodynamics:

The first law does **not** capture the directionality we experience in the flow of energy. It seems that no matter what type of energy we start out with, as time passes and the energy is transferred from one form to another, more and more of it goes into a form we call heat. And once it's in the form of heat, there are additional limits (beyond that of conservation of energy) on how much of this energy can be recovered into other forms useful for tasks we want to accomplish.

So, formulations of the second law of thermodynamics attempt to capture this experience that as time passes, energy tends to "spread out" and become less accessible, less able to be harnessed for any given task, even though there may be plenty of energy available (to satisfy the first law).

To see how pervasive this additional restriction is in our lives, we need only look at a few examples…

Common observations about the world pointing to the underlying principle embodied in the second law:

- I can’t run my projector for the next 5 minutes by using the heat it has generated during the last 5 minutes as the energy source.

- More generally, modern society is dominated by the need to find concentrated sources of energy (petroleum, for example) and to “conserve” them.

- When I drop a ball, it settles down to rest on the ground. I never see it spontaneously rise from the ground back up into my hand.

- If your room is warmer than the outside temperature, it takes effort to keep the room from cooling off.

Common observations (continued)…

• All else being equal, a car with a diesel engine gets better mileage than a car with a gasoline engine.

• Your home or office becomes disorganized unless you put effort into keeping it orderly.

• Recycling is important.

• Time has a direction: we can't "take back" our actions, we remember the past but not the future, we forget things as time passes, etc.

Formalized Ways of Stating the Second Law:

> "We dance round in a ring and suppose,
> But the Secret sits in the middle and knows."
> — Robert Frost

- Heat energy flows spontaneously from a hot object to a cold object, and not vice versa.

- Kelvin (1852): "It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects."

- Carnot (1824 - later refined by Clausius in the 1850s): Heat engines (which convert heat energy into work – an automobile engine is a common example) always waste some heat. They never convert 100% of the heat energy into work. More precisely, the maximum efficiency of a heat engine depends only on the ratio of the cooler temperature at which waste heat is discarded, to the higher temperature at which heat is taken in:

$$\text{maximum efficiency} = \frac{\text{work produced}}{\text{heat input}} = 1 - \frac{T_c}{T_h}$$

Statements of the Second Law (continued)

- The total entropy of the universe never decreases (as time moves forward); it can only increase or remain constant.

In order to state the second law in its modern form (which is more general and more precise), Clausius (~1865) defined a quantity he called **entropy** (from the greek word for transformation).

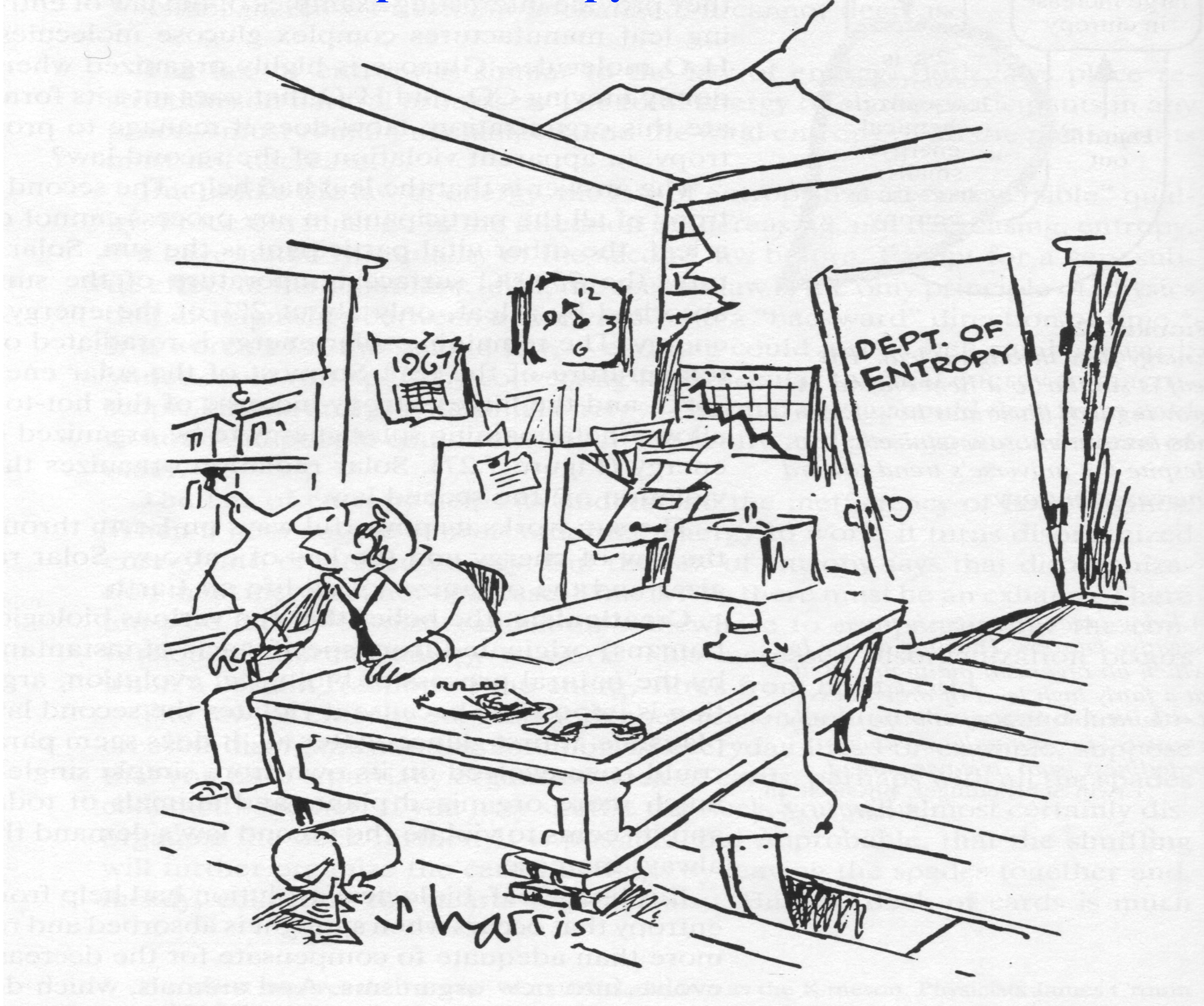
Whenever heat energy flows into an object, the entropy change (ΔS) is given by the amount of heat flow (ΔQ) divided by the temperature (T, on the Kelvin scale) at which the heat transfer occurs:

$$\Delta S = \frac{\Delta Q}{T}$$

But while this allows us to state the second law in a simple form, entropy is a rather mysterious and non-intuitive quantity…what does "*heat energy tranferred* divided by *temperature*" really mean??

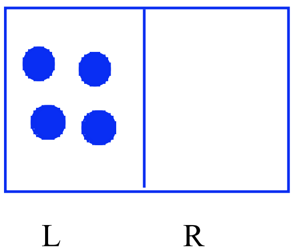
So our next task is to gain a better understanding of entropy…

An intuitive concept of entropy as "disorder"…



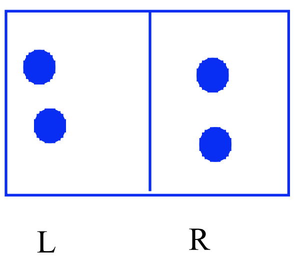
Boltzmann: Relating Entropy to Microscopic Physics

A simple example to illustrate the idea of entropy as a precise measure of "disorder":



Our observation: "All 4 balls on the left side of the box"

Number of ways of realizing this state: **1**



Our observation: "2 balls on each side of the box"

Number of ways of realizing this state: **6**

Interpret entropy as ~ "number of microscopic ways to realize an observed state"


S = k. log W
LVDWIG
BOLTZMANN
1844 – 1906
ARTHUR
LVDWIG
1925 – 1943

Boltzmann's interpretation of entropy provides new perspective on why entropy tends to increase (or equivalently, why heat energy flows from hot things to cold things)…

It's for the same reason that your files become disorganized if you stuff them randomly back into the drawer after looking at them! There are many ways (detailed arrangements of the files) for them to be disorganized, but very few ways for them to be organized, so the probability is very low that they will just happen to end up in an organized state.

To see the connection between Boltzmann's entropy and Clausius' entropy, interpret temperature as a measure of how many new states become accessible to a system when you give it a little bit of energy (remember energy is like the currency that allows a system to gain access to certain states).

Then Clausius' mysterious "heat divided by temperature" becomes Boltzmann's "number of microscopic states" and we can say that…

Heat flows from hot to cold simply because it is much more probable (it makes more microscopic states available) than if heat were to flow in the reverse direction.

A few observations, questions, and loose ends to ponder…

- Is it reasonable to assume that systems in nature are randomly exploring all the microscopic states available to them?

- Maxwell's Demon (posed in 1867; lively discussion continues in the physics community today)
  - Are entropy and heat "subjective?" What happens when we can control the motions of molecules on the microscopic level?

- Link between concept of entropy and information theory/computation: increasing entropy amounts to losing information about the detailed state of a system.

- Why can't energy reorganize itself (e.g. why can't the heat energy in the room that was produced when I dropped a ball, collectively reorganize to raise the ball back into my hand?) Appears that fundamentally, molecules "forget" information about their history. They no longer know where they came from, so the information is no longer recorded or stored anywhere, that would be needed to recover the original state (like the ball in my hand). Why is this the case? What exactly does it mean for nature to truly forget information about the state of things?

- Recent challenges to the second law make these foundational issues more pressing (quantum coherence, July 2002 conference)

- Link to our own experience of "forgetting" and the direction or arrow of time we experience

> "Time flows on, never comes back. When the physicist is confronted with this fact he is greatly disturbed." – Leon Brillouin

- Why do things forget? What’s the mechanism for this?

- Systems tend to spread out as much as they can within constraints. Is this related to quantum theory?

- What would we have to change about the laws of nature in order to “turn off” the second law?

For Further Investigation…

- von Baeyer, Hans Christian. *Warmth Disperses and Time Passes: The History of Heat*. New York: Random House, 1998.

- Hobson, Art. *Physics: Concepts and Connections.* New Jersey, Prentice Hall, 1995. (Chapter 7).

- Brush, S. G., *The Kind of Motion We Call Heat* (2 volumes), North-Holland, Amsterdam, 1976. (History of the subject with translations of many significant original papers)

- Leff, Harvey. "Thermodynamic entropy: the spreading and sharing of energy," *American Journal of Physics*, Oct. 1996, p.1261.

- Leff and Rex, *Maxwell's Demon 2.* Institute of Physics, 2003. A great compilation of the history of Maxwell's Demon and related topics.

- *Entropy* (on-line journal) – http://www.mdpi.org/entropy/

- *Challenges to the Second Law of Thermodynamics,* by V. Capek and Daniel P. Sheehan, Springer Fundamental Theories of Physics Series (Volume 146, 2005). Discusses many aspects of the second law including issues of time and fundamental physics.

Maxwell’s Demon

“Suppose that a body contains energy in the form of heat. What are the conditions under which this energy or any part of it may be removed from the body? If heat in a body consists in a motion of its parts, and if we were able to distinguish these parts, and to guide and control their motions by any kind of mechanism, then by arranging our apparatus so as to lay hold of every moving part of the body, we could, by a suitable train of mechanism, transfer the energy of the moving parts of the heated body to any other body in the form of ordinary motion. The heated body would thus be rendered perfectly cold, and all its thermal energy would be converted into the visible motion of some other body.

Now this supposition involves a direct contradiction to the second law of thermodynamics, but is consistent with the first law. The second law is therefore equivalent to a denial of our power to perform the operation just described, either by a train of mechanism, or by any other method yet discovered. Hence, if the heat consists in the motion of its parts, the separate parts which move must be so small or so implpable that we cannot in any way lay hold of them to stop them.”