8.044 Lecture Notes
Chapter 1: Introduction to Thermodynamcs and Statistical Mechanics

Lecturer: McGreevy*

Reading: PW Atkins, *The Second Law*, on course webpage.

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*These notes owe a great deal to previous 8.044 lecturers, especially Prof. Krishna Rajagopal.

What is 8.044 about?

This class is about the physics of matter and energy as we actually experience it – at everyday time-scales and length-scales (seconds, meters, grams...). This means that it is about the physics of *lots* of particles. (On pset 1 you'll think about how many.)

'Lots' here means numbers like 10^{25}. As you can imagine, solving the equations of motion for each of those particles is hard – really, impossible. (And the answer would be useless! We don't want to know the wavefunctions of all the particles, we want to know much more simple-minded things about it – whether the system is squishy or hard, whether it is a magnet or not ...) We'll have to figure out how to use the largeness of this number as an advantage.

We will also consider the physics of lots of particles in some more extreme circumstances, like high temperature and low temperature.

New phenomena and new concepts will arise. The slogan[1] is "More is different", and the brand-name is "emergence".

The simplest example is the fact that the future is different from the past. For example, if you watch these videos of melting things, you can tell which one is being played backwards. From a still photograph of this melting stuff, you can guess pretty well how it looked a few minutes earlier, and how it will look in the future. This time asymmetry is not apparent in Newton's laws or Maxwell's equations or the Schrödinger equation.

In fact, it's really absent in their simple applications to few-body systems (consider looking at a still photograph of a pendulum and trying to predict its earlier state). But this arrow of time does in fact follow as a very non-obvious consequence of the physics of many particles.

Related novel concepts we must confront immediately: temperature, entropy.

To see that these concepts are new, notice that the phrase "the temperature of a particle" doesn't even make sense. Temperature is not a property of systems with just a few particles.

Many other questions arise from this phenomenon of emergence, and are crucial for understanding the physics of the world around us, some of which we will touch on in 8.044. Why is a solid rigid? What's the difference between solid/liquid/gas?, between conductors and insulators?, How to understand the properties of magnets, of superfuids and superconductors, of white dwarves and neutron stars, the stretchiness of rubber bands...? None of these is apparent in Newton, Maxwell, Schrödinger.

8.044 is the jumping-off point for many branches of physics, only some of which we'll get to touch on briefly. Our job is to develop the general theoretical machinery.

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[1]due to the condensed matter physicist PW Anderson

This machinery has two parts, each with its own language:

Thermodynamics is the machinery for describing the macroscopic viewpoint: entropy, temperature, magnetization... and relations between them

MACRO: what phenomena are we describing?

Statistical mechanics is the machinery for describing the microscopic picture: what are each of the 10^{24} degrees of freedom doing?

MICRO: why do the macro phenomena happen?

We need both of these, and we'll go back and forth between them many times, being careful to identify which concepts belong to each. By the end, we'll have developed enough facility going back and forth that we can safely talk about them all at once.

Both perspectives are very powerful. In this introduction, we give a quick tour through the ideas involved in each. Then we come back and build the foundations, see the full power and generality, over the rest of the semester.

1.1 Carnot's discovery: Nature's asymmetry

The founder of this subject, unbeknownst to himself, was Sadi Carnot[2].

Sadi Carnot (1796-1832) was a soldier in Napoleon's army as a teenager. The defeat of this army by England's in 1814 was a formative experience for him, and he became obsessed with understanding *why* they had been defeated. The answer he arrived at was England's mastery of steam engines. Steam engines made possible the mining of coal and hence of iron and hence the production of better weapons for the killing of French people.

Initially Carnot's interests were technological, on devices for dramatic extension of human capabilities. But these interests led him to the following very fruitful question:

Q: Is there a limit to the efficiency of a steam engine?

A: In fact there is an *intrinsic* inefficiency in the conversion of heat into work.

(The steam engine is just one way of doing this.) Carnot was very ambitious, attacking a big problem of his age. Though his intention was not to do basic science, this result led to an intellectual revolution, whose consequences we pursue in 8.044.

Carnot discovered the Second Law of Thermodynamics without understanding the First Law! He didn't know that energy is conserved.

It took Joule, Kelvin, Clausius and others to sort out the relations between heat, work, energy – indeed, to realize that there were such relations – establishing a modern understanding (by 1850 or so) of **thermodynamics:**, the study of the transformation of energy in all its forms.

Clausius speculated that maybe heat has to do with random motions of atoms or particles of which matter is made. (The existence of such objects was itself a speculation at the time.)

Boltzmann (1844-1906) provided a mechanistic explanation for thermodynamics: **statistical mechanics** (answering the question: what are all the particles doing that corresponds to heat, temperature, *etc*?). His motivation *was* a basic science question: "what is matter made of?" (This contrasts sharply with Carnot's technical engineering starting point: "what did France do wrong?")

Atkins: "Statistical physics is the child of the steam engine and the atom."

This rich interplay between technology and basic science continues, and we'll see both threads repeatedly in 8.044. At the end of the course we will discuss some fundamental

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[2]See Atkins for more of the interesting history.

physics discoveries of the 1990s [Ketterle], coming soon to your iPhone[3].

It's worth mentioning at this point that statistical mechanics and thermodynamics have played a crucial role in the development of fundamental physics. In developing statistical mechanics, Boltzmann had to struggle against the fact that the existence of atoms was not yet established; the success of his theory at deriving thermodynamic laws from this starting point should have been taken (in a rational world) as evidence in favor of the existence of atoms. Just a little later, the application of statistical mechanics to a box of light (the subject of our Chapter 7) and to electrons in a solid (Chapter 9) were the two crucial clues that led to quantum mechanics. Much more recently, the existence of a strong analogy between the laws of thermodynamics and the physics of black holes has led to our best progress on the understanding of quantum gravity. This story is not over.

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[3]OK, this is a small exaggeration.

Laws of Thermodynamics
(a first glimpse, and an explanation of our motivation for beginning with the 2nd Law).

- **0th Law:** is a precise definition of temperature.
  We can put this one off because of your familiarity with thermometers. So you all think you understand it already.
  For now: temperature is what you measure with a thermometer.

- **1st Law:** Energy is conserved.
  This is by now a familiar statement to you, but as you will see it is a bit more subtle in thermodynamics than in 8.01.
  The fact that it's true in simple mechanical systems is pretty simple, but its elevation to a Law of macroscopic systems was very non-obvious, given the ubiquity of friction. More later.

- **2nd Law:** There exists a fundamental asymmetry in nature.
  Hot objects cool to room temperature; room-temperature objects don't heat up on their own.
  Bouncing balls come to rest.
  Ice cream melts while you eat it.
  Work can be fully converted into heat[4], but not vice versa.

  Quantity of energy is conserved, but its distribution among kinds of energy (kinetic energy or potential energy, and thermal energy) can change irreversibly.

  There is nothing like this in Newton or Maxwell. The basic example of "more is different."

- **3rd Law:** It is not possible to cool a system to $T = 0$ in a finite number of steps. This one we postpone for a long time.

Why start with the 2nd Law? It's the most interesting part!

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[4]Actually, this was the major contribution of Joule and Mayer, the latter of whom used the color of blood to demonstrate it (biophysics!). See here, page 124, or here for more on this history.

Q: How did Carnot identify this asymmetry?

A thought experiment:
Carnot engine (or "Carnot cycle").

Def: An **engine** is a device that converts heat to work cyclically.

This definition has three words to explain (work, heat, cyclically). We'll do two out of three now:

Work: Any process equivalent to lifting a weight. (Exerting a force through a distance. Couple it by some series of pulleys etc)

Heat: We postpone this definition. It has a colloquial meaning which isn't too wrong, so you have some idea what you think it means.

Cyclically: Returns periodically to its initial state.

The Carnot cycle is an abstract engine, not a description of a real car engine or steam engine. It is (hopefully) easy to understand, makes manifest the 2nd Law. It is implemented as in Fig. 1. The "hot source" and "cold sink" can be moved into and out of contact with a sealed cylinder containing a fixed quantity of gas[5], whose volume may be changed by the motion of the piston.

The cycle is a sequence of steps of motion of piston and sources and sink, which we describe below.

(recall 8.01: work = force · distance.) Work done by gas =

$$ P \quad \cdot \quad \Delta V $$

$$ = \left(\text{pressure} = \frac{\text{force}}{\text{area of piston}} \right) \quad \cdot \quad \left(\text{area of piston} \times \text{distance piston moves} \right) $$

(More precisely, $W = \int_{V_1}^{V_2} P(V)dV$.)

Figure 1: A Carnot engine, adapted from Atkins.

This contraption is rigged up so that the expansion of the gas lifts the weight (gas does work), and lowering the weight compresses the gas (weight does work on gas). That is:
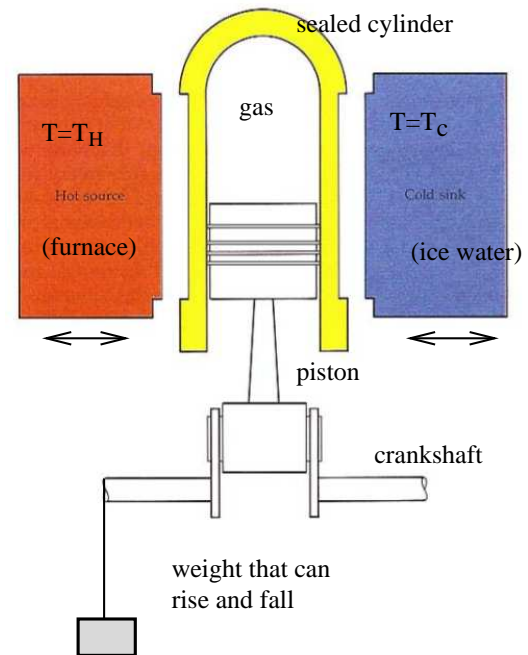
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[5]This makes the Carnot engine unlike a car engine or a steam engine, but it is something can actually be built.

V increases $\implies$ gas does work.
V decreases $\implies$ weight lowers, does work on gas.

Q: What's the point of the cold sink?

Ideal gas: Now we appeal to high school chemistry for the ideal gas law: $PV = NkT$. The important content for us here is:

$$P = \text{const} \cdot T \cdot \frac{1}{V}.$$

Figure 2: Two isotherms for an ideal gas.

This is the answer to several questions, one of which is: If we fix the temperature of the gas, by putting it in contact with a giant heat bath at temperature T_H, and change the volume by moving the piston, how does the pressure of the gas change. The resulting curve is an *isotherm*. (Real gas: isotherms are not precisely hyperbolae.) A reason to care about this is if we want to make an energy budget.

Compression at T_H: work done *on* gas = area under curve.

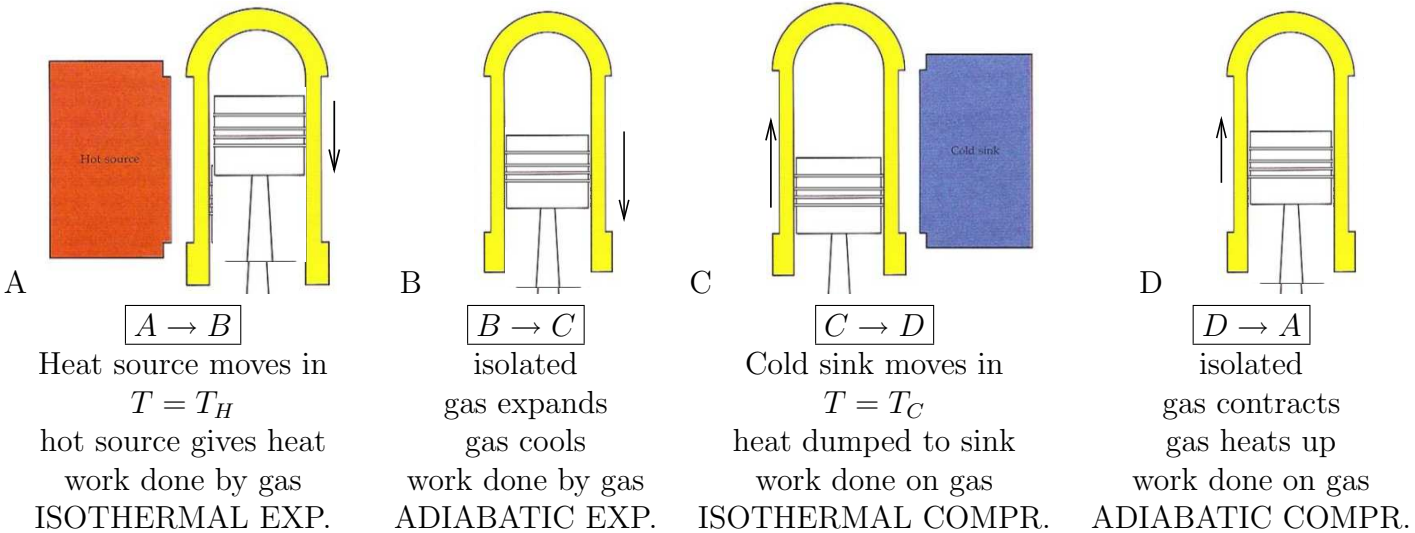Expansion at T_H: work done *by* gas = *same* area under curve.

If we compress and expand at the same temperature, we get no net work.

To go back to the same temperature and volume (cycle!), we must put all the energy back. But we don't want to do it in the same way. This is the purpose of the cold sink.

The Carnot Cycle:

Begin the cycle in 'state A' of the engine. This is when the piston is in its highest position, and $T = T_H$. Then $P = \text{const} \cdot T \cdot \frac{1}{V}$.

Here is the cycle all at once:

A	B	C	D
$\boxed{A \rightarrow B}$	$\boxed{B \rightarrow C}$	$\boxed{C \rightarrow D}$	$\boxed{D \rightarrow A}$
Heat source moves in	isolated	Cold sink moves in	isolated
$T = T_H$	gas expands	$T = T_C$	gas contracts
hot source gives heat	gas cools	heat dumped to sink	gas heats up
work done by gas	work done by gas	work done on gas	work done on gas
ISOTHERMAL EXP.	ADIABATIC EXP.	ISOTHERMAL COMPR.	ADIABATIC COMPR.

Net work done by engine in one cycle = area enclosed in P-V diagram.

$A \rightarrow C$ gas does work, area under ABC curve.

$C \rightarrow A$ weight doing work on gas, area under CDA curve.

Note the crucial role of the cold sink. Dumping heat into the cold sink was the key to opening nonzero area on the PV diagram. We have to pay a tax (here, the heat lost to the cold sink) to get some work out. This a crude statement of the 2nd Law, in this example. Even though you don't believe me yet (if you don't spend a lot of time playing with heat engines), this claim is consistent with your experience.

Figure 3: Two isotherms for an ideal gas, with work done on gas during a Carnot cycle between them (volume of shaded region).

Our next goal is to convince you that this conclusion drawn from thinking about pistons and stuff is actually general. You could imagine

1-9
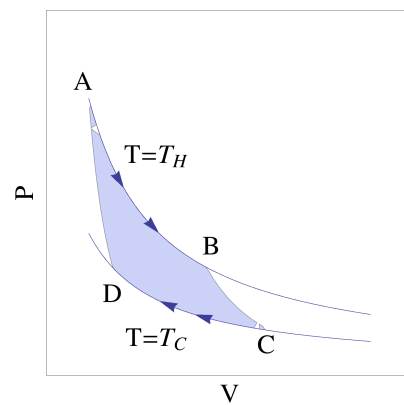
doing the cycle in other ways and tracing out other loops on the PV diagram. (Many of these have names: Otto Cycle, Deisel Cycle...) You could imagine that the amount of gas was allowed to change, you could imagine something other than a volume of gas was involved... The general statement we want to defend (which has nothing to do with these details) is...

Some notational simplification to summarize what we've done. Use the symbol Q to denote a quantity of heat.

hot source

Q_H

engine

net work done

Q_C
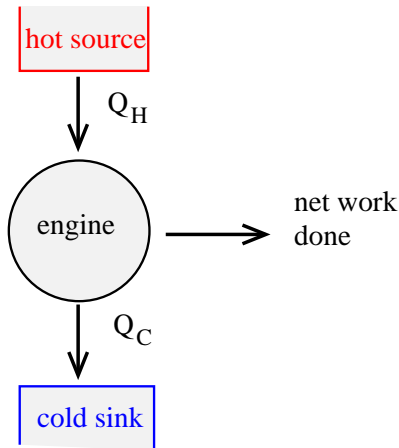
cold sink

Applied to this situation, the statements of the 1st and 2nd Laws are:

1st Law: $Q_H = Q_C + $ net work.

2nd Law: Q_C can't be zero unless net work $= 0$.

2nd Law, more precisely: In every engine, there is a cold sink, and heat has to be dumped into it at some point in the cycle.

Observation: power plants are always built near a body of water.

1.2 Work, heat, the 2nd Law, and entropy

First let's define these four terms.

Work: we already defined.

To **heat** an object is to transfer energy to it, making use of a temperature difference between a hot source and the heated object.

To **cool** an object is to transfer energy out of it, making use of a temperature difference between a cold sink and the cooled object.

Heat is NOT a form of energy. It is really a verb. If we must use it as a noun, it is "energy in motion" – a means of transferring energy. [6]

The same is true of **work**. Both are processes. (Work is any means of transferring energy *other* than a temperature gradient.)

Colloquial: "Heat was transformed into work."

Precise: "Energy was transferred from the hot source to engine by heating, and from engine to weight by doing work."

[End of lecture 1.]

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[6]This took a long time for humans to understand. At the time Carnot was working, the popular theory of thermodynamics (due to Lavoisier) centered on a quantity called 'caloric' which was believed to flow from hot bodies to cold ones because it repels itself. A fatal flaw of this theory is that this quantity is not *conserved*. For example, a body can be warmed by mechanical work (*e.g.* you rub your hands together on a cold day). This argument is due to Count Rumford of the Holy Roman Empire (who observed that no matter how many times you shoot a cannon, you can still squeeze more caloric out of it), but to quote Yosi Avron, "Rumford was an obnoxious character and history obscured his role in laying caloric theory to rest." Rumford's real name was Benjamin Thompson; he was born in Woburn, MA. After killing Lavoisier's theory of caloric, Rumford married Lavoisier's widow (Lavoisier had in the meantime been beheaded by the French Revolution). I promise I didn't make this stuff up.

(Recap) **2nd Law:** Work can be converted fully into heat, but not vice versa.

The quantity of energy is conserved, but its distribution changes irreversibly.

Next: several useful re-statements of the 2nd Law.

SECOND LAW (Kelvin's Version)

hot source

Q_H

anti–
Kelvin
engine

net work
done

Figure 4: Kelvin says no to this.
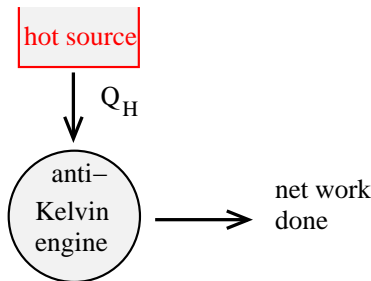
No process is possible whose *sole result* is absorption of heat from a reservoir and its *complete conversion* into work.

reservoir ≡ big hot source, so big that its temp is not affected by donating energy.

Note that we're using the colloquial abbreviation of "heat" as a noun already.

Note that the fact that the operation of an engine is defined to by cyclical is important here. That's part of "sole result".

This defines an "antiKelvin engine".

This is a fundamental asymmetry of nature: Nature exacts a tax for converting heat to work. By contrast, there is no tax for converting work completely into heat. For example: friction. Work and heat are both manners of transferring energy, but they are not equivalent.

Law ≡ a fact we know from experience.
In thermodynamics, the 2nd Law is a law.
In stat mech, our job is to explain this phenomenon in terms of more elementary laws.

You may be thinking that the absence of antiKelvin engines has not been a fundamental aspect of your experience of the world so far.

SECOND LAW (Clausius's Version)
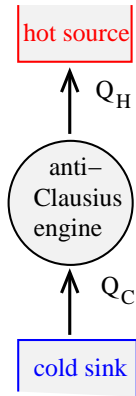
No process is possible whose *sole result* is (same so far) the transfer of energy from a cooler body to a hotter body.

The action of your refrigerator on the food in it is excluded by "sole result": the fridge is plugged in.

Clausius' statement comes from your experience of the world. And it is equivalent to Kelvin's statement.
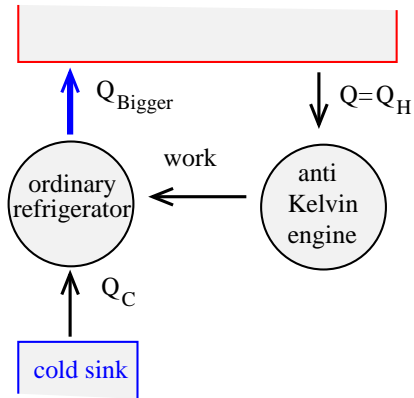
hot source

Q_H

anti–
Clausius
engine

Q_C

cold sink

Figure 5: Clausius says no to this.

Figure 6: How to make an antiClausius engine using an antiKelvin engine and a refrigerator.

The proof of equivalence of the two statements [Atkins book] goes in two steps. It's a completely rigorous argument which is also extremely simple and just uses pictures.

Step 1. If you have an antiKelvin engine, you can build an antiClausius engine, by combining it with an ordinary engine (a refrigerator) whose existence no one disputes.

The combined result of this, if we choose the amounts of heat to add up right ($Q_C = Q_{\text{Bigger}} - Q_H$, so the First Law is satisfied), is an antiClausius engine.

Step 2. If you have an antiClausius engine, you can build an antiKelvin engine, by combining it with an ordinary engine whose existence no one disputes.

(Small exercise: what relation does the First Law imply between Q, Q_{bigger} and the work done in the figure?)
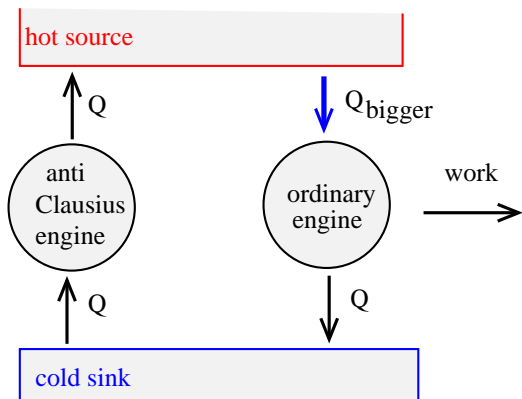
Figure 7: How to make an antiKelvin engine using an antiClausius engine and an ordinary engine.

Entropy

The title of this chapter section 2.1 involves one more term that we haven't defined: entropy. Before saying what it is, let's say what it's for.

Entropy is the answer to the following plea: It would be helpful to have a quantity which says *how* allowed something is according to the 2nd law.

Entropy will be the property of state that tells us whether a particular change of state is allowed by the second law, *i.e.* whether it can happen spontaneously.
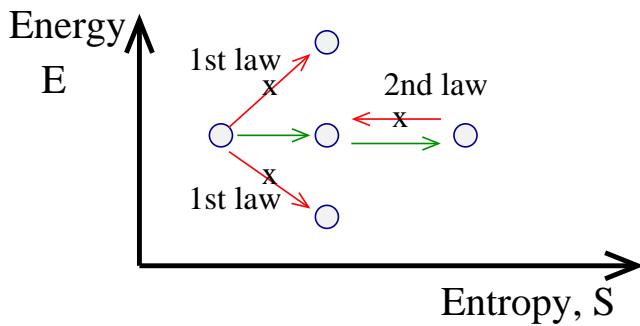
SECOND LAW (entropy version): Natural processes are never accompanied by a decrease in the entropy of "the universe".

"universe" $\equiv$ isolated system.

Entropy *quantifies* the second law.

Actual definition next.

Fundamental role in physics: defends us from perpetual motion machines, and their inventors.

Figure 8: Plotted here are the energy and entropy of an *isolated* system. Processes which change the total energy don't happen spontaneously by the first law. Processes which *decrease* the total entropy don't happen spontaneously by the second law.

Note that **entropy** is a property of the state of a system. Let's reverse-engineer the definition which accomplishes this.

Bad guess: entropy $\overset{?}{=}$ temperature. Here's a counterexample.
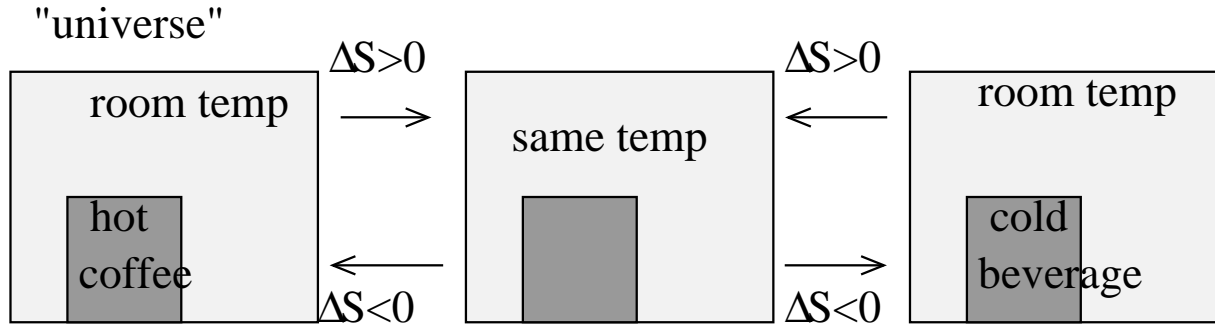
Both directions are allowed by conservation of energy.

Only the ones with $\Delta S > 0$ happen (that's how we decided how to label them): hot coffee reaches room temperature (and warms the room slightly), a cold beverage reaches room temperature (and cools the room slightly).

Recall Kelvin's statement of the 2nd Law: No antiKelvin machines. We'd like to define entropy so that this is a consequence of $\Delta S \geq 0$ for things that happen.
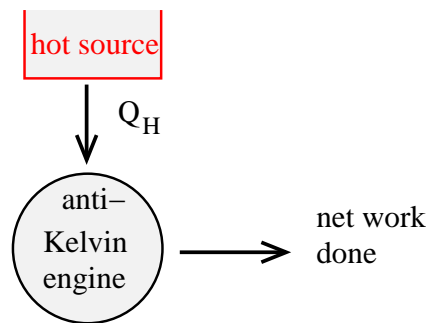
This suggests that the entropy of a system increases when it is heated, remains the same when work is done, and decreases when cooled.

That is, the antiKelvin engine cools a hot source; if this in turn decreases the entropy, it will be forbidden in our new formulation.

So if entropy increases when we heat something, decreases when we cool something, and is unchanged when work is done,

$$\Delta S \geq 0 \implies \text{Kelvin's statement of 2nd Law}.$$

Why: $\Delta S(\text{hot source}) < 0$: the hot source is being cooled, so according to the proposal, its entropy decreases.
$\Delta S(\text{work}) = 0$
Key point: Engines are cyclical: their entropy does not change after a cycle is completed. Remember – we want to define entropy to be a property of the *state* of the system. When the engine returns to the original state, it returns to the same entropy: $\Delta S(\text{engine}) = 0$.
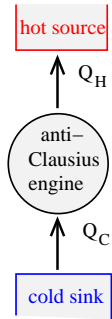
On the other hand, Clausius' statement of the 2nd Law suggests that the higher the temperature at which heat enters/leaves an object, the *smaller* the resulting increase/decrease in entropy.

Why: $\Delta S(\text{source}) \geq 0$ (hot source is being heated, at temperature T_H).
$\Delta S(\text{sink}) \leq 0$ (cold source is being cooled, at temperature T_C).
Since $T_C < T_H$, our hypothesis implies that $|\Delta S(\text{source})| < |\Delta S(\text{sink})|$.
Therefore, the total entropy

$$\Delta S_{\text{total}} = \Delta S(\text{source}) + \Delta S(\text{sink}) + \Delta S(\text{engine}) = \Delta S(\text{source}) + \Delta S(\text{sink})$$

decreases by *more* than it increases.
Therefore, this process is forbidden by our entropy version of the 2nd Law. So

$$\Delta S \geq 0 \implies \text{Clausius' statement of 2nd Law.}$$

A simple possible definition which works is:

$$\boxed{\Delta S \equiv \frac{\Delta Q}{T}}.$$

ΔS = change in entropy of the system,
ΔQ = heat transferred INTO system,
T = temperature at which heat is transferred.

Later: we will further justify this definition in thermodynamics (Chapter 3),
Even later: we will justify it microscopically (Chapter 4). For now, it works, in the sense that: with this def'n,

$$\Delta S \geq 0 \implies \text{Clausius' and Kelvin's statements of 2nd Law.}$$

Caveat. This is the correct definition only for $\boxed{\text{quasistatic processes}}$.
Pistons must move arbitrarily slowly,
heat must be absorbed arbitrarily slowly,
temperature gradients must be infinitesimal...
Quasistatic processes are limits of real processes, carried out ever more slowly.

"Correct": for our present purposes, any monotonic function of $\Delta Q/T$ would work. ($\Delta Q/T^2$ would not.) $e^{\Delta S}$ is in some ways the more natural thing.

Measuring entropy

A liter of hot water has higher entropy than a liter of cold water. Why are we all more comfortable with T than with S? Because we are used to thermometers, but not so much entropomometers. (I guess it should be "entropometers", but my familiarity with thermometers is even influencing my neologism.)
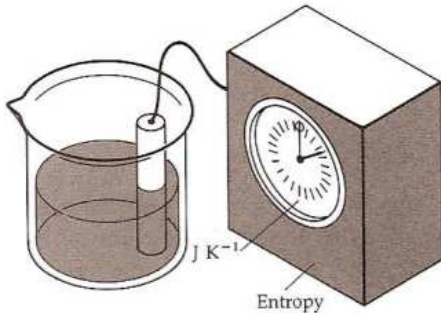
An entropometer consists of a probe with a heater and thermometer in it. Here's the protocol:
measure the initial temperature T.
Send in little pulses of heat, dQ
(Wait long enough so that we are in the quasistatic regime. Then...)
Measure the new T after each.
Calculate ΔS as in Fig. 9.

The area under the curve is the change in entropy, ΔS, associated with heating this liquid from T_i to T_f.

Notes: keep the thing insulated.

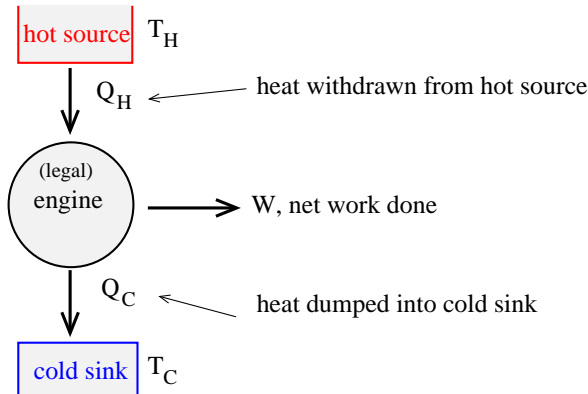There's no obstacle to actually doing it.

Nothing mysterious.

This measures *differences* in entropy. What about the overall constant? This is the subject of the 3rd Law. Later. (Recall that only differences in energy are meaningful (except when General Relativity is involved).)
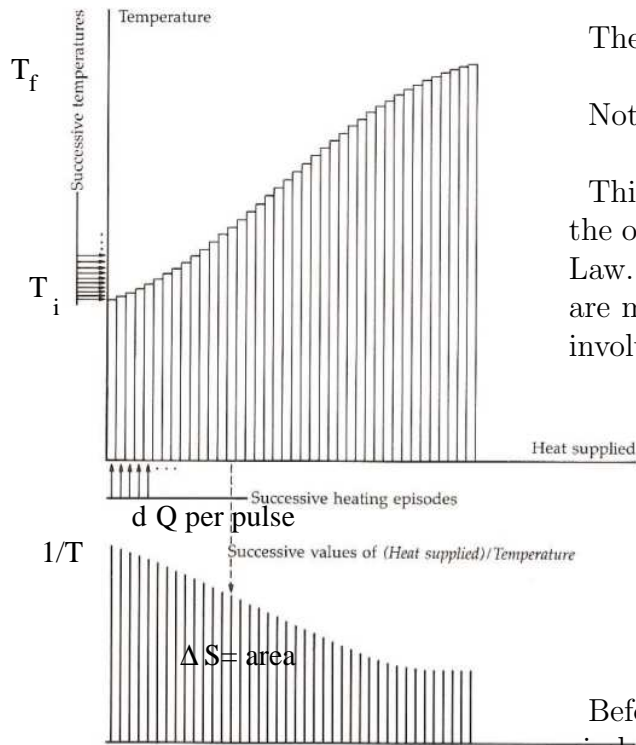
Before we go "under the hood", we must close the circle: what did Carnot actually discover? We'll show next that our notion of entropy (not derived) implies Carnot's result.

Figure 9: From Atkins.

Ceiling of Efficiency

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hot source  T_H
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Q_H ← heat withdrawn from hot source

(legal) engine → W, net work done

Q_C ← heat dumped into cold sink

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cold sink  T_C
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$$\Delta S_H = -\frac{Q_H}{T_H}$$

$$\Delta S_{\text{engine}} = 0 \quad (\text{cyclical, } \Delta S_{\text{work}} = 0)$$

$$\Delta S_C = +\frac{Q_C}{T_C}$$

(Beware signs! Here $Q_H, Q_C > 0$.)

1st Law: conservation of energy. $Q_H = W + Q_C$

2nd Law: $0 \leq \Delta S_{\text{total}} = \Delta S_C + \Delta S_H + \Delta S_{\text{work}} \Leftrightarrow \frac{Q_C}{T_C} \geq \frac{Q_H}{T_H} \Leftrightarrow \boxed{\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H}}$

$$\textbf{Efficiency} \equiv \frac{W}{Q_H} = \frac{\text{thing I want to optimize}}{\text{thing I'm expending}}$$

Note: efficiency $= 1 \Leftrightarrow W = Q_H \overset{\text{1st Law}}{\Longrightarrow} Q_C = 0$.

$$\textbf{Efficiency} \overset{\text{1st Law}}{=} \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \overset{\text{2nd Law}}{\leq} 1 - \frac{T_C}{T_H}.$$

This was Carnot's result. To maximize efficiency, make $\frac{T_C}{T_H}$ as small as possible – cold sink cold and hot source hot.

We won't discuss how Carnot arrived at this result. Even with only partial understanding, one can sometimes still arrive at a correct conclusion.

We'll see later that the Carnot cycle *saturates* this inequality: $\text{Efficiency}_{\text{Carnot}} = 1 - \frac{T_C}{T_H}$. Real engines get to within a factor of two.

Words: "quality of energy" decreases as it goes through the engine.

Energy stored at a higher temperature is higher quality: this energy is available to do work, as long as you dump it into a cold sink. The energy in the cold sink is useless unless you have a colder sink.

"quality" $\sim \frac{1}{\text{entropy}}$.

Comment on "Energy Problem" that is so much talked-about: There isn't one – energy is conserved. Really it's an entropy problem. We have a lack of high-quality (low-entropy) energy.

This is the end of the introduction to the MACROSCOPIC aspect of the subject. Read in Atkins about generalizations to other processes (chemical, nuclear...).

Next: What the heck is going on microscopically? A taste of statistical mechanics. Maxwell, Newton, Schrödinger are invariant under running the movie backwards. How can it be that thermodynamics follows from these, but distinguishes between future and past?

1.3   Nature's asymmetry at a microscopic level

Key: Thermodynamics deals with a vast number of particles.
e.g. $N_{\text{Avogadro}} = 10^{23} \cdot 6 =$ number of atoms in 12g of carbon.

Thermodynamic properties are *averages* over large assemblies of particles.

Fluctuations become negligible in the "thermodynamic limit" of such large numbers of particles. (Think about the last problem on pset 1 in this light.)

e.g.: Consider the air in room, and in particular what we mean by its energy.

Energy of thermodynamic system = sum of kinetic and potential energies of all particles in it.

With 10^{24} particles, there is a distinction between all the particles moving together (*e.g.* lift a piece of chalk) – coherent motion, the result of *work*
vs
random "thermal motion" of individual particles, the result of *heating*.

This distinction is meaningless for two particles.

This distinction is the first crucial new element in thermodynamics, compared to few-particle (always reversible) dynamics.

To go further, we need a simple system to discuss. Chalk is too difficult, gas in a room is close. Here is a simple system which Atkins (over)uses, which captures much of the essence of the 2nd Law: a grid of squares, which can be on or off (red or white).
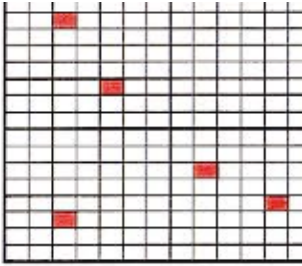
In each of N cells in a grid, an "atom" can be in one of **two** states, which have different energies. Call the states ON and OFF.
(In the picture above, 5 atoms are ON.)

Total number of ON atoms is conserved (1st Law). The ON-ness can move around.

A state of this system, specified by enumerating exactly which atoms are ON (and which are OFF) is called a "microstate".

For our present purposes, the details of the microscopic laws governing these atoms are not so important. What we really require of them is merely that:

- the microstate can change as a function of time (ON-ness can move)

- microscopic laws are time-reversal invariant (otherwise an arrow of time wouldn't surprise us.)

- given enough time, the system will explore all possible microstates (at least a representative sample) It's important here that there's no secret Law that says that some large class of microstates is inaccessible, *e.g.* that the ON-ness can't go certain places.

- over a long period of time all microstates are equally probable. (In about a month, just from this starting point, we can derive *e.g.* $PV = NkT$; it is a (possible) basis of stat mech, from which we can derive all of thermodynamics.)

The generality of the result means that we need not say much about the update rules for *how* the ONness moves around.

We could also consider this as a crude model of a gas: atoms $\leftrightarrow$ red squares
update rule = (discretized version of) Newon's laws.

[End of Lecture 2.]

Let's consider the case of $N = 40 \times 40 = 1600$ squares, with 40 atoms ON.

Furthermore, suppose initially all 40 ONs are in the top left 10×10 box. Call this "System 1". Call the rest "System 2". System 1 here is a proxy for a hot cup of coffee, in a room represented by System 2. This is a special starting point.

Initially: $N_{ON}^1 = 40, N_{OFF}^1 = 60$. $N_{ON}^2 = 0, N_{OFF}^2 = 1500$. What happens?
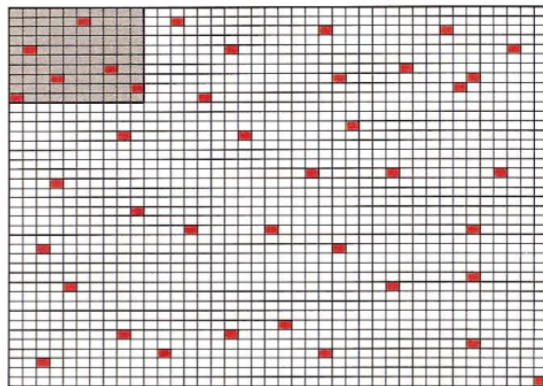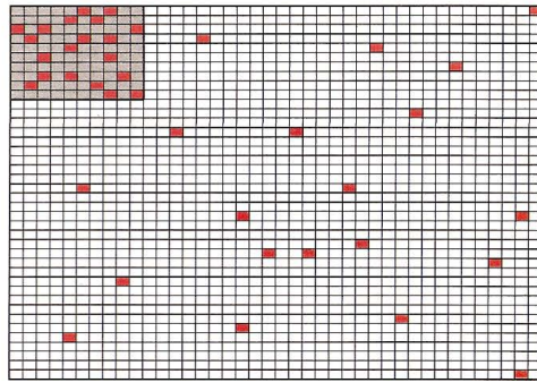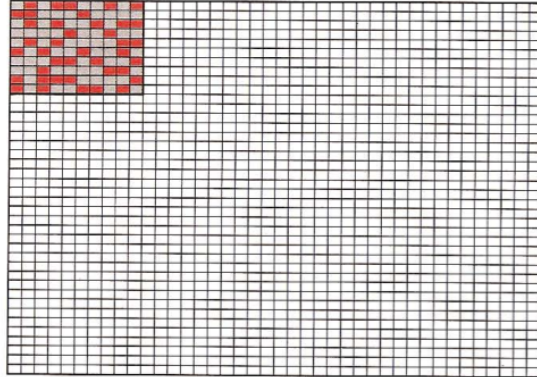
What happens? ON-ness diffuses out of System 1. There is no final microstate: the jostling continues forever.

Working Def: A *thermodynamic observer* is someone sitting in the back of the room, without their glasses, who can't distinguish the individual red dots, so only sees (a smaller amount of) macroscopic information about the system.

There is no final microstate, but:
to a *thermodynamic observer*, equilibrium ($\equiv$ the end of change) occurs when differences between the microstates can no longer be resolved.

In particular, thermodynamic observers no longer see any change when the ON-ness is uniformly distributed:

$$\frac{N^1_{ON}}{N^1_{OFF}} = \frac{N^2_{ON}}{N^2_{OFF}} \quad \text{in "thermal equilibrium"}.$$

The irreversibility of this process of dispersal of ON-ness from the corner – "equilibration" – arises from the lack of special rules for how the ON-ness moves around, and the largeness of the number of squares.

The 2nd Law, in this model, is a consequence, for thermodynamic observers, of the purpose-less shuffling of the energy. Specifically, Clausius' version, that heat doesn't spontaneously go from cold to hot, follows from: [7]

- the lack of any special rules favoring some class of microstates

- the vastness of the system

The microscopic laws for the shuffling can be perfectly time-reversal invariant, but the result for the thermodynamic observer is irreversible: the probability of getting back to the starting point, with all (or even most) of the ONs in System 1, is **very small** (see pset 2). The 2nd Law (at least Clausius' version) is probabilistic, not exact. It is not always true! But the probability that it is violated is **very small**, and goes to zero in the *thermodynamic limit* – for Atkins model, this is when the number of squares in the grid $\to \infty$.

(An identical argument explains why we don't worry about all the air in the room accumulating in the corner.)

This is how we obtain (overwhelmingly-likely-to-be) irreversible dynamics for thermodynamic observers, from reversible microscopic dynamical laws.

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[7] To do Kelvin's version, we would need some notion of work in this model. Atkins does show how to add them in; see the very end of this chapter.

Temperature: We've just described a hot object cooling, by transferring heat (the energy of the ON squares) to an initially cold environment. We can infer from this that T should be an increasing function of $\frac{N_{ON}}{N_{OFF}}$. The density on ON for the hot spot decreases, and the density of ON for the initially-colder environment increases.

(We'll see later that consistency of thermodynamics will require the specific relation

$$T = \frac{A}{\ln\left(\frac{N_{OFF}}{N_{ON}}\right)}.$$

for some constant A with units of temperature (whatever those might be); "ln" means logarithm base e.)

Entropy: Boltzmann's bridge

Boltzmann realized that

$$S = k_B \ln \Omega$$

$\Omega \equiv$ the number of possible microstates that a thermodynamic observer sees as equivalent

(*e.g.* number of ways to put 40 pink squares into a 10×10 grid) [8].

k_B is Boltzmann's constant, and can be set to 1 and ignored by a good choice of units (for temperature).

This is a big deal: on the LHS is a thermodynamic concept, entropy (Recall: $dS = dQ/T$). On the RHS is something we can just determine by counting.
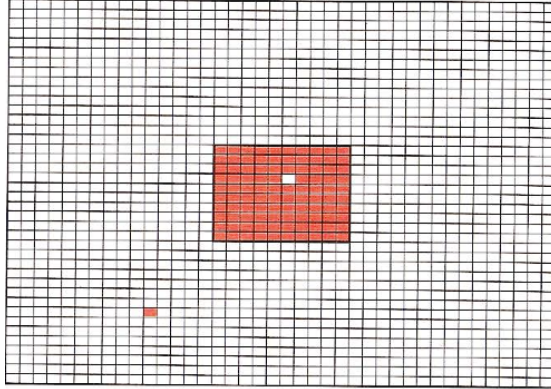
An example:

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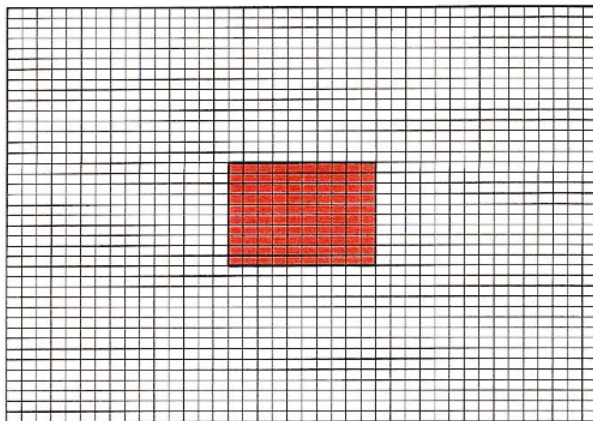
[8]Ω is called W by Boltzmann (and Atkins), but not being in Germany we'll use W for work.

Initial state: all 100 ON in System 1, all 1500 OFF in System 2.

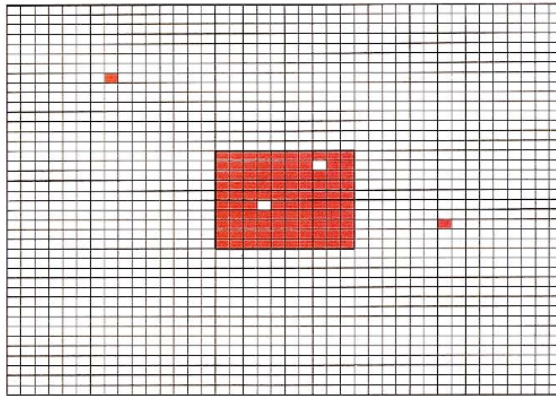$$\Omega_1 = 1, S_1 = \ln \Omega_1 = \ln 1 = 0, \quad \Omega_2 = 1, S_2 = \ln \Omega_2 = \ln 1 = 0.$$

Another state: one OFF in System 1, one ON in System 2.

$$\Omega_1 = 100, S_1 = \ln \Omega_1 = \ln 100 = 4.61, \quad \Omega_2 = 1500, S_2 = \ln \Omega_2 = \ln 1500 = 7.61$$
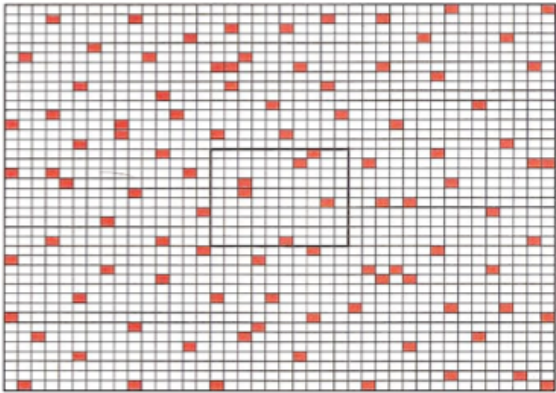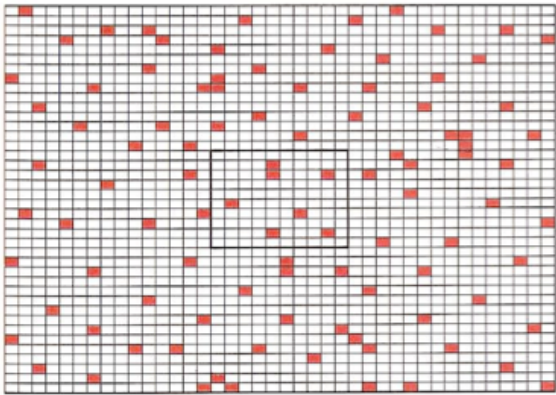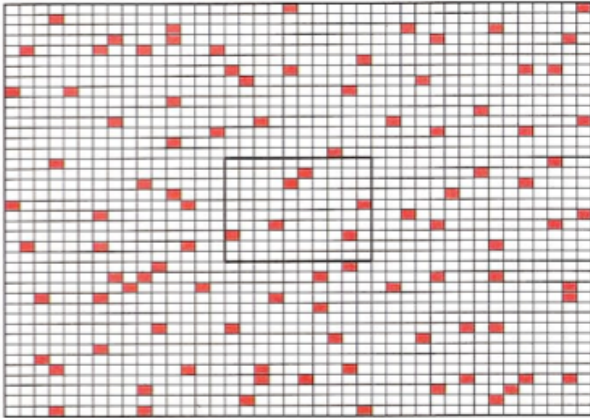
$$\Omega_{\text{whole system}} = \Omega_1 \cdot \Omega_2 \implies S_{\text{total}} = S_1 + S_2.$$

because the counting of configurations of 1 and 2 are independent, the entropies add.

$$\Omega_1 = \frac{100 \cdot 99}{2}, S_1 = 8.91, \Omega_2 = \frac{1500 \cdot 1499}{2}, S_2 = 13.93.$$
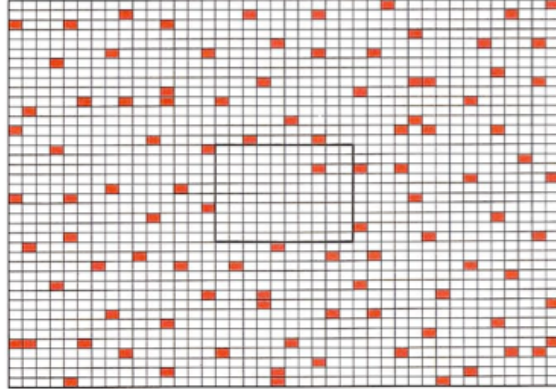
Soon after this, the situation looks like this:

Pictures (of three different microstates) which look the same to thermodynamic observers.
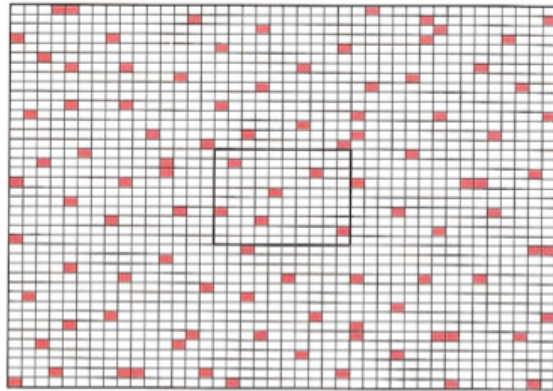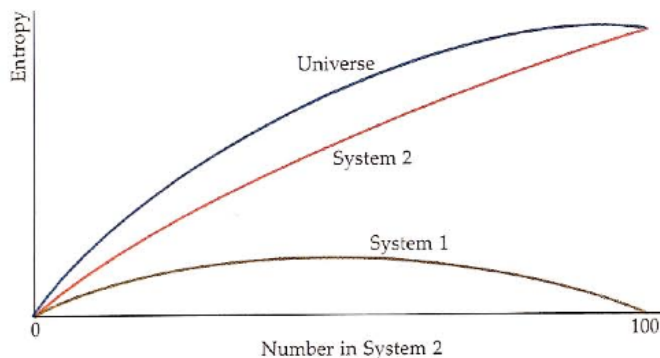
another example: start with a cold spot in a room.

Start with $N_2^{ON} = 99$, $N_1^{ON} = 1$.
Then $S_1 = \ln(100)$ is small.

$\downarrow$

It warms up:

Number in System 2

"Universe" here denotes $S_{\text{total}} \equiv S_1 + S_2$. Note that S_2 is still rising all the way to $N_2^{ON} = 100$: the number of ways to sprinkle N_2^{ON} pink squares among 1500 spots is still growing rapidly there. S_1 on the other hand is starting to die off: $N_2^{ON} = 100$ here means $N_1^{ON} = 0$, and if all the squares in System 1 are white, then there's only one state of System 1.

Note: S_{total} has a maximum. Zoom in:

From the plot [and pset 2]: max occurs at $N_2^{ON} \sim$ 93.75 (There is small typo in Atkins).

Combine intuitions:

1. entropy increases

2. we should end up in a macrostate where nothing happens, nothing changes (equilibrium).
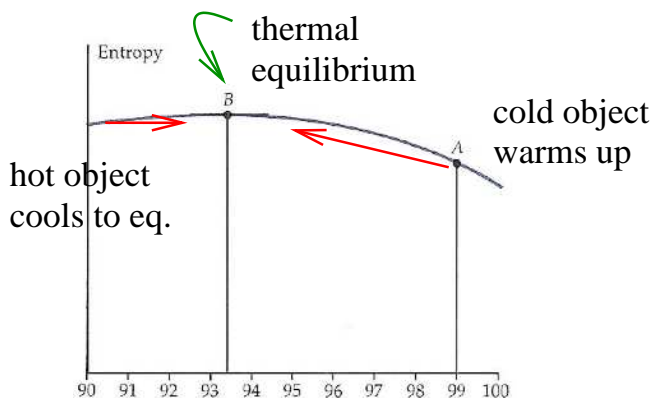
$$\implies \boxed{S = S_{\text{max}} \text{ is equilibrium.}}$$

Warming to equilibrium = increasing $S_{\text{total}} = S_1 + S_2$ to S_{max}.

From this information, we can (and you will on pset 2) compute the number of red dots in System 1 in equilibrium. You'll conclude from Boltzmann's law that equilibrium occurs when

$$\frac{N_1^{ON}}{N_1^{OFF}} = \frac{6.25}{93.75} \overset{!}{=} \frac{N_2^{ON}}{N_2^{OFF}} = \frac{93.75}{1406.25} \ .$$

the density of ON-ness is the same in systems 1 and 2. We'll eventually see this as a special case of $T_1 = T_2$. (We'll actually use this criterion to define temperature.)

Thermal equilibrium:

- All objects (which are able to exchange energy) have the same temperature

- The most probable macroscopic state. (max of distribution = most probable value)

Left for us to show: these two criteria are the same.

Where we are so far: • 2nd Law comes from probability, not certainty. (But: very high probability, super-exponentially probable in number of particles involved. This is our first example of using the large number of particles to our advantage.)

$$\bullet \qquad S = k_B \ln \Omega$$

is the bridge between the thermodynamic description and the statistical description.

You may be wondering: in what sense is this a discovery and not a definition. The discovery is that this expression for the entropy agrees with the thermodynamic definition that we gave earlier for changes in entropy $\Delta S = \Delta Q / T$. In a small number of weeks, this will be clear to you.

For fun: Carnot cycle with red squares. To make motors: introduce barriers across which pink squares can't go. (see slides for animation.)
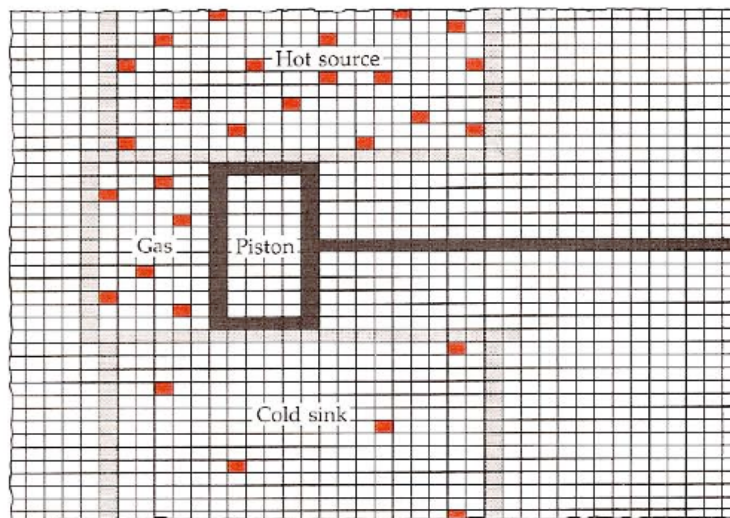
Punchline: Entropy is ignorance. Specifically, ignorance about the microstate.

Better: Entropy is a quantification of ignorance. How many further bits of information are required to specify the microstate, given what we know about the macrostate.

Carnot is an idealized engine. More in Atkins about realistic engines (Stirling, Internal Combustion,...).

Demonology

A natural and very good question which arises from the claim that "entropy is ignorance" is "Can't we subvert the 2nd Law by keeping careful track of the microstate?" An individual who tries to do this is called a *Maxwell Demon*[9] Imagine we hire a tiny person to follow around each of the atoms, for example during the process of cooling a cup of coffee. In this way, the entropy of the system of atoms does not change. However, a crucial extra ingredient is that the Demon itself must be included as part of the system. And here we have a choice: either we must provide the Demon with an exceptionally good memory, to keep track of all the data of the particles, or we must provide the Demon with a mechanism to *erase* his knowledge and rewrite to his limited memory. It turns out that this step of erasure is not so innocuous. This is a deep connection between thermodynamics and information theory, made by Szilard. For further reading, I recommend Charles H. Bennett, *Notes on Landauer's Principle, Reversible Computation, and Maxwell's Demon.*

This is the end of the introduction. You can see that we'll need to learn about probability. That's next (Chapter 2), then we lay more formal foundations for thermodynamics (Chapter 3). Then we do statistical mechanics for real (Chapter 4).

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[9]This is to be distinguished from a Boltzmann Demon, whose job is much more prosaic. A Boltzmann Demon merely implements the microscopic time-reversible laws of dynamics.