Thermodynamics
Second Law
Entropy

Lana Sheridan

De Anza College

May 9, 2018

Last time

- entropy (macroscopic perspective)

Overview

- entropy (microscopic perspective)

Reminder of Example from Last Lecture

What is the entropy change during an adiabatic free expansion of an isolated gas of n moles going from volume V_i to volume V_f? (Note: such a process is not reversible.)

Reminder of Example from Last Lecture

What is the entropy change during an adiabatic free expansion of an isolated gas of n moles going from volume V_i to volume V_f? (Note: such a process is not reversible.)

In an adiabatic free expansion $Q = 0$, and since its isolated, $W = 0$, and therefore $T_f = T_i$.

$$\Delta S = nC_v \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

Reminder of Example from Last Lecture

What is the entropy change during an adiabatic free expansion of an isolated gas of n moles going from volume V_i to volume V_f? (Note: such a process is not reversible.)

In an adiabatic free expansion $Q = 0$, and since its isolated, $W = 0$, and therefore $T_f = T_i$.

$$\Delta S = nC_v \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

using $\ln 1 = 0$ becomes

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$

Clausius Equality

Clausius found that the entropy change around any reversible cycle (closed path) is zero.

This is called the Clausius Equality:

$$\Delta S = \oint \frac{dQ_r}{T} = 0$$

And moreover that since real engines can never quite conform to this ideal, for all engines the Clausius Inequality holds:

$$\Delta S_{sys+env} = -\oint \frac{dQ}{T} \geqslant 0$$

(If the system entropy decreases the environment's entropy *must* increase.)

Entropy in an isolated system

This gives us another way to state the second law:

2nd Law

In an isolated system, entropy does not decrease.

In a non-isolated system (either closed or open) entropy can decrease, but only by increasing the entropy of the environment at least as much.

Entropy Microscopically

Entropy is a measure of disorder in a system.

It can also be used as a measure of information content.

Intriguingly, entropy was introduced separately in physics and then later in information theory. The fact that these two measures were the same was observed by John von Neumann.

Entropy

According to Claude Shannon, who developed Shannon entropy, or information entropy:

"I thought of calling it 'information', but the word was overly used, so I decided to call it 'uncertainty'. [...] Von Neumann told me, 'You should call it entropy, for two reasons. In the first place your uncertainty function has been used in statistical mechanics under that name, so it already has a name. In the second place, and more important, nobody knows what entropy really is, so in a debate you will always have the advantage.' "

So what is entropy?

Consider the Yo. app (valued at $5-10 million in 2014).

You can only use it to send the message "yo."

If you get a message on the app, you can guess what it will say.

So what is entropy?

Consider the Yo. app (valued at $5-10 million in 2014).

You can only use it to send the message "yo."

If you get a message on the app, you can guess what it will say.

The message has no information content, and it is perfectly ordered, there is no uncertainty.

The message is a physical system that can only be in one state.

So what is entropy?

But what if the message is only sent with 50% probability?

"If you get the message, let's meet for drinks, if not, I'm still in a meeting and can't join you."

So what is entropy?

But what if the message is only sent with 50% probability?

"If you get the message, let's meet for drinks, if not, I'm still in a meeting and can't join you."

Now you learn something when you get the message.

The information content is 1 bit.

So what is entropy?

(Shannon) Entropy of a message m:

$$H(m) = -\sum_i p_i \log p_i$$

where p_i is the probability of receiving message i.

So what is entropy?

(Shannon) Entropy of a message m:

$$H(m) = -\sum_i p_i \log p_i$$

where p_i is the probability of receiving message i.

For the fully-determined message "yo":

$$
\begin{aligned}
H(m) &= -1 \log 1 - 0 \log 0 \\
&= 0 \quad \text{bits}
\end{aligned}
$$

So what is entropy?

(Shannon) Entropy of a message m:

$$H(m) = -\sum_i p_i \log p_i$$

where p_i is the probability of receiving message i.

For the fully-determined message "yo":

$$
\begin{aligned}
H(m) &= -1 \log 1 - 0 \log 0 \\
&= 0 \text{ bits}
\end{aligned}
$$

For the "yo"-or-no message:

$$
\begin{aligned}
H(m) &= -\frac{1}{2} \log \frac{1}{2} - \frac{1}{2} \log \frac{1}{2} \\
&= \log 2 \\
&= 1 \text{ bit}
\end{aligned}
$$

Entropy in Thermodynamics

In physics, we express entropy a little differently:

$$S = -k_B \sum_i p_i \ln p_i$$

p_i is the probability of being in the ith microstate, given you are in a known macrostate.

k_B is called the Boltzmann constant.

$$k_B = 1.38 \times 10^{-23} \text{J K}^{-1}$$

Notice that this changes the units of entropy to J / K.

Entropy in Thermodynamics

Consider the atmosphere, it is mostly Oxygen and Nitrogen.

Have you ever walked into a room and been unable to breathe because all of the oxygen in on the other side of the room?

Entropy in Thermodynamics

Consider the atmosphere, it is mostly Oxygen and Nitrogen.

Have you ever walked into a room and been unable to breathe because all of the oxygen in on the other side of the room?
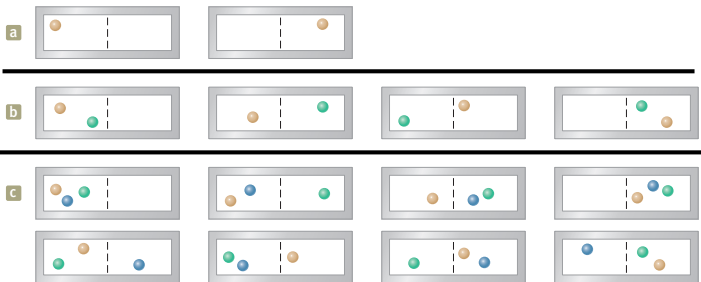
As more oxygen molecules are added, the probability that there is oxygen is on both sides increases.

Macrostates and Microstates

A **macrostate** is something we can observe on a large scale.

The macrostates here could be:
- all oxygen on the left
- all oxygen on the right
- oxygen mixed throughout the room.

Macrostates and Microstates

A **microstate** is a state too small / complex to easily observe, but represents one way a macrostate can be achieved.

We want to consider the number of microstates for each macrostate.

The macrostates here could be:

- all oxygen on the left — 1 microstate
- all oxygen on the right — 1 microstate
- oxygen mixed throughout the room — 6 microstates

Suppose all of the microstates are equally likely. If so, even with only 3 molecules, we would expect to find the oxygen distributed throughout the room (75% probability).

$$S = -k_B \sum_i p_i \ln p_i$$

Entropy of the "all on the left" macrostate:

$$S_L = k_B \ln 1 = 0$$

Entropy of the "mixed" macrostate:

$$S_M = k_B \ln 6 \approx 1.8 k_B$$

The entropy of the "mixed" macrostate is higher!

Boltzmann's formula

The entropy of a macrostate can be written:

$$S = k_B \ln W$$

where W is the number of microstates for that macrostate, assuming all microstates are equally likely.

W is the number of *ways* the macrostate can occur.

Entropy and disorder

A macrostate that has very many microstates can be thought of as a disordered state.

If all the oxygen is on the left of the room, all the nitrogen on the right, the room is organized, or ordered.

But this is very unlikely!

Even if a room starts out ordered, you would expect it to become disordered right away, because a disordered room is more probable.

Entropy example

Imagine throwing two dice. The score of the dice will be the sum of the two numbers on the dice.

What score should you bet on seeing?

[1]Hewitt, 'Conceptual Physics', Problem 8, page 331.

Entropy example

Imagine throwing two dice. The score of the dice will be the sum of the two numbers on the dice.

What score should you bet on seeing?

What is the number of microstates associated with that score?

What is the number of microstates associated a score of 2?

Entropy example

Imagine throwing two dice. The score of the dice will be the sum of the two numbers on the dice.

What score should you bet on seeing?

What is the number of microstates associated with that score?

What is the number of microstates associated a score of 2?

The macroscopic world is like a game in which there are $\sim 10^{23}$ dice, but you only ever see the (approximate) score, not the result on each dice.

---

[1]Hewitt, 'Conceptual Physics', Problem 8, page 331.

Second Law of Thermodynamics

This gives us another perspective on entropy and the second law.
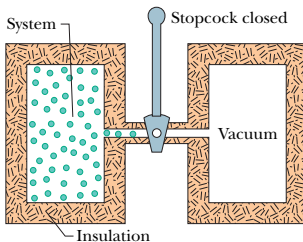
Heat must flow from hotter to colder because there are more ways to distribute energy evenly than to keep it in one place only.

$$\frac{\Delta S}{\Delta t} \geqslant 0$$

As time goes by, things tend to disorder.

Second Law of Thermodynamics
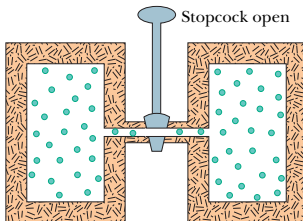
ordered,
less probable,
low entropy

System
Stopcock closed

Vacuum

Insulation

(*a*) Initial state *i*

Irreversible
process

disordered,
more probable,
high entropy

Stopcock open

(*b*) Final state *f*

Example (Microscopic Entropy Analysis)

What is the entropy change during an adiabatic free expansion of an isolated gas of n moles going from volume V_i to volume V_f? (Note: such a process is not reversible.)

Two approaches: microscopic and macroscopic (seen earlier).

Now for **microscopic**. We need some way to count microstates of the gas.

Let's break up our volume, V, into a grid and say there are m different locations a gas particle could be in.[1] Let N be the number of particles and $m \gg N$.

---

[1]Serway & Jewett, pg 671.

Example

Let V_m be the volume of one grid unit, so $m = V/V_m$.

How many ways can we place the particles? The first can be placed in any of $w = V/V_m$ places. For each of those positions, the second can be placed in w locations, giving w^2 ways in total.

For N, there are $w^N = \left(\frac{V}{V_m}\right)^N$ ways the particles can be arranged in the volume V.

This gives

$$S = Nk_B \ln\left(\frac{V}{V_m}\right)$$

Example

There are reasons to quibble over how we counted the microstates, but let us think what this gives us for the change in entropy.

We have a final volume V_f and an initial volume V_i:

$$\Delta S = N k_B \ln \left(\frac{V_f}{V_m} \right) - N k_B \ln \left(\frac{V_i}{V_m} \right)$$

Example

There are reasons to quibble over how we counted the microstates, but let us think what this gives us for the change in entropy.

We have a final volume V_f and an initial volume V_i:

$$\Delta S = N k_B \ln \left(\frac{V_f}{V_m} \right) - N k_B \ln \left(\frac{V_i}{V_m} \right)$$

So,

$$\Delta S = N k_B \ln \left(\frac{V_f}{V_i} \right)$$

The same as for the macroscopic analysis!

Summary

- entropy (microscopic perspective)

Test Monday, May 14.

Homework Serway & Jewett:

- new: Ch 22, onward from page 679. Probs: 39, 49
- will set tomorrow: Ch 22, OQs: 1, 3, 7; CQs: 1; Probs: 1, 3, 9, 15, 20, 23, 29, 37, 67, 73, 81