Lecture 15: Entropy I

- Entropy from the microscopic viewpoint
- Macrostates & microstates
- Probability and multiplicity
- Calculating the multiplicity
- A physical example – the 1D spin chain
- The coin flipping demo
- Likelihood of macrostates, disorder & the 2^{nd} law
- Evolution with time
- Boltzmann's entropy
- An unlikely arrangement

Entropy is about spontaneity.

The Second Assignment

PHYS2060 – Thermal Physics
Session 2 - 2008
Assignment 2

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Assignment (marked out of 50 but worth 10% of the final mark)
Due date – Must be in my office by 5pm on Wednesday 15th October 2008 (i.e., Week 11)
All answers must be fully justified (i.e., no guesses) and should be of sufficient detail that a fellow student could follow your reasoning.
NO EXTENSIONS – Penalty for late submission is 25 marks/day (i.e., out of 25 marks if submitted Thursday, zero if Friday or later)
(Note: Superscript numbers in the assignment refer to the end-notes on the last page.)

The assignment will look long and complex, but it actually isn't. But you will need to think about some of the problems and possibly do a little background research.

Entropy from the microscopic viewpoint

- **You'll remember in the last lecture that we found an important relationship between the reservoir temperatures and heat input/output for a Carnot engine:**

$$\frac{Q_c}{T_c} = \frac{Q_h}{T_h} \qquad \textbf{(14.12)}$$

In other words, the ratio *Q*/*T* is conserved, and this is something we call the entropy *S*, making the Carnot cycle an *isentropic* (or constant entropy) process.

But probably one of the most significant questions in thermodynamics is: What exactly is entropy, and does it have some physical meaning beyond Eqn 14-12? This is one of the harder questions in physics, as entropy is a rather abstract concept.

To get a feeling for what entropy is, we need to delve a little bit into statistical mechanics. From a statistical mechanics perspective, we can loosely say that the 2nd law states that isolated systems tend toward disorder and that entropy is a measure of this disorder (n.b. at the end of this lecture I will abandon 'disorder' so don't get used to it).

But what do we mean by disorder? To answer that, we need to think about probability and we need to distinguish between the *microstates* and *macrostates* of a system.

Macrostates and Microstates

- A ***microstate*** is a particular configuration of the individual constituents of a system.

- A ***macrostate*** is a description of the conditions of the system from a macroscopic point of view. Let's see two examples so this makes some sense.

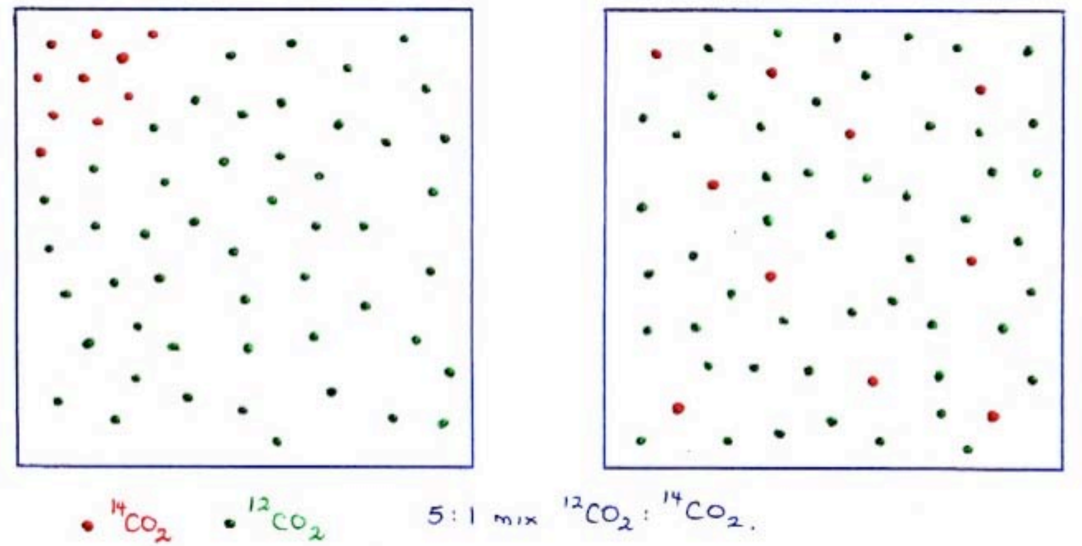
Example 1 – A gas: **Consider 1 mol. of He gas at *P* = 1 atm and *T* = 298K. This is the macrostate of the gas – its condition described in terms of macroscopic parameters This gas has only *one* macrostate, if we change any of those macroscopic parameters, it's a different macrostate.**

For each microstate, we'd have to fully describe the configuration of each of the 6.022×10^{23} molecules. To do this we need to know its location (3 coordinates), velocity (3 coordinates) and time (1 coordinate for the whole system). A total of $(6 \times 6.022 \times 10^{23}) + 1 = 3.6 \times 10^{24}$ coordinates.

Note that a number of different microstates can have the same macrostate. The best way to realise this is to take our gas and move one of the atoms slightly – this is a new microstate as one of the microscopic parameters has changed, but the effect on the macroscopic parameters is infinitesimal, hence it's the same macrostate.

Macrostates and Microstates

But it's more interesting to see the relationship between micro- and macrostates the other way around. A gas in one particular macrostate could be in any of an infinite number of possible microstates.



To give two out of an infinite number of examples – suppose I have a mixture of $^{14}CO_2$ in $^{12}CO_2$, one possible microstate has all of the $^{14}CO_2$ in one corner of the volume, another has them evenly distributed throughout the gas. Both of these are the same macrostate, the gas has the same *U*,*P*,*V*,*T*,*N*, etc., but different microstates.

Both are possible, so why is it we never see the first case and almost always see the second case? To answer that, we should look at the second example.

The coin flipping demo

We're now going to do a quick exercise playing with the flipped coin system. We've already done the 3-coin system, it's kind of trivial, but on the flipside, the 100-coin is a bit big to handle, so we'll reduce it to a 10-coin system.

Our plan is to let our system 'spontaneously' evolve via a set of random 'state-flips' over time and see what happens. You will each get a sheet to do this on and you will need a pen, a calculator, a coin (I have some in case you don't) and your brain.

What did people notice?

Macrostates and Microstates

Example 2 – Coin tossing: Let's switch for a few moments to a system that's a bit easier to handle (because there are only 8 configurations, not 10^{24}). Let's make it three coins, say a 1c coin, a 5c coin and a $2 coin (bronze, silver and gold, so that we can keep track of them easily). If we toss the three coins enough times, we'll soon realise that there are 8 possible outcomes, which are shown in the table below.

1¢	5¢	$2	
H	H	H	n_{heads} = 3 (has 1 possible microstate)
H	H	T	
H	T	H	n_{heads} = 2 (has 3 possible microstates)
T	H	H	
H	T	T	
T	H	T	n_{heads} = 1 (has 3 possible microstates)
T	T	H	
T	T	T	n_{heads} = 0 (has 1 possible microstate)

Each of the eight outcomes are our microstates, and we have four macrostates corresponding to the number of heads (n_{heads} = 0, 1, 2 or 3) in our system. As you can see in the table, the macrostates with 0 and 3 heads have only one possible microstate, and the macrostates with 1 or 2 heads have three possible macrostates.

Probability and Multiplicity

The number of microstates corresponding to a given macrostate is called the *multiplicity* Ω of that macrostate, in the two cases above this is Ω (n_{heads} = 0, 3) = 1 and Ω (n_{heads} = 1, 2) = 3, respectively.

Another point of note here is that if you know the microstate of a system then you know the macrostate of the system (for example, if it's HHT then n_{heads} = 2), but if you know the macrostate then you don't necessarily know the microstate (for example, if n_{heads} = 1, is it TTH, THT or HTT?). There is a lot of 'information' contained in a microstate.

1¢	5¢	$2
H	H	H
H	H	T
H	T	H
T	H	H
H	T	T
T	H	T
T	T	H
T	T	T

Let's think a bit more about our coin example. The total multiplicity of all four possible macrostates is 1 + 3 + 3 + 1 = 8 = Ω(all), the total number of microstates. We can then write the probability of any particular microstate as:

$$P(n\ \text{heads}) = \frac{\Omega(n)}{\Omega(\text{all})} \qquad \textbf{(15.1)}$$

For example, *P*(2 heads) = Ω(2)/Ω(all) = 3/8, which makes sense if you look back at the table above.

Calculating the multiplicity

Suppose we have 100 coins now, the total number of microstates is quite large: 2^{100}, since each of the 100 coins has two possible states. The number of macrostates is 101: 0 heads, 1 head … up to 100 heads. What are the multiplicities of these macrostates?

0-heads: in this case, every coin lands tails up. Of course, there is only one possible microstate for this TTTTTTTT...TTTTTTTT, so $\Omega(0) = 1$.

1-head: the heads-up coin could be in any one of 100 positions, so $\Omega(1) = 100$.

2-heads: to find $\Omega(2)$, we need to think a little more carefully. You have 100 choices for the first coin, and for each of these choices you have 99 remaining choices for the second coin, but you could choose any pair in either order, so the number of distinct pairs is $\Omega(2) = (100 \times 99)/2$.

3-heads: here, you have 100 choices for the first, 99 for the second, 98 for the third, but any triplet can be chosen in several ways, 3 choices for the first flip and then 2 for the second flip, so the number of distinct triplets is $\Omega(3) = (100 \times 99 \times 98)/(3 \times 2)$.

Calculating the multiplicity

By now, you can probably spot the pattern forming that will give us a general result.

$$\Omega(n) = \frac{100.99...(100-n+1)}{n...2.1} = \frac{100!}{n!(100-n)!} = \binom{100}{n} \qquad \textbf{(15.2)}$$

where *n*! is a factorial. We can take this one step further and arrive at a general expression for the multiplicity of a system with *N*-coins, which gives:

$$\Omega(N,n) = \frac{N!}{n!(N-n)!} = \binom{N}{n} \qquad \textbf{(15.3)}$$

which is the number of ways of choosing *n* objects out of *N*.

Lets just check this: Suppose we want the multiplicity for 2 coins in our 3 coin set. Ω(3,2) = 3!/[2!(3-2)!] = 6/[2*1] = 3, which is exactly as we'd expect.

1¢	5¢	$2
H	H	H
H	H	T
H	T	H
T	H	H
H	T	T
T	H	T
T	T	H
T	T	T

A physical example – the 1D spin chain

- Finally, just to show this isn't about coins, this can be applied directly to magnetic systems. For example, consider the 1-dimensional spin chain below.

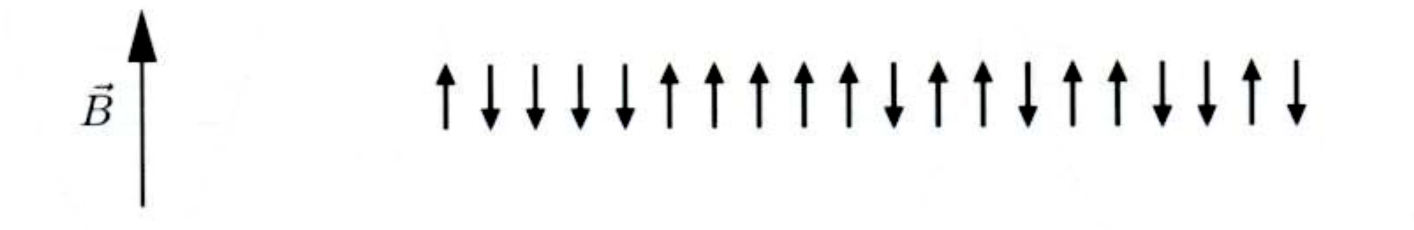


Figure 2.1. A symbolic representation of a two-state paramagnet, in which each elementary dipole can point either parallel or antiparallel to the externally applied magnetic field.

The multiplicity for any macrostate of this 1D spin chain is just:

$$\Omega(N, N_{\uparrow}) = \binom{N}{N_{\uparrow}} = \frac{N!}{N_{\uparrow}!(N - N_{\uparrow})!} = \frac{N!}{N_{\uparrow}!N_{\downarrow}!} \qquad \textbf{(15.4)}$$

We can see that the maximum multiplicity will occur when $N_{\uparrow} = N_{\downarrow}$, and later we'll see that this corresponds to the state with the highest entropy. This is the very beginnings of a subject called statistical mechanics (PHYS3020), so I'll leave this discussion here.

Likelihood of macrostates, disorder & the 2nd law

- Let's go back to our coins. You'll probably have noticed that if I take the three coins and throw them up in the air, that the macrostates n_{heads} = 1 or 2 (probability 3/8^{ths} each) are more likely than n_{heads} = 0 or 3 (probability 1/8th each). And if I take 100 coins, I'm far more likely to get 49, 50 or 51 heads than get 0, 1, 99 or 100 heads.

But in either case, if I choose any of the 8 or 10^{30} possible microstates, then they are all equally likely (probability 1/8 or 10^{-30} – 100-coins have $2^{100} \approx 10^{30}$ microstates). So now you can probably spot a general rule here:

The most likely macrostate for a system is the one with the largest number of microstates.

Another thing you might have noticed with the coins is that the n_{heads} = 0 or 3 macrostates are more ordered (i.e. are HHH or TTT) than the n_{heads} = 1 or 2 macrostates (e.g HHT, HTH, TTH, etc), and that the more disordered macrostates (n_{heads} = 1 or 2) are more likely, because they contain more microstates. This is because there are usually more ways of configuring the system if it's got more disorder. Hence you could also say:

The most likely macrostate of the system is the one with the most 'disorder'.

Evolution with time

- **Now lets consider how a system evolves with time, with our 100 coins, but this time we start with all coins as heads (one microstate).**

If each second, I randomly choose one coin and flip it at random, gradually the system evolves towards an equilibrium macrostate with ~ 50 heads and 50 tails organised at random (this macrostate has 100!/(50!50!) = 10^{29} microstates). This is a highly disordered state compared to our initial highly ordered 'all heads' microstate.

If the system continues to evolve, it will fluctuate a bit (e.g., we may have 48 heads and 52 tails, sometimes), but we have to wait a *long* time to get all the heads back. Even if we were flipping all 100 coins each second, we'd expect to have to wait 10^{30}s (or $10^{12} \times$ the age of the universe) before we got 'all heads' back.

For the moment you'll need to trust that this idea translates across to other systems like gases, but already we can see a general rule emerging from our 'coin' system:

Any large isolated system will spontaneously 'evolve' over time from non-equilibrium macrostates (those with a smaller number of microstates, lower multiplicity and low 'disorder) towards equilibrium macrostates (those with the largest number of microstates, the highest multiplicity and the highest 'disorder').

This is just a more general statement of the 2nd law. But where does entropy come into this? To resolve this, we need some work by Ludwig Boltzmann.

Boltzmann's entropy

- **Ludwig Boltzmann was an Austrian physicist working on the kinetic theory of gases in the late 1800s. His two main contributions were the velocity distribution of particles in a gas (i.e., the Maxwell-Boltzmann distribution) and the following connection between the microscopic properties of a system and its entropy.**

  In fact, this latter result is what Boltzmann is best remembered for, and he felt it was so important that it be engraved on his tombstone.

So what is this equation that we see written on Boltzmann's tombstone? It is:

$$S = k_B \ln \Omega \ \text{ or } \ k_B \log W \qquad \textbf{(15.5)}$$

where S is the entropy, k_B = 1.38 × 10^{-23} J/K is Boltzmann's constant and W is the number of microstates corresponding to the macroscopic state of the system – this is just the multiplicity Ω that we developed earlier. Note that the log is an exponential/natural log (or ln) not a base 10 log.

Boltzmann's version of the 2nd law

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If we apply Boltzmann's law to the general result we just arrived at, we obtain:

Any large isolated system in equilibrium will be found in the macrostate with the greatest entropy (aside from fluctuations normally too small to measure), and non-equilibrium systems with lower entropy will spontaneously evolve towards this maximally-entropic, equilibrium state.

This is something known as the entropic statement of the 2nd law or the principle of increase in entropy (some will also call it Boltzmann's statement of the 2nd law).

Horribly Large Numbers!!

The standard entropy for a mole of ice ΔS_0 at 273K is 41 J/K, let's follow this through the Boltzmann equation.

So, $\ln \Omega = \Delta S_0/k_B = 41/1.38\times10^{-23} = 2.9\times10^{24}$

giving $\log_{10} \Omega = 0.43 \times 2.9\times10^{24} = 1.3\times10^{24}$

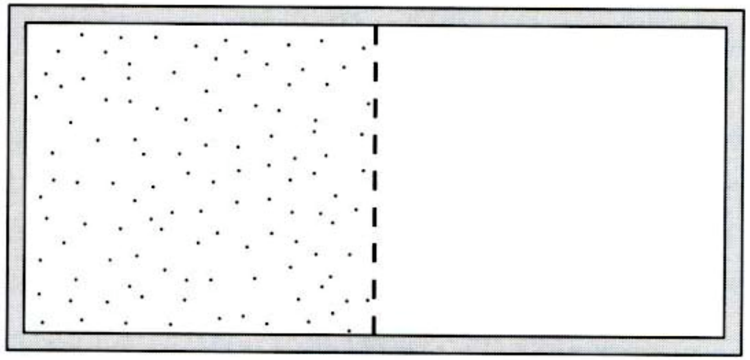
and so $\Omega = 10^{1.3\times10\text{^}24} = 10^{1,300,000,000,000,000,000,000,000}$!!!! This is a **HUGE** number, for example, there are only about 10^{70} particles in the entire universe.

Now if we consider water at 273K, then ΔS_0 = 63 J/K, and this gives a larger $\Omega = 10^{2,000,000,000,000,000,000,000,000}$, this is bigger, but not to a massive extent.

With these sorts of numbers in mind, any idea of 'order' and 'disorder' goes out the window. Be really careful with these two terms – they work great as a way to get the concept, but they are actually wrong, and so once you understand it, they are best abandoned for other descriptions of entropy.

An unlikely arrangement

- Suppose we have a gas in a box, how long would we have to wait for it to end up in a microstate where all of the gas is in one half of the box, as shown to the right.



A very unlikely arrangement of gas molecules.

Note this is equivalent in the 100-coin system to a macrostate with 100 heads and 0 tails, which is very rare because it's the most ordered of ~10^{30} possible microstates.

This might seem like we're stretching the coin analogy too far, but its not. If we wanted to, we could just represent this system with L = particle in the left side and R = particle in the right side, instead of H and T – it's exactly the same as the coins!

What we're doing is to effectively halve the volume of the gas. If we look at Eqn. 20.6, replacing V by $V/2$ reduces the multiplicity by a factor of 2^N. In other words, the probability of all the molecules being on the left is 2^{-N}. For $N = 100$, this probability is ~10^{-29}, and you would have to check a trillion times a second for the age of the universe before finding such an arrangement once.

For ~1 mol. of a gas, $N \sim 10^{23}$ and so the probability might is infinitesimally small and we can fairly safely expect to never see a gas occupying half a volume.

Summary

- **While entropy can be described macroscopically as the ratio *Q*/*T*, it also has a microscopic description.**

- **A *microstate* is a particular configuration of the individual constituents of a system. A *macrostate* is a description of the conditions of the system from a macroscopic viewpoint.**

- **A system can have a number of possible macrostates, each with its own microstates. A number of different microstates can have the same macrostate, and a macrostate can have anything from one to an infinite number of microstates.**

- **Based purely on probability, it is possible to say that the most likely macrostate for a system is the one with the largest number of microstates.**

- **Boltzmann's law relates entropy to the multiplicity of microstates of a system via $S = k_B \ln\Omega$. This results in the entropic statement of the 2nd law (or principle of increasing entropy) which states that *any large system in equilibrium will be found in the macrostate with the greatest entropy* (aside from small fluctuations).**

In the next lecture we will look at the second law from the macroscopic viewpoint of entropy and try to link the two pictures together.