213 Midterm coming up...

Monday April 8 @ 7 pm (conflict exam @ 5:15pm)

Covers:

Lectures 1-12 (not including thermal radiation)

HW 1-4

Discussion 1-4

Labs 1-2

Review Session

Sunday April 7, 3-5 PM, 141 Loomis

HW 4 is not due until Thursday, April 11 at 8 am, but some of the problems are relevant for the exam.

Lecture 7

Entropy and Exchange between Systems

- Counting microstates of combined systems

- Volume exchange between systems

- Definition of Entropy and its role in equilibrium

Reference for this Lecture:
Elements Ch 6

Reference for Lecture 8:
Elements Ch 7

Review: Some definitions

State:

The details of a particular particle, e.g.:
. what volume bin it is in
. the orientation of its spin
. its velocity

Microstate:

The configuration of states for a set of particles, e.g.:
. which bin each particle is in
. the velocities of all the particles
. the orientation of all the spins -- ↑↑↓↑↓

Macrostate:

The collection of all microstates that correspond to a particular macroscopic property of the system, e.g.:
. all the particles on the left side
. A box of gas has a particular P, V, and T
. 1/3 of the particles with their spins "up"
. no particles as a gas: all as liquid

ACT 1: Microstates

Consider 10 coin flips. Which sequence is least likely?

a. H H H H H H H H H H
b. H H H H H T T T T T
c. H T H T H T H T H T
d. H H T H T T T H H H
e. T T H T H H H T T H

ACT 1: Solution

Consider 10 coin flips. Which sequence is least likely?

  a. H H H H H H H H H H
  b. H H H H H T T T T T
  c. H T H T H T H T H T
  d. H H T H T T T H H H
  e. T T H T H H H T T H

Each sequence is equally likely!

Now, imagine that the coins are being flipped by random thermal motion. Each sequence is a microstate of the 10-coin system.

In thermal equilibrium, every microstate is equally likely!

If instead we ask which macrostate is least likely, it is the one with all the coins 'heads' (or 'tails').

Why? Because there is only one corresponding microstate.

ACT 1'

Consider 10 coin flips, and 50 coin flips. Are you more likely to see 4/10 heads, or 20/50 heads?

a. 4 out 10 is more likely
b. 20 out of 50 is more likely
c. 4/10 is as likely as 20/50

ACT 1: Solution

Consider 10 coin flips, and 50 coin flips. Are you more
likely to see 4/10 heads, or 20/50 heads?

a. 4 out 10 is more likely
b. 20 out of 50 is more likely
c. 4/10 is as likely as 20/50

Although in both cases it's 40% heads, the two distributions look
very different. The uncertainty in the average number of heads is
proportional to the sqrt(average number of heads). Here it's the
relative uncertainty that's important, that varies as $1/\sqrt{N_{heads}}$.
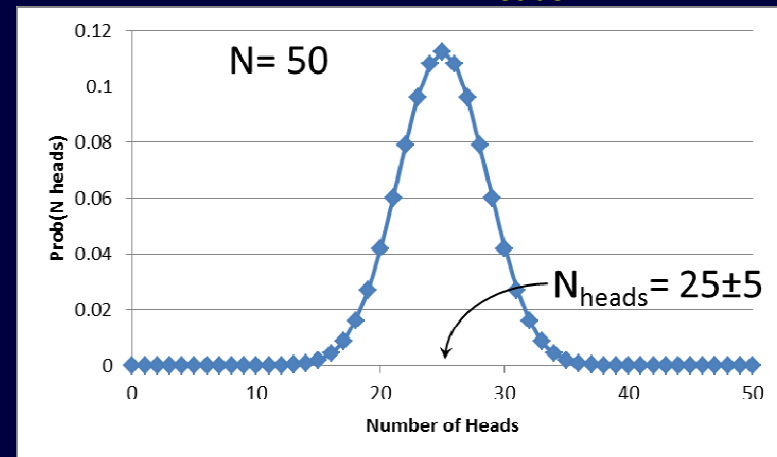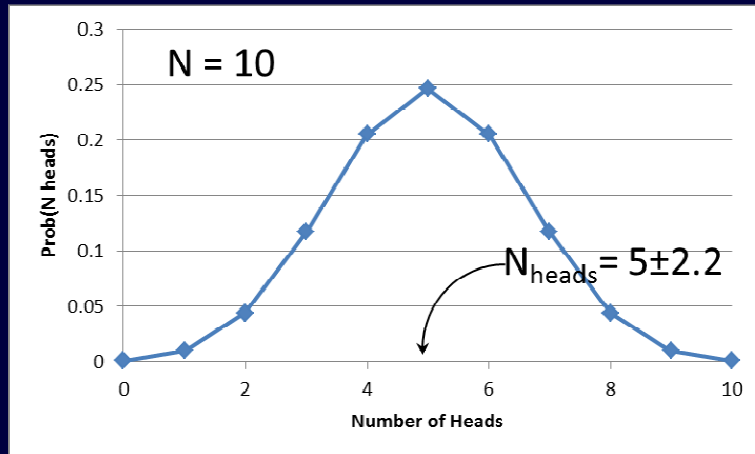
The usual case in thermal systems – they are big enough that the
distribution is VERY narrowly peaked about the most likely macrostate.

A New Definition

In an isolated system in thermal equilibrium, each microstate is equally likely.
We'll learn later why the system must be isolated.

So, the probability that you find some *macro*state A is just
the fraction of all the microstates that correspond to A:

$$P(A) = \Omega(A)/\Omega_{total}.$$

To keep track of the large numbers of states,
we define entropy, σ:

$$\sigma(A) \equiv \ln(\Omega(A))$$
$$\Rightarrow \; P(A) \propto e^{\sigma(A)}$$

Entropy is the logarithm
of the number of microstates.

In thermal equilibrium,
the most likely macrostate is the one with the biggest entropy σ.
We call that the "equilibrium state" even though there are really
fluctuations around it. If the system is big (many particles), the
relative size of these fluctuations is negligible.

Counting Microstates (revisited)

Last week we considered binomial (two-state) systems:

Coins land with either heads or tails, electronic spins have magnetic moments m pointing either with or against an applied field, and 1-dimensional drunks can step a distance either left or right.
We defined the terms "microstate" and "macrostate" to describe each of these systems:

System	One particular microstate	Macrostate (what we measure)
Spins	U D D U D U U U D U	Total magnetic moment = $\mu(N_{up} - N_{down})$
Coins	H T T H T H H H T H	$N_H - N_T$
Steps	R L L R L R R R L R	Net displacement = $\ell(N_R - N_L)$

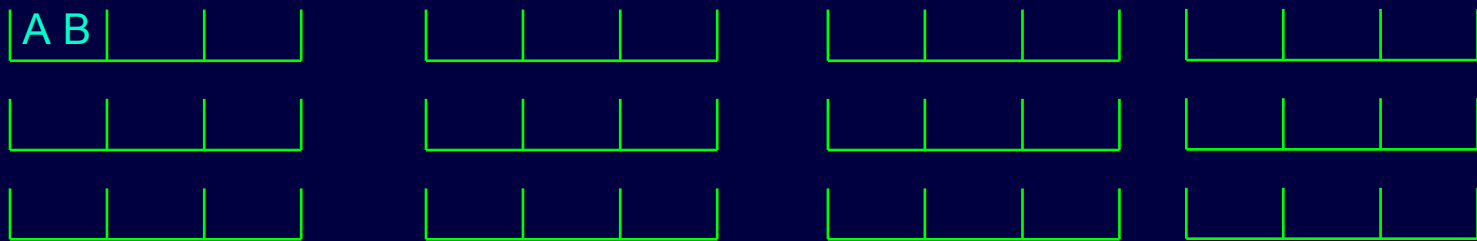Now we will study systems that have more than two states:

Each particle can be placed in any of many bins.
This "bin problem" is directly related to particles in gases and solids.

Counting Arrangements of Objects

Problem 1: Distinct objects in bins with unlimited occupancy.

How many ways can you arrange 2 distinct objects (A and B) in 3 bins?

Work space:

| A B | | |

arrangements (# microstates) Ω =

Suppose we throw the 2 objects up and let them land randomly.

What is the probability of getting a specified microstate?   P =

How many microstates for N different objects in M bins? Ω =

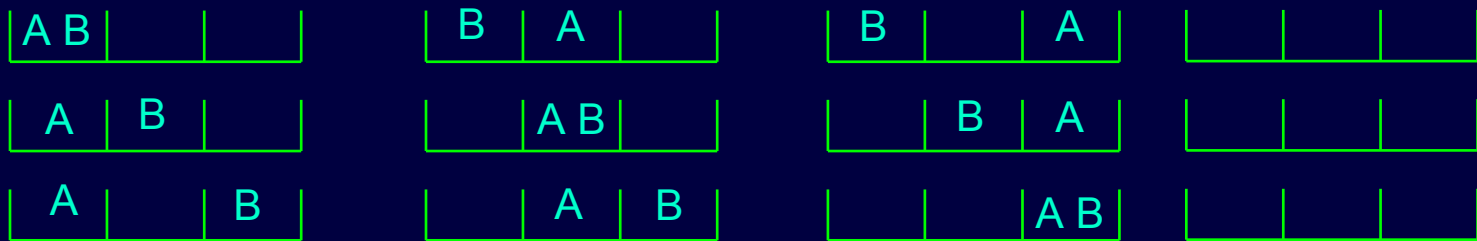Find Ω for two identical objects (A and A) in 3 bins. Ω =

Identical *vs* distinct
(or distinguishable) is important!

Solution

Problem 1: Distinct objects in bins with unlimited occupancy.

How many ways can you arrange 2 distinct objects (A and B) in 3 bins?

Work space:

| A B | | | | B | A | | | B | | A | | | | |

| | A | B | | | | A B | | | | B | A | | | | |

| | A | | B | | | A | B | | | | A B | | | | |

arrangements (# microstates) $\Omega = 9$

Now throw the 2 objects up and let them land randomly.

What is the probability of getting a specified microstate? $P = 1/9$

How many microstates for N different objects in M bins? $\Omega = M^N$

Find Ω for two identical objects (A and A) in 3 bins. $\Omega = ???$

Identical *vs* distinct
(or distinguishable) is important!

ACT 2: Effect of Indistinguishability

Consider 2 particles in a box with two bins (multiple occupancy allowed). Compare the total number of microstates Ω_d if the particles are distinguishable, with Ω_i, the total number of microstates if the particles are identical (indistinguishable).

a) $\Omega_i < \Omega_d$ b) $\Omega_i = \Omega_d$ c) $\Omega_i > \Omega_d$

Solution

Consider 2 particles in a box with two bins (multiple occupancy allowed). Compare the total number of microstates Ω_d if the particles are distinguishable, with Ω_i, the total number of microstates if the particles are identical (indistinguishable).

a) $\Omega_i < \Omega_d$ b) $\Omega_i = \Omega_d$ c) $\Omega_i > \Omega_d$

For distinguishable particles ("a" and "b"), the states are:

|ab| | | |ab| |a|b| |b|a|

For indistinguishable particles ("a" and "a"), the states are:

|aa| | | |aa| |a|a|

This is a general result – indistinguishable particles typically have fewer microstates.

Why Do We Consider Identical Particles?

Many microscopic objects are identical:

- All elementary particles of a given type are identical (indistinguishable).
  Electrons, protons, neutrons, etc.

- All atoms of a given type are identical.
  E.g., ^{235}U, ^{12}C.

- All molecules of a given type are identical.
  E.g., O_2, N_2, H_2O, C_6H_6.

"Type" includes isotope and any other internal structure.

Macroscopic objects (*e.g.*, baseballs) are never identical, because their internal structure is too complicated ever to be exactly the same.

Single occupancy (1)

In many situations, each bin can only hold a single object.

Problem #2: Distinct objects in single-occupancy bins.
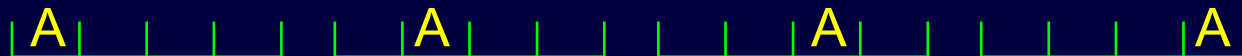How many ways can you arrange 2 distinct objects (A,B) in 4 bins?

Solution

In many situations, each bin can only hold a single object.

Problem #2: Distinct objects in single-occupancy bins.
How many ways can you arrange 2 distinct objects (A,B) in 4 bins?

|A| | | | | |A| | | | | |A| | | | | |A|

There are 4 ways to put A in. (A has 4 possible states.)
For each of these, there are 3 states for B.
Therefore, the total number of microstates is: $\Omega = 4 \times 3 = 12$.

What if we have 3 particles (A,B,C)?
For each (A,B) microstate, C has 2 states (empty bins).
Therefore, $\Omega = 4 \times 3 \times 2 = 24$.

For N distinguishable objects in M single-occupancy bins:
$$\Omega = M! / (M-N)!$$

Single occupancy (2)

What happens if the particles are identical?

Problem #3: Identical objects in single-occupancy bins.

First, look at a specific distinct particle problem 4 particles in 10 bins:

$$\Omega = M! / (M-N)! = 10! / 6! = 5040$$

Look at a particular microstate:

A		B				C	D			

If the particles are all identical,
we have over counted the microstates.
By what factor?

A		A				A	A			

swap

Swapping "A"s doesn't give a new microstate, so we must divide by the number of permutations of A particles, namely 4! = 24.

The number of microstates for identical particles is:

$$\Omega = M! / (M-N)!N! = 10! / 6!4! = 210$$

Summary of Bin Occupancy and Particle Type

The possible occupancy rules for bins:
- unlimited occupancy
- single occupancy

4 cases

The possible particle types are
- distinct   (distinguishable)
- identical   (indistinguishable)

For N << M, the occupancy rule doesn't matter
because multiple occupancies are rare. (Remember: N objects and M bins)

Example:
Compare M^N with $M!/(M-N)!$ when M = 30 and N = 2:
Multiple occupancy: 30^2 = 900   The single occupancy
Single occupancy: 30!/28! = 870   requirement loses 30 microstates.

Summary of Bin Counting

Number of microstates for N objects in M bins:

|	Unlimited occupancy	Single occupancy	N << M Dilute gas
Distinguishable	M^N	$\dfrac{M!}{(M-N)!}$	M^N
Identical	$\dfrac{(N+M-1)!}{(M-1)!\,N!}$	$\dfrac{M!}{(M-N)!\,N!}$	$\dfrac{M^N}{N!}$

Needed at high densities (liquids and solids) OK for gases, too.

OK at low densities (gases only)

This one is derived in the Appendix

Example: Gas Molecules

- This is a "real world" problem. Consider gas molecules in a container. We are going to count the microstates and use the result to determine the condition for equilibrium when two containers are in contact.

Container

• molecule

Volume V

- In each volume V, the number of states, M, available to a particle is proportional to V, as you would expect. Write: $M = n_T V$.

- n_T is the proportionality constant. The subscript reminds us that, because particles with different velocities are in different states, n_T depends on temperature.

- We will be working in the dilute gas limit, i.e. M>>N. For *indistinguishable* particles, the number of microstates is given by: $\Omega = M^N/N!$. If we are dealing with problems where the number of particles is fixed, the factor of N! drops out. Therefore, we can simplify the math by using the result for *distinguishable* particles: $\Omega = M^N$.

- In realistic problems, the number of microstates is going to be enormous*. Suppose that M = 100, and that we have a mole of gas. Then

- $\Omega = M^N \sim 100^{10^{24}}$ This is an incredibly large number I would say "astronomical", but astronomical numbers are puny in comparison.
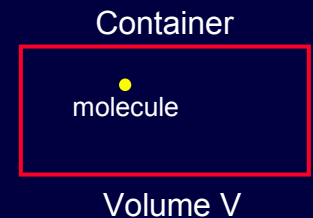
*Why not an uncountable infinity of states? Quantum mechanics!($\Delta x \, \Delta p > \hbar$)

ACT 3: Counting states

Consider N particles in a box of volume V. It has a total number of states (*i.e.*, bins) M, and a total number of microstates $\Omega = M^N$. If we double the volume (2V), what is the new number of microstates Ω'?

a) $\Omega' = \Omega$ b) $\Omega' = 2\,\Omega$ c) $\Omega' = 2^N\Omega$ d) $\Omega' = \Omega^2$

Solution

Consider N particles in a box of volume V.   It has a total number of states (*i.e.*, cells) M, and a total number of microstates $\Omega = M^N$. If we double the volume (2V), what is the new number of microstates Ω'?

a) $\Omega' = \Omega$ b) $\Omega' = 2\,\Omega$ c) $\Omega' = 2^N\Omega$ d) $\Omega' = \Omega^2$

If you double the volume, M doubles. $\Omega' = (2M)^N = 2^N\,M^N = 2^N\Omega$

To get a feeling for how rapidly Ω varies with volume, suppose the volume increases by 0.1%:

$\Omega' = (1.001\ M)^N = 1.001^N\,\Omega$

If $N = 10^{24}$ (*e.g.*, gas in a room), this increase in the number of states is enormous: $(1.001)^N$ will overflow your calculator.

Counting States:
Two Interacting Systems

Divide a box of volume V into two parts, volumes V_1 and V_2: $V = V_1 + V_2$

Put N_1 particles in V_1 and N_2 particles in V_2. $N = N_1 + N_2$

The partition can move. Its position (the value of V_1) describes the macrostate.

V_1	$V_2 = V - V_1$	$\Omega_1 = (n_T V_1)^{N_1}$
N_1	$N_2 = N - N_1$	$\Omega_2 = (n_T V_2)^{N_2}$

moveable partition
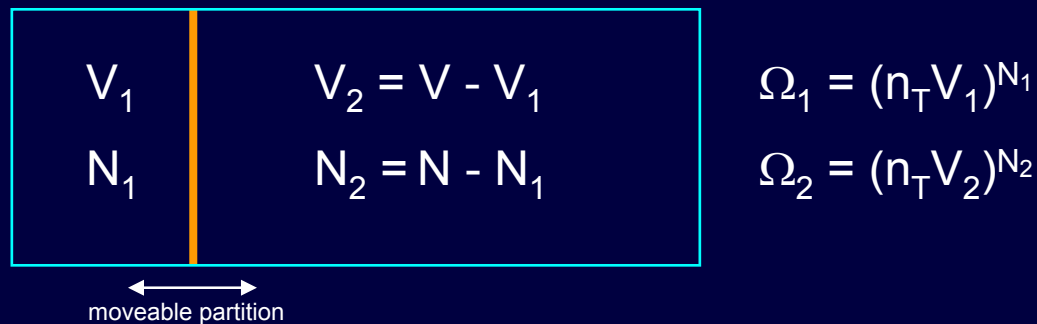
The total number of microstates depends on the position of the partition
(*i,.e.*, on V_1 and V_2):

$$\Omega_{tot} = \Omega_1 \cdot \Omega_2 = (n_T V_1)^{N_1} (n_T V_2)^{N_2} = (n_T)^N V_1^{N_1} V_2^{N_2}$$

Ω_{tot} is the product, because microstates in V_1 are independent of microstates in V_2.

Equilibrium of Volume Exchange

The partition can move, so let's ask:
What is the most probable macrostate?
(the most likely V_1)

$$\boxed{V_1 \quad \leftarrow|\rightarrow \quad V - V_1}$$

Solution:

Find the value of V_1 that maximizes Ω_{tot}:

$$\Omega_{tot} = (n_T)^N V_1^{N_1} V_2^{N_2} = \text{constant} \cdot V_1^{N_1} \cdot V_2^{N_2} = \text{constant} \cdot V_1^{N_1}(V-V_1)^{N_2}$$

It is simpler to maximize the logarithm:

$$\ln(\Omega_{tot}) = \text{constant} + N_1 \ln V_1 + N_2 \ln(V-V_1)$$

Remember that we have defined this to be the entropy: $\sigma = \ln(\Omega)$.
So we will be maximizing the entropy:

$$\frac{d\ln(\Omega_{tot})}{dV_1} = \frac{d\sigma_{tot}}{dV_1} = 0$$

The condition for equilibrium when volume is exchanged.

Volume Equilibrium

Let's solve the problem. Use $\dfrac{d\ln(V_1)}{dV_1} = \dfrac{1}{V_1}$

$$\frac{d\ln(\Omega_{tot})}{dV_1} = \frac{d\ln(\Omega_1)}{dV_1} + \frac{\partial\ln(\Omega_2)}{\partial V_1} = \frac{d\ln(\Omega_1)}{dV_1} - \frac{\partial\ln(\Omega_2)}{\partial V_2} = \frac{N_1}{V_1} - \frac{N_2}{V_2} = 0$$

$$\Rightarrow \frac{N_1}{V_1} = \frac{N_2}{V_2}$$

This is the ideal gas law result. The ideal gas law is $p = \dfrac{N}{V}kT$
In equilibrium, the pressures will be equal, and we assumed that the temperatures were equal (same n_T), so the densities will be equal as well.

The important general result here is that when volume is exchanged between two systems, the equilibrium condition is

$$\frac{d\ln(\Omega_1)}{dV_1} = \frac{\partial\ln(\Omega_2)}{\partial V_2}, \text{ or } \frac{d\sigma_1}{dV_1} = \frac{\partial\sigma_2}{\partial V_2}$$

A similar relation will hold when any quantity is exchanged.
Just replace V with the exchanged quantity.

Entropy

We have defined entropy to be the natural log of the number of accessible microstates.

$$\sigma = \ln \Omega$$

Why is this useful? Why not just use Ω?

A property of system 1

A property of system 2

- Entropy is additive: $\sigma_{tot} = \ln \Omega_{tot} = \ln(\Omega_1\Omega_2) = \sigma_1+\sigma_2$
  Conceptually simpler. Simplifies the math as well.

- The numbers are much more manageable.
  Compare $2^{10^{24}}$ with $10^{24}\ln2$.

Note: σ and Ω are state functions. If you know the macrostate of a system you can, in principle, calculate the number of corresponding microstates.

Summary

- The total entropy of an isolated system is maximum in equilibrium.
- So if two parts (1 and 2) can exchange V, equilibrium requires:

$$\frac{\partial \sigma_1}{\partial V_1} = \frac{\partial \sigma_2}{\partial V_2}$$

This is a general equilibrium condition.
A similar relation holds for any
exchanged quantity.

Entropy of an ideal gas:

For N distinguishable particles in volume V: $\Omega \propto V^N \Rightarrow \sigma = N\ln V + \text{const}$

You can't calculate the constant (that requires quantum mechanics),
but it drops out of problems where one only needs the entropy change.
For example, if the temperature is constant:

$$\sigma_f - \sigma_i = N\ln V_f - N\ln V_i = N\ln(V_f/V_i)$$

Next lecture, you'll learn about the temperature dependence of σ.

Next Lecture

- The Second Law of Thermodynamics

- Energy exchange

- General definition of temperature
  (not just ideal gases)

- Why heat flows from hot to cold

Appendix:

Microstate Counting for Identical Particles in Multiple-Occupancy Bins

A picture is worth 1000 words. Here's one microstate:

$$|\bullet\bullet\bullet|\bullet|\bullet\bullet\bullet\bullet||\bullet\bullet\bullet\bullet\bullet|\bullet\bullet|\bullet\bullet\bullet\bullet|\bullet\bullet\bullet|$$

In this example, there are N=22 particles (the $\bullet$) and M=8 bins.
There are M-1=7 internal walls (the |).
Note that in this microstate, the 4th bin is empty.

If everything were distinguishable, there would be (N+M-1)! arrangements
of particles and internal walls. However, we must divide by N!, the number
of particle permutations, and by (M-1)!, the number of wall permutations
(because walls are also indistinguishable).

Thus, Ω = (N+M-1)! / (M-1)!N!