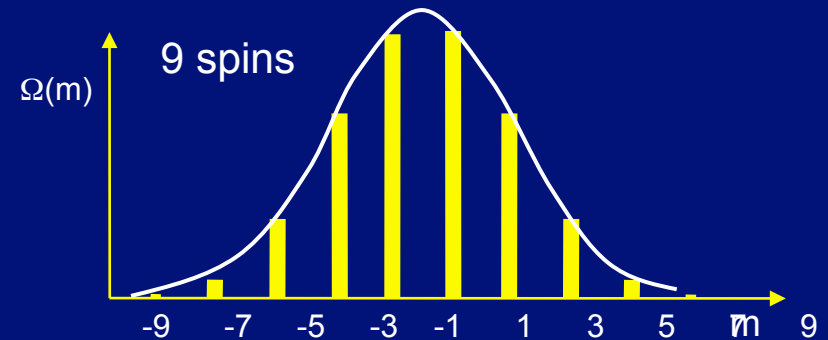


Lecture 6

Statistical Processes

- Irreversibility
- Counting and Probability
- Microstates and Macrostates
- The Meaning of Equilibrium



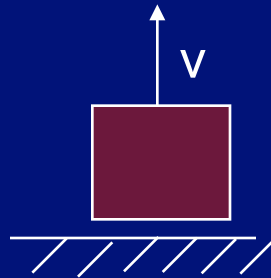
Irreversibility

Have you ever seen this happen?

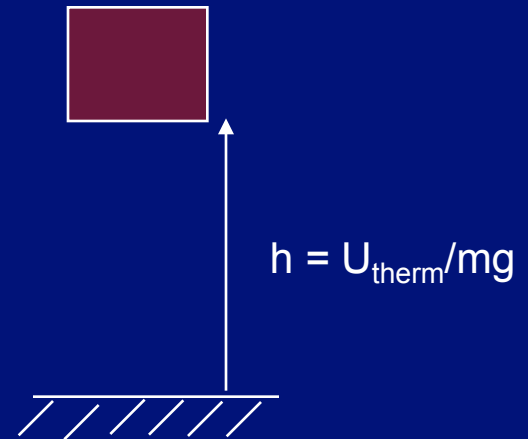
(when you weren't asleep or on medication)



Thermal energy in block
converted to CM KE



$$\frac{1}{2} mv^2 = U_{\text{therm}}$$



End with $v = 0$
 $mgh = U_{\text{therm}}$

Thermal energy $\longrightarrow$ Kinetic energy $\longrightarrow$ Potential energy

Which stage never happens?

Act 1: Irreversibility

Replace the block in the last problem with an ice cube of the same mass. Will that stuff jump off the table?

A) Yes

B) No

Solution

Replace the block in the last problem with an ice cube of the same mass. Will that stuff jump off the table?

A) Yes

B) No

You probably forgot that the ice will melt and then evaporate!

What won't happen is for all the ice to jump up *as one object*. It will certainly all jump up, *molecule-by-molecule*.

Why does one process happen, but not the other?

There are lots of different ways for the water to evaporate, but only one way to jump up as a block.

This is our first hint that:

Which event will happen is determined by the number of different ways the various events could happen.

The Direction of Time

In Physics 211 (Classical Mechanics), most of the processes you learned about were **reversible**. For example, watch a movie of a pendulum swinging or a ball rolling down a plane. Can you tell from the action whether the movie is being played forwards or backwards?

The real world is full of **irreversible** processes. *E.g.*, a block sliding across a rough surface or a rocket being launched. You know whether a movie of those is being played backwards or forwards.

Time has a direction.

Consider the free expansion of a gas. On a microscopic scale motion is reversible, so

How can you in general know which way is forward?

Our answer will be that **total entropy never decreases**.

Which of the following are irreversible processes?

An object sliding down a plane

A basketball bouncing on the floor

A balloon popping

Rusting: $\text{Fe} + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$

Act 2

To illustrate how large, many-particle systems behave, consider a familiar system, the air in this room.

Why does the air spread out to fill the room?

- a) The atoms repel each other, so the gas expands to fill up the available space.
- b) The atoms move around randomly, so they just end up all over the place by accident.
- c) The energy of the system is lowered when the gas fills all the available space.

Solution

To illustrate how large, many-particle systems behave, consider a familiar system, the air in this room.

Why does the air spread out to fill the room?

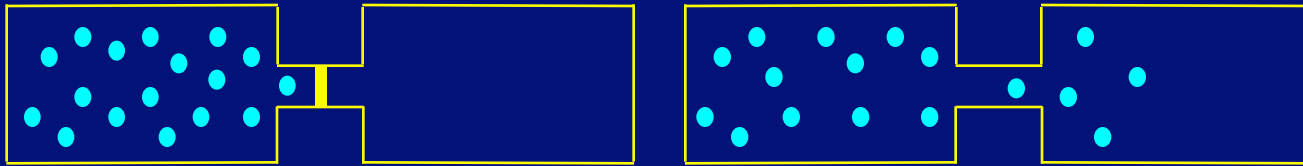
- a) The atoms repel each other, so the gas expands to fill up the available space.
- b) The atoms move around randomly, so they just end up all over the place by accident.
- c) The energy of the system is lowered when the gas fills all the available space.

Choices a and c are wrong. In fact, there is a small *attraction* between molecules.

The molecules just distribute themselves randomly and quite uniformly. There are simply **more ways to spread out** the gas than to compress it.

Act 3: Free Expansion of a Gas

Free expansion occurs when a valve is opened allowing a gas to expand into a bigger container.

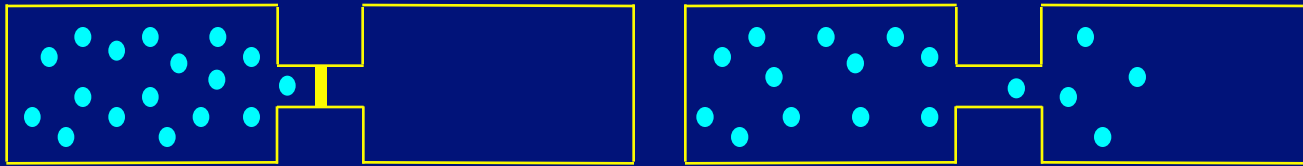


Such an expansion is:

- A) Reversible, because the gas does no work and thus loses no energy.
- B) Reversible, because there is no heat flow from outside.
- C) Irreversible, because the gas won't spontaneously go back into the smaller volume.

Solution

Free expansion occurs when a valve is opened allowing a gas to expand into a bigger container.



Such an expansion is:

- A) Reversible, because the gas does no work and thus loses no energy.
- B) Reversible, because there is no heat flow from outside.
- C) Irreversible, because the gas won't spontaneously go back into the smaller volume.

Because there are many fewer “microstates”.

But WHY do we necessarily get half of the molecules on each side...

Counting and Probability

We've seen that nature often picks randomly from the possible outcomes:

- Position of a gas atom

- Direction of a gas atom velocity

We will use this fact to calculate probabilities.

- This is a technique that good gamblers know about.

- We will use the same counting-based probability they do.

This is not like the stock market or football!

We will end up with extremely precise and very general laws-not fuzzy guesswork.

Act 4: Rolling Dice

Roll a pair of dice . What is the most likely result for the sum?
(As you know, each die has an equal possibility of landing on 1 through 6.)

A) 2 to 12 equally likely B) 7 C) 5

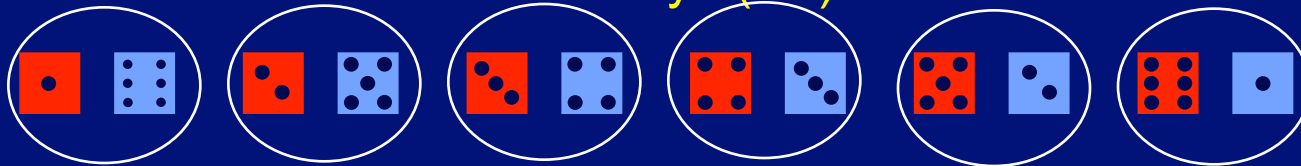
Solution

Roll a pair of dice . What is the most likely result for the sum?
(As you know, each die has an equal possibility of landing on 1 through 6.)

A) 2 to 12 equally likely **B) 7** C) 5

Why is 7 the most likely result?

Because there are more ways (six) to obtain it.



How many ways can we obtain a six? (only 5)



Important Nomenclature Slide

When we roll dice, we only care about the sum, not how it was obtained. This will also be the case with the physical systems we study in this course. For example, we care about the internal energy of a gas, but not about the motion of each atom.

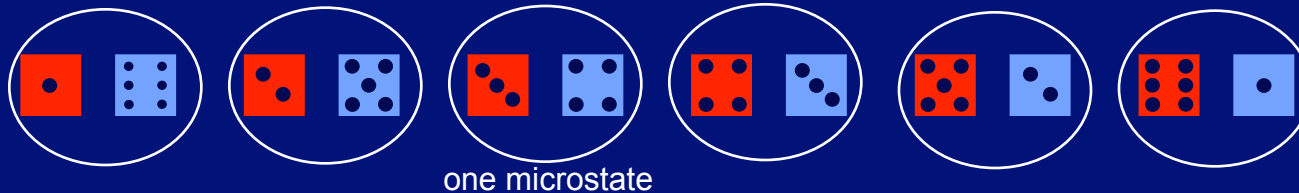
Definitions:

Macrostate: The set of quantities we are interested in (e.g., p , V , T).

Microstate: A specific internal configuration of the system, with definite values of all the internal variables.

Dice example:

These microstates all correspond to the “seven” macrostate.



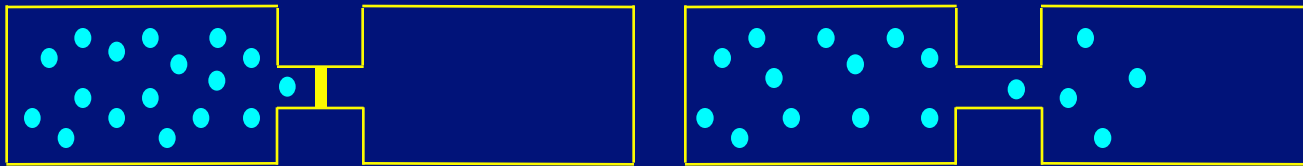
Due to the randomness of thermal processes:

Every microstate is equally likely. Therefore the probability of observing a particular macrostate is proportional to the number of corresponding microstates.

The Meaning of Equilibrium (1)

An Introduction to Statistical Mechanics

In the free expansion of a gas, why do the particles tend towards equal numbers in each equal-size box?



Let's study this mathematically.

Consider four particles, labeled A, B, C, and D. They are free to move between halves of a container. What is the probability that we'll find three particles on the left and one on the right? (That's the macrostate).

A complication that we can ignore:

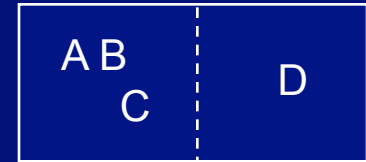
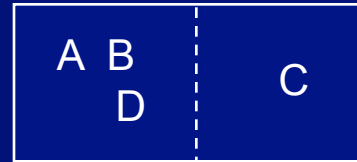
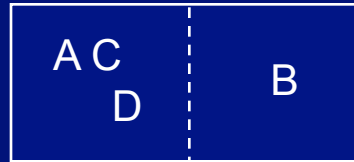
We don't know how many 'states' a particle can have on either side, but we do know that it's the same number on each side, because the volumes are equal. To keep things simple, we'll call each side one state. This works as long as both sides are the same.



one microstate

The Meaning of Equilibrium (2)

Four microstates have exactly 3 particles on the left:



We'll use the symbol $\Omega(N, N_L)$ to represent the number of microstates corresponding to a given macrostate. $\Omega(4, 3) = 4$.

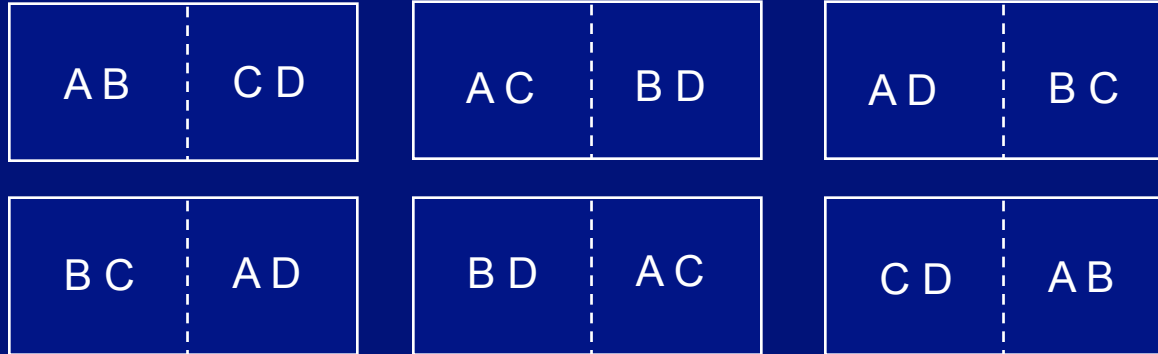
How many microstates are there with exactly 2 particles on the left?



Use the workspace to find $\Omega(4, 2) = \underline{\hspace{2cm}}$.

Solution

$$\Omega(4,2) = 6:$$



This can be solved using the binomial formula, because each particle has two choices.

$$\Omega(N, N_L) = {}_N C_{N_L} \equiv \frac{N!}{N_L!(N - N_L)!} = \frac{4!}{2!(4 - 2)!} = 6$$

Many systems are described by binary distributions:

- Random walk
- Coin flipping
- Electron spin

The Meaning of Equilibrium (3)

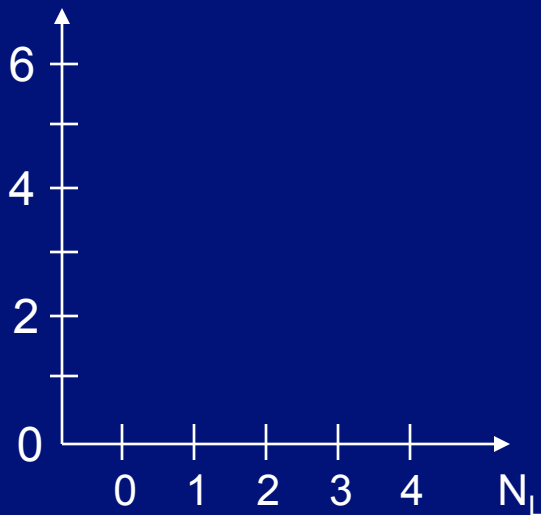
Now you can complete the table:

N_L	0	1	2	3	4
$\Omega(4, N_L)$					

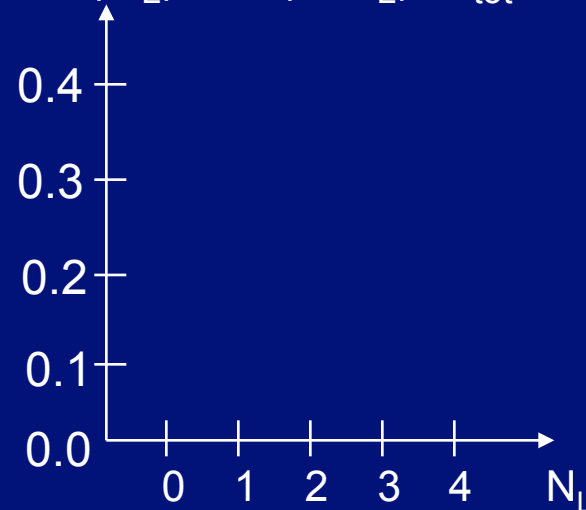
The total number of microstates for this system is $\Omega_{\text{tot}} =$ _____

Plot your results:

$\Omega(4, N_L)$ # microstates



$P(N_L) = \Omega(4, N_L) / \Omega_{\text{tot}}$ Probability



Solution

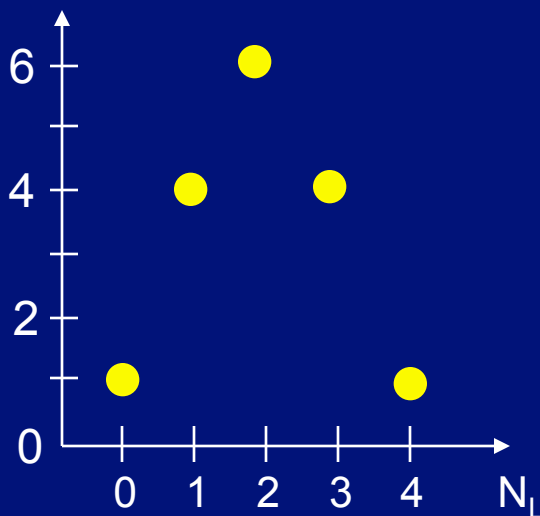
Now you can complete the table:

N_L	0	1	2	3	4
$\Omega(4, N_L)$	1	4	6	4	1

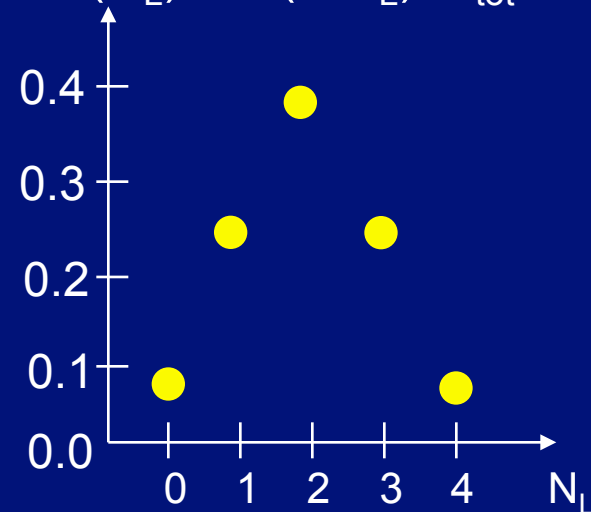
The total number of microstates for this system is $\Omega_{\text{tot}} = \underline{2^N = 16}$

Plot your results:

$\Omega(4, N_L)$ # microstates



$P(N_L) = \Omega(4, N_L) / \Omega_{\text{tot}}$ Probability



The Meaning of Equilibrium (4)

You just plotted what is called an **Equilibrium Distribution**.
It was done assuming that all microstates are equally likely.

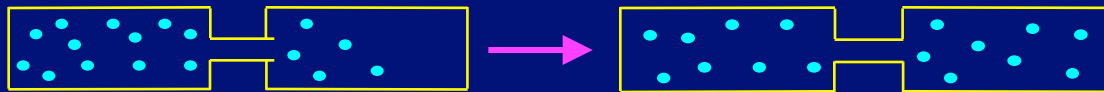
The basic principle of statistical mechanics:

For an isolated system in thermal equilibrium,
each microstate is equally likely.

An isolated system that is out of thermal equilibrium
will evolve irreversibly toward equilibrium.

We'll understand why this is as we go forward.

For example, a freely expanding gas is not in equilibrium
until the density is the same everywhere.



This principle also explains why heat flows from hot to cold.

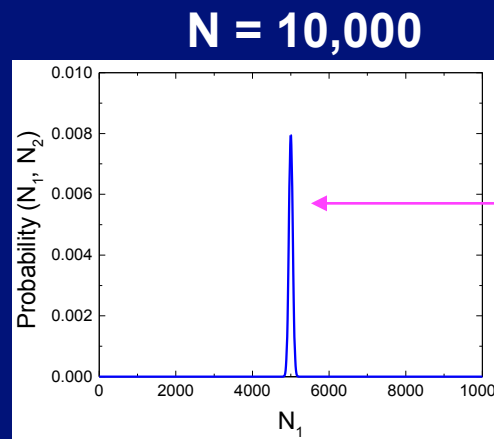
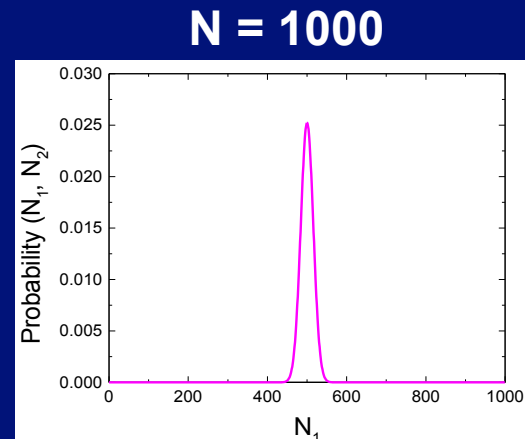
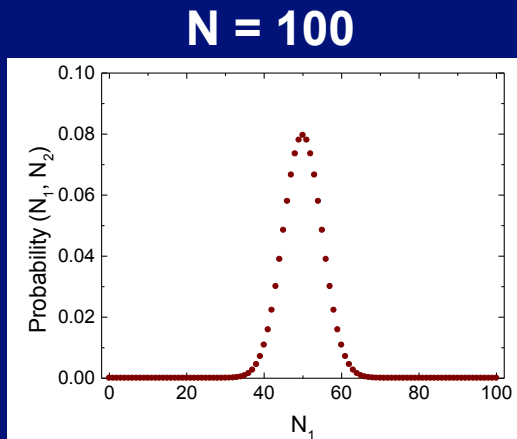
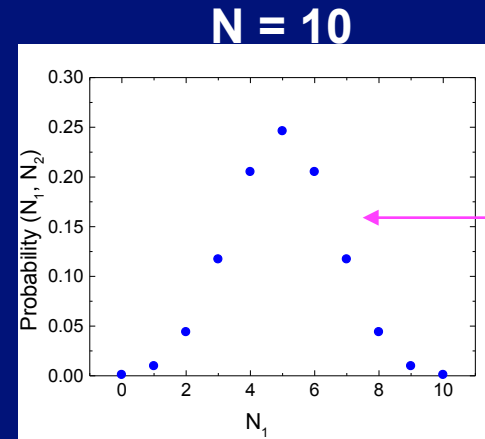
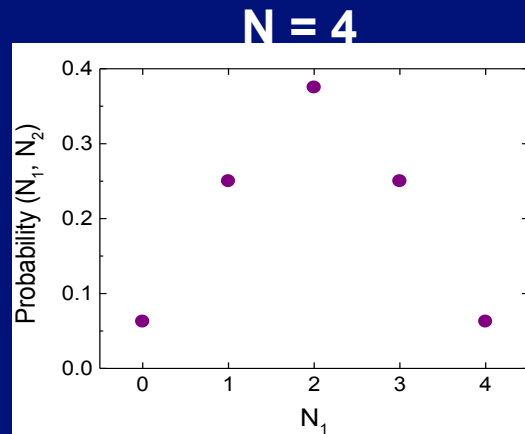
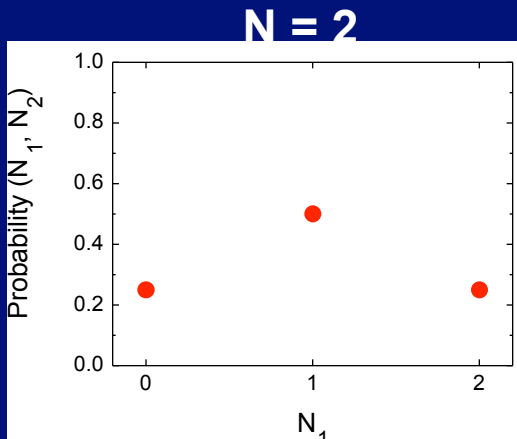
Equilibrium for Large N

Here are the probability distributions for various number of particles (N).

- The width of a peak is proportional to $\sqrt{N}$.
- The fractional width is proportional to $\sqrt{N}/N = 1/\sqrt{N}$.

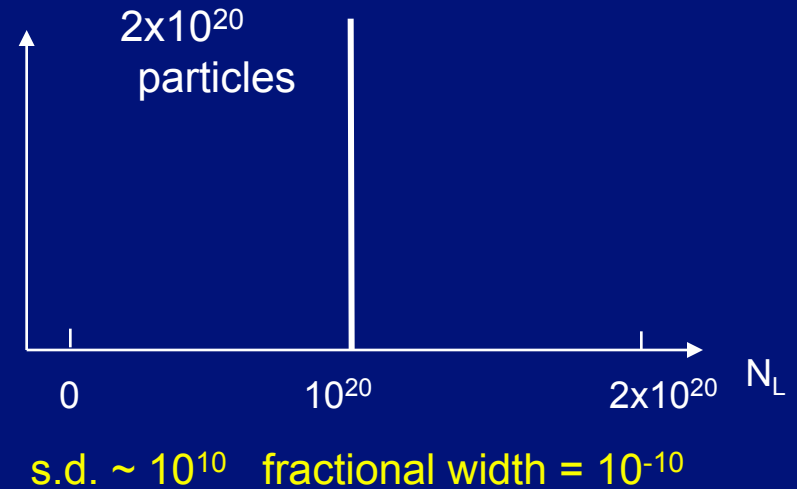
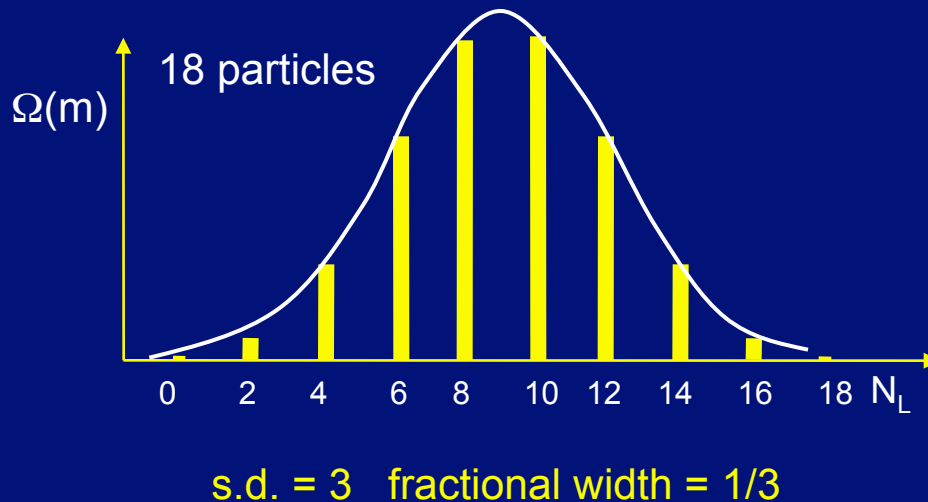
This means that for very large N (e.g., 10^{23}), the effects of randomness are often difficult to see.

$$P(N, n_L) = \frac{{}_N C_{n_L}}{2^N} = \frac{N!}{(N - n_L)! n_L!} \frac{1}{2^N}$$



Equilibrium Values of Quantities

We have seen that thermal equilibrium is described by probability distributions. Given that, what does it mean to say that a system has a definite value of some quantity (e.g., particles in left half of the room)? The answer comes from the large N behavior of the probability distribution.



For large N , the equilibrium distribution looks remarkably sharp. In that case, we can accurately define an “Equilibrium Value”. The equilibrium value here is $N_L = N/2$.

Equilibrium Summary

Definitions:

Macrostate: The set of quantities we are interested in (e.g., p , V , T).

Microstate: A specific internal configuration of the system, with definite values of all the internal variables.

Assume:

Due to the randomness of thermal processes,

every microstate is equally likely. Therefore the probability of observing a particular macrostate is proportional to the number of corresponding microstates.

$$P(A) = \Omega_A / \Omega_{\text{tot}}$$

If we have systems with large numbers of particles, then the resulting probability distribution can be very peaked $\rightarrow$ equilibrium (single) 'value'

Many systems are described by *binary* distributions:

- Random walk
- Coin flipping
- Electron spin

This can be solved using the binomial formula, because each particle has two choices:

$$\Omega(N, N_L) = {}_N C_{N_L} \equiv \frac{N!}{N_L! (N - N_L)!}$$

$$\Omega_{\text{tot}} = 2^N$$

Example: Electron Spin

Electrons have spin and associated magnetic moment μ .
They can only point “up” or “down”:*

↑ or ↓

Consider a system of $N=9$ spins: ↑ ↑ ↓ ↓ ↑ ↓ ↑ ↑ ↓

One
microstate

Similar to HHTTHTHHT
in a coin flipping experiment:

The total magnetic moment (what we can measure) is:

$$M = (N_{\text{up}} - N_{\text{down}})\mu \equiv m\mu$$

$$m = \text{“spin excess”} = N_{\text{up}} - N_{\text{down}}$$

A macrostate is described by m . The microstate above has $m = +1$.

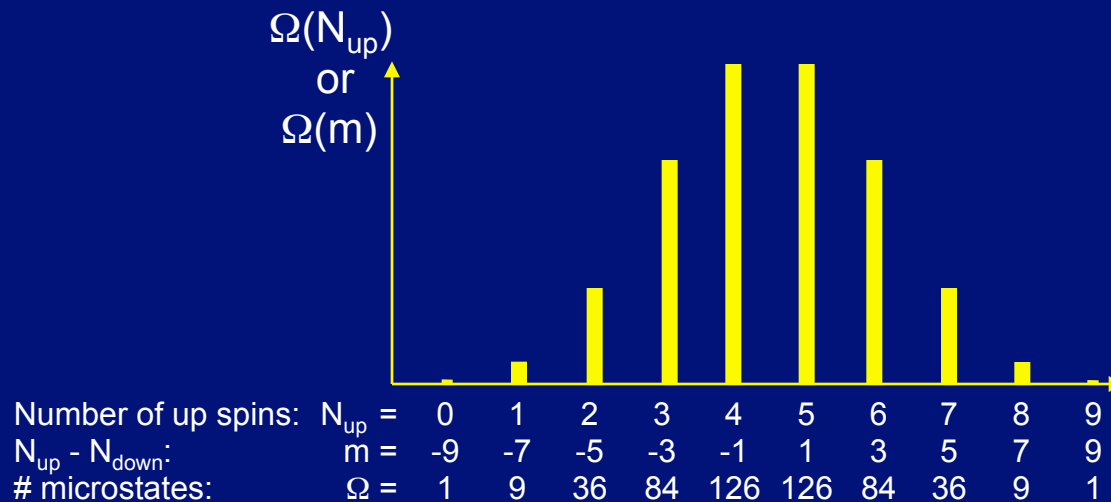
*This is a result from P214 that you’ ll have to take on faith.

Electron Spin (2)

Count microstates for each value of m :

$$\Omega(N_{\text{up}}) = \frac{N!}{N_{\text{up}}! N_{\text{down}}!} \Rightarrow \Omega(m) = \frac{N!}{\left(\frac{N+m}{2}\right)! \left(\frac{N-m}{2}\right)!}$$

$$P(N_{\text{up}}) = \frac{N!}{N_{\text{up}}! N_{\text{down}}!} \left(\frac{1}{2^N}\right)$$



Each macrostate is described by m .
(what we measure).

This problem will become more interesting later in the course. We will put the spins in a magnetic field. The energy of spin up will not equal the spin down energy, and the probabilities will change.

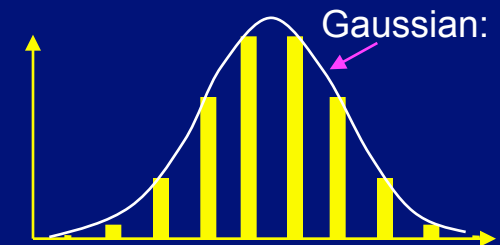
Gaussian Approximation to the Binomial Distribution

When N is large, the binomial formula becomes impossible to evaluate on a calculator.

$$\Omega(N_{\text{up}}) = \frac{N!}{N_{\text{up}}! N_{\text{down}}!} \Rightarrow P(N_{\text{up}}) = \frac{N!}{N_{\text{up}}! N_{\text{down}}!} \left(\frac{1}{2^N} \right)$$

Fortunately, when N is large the shape of the distribution becomes a Gaussian:

$$\Omega(m) = 2^N \left(\frac{2}{\pi N} \right)^{1/2} e^{-m^2 / 2N} \Rightarrow P(m) = \left(\frac{2}{\pi N} \right)^{1/2} e^{-m^2 / 2N}$$



This expression can be evaluated for very large N (e.g., 10^{23}).

Does it work? Try $N = 20$, $m = 2$:

Binomial: $\Omega(1) = 167960$, $P(1) = 0.160$

Gaussian: $\Omega(1) = 169276$, $P(1) = 0.161$

Ex:

$N = 10^{10}$, $m = 10^5$

$P(m) = 8.0 \times 10^{-6}$

The agreement improves as N increases.

Next Week

Entropy and Exchange between systems

- Counting microstates of combined systems
- Volume exchange between systems
- Definition of Entropy and its role in equilibrium

Exercise: Random Walk

Suppose that a particle is undergoing a 1-dimensional random walk (equally likely steps in the + or minus directions.)

What is the probability:

1) that after N steps it is exactly where it started? Evaluate it for $N=10$.

2) that after N steps it is within 2 steps of the maximum possible positive position? Evaluate it for $N=10$.

Solution

Suppose that a particle is undergoing a 1-dimensional random walk (equally likely steps in the + or minus directions.)

What is the probability:

1) that after N steps it is exactly where it started? Evaluate it for $N=10$.

There are 2^N total microstates. We want $N_+ = N_- = N/2$. The probability that this happens is:

$$P(0) = \frac{N!}{\left(\frac{N}{2}!\right)^2 2^N} = 0.246$$

2) that after N steps it is within 2 steps of the maximum possible positive position? Evaluate it for $N=10$.

Solution

Suppose that a particle is undergoing a 1-dimensional random walk (equally likely steps in the + or minus directions.)

What is the probability:

1) that after N steps it is exactly where it started? Evaluate it for $N=10$.

There are 2^N total microstates. We want $N_+ = N_- = N/2$. The probability that this happens is:

$$P(0) = \frac{N!}{\left(\frac{N}{2}!\right)^2 2^N} = 0.246$$

2) that after N steps it is within 2 steps of the maximum possible positive position? Evaluate it for $N=10$.

We must sum the three probabilities: $P(N) + P(N-1) + P(N-2)$.

$P(N)$	$= 1/2^N$	one microstate
$P(N-1)$	$= 0$	$N_+ - N_-$ must be even when N is even.
$P(N-2)$	$= N/2^N$	N microstates: $N_+ = N-1$ and $N_- = 1$.

The sum is $P(N-2:N) = \frac{N+1}{2^N} = 0.011$

Exercise: Random Walk (2)

Do the previous exercise when $N = 10^6$.

For what value of m is $P(m)$ half of $P(0)$?

Solution

Do the previous exercise when $N = 10^6$.

There is no way that we are going to evaluate $2^{1,000,000}$.

We must use the Gaussian approximation: $P(m) = \left(\frac{2}{\pi N}\right)^{1/2} e^{-m^2/2N}$

$$1) m = 0: P(0) = \left(\frac{2}{\pi 10^6}\right)^{1/2} = 8 \times 10^{-4}$$

$$2) m = N \text{ and } m = N-2: P(N) = \left(\frac{2}{\pi 10^6}\right)^{1/2} e^{-10^6/2} = 0 \text{ for all practical purposes.}$$

For what value of m is $P(m)$ half of $P(0)$?

$$\text{We want } e^{-m^2/2N} = \frac{1}{2} \Rightarrow m = \sqrt{2 \ln(2)} \sqrt{N} = 1.177 \sqrt{N} = 1177$$

Example: Probability & Microstates

The typical baseball player gets a hit 25% of the time. If this player gets several hits in a row, he is said to be “on a streak”, and it’s attributed to his skill.

1) What is the probability that this player will get a hit exactly 25% of the time if he tries 20 times (i.e., 5 hits and 15 misses)?

2) What is the probability that this player will get five hits (no misses) in a row?

Solution

The typical baseball player gets a hit 25% of the time. If this player gets several hits in a row, he is said to be “on a streak”, and it’s attributed to his skill.

1) What is the probability that this player will get a hit exactly 25% of the time if he tries 20 times (i.e., 5 hits and 15 misses)?

The probability of obtaining a particular microstate (five hits and 15 misses, in a specific order) is $0.25^5 \times 0.75^{15} = 1.3 \times 10^{-5}$. Now, count microstates (different orderings of hits and misses): $N = 20! / (5! \times 15!) = 15,504$. Each microstate is equally likely, so the probability is $1.3 \times 10^{-5} \times 15,504 = 0.20$.

Here’s one microstate: MMMMMHMHMMMHHMMMMHMM

2) What is the probability that this player will get five hits (no misses) in a row?

There is only one way to do this (one microstate). The probability is: $P = 0.25^5 = 0.00098$. That’s fairly small (about one in a thousand) for a particular player, but not unlikely to happen by chance somewhere on a particular day, if one remembers that there are more than 1000 “at bats” every day in major league baseball.