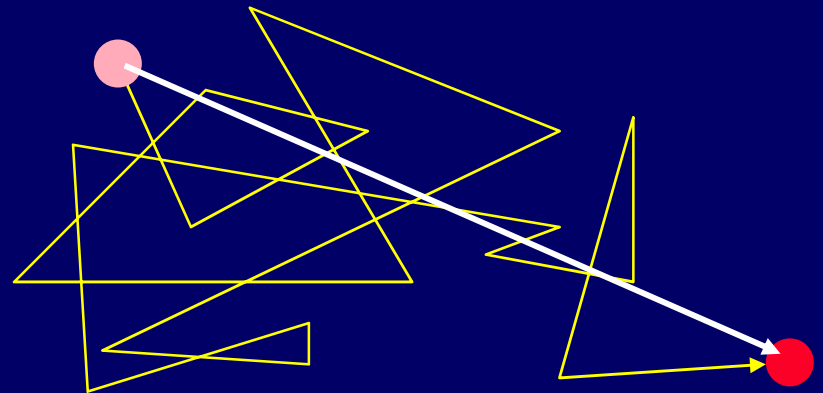


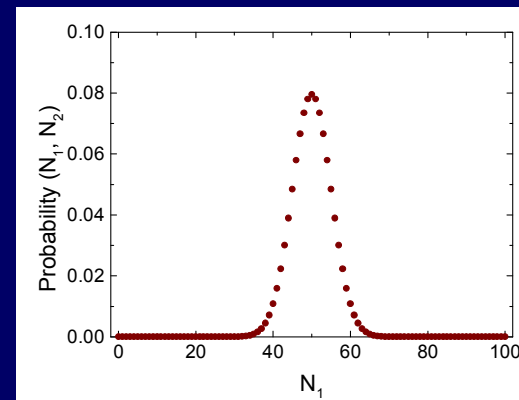
# Lecture 5:

## Statistical Processes

- Random Walk and Particle Diffusion
- Counting and Probability
- Microstates and Macrostates
- The meaning of equilibrium



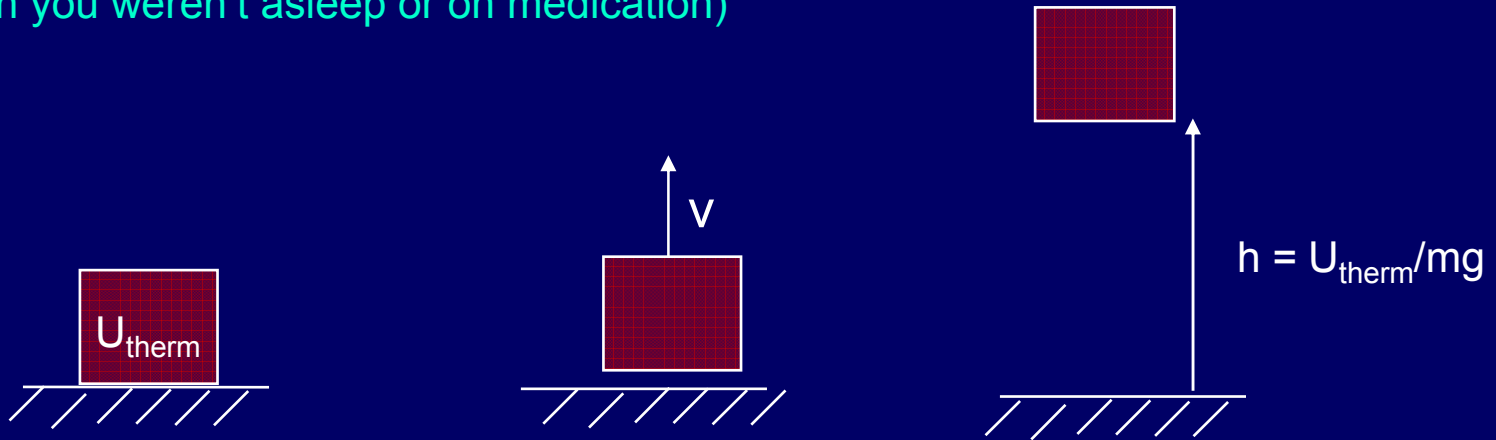
Reading: Elements Ch. 5



# 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 (movie). 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:  $\text{Fe} + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$

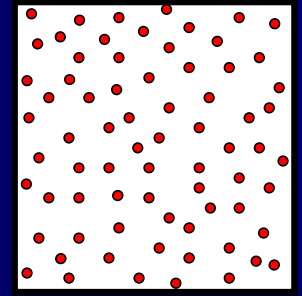
# Brownian Motion

- 1828 Robert Brown (English botanist) noticed that pollen seeds in still water exhibited an incessant, irregular “swarming” motion.
- There were several suggestion explanations, but none really worked until...
- 1905: Einstein, assuming the random motion of as-yet-unobserved molecules making up the water, was able to precisely explain the motion of the pollen --- as a diffusive random walk.
- Einstein’s concrete predictions (he suggested measuring the mean-square displacements of the particles) led Jean Perrin to experiments confirming kinetic theory and the existence of atoms!

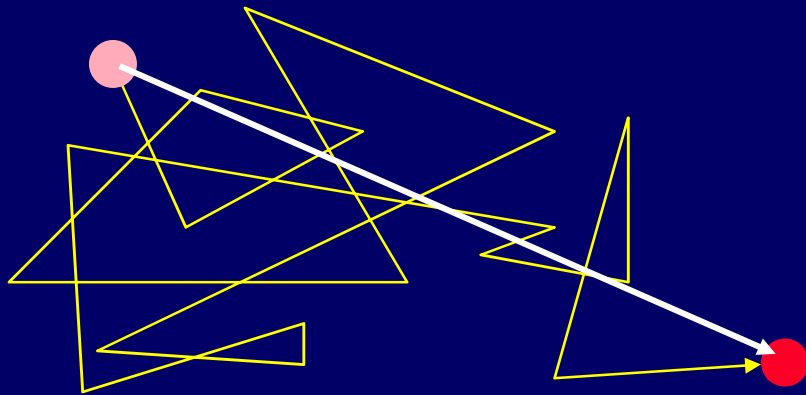
# The Random Walk Problem (1)

We'll spend a lot of time in P213 studying random processes.

As an example, consider a gas. The molecules bounce around randomly, colliding with other molecules and the walls.



How far on average does a single molecule go in time?



This picture can also apply to:

- impurity atoms in an electronic device
- defects in a crystal
- sound waves carrying heat in solid!

The motion that results from a random walk is called diffusion.

# The Random Walk Problem (2)

We'll analyze a simplified model of diffusion.

A particle travels a distance  $\ell$  in a straight line, then scatters off another particle and travels in a new, random direction.

Assume the particles have average speed  $v$ . As we saw before, there will be a distribution of speeds. We are interested in averages.

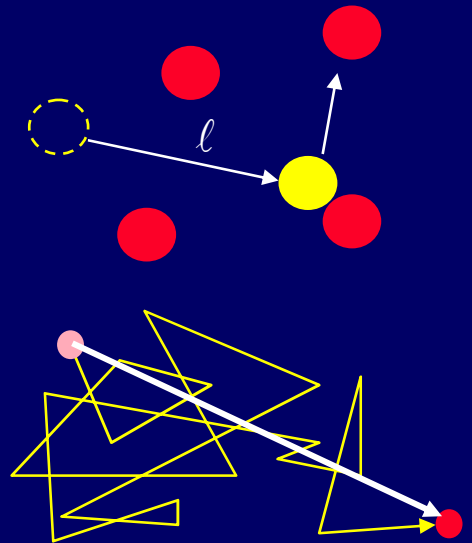
Each step takes an average time  $\tau = \frac{\ell}{v}$

Note:  $\ell$  is also an average, called the "mean free path".

We'd like to know how far the particle gets after time  $t$ .

First, answer a simpler question:

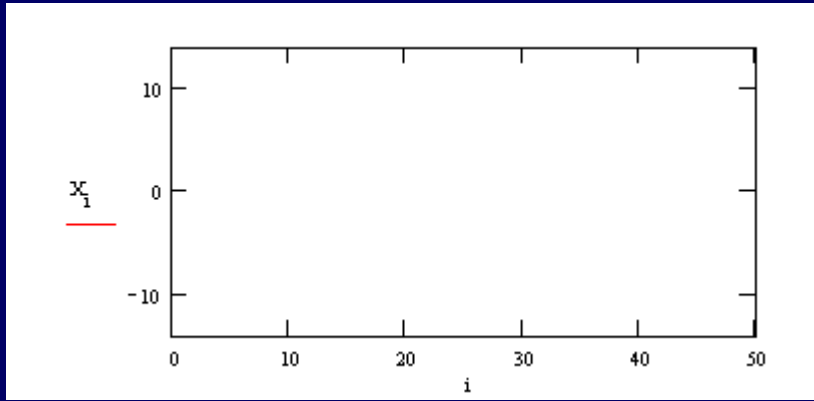
How many steps,  $M$ , will the particle have taken?  $M = \frac{t}{\tau}$



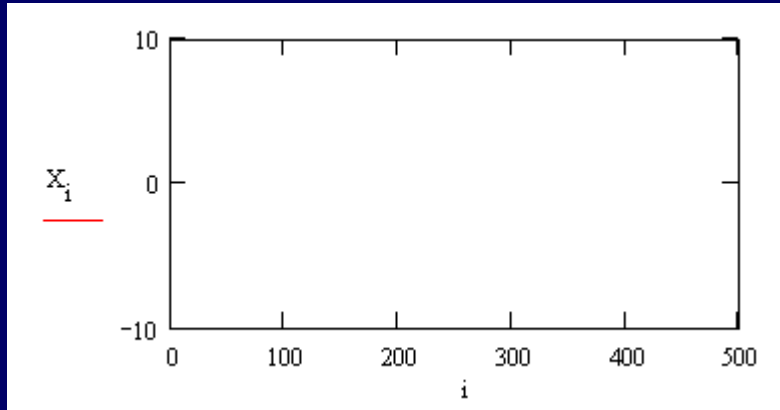


# Random Walk Simulation

Random walk with constant step size ( $\ell$  always the same):



Random walk with random step size ( $\ell$  varies, but has the same average):

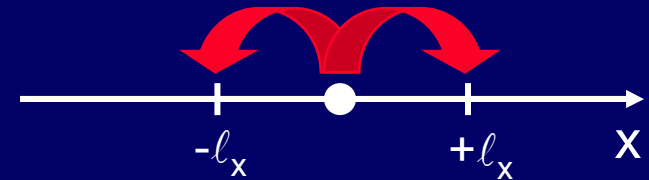


# The Random Walk Problem (3)

Simplify the problem by considering 1-D motion and constant step size.

At each step, the particle moves  $s_i = \pm l_x$

After M steps, the displacement is  $x = \sum_{i=1}^M s_i$



Repeat it many times and take the average:

The average (mean) displacement is:  $\langle x \rangle = \left\langle \sum_{i=1}^M s_i \right\rangle = 0$

Cross terms cancel,  
due to randomness.

The average squared displacement is:  $\langle x^2 \rangle = \left\langle \sum_{i=1}^M s_i \sum_{j=1}^M s_j \right\rangle = \left\langle \sum_{i=1}^M s_i^2 \right\rangle + \left\langle \sum_{i \neq j} s_i s_j \right\rangle = M l_x^2$

The average distance is the square root

(the “root-mean-square” displacement)  $x_{\text{rms}} = \sqrt{\langle x^2 \rangle} = M^{1/2} l_x = \sqrt{\frac{t}{\tau}} l_x$

The average distance moved is proportional to  $\sqrt{t}$ .

Note:

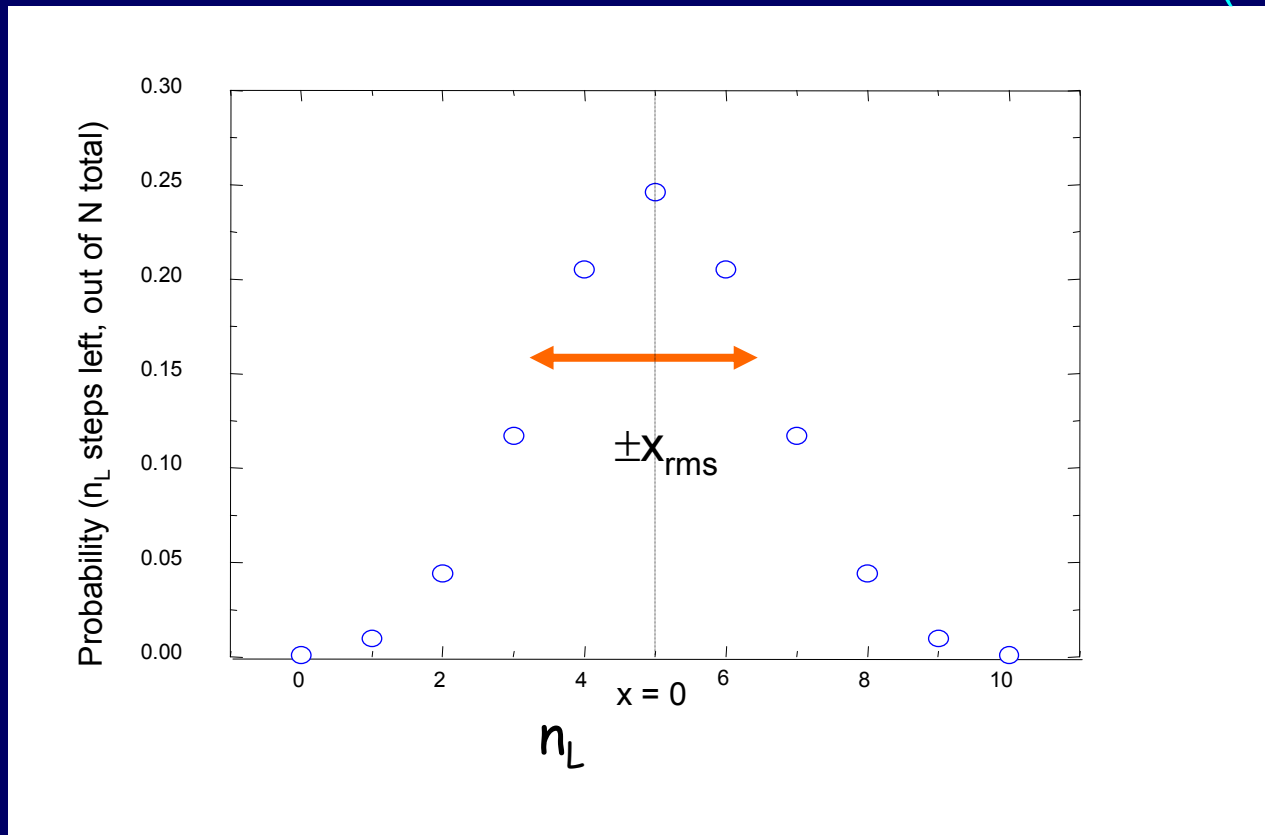
This is the same square root we obtained last lecture when we looked at thermal conduction. It's generic to diffusion problems.

# The Random Walk Problem (4)

Look at the distribution of displacements after 10 steps.

$n_L = \#$  steps left.  $x = 0$  when  $n_L = 5$

$$P(n_L) = \frac{{}^{10}C_{n_L}}{2^{10}} = \frac{10!}{(10-n_L)!n_L!} \frac{1}{2^{10}}$$



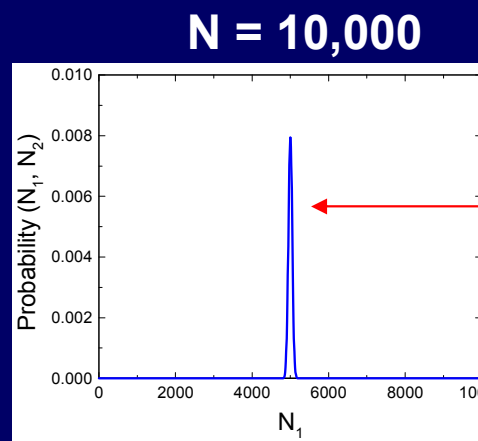
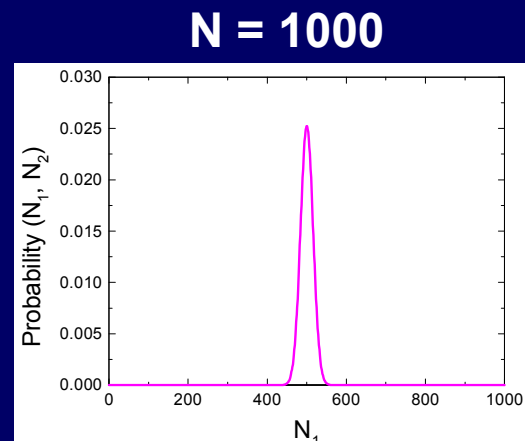
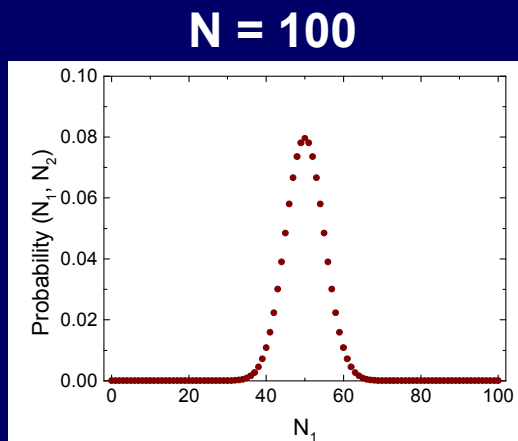
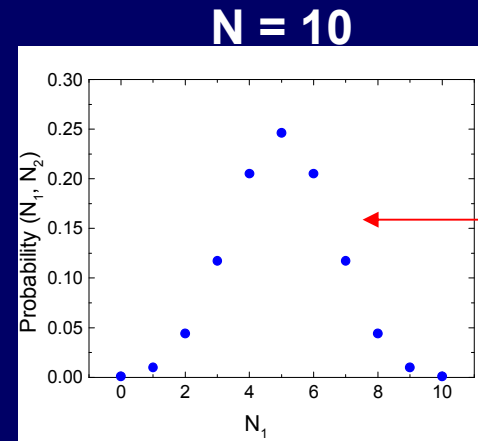
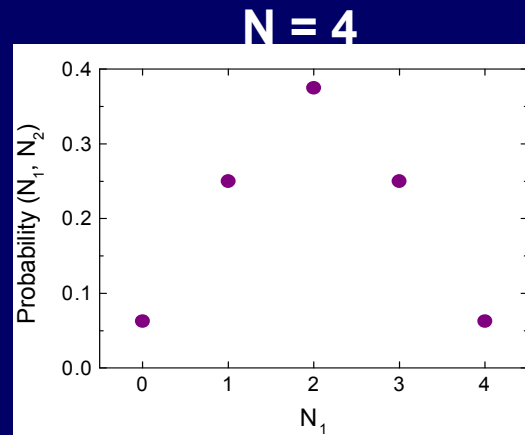
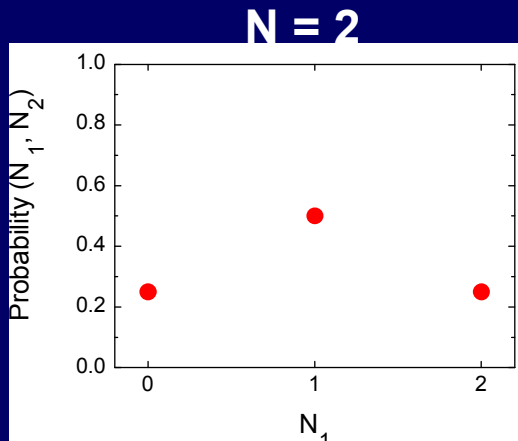
Consider what happens to this distribution as the number of steps becomes large.

# The Random Walk Problem (5)

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

- The width ( $x_{\text{rms}}$ ) 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.

Important to remember:  
These peaks are all centered at  $x = 0$ .  
The distribution spreads out with time.



# The Diffusion Constant

The solution to the 3-D random walk, with varying  $\ell$  and  $v$ , is similar (but the math is messier).

The mean square displacement along  $x$  is still proportional to  $t$ :

$$\langle x^2 \rangle = 2Dt, \text{ where } D = \frac{\ell^2}{3\tau} = \frac{1}{3}v\ell$$

These are the average values of  $\tau$ ,  $v$ , and  $\ell$ .

$D$  is called the diffusion constant\*.

$$x_{rms} = \sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$$

The 3-D displacement (along  $x$ ,  $y$ , and  $z$  combined) is:

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 6Dt$$

\* The numerical coefficients in general depend on the *distribution* of distances and time intervals. For Phys. 213 we'll use the form above.

# ACT 2: Lifetime of batteries

Batteries can lose their charge when the separated chemicals (ions) within them diffuse together. If you want to preserve the life of the batteries when you aren't using them, you should...

(A) Refrigerate them

(B) Slightly heat them

# Solution

Batteries can lose their charge when the separated chemicals (ions) within them diffuse together. If you want to preserve the life of the batteries when you aren't using them, you should...

(A) Refrigerate them

(B) Slightly heat them

The diffusion time  $t \sim \langle x^2 \rangle / 2D$ .

$$D = \frac{1}{3} v \ell$$

From equipartition:

$$\frac{1}{2} m v^2 = \frac{3}{2} kT \Rightarrow v = \sqrt{3kT/m}$$

Therefore  $t \sim 1/D \sim 1/v \sim 1/\sqrt{T} \rightarrow$  cooling the batteries can reduce the diffusion constant, increasing the lifetime.

## FYI: Batteries...

Does putting batteries in the freezer or refrigerator make them last longer?

- It depends on which type of batteries and at what temperature you normally store them.
- Alkaline batteries stored at  $\sim 20^{\circ}\text{C}$  (room temp) discharge at about 2%/year. However, at  $38^{\circ}\text{C}$  ( $100^{\circ}\text{F}$ ) the rate increases to 25%/year.
- NiMH and Nicad batteries, start to lose power when stored for only a few days at room temperature. But they will retain a 90% charge for several months if you keep them in the freezer after they are fully charged. *If you do decide to store your charged NiMH cells in the freezer or refrigerator, make sure you keep them in tightly sealed bags so they stay dry. And you should also let them return to room temperature before using them.*



# 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 3: 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

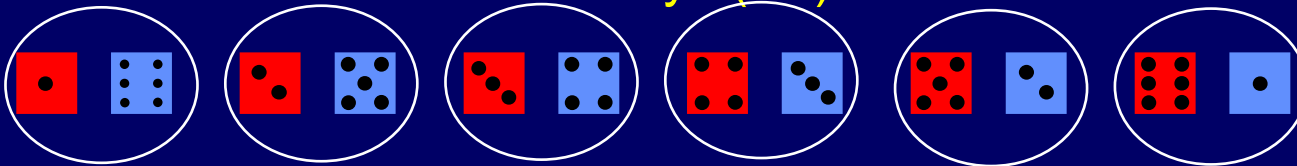
# Solution

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.)

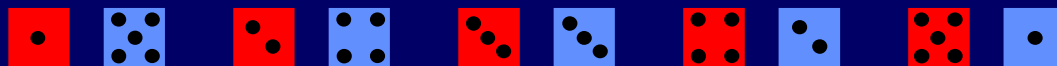
A) 2 to 12 equally likely   **B) 7**   C) 5

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.

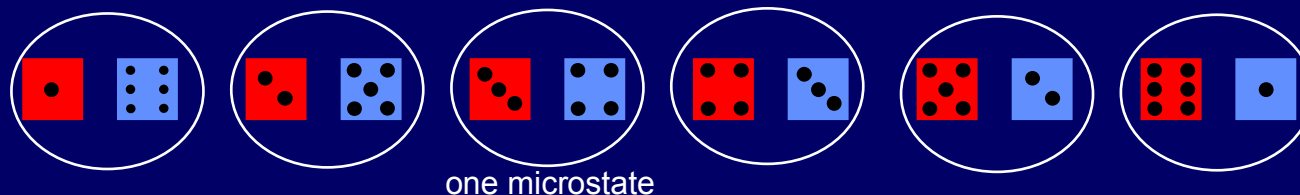
Definitions:

**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.



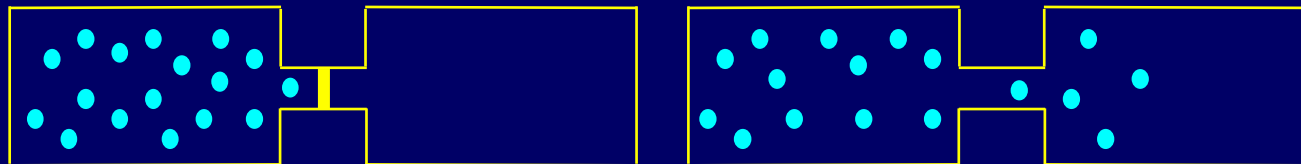
Due to the randomness of thermal processes:

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?



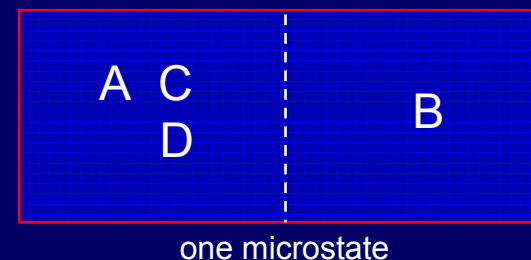
Let's study this mathematically.

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).

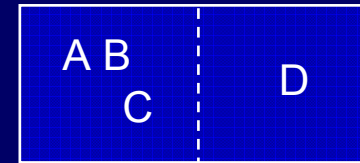
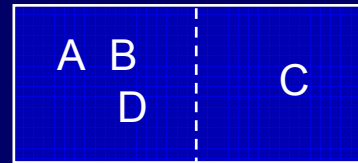
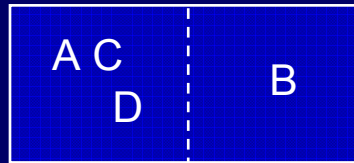
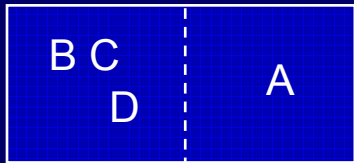
A complication that we can ignore:

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.



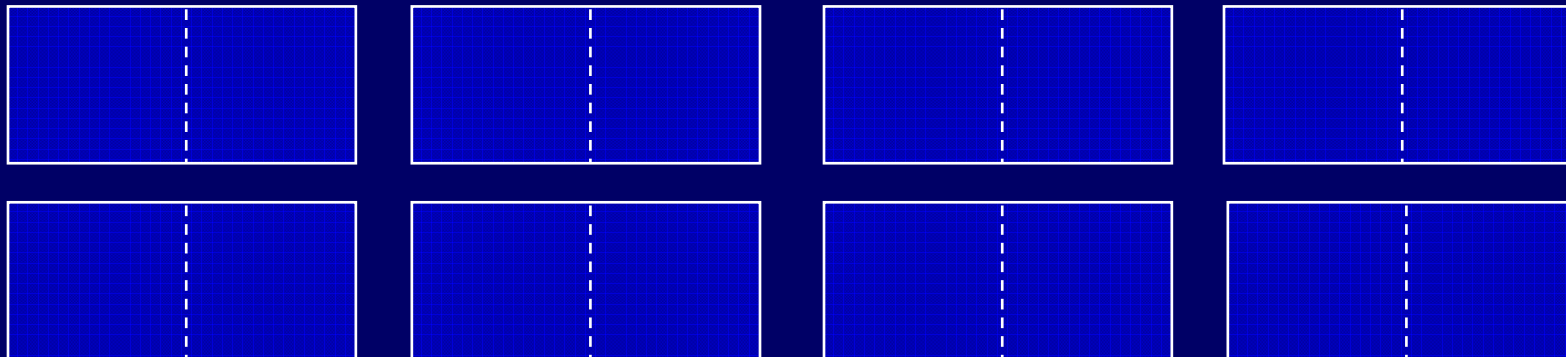
# The Meaning of Equilibrium (2)

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.  $\Omega(4, 3) = 4$ .

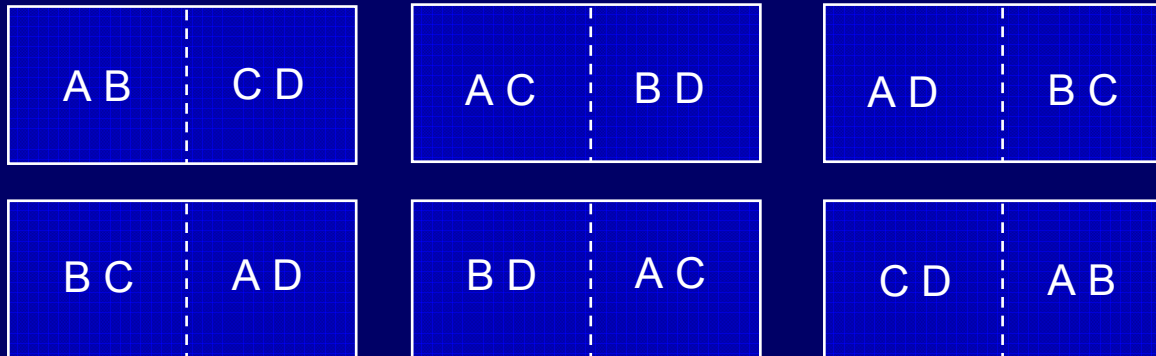
How many microstates are there with exactly 2 particles on the left?



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

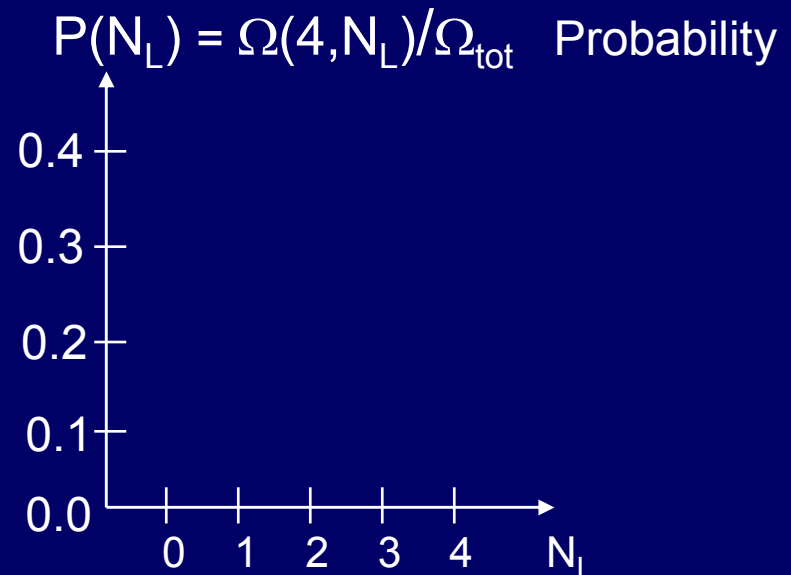
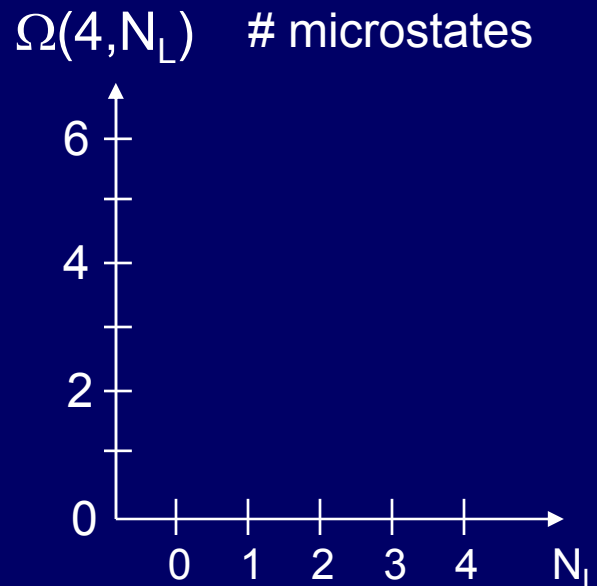
# The Meaning of Equilibrium (3)

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  $\Omega_{\text{tot}} = \underline{\hspace{2cm}}$

Plot your results:





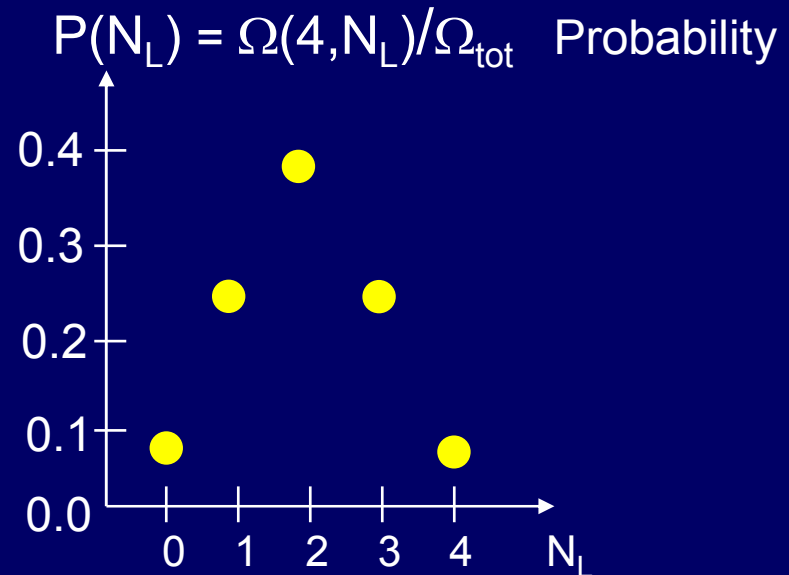
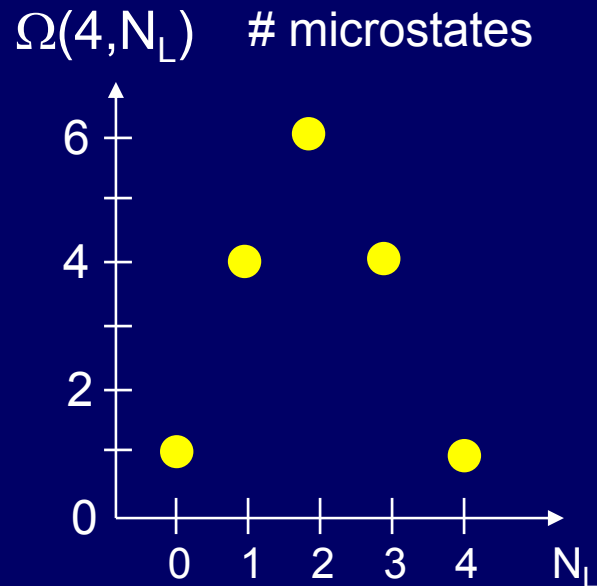
# Solution

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:



# The Meaning of Equilibrium (4)

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

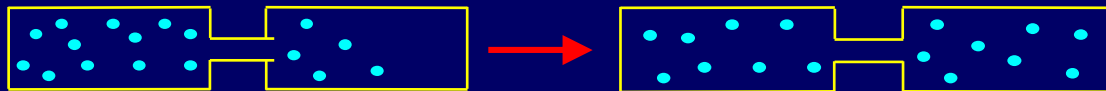
The basic principle of statistical mechanics:

**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.

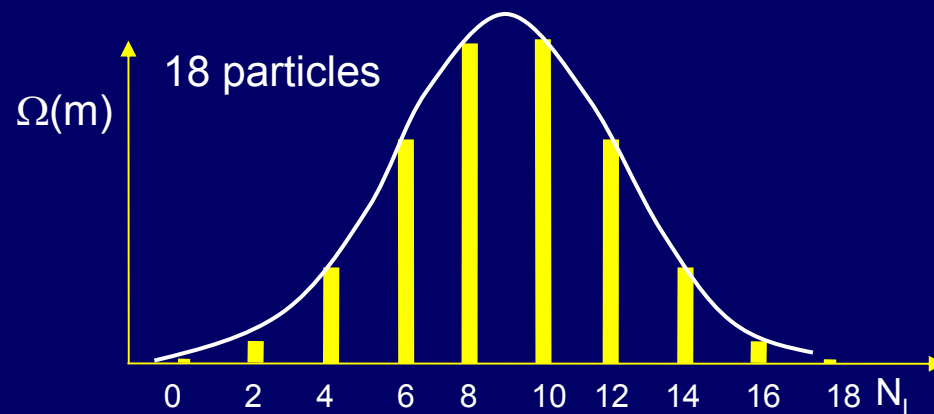
For example, a freely expanding gas is not in equilibrium until the density is the same everywhere.



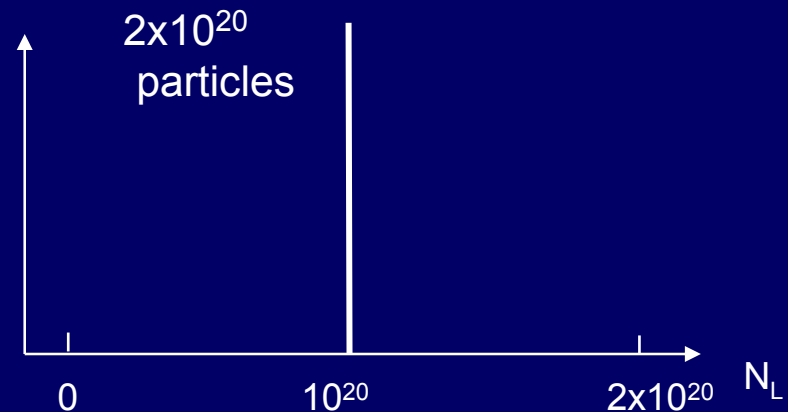
This principle also explains why heat flows from hot to cold.

# Equilibrium 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.



s.d. = 3 fractional width = 1/3



s.d.  $\sim 10^{10}$  fractional width =  $10^{-10}$

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

# Next Week

## Entropy and Exchange between systems

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