Review

- We discussed the number of ways to combine things - distinguishable things (like cars)
- We added a dimension to this question, grouping some of the things under a category and asking how many combinations exist such that you can rearrange things in the group and not change the order of things outside the group
- We derived some useful formulas:
  - $W = N!$ (number of ways to combine $N$ unique things in $N$ micro-states)
  - $W = N!/N_i!$ (number of ways to combine $N$ unique things, where $N_i$ of them lie in a group whose order doesn't affect the order of the other things)
  - $W = N!/\prod_{i=1}^{M} N_i!$ (number of way to combined $N$ unique things when $M$ groupings are present, such that the order or things in each group doesn't affect the order of things outside the groups)
- Two-state case:
  $$ W_n^N \equiv \binom{N}{n} = \frac{N!}{n!(N-n)!} $$
  (the binomial coefficient)

Definitions

- Micro-state: each individual way of obtaining a distribution
  - Consider four distinguishable objects. There are $4!$ micro-states
- Macro-state: the property of the system that doesn't depend on the exact microscopic states
  - e.g. in our analogy, "getting free food for cars 1,2,3" doesn't depend on how those cars are ordered in the free-food parking
spots.
- for physics: volume, number of particles, energy, average pressure, average temperature, average density

**The Most Probable State**

In our example, we assumed that any micro-state was equally likely (e.g. there is no reason to prefer 1,2,3,4 over 1,2,4,3, etc.). Under that condition, we find that there are macro-states that can be obtained by a maximum number of micro-states. The macro-state that can be obtained by the maximum number of micro-states is defined as EQUILIBRIUM.

Some examples of equilibrium:

- Start all the air in a room on one side of the room (say, by imposing a thin but impenetrable barrier in the center of the room, filling one half, and then sliding the barrier out of the way. Assuming no external forces act on the room, the gas will reach a state where equal numbers of molecules lie on either side of the room. This happens because that macro-state can be achieved by the most number of micro-states, and so is the most likely.

- More generally, begin a bunch of individual particles in different energy states - say, half in their ground states and half in their 37th quantum level - and over time the system will enter into its equilibrium (most likely) macro-state.

**Discussion about Probability**

Let's continue thinking about distinguishable particles a bit longer. Specifically, consider a large number of distinguishable particles in equilibrium. With such systems, we are very interested in the following questions:

- **QUESTION:** How is energy distributed among the particles in the system when it is in equilibrium?

We can explore that question conceptually for a moment. What do we need to know?

**DISCUSSION:** What do we need to know to compute the probability of
finding a particle in a given energy state?

GUIDE:

- in general, probability is given by the "number of ways of obtaining a subset, $a$" divided by the "total number of ways to obtain all possibilities".
- In our specific case, we want to know "the number of ways energy can be distributed with $n_i$ fixed" divided by the "total number of ways energy can be distributed"

All ways of distributing energy are assumed to be equally likely.

Exact Probabilities and Energy

Harris does an example treatment using EXACT probabilities, based on these "ways of combining" formulas that we've been discussing. I only want to demonstrate his conclusion, as applied to energy for a collection of harmonic oscillators (which are easier to think about mathematically):

CONCLUSION: In a system of particles, varying the energy of just one particle causes sharp changes in the way energy is then distributed amongst all the other particles. The greatest freedom to distribute energy amongst particles occurs when that one particle under consideration has the least energy possible. Therefore, the more probable state for a given particle, the state in which the number of ways of distributing energy among all particles is greatest, is one of lower energy.

The Boltzmann Distribution

In the limit of large systems of distinguishable particles ($N=10$ and $M=50$ is already "large enough"), this probability is given by the Boltzmann Distribution:

$$P(E_n) = A e^{-E_n/k_BT}$$

where $A$ is a factor to be determined.

DISCUSSION: How might we determine this factor, $A$?
GUIDE: Normalization of probability is the key, $\sum_n P(E_n) = 1$.

RESULT:

$$P(E_n) = \frac{e^{-E_n/k_B T}}{\sum_n e^{-E_n/k_B T}}$$

**NOTE:** there is a mistake in Harris when he computes this factor - he accidentally leaves $A$ in when he inverts the normalization equation to solve for $A$

Average Energy in the Boltzmann Treatment

QUESTION: how can we compute the average energy of a system?

GUIDE: how do we compute the average, or expectation value, of a wave function? For instance, the average position? The same applies here:

$$\bar{E} = \sum_{n=0}^{\infty} E_n P(E_n)$$

(for closely spaced states, e.g. when the temperature is very large compared to the energy of the states, this can be written as an integral)

A Boltzmann Treatment of the Harmonic Oscillator

Using a system of harmonic oscillators will help us to reveal some of the properties of this energy distribution. Consider a system of such oscillators, where the energy of each state $n$ in an oscillator is given by:

$$E_n = (n + \frac{1}{2})\hbar\omega_0$$

I will shift the overall potential energy of the problem to $\frac{1}{2}\hbar\omega_0$ to simplify this energy:

$$E_n = n\hbar\omega_0$$
We can compute the average and we find:

$$\overline{E} = \frac{\hbar \omega_0}{e^{\omega_0/k_BT} - 1}$$

We can then see how the distribution of energy goes as the temperature changes (see slides).

**OCCUPATION NUMBER**

We are very often interested not in the probability of finding a particle in a state of energy $E_n$, but how many particles are in a state of energy $E_n$. This is called the OCCUPATION NUMBER and is given simply by:

- **OCCUPATION NUMBER**:

  $$\mathcal{N}(E_n)_{\text{Boltzmann}} = N A e^{-E/k_BT}$$

  where $n$ represents the full set of quantum numbers needed to specify a given state.

- It is important to note that this is NOT the same as the "number of particles with an energy, $E_n$" - it is possible that several states may have the same energy ($E_n = E_n' \equiv E$), and if that is the case you have to add the occupation numbers of those states together to get the "number of particles of energy $E$".
- Let's codify this:
  - "The number of particles of energy $E$" = "the occupation number (the number of particles in a given state of energy $E$)" times "the number of states with energy, $E$"

This latter quantity, "the number of states with energy, $E$", is called the DENSITY OF STATES.

**Quantum Distributions**

The Maxwell distribution applies when the particles are distinguishable.
QUESTION: how might a collection of particles, like electrons (which are identical), achieve "distinguishability" in the real world?

GUIDE: what is an electron - a particle or a wave? As a wave, it has an extent to its location in space. Two electrons that are very close, such that their wave functions overlap, risk being "indistinguishable" because you are no longer confident that "one is here and the other is there" by measurement. If, instead, they are very far apart, such that their motion is not so fast that you can't decisively establish "one is here and the other is there," they achieve distinguishability.

CONDITION: the condition for the application of the Boltzmann distribution is when:

\[(\lambda/d)^3 << 1\]

or more precisely

\[(N/V)\frac{\hbar^3}{(mk_B T)^{3/2}} << 1\]

What happens when they are not? Let's do a counting exercise to illustrate how distinguishability and indistinguishability influence counting/probability.

QUESTION: There are two kinds of quantum particle, depending on their spin. Name them.

QUESTION: What is the exclusion principle, and to which class of particles does it apply?

EXERCISE: consider 4 objects. Begin with them being distinguishable. Let's pretend there are quantum states, \(n_i = 0, 1, 2\) into which each particle can be placed. Designate the energy of each state by \(E_i = n_i \hbar \omega_0\). How many ways can be combine them to achieve a total energy of \(E = 2\hbar \omega_0\)?

**The Case-Specific Probabilities**

We've already see the Boltzmann distribution for distinguishable particles in equilibrium.

- **Bose-Einstein** (bosons, indistinguishable):
\[ N(E) = \frac{1}{Be^{E/k_BT} - 1} \]

- **Fermi-Dirac** (fermions, indistinguishable):
\[ N(E) = \frac{1}{Be^{E/k_BT} + 1} \]

**Notes:**
- \( B \) is a factor dependent on temperature (we'll see a case of this shortly).
- For a state whose energy \( E < k_BT \), the occupation number of fermions in that state is typically smaller than for bosons.
- For a state whose energy \( E > k_BT \), the occupation number of fermions in that state is typically higher than for bosons.
- If you instead compute the average energy, you find that in general fermion systems tend to have more energy, on average, than boson systems for the same temperature, and at low temperatures fermions approach a minimum non-zero energy.

**The Fermi Energy**

A useful concept going forward is "The Fermi Energy." We will need this in our next discussion of solids, and why some solids make good conductors, semi-conductors, or very bad conductors (insulators).

The Fermi Energy is defined as follows:
- For a given temperature, the FERMI ENERGY is the energy at which the occupation number is 1/2. This signifies an energy below which the occupation number is 1 and above which the occupation number is 0 (see slides). It's the "top" of the filled states, and is a good reference point in the energy spectrum for thinking about what it means to impart energy to such a system in order to raise the energy of a fermion, or remove one entirely.

At the Fermi Energy, you can solve for \( B \) (since \( N(E_F) = \frac{1}{2} \)). From this, we obtain:
\[ N_{FD}(E) = \frac{1}{e^{(E-E_F)/k_BT} - 1} \]
We see that the FERMI ENERGY is a good reference point - the sign of the exponent changes depending on whether you are above or below the Fermi Energy (for a given T).

DISCUSSION: What happens to a Fermi Gas when T=0?
GUIDE: Think about that happens to the exponent. Now, what happens to the sign of the exponent on either side of the fermi energy? Sketch the resulting occupancy number vs. energy graph for different Temperatures (0, 0.1, and 0.6 of the Fermi Energy).

**Conduction Electrons in a Metal: Classical vs. Quantum**

Conductors are an everyday example of how quantum mechanics is VITAL to the modern world. They are so common, we take them for granted, but did you know that treating conduction electrons in a metal as a classical gas of fermions is completely unrealistic? Here’s why.

DISCUSSION: How might we model silver metal?
GUIDE: Think about the Coulomb Potential for a single atom (1/r). Now pack a bunch of atoms next to each other. A finite square well emerges. Each Nth atom contributes 1 electron, so there are as many conduction electrons as silver atoms. Harris works through this calculation and finds a Fermi Energy of 5.5eV.

DISCUSSION: What does a Fermi Energy of 5.5eV mean?
GUIDE: above the Fermi energy, the occupation number drops to 0. So that means all states in the metal "finite square well" below 5.5eV are filled. If the classical treatment of the same "gas" of fermions predicts less energy than the quantum treatment, we know we can’t describe conduction as a classical physics phenomenon because electrons below 5.5eV aren’t mobile - they are happily occupying the lowest energy state and have no reason to go anywhere.

DISCUSSION: Harris works through the details in under classical considerations and finds the average energy of the gas to be $\frac{3}{2}k_B T = 0.04 eV$. This is far below 5.5eV, and there is no way conduction (the behavior of these electrons) can be described by classical physics.

To electrons in a metal, room temperature is very cold.

**More Consequences**

This picture of metal also helps us understand the "Work Function"
introduced by Einstein in the photoelectric effect - it is merely the difference in energy between the top of the "metal square well" and the electrons sitting just below the Fermi Energy. If you impart that much energy to such an electron, you can free it from the metal entirely, and the rest of the energy from the photon goes into its kinetic energy.

The boson statistics also has an interesting connection back to the birth of quantum mechanics: the Planck Blackbody Distribution. Why is thermal energy radiated by a blackbody distributed as Planck empirically derived, using energy quantization? Not mere quantization, but the fact that Photons are BOSONS, leads to this result for the spectrum of blackbody radiation. (See slides)

**Next Time**

- Solid-state physics:
  - when atoms meet
  - crystals (when MANY atoms meet regularly)
  - conductors
  - Later: semi-conductors, insulators