LECTURE 12
Maxwell Velocity Distribution

Suppose we have a dilute gas of molecules, each with mass m. If the gas is dilute enough, we can ignore the interactions between the molecules and the energy will not depend on the positions of the molecules. Let $f(\vec{r},\vec{v})d^3rd^3v$ be the mean number of molecules with center of mass position between $\vec{r}$ and $\vec{r}+d\vec{r}$ and velocity between $\vec{v}$ and $\vec{v}+d\vec{v}$. Then

$$f(\vec{r},\vec{v})d^3rd^3v = Ce^{-\beta(mv^2/2)}d^3rd^3v \tag{1}$$

where C is a constant determined by normalization. Here we have used the Boltzmann distribution $e^{-\beta E}$ with the energy E being the kinetic energy of the system $mv^2/2$. The contribution to the energy from internal states or degrees of freedom doesn't affect the velocity; these internal states are summed over ($\sum_r \exp(-\beta\epsilon_r)$) and will just contribute to C. The constant C is determined by the condition

$$\int d^3r \int d^3v f(\vec{r},\vec{v}) = N \tag{2}$$

We can evaluate the integrals to obtain C:

$$\begin{aligned} C\int d^3r \int d^3v e^{-\beta(mv^2/2)} &= CV\left(\int_{-\infty}^{\infty} e^{-\beta(mv_x^2/2)}dv_x\right)^3 \\ &= CV\left(\frac{2\pi}{\beta m}\right)^{3/2} \\ &= N \end{aligned} \tag{3}$$

or

$$C = n\left(\frac{\beta m}{2\pi}\right)^{3/2} \tag{4}$$

where $n \equiv N/V$ is the total number of molecules per unit volume. Hence

$$f(\vec{v})d^3rd^3v = n\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\beta mv^2/2}d^3rd^3v \tag{5}$$

or

$$f(\vec{v})d^3rd^3v = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}d^3rd^3v \tag{6}$$

We have omitted $\vec{r}$ from the argument of f since f doesn't depend on $\vec{r}$. Equation (6) is known as the Maxwell velocity distribution for a dilute gas in thermal equilibrium. Notice that it is a Gaussian distribution centered at $\overline{v}=0$. Recall that the exponential factor in a Gaussian distribution has the form $\exp(-x^2/2\sigma^2)$ where 2σ is the width of the distribution. Then the width of the Maxwell velocity distribution is $\sigma = \sqrt{kT/m}$. Notice that the width increases as the temperature increases. This means there are more hot molecules at higher temperatures. By "hot" molecules I mean ones with large $|v|$.

This applies for both positive and negative velocities because in (6) $v^2 = v_x^2 + v_y^2 + v_z^2$ and each component of velocity can be positive or negative.

Quantum Statistics

So far we have mostly concentrated on systems where classical mechanics is applicable. We have invoked quantum mechanics only to the extent that we had to acknowledge that quantum mechanically systems have discrete states and discrete energy levels. This becomes particularly apparent at low temperatures. We also noted that identical particles are indistinguishable. That's how we resolved the Gibbs paradox. Now we need to include some more quantum mechanics in order to treat the statistics of systems of identical particles where the classical approximation no longer is valid. Before we get to quantum statistics, let's go over some preliminaries.

Quantum Numbers

In your quantum mechanics course, when you solved the problem of a particle in a one dimensional box, you labelled the eigenvalues and eigenvectors with an integer n.

$$H\psi_n = E_n\psi_n \tag{7}$$

where

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{8}$$

with $n = 1, 2, 3, ...$ n is an example of a quantum number. It's a number which characterizes an eigenstate of the system. It changes from eigenstate to eigenstate, but if the system is in that eigenstate, it remains in that eigenstate and the quantum numbers describing that state don't change either. This is why an eigenstate is called a stationary state. Typically the quantum numbers are associated with symmetries. Symmetry means that the system looks the same under certain operations. For example if the system is invariant under time translation, then the Hamiltonian is time independent, and energy is conserved. This was true of the case of a particle in a box, and we labelled the energy eigenstates by n.

Another possible symmetry is spatial translation. If the potential is invariant under spatial translation, then momentum is a good quantum number. This would be true of a constant potential or if there were no potential. Classically momentum is conserved as long as the system is not subjected to a force. So if $\vec{F} = d\vec{p}/dt = 0$, then $\vec{p} =$ constant. The force is the gradient of the potential: $\vec{F} = -\nabla V(\vec{r})$. So momentum is a good quantum number as long as the potential does not vary spatially, i.e, as long as it's constant. (We don't usually refer to forces in quantum mechanics.) If the potential is constant or zero, then we have a free particle with momentum $\vec{p}$, energy $E = p^2/2m$ and $\psi \sim \exp(i\vec{p} \cdot \vec{r}/\hbar)$.

Another way to define a conserved quantity is to recall the Heisenberg equation of motion. For wavefunctions, it takes the form

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \tag{9}$$

There is also an equation of motion for operators. Let $\hat{A}$ be some operator. Its equation of motion is

$$i\hbar \frac{\partial \hat{A}}{\partial t} = [\hat{A}, \hat{H}] \tag{10}$$

So if $i\hbar \partial \hat{A}/\partial t = 0$, then we must have $[\hat{A}, \hat{H}] = 0$. This is the condition that A is a constant of the motion and is a conserved quantity. So if momentum is a conserved quantity, then it commutes with the Hamiltonian:

$$[\hat{H}, \hat{p}] = \hat{H}\hat{p} - \hat{p}\hat{H} = 0 \tag{11}$$

But this is getting too technical.

Angular Momentum

Angular momentum is another quantity that is conserved. There are two basic types of angular momentum: orbital and spin. Classically the orbital angular momentum is conserved as long as there is no torque on the system. In quantum mechanics we don't usually talk about torque. Rather we say that orbital angular momentum is a good quantum number if the system has continuous rotational symmetry. By rotational symmetry, I mean that if you rotate the system in some way, like by an angle θ about the z axis, it still looks the same. An atom is a spherical kind of object, and it has rotational symmetry.

Spin angular momentum is an internal angular momentum that is associated with a particle. (If the particle has rotational symmetry in spin space, then spin is a good quantum number.) The spin operator is denoted by $\vec{S}$. There are 2 quantum numbers associated with spin angular momentum: s and s_z. Sometimes s_z is denoted by m_s. If spin is a good quantum number, then the energy eigenstate ψ_n is also an eigenstate of $\hat{S}^2$ and $\hat{S}_z$:

$$\hat{S}^2 \psi_n = \hbar^2 s(s+1)\psi_n \tag{12}$$

and

$$\hat{S}_z \psi_n = \hbar s_z \psi_n \tag{13}$$

(In terms of commutators, $[\hat{H}, \hat{S}^2] = 0$, $[\hat{H}, \hat{\vec{S}}] = 0$, and $[\hat{S}^2, \hat{\vec{S}}] = 0$.) It turns out that s_z has a range of values:

$$s_z = -s, -s+1, ..., s-1, s \tag{14}$$

There are $2s+1$ values of s_z. s can be either an integer or a half–integer. Particles with integer spin are called *bosons* and particles with half–integer spin are called *fermions*. An example of a fermion is an electron. An electron is a spin-1/2 particle, i.e., $s = 1/2$, and it has 2 spin states: spin up (which corresponds to $s_z = +1/2$) and spin down (which corresponds to $s_z = -1/2$). Protons and neutrons are also spin–1/2 particles and are therefore fermions.

An example of a boson is a photon. A photon is a spin–1 particle, i.e, $s = 1$, and it has $s_z = -1$ or $s_z = +1$. It turns out not to have $s_z = 0$. This is related to the fact that there are 2 possible polarizations of the electric field $\vec{E}$ and that $\vec{E} \perp \vec{k}$, where $\vec{k}$ points in the direction of propagation of the electromagnetic wave.

Adding Angular Momenta

One can add angular momenta. For example one can add the spin angular momenta of two independent particles, say the spin of the proton and the neutron in a deuteron:

$$\hat{\vec{S}} = \hat{\vec{S}}_1 + \hat{\vec{S}}_2 \tag{15}$$

The total angular momentum also has 2 quantum numbers associated with it: S and S_z. If these are good quantum numbers, then the energy eigenstate ψ_n satisfies:

$$\hat{S}^2 \psi_n = \hbar^2 S(S+1)\psi_n \tag{16}$$

and

$$\hat{S}_z \psi_n = \hbar S_z \psi_n \tag{17}$$

One can also add orbital angular momenta. The rules for angular momentum addition are the same for all types of angular momentum. But the rules for adding angular momenta in quantum mechanics are a little tricky. You might think that if one particle has angular momentum s_1 (be it spin or orbital or total) and another independent particle has angular momentum s_2, the total is $s = s_1 + s_2$. This is not necessarily so. Classically you don't add two vectors by adding their magnitudes: $\vec{s}_1 + \vec{s}_2 \neq |s|_1 + |s|_2$. You don't do this in quantum mechanics either. In quantum mechanics the rule is that if you add s_1 and s_2, the total s obeys

$$|s_1 - s_2| \leq s \leq s_1 + s_2 \tag{18}$$

The z component s_z still runs from $-s$ to $+s$ in integer steps; there are $2s+1$ values of s_z. So if we add the spin angular momentum of 2 spin–1/2 particles, the total spin S of the system is $S = 0$ (we call this a singlet) or $S = 1$ (we call this a triplet). The singlet state has $s_z = 0$ and the triplet state has 3 possible values of s_z: -1, 0, $+1$. In this way one can make a composite particle that is a boson out of fermions. For example, ^{4}He is a boson because if you add the spin of the proton, neutron, and 2 electrons, you always will get an integer. On the other hand ^{3}He is a fermion.

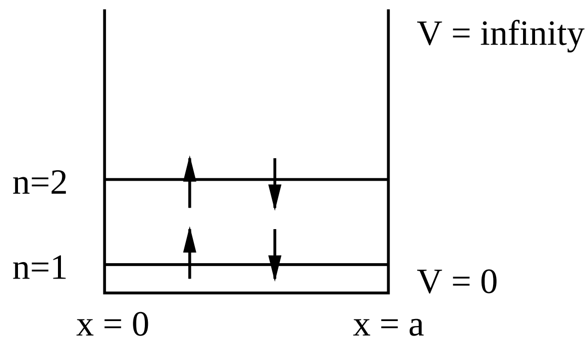
Many Particle States versus Single Particle States

Before proceeding, I want to clarify the difference between eigenstates of the entire system and single particle eigenstates. When we summed over microstates r in the past, we were thinking that each microstate was a many particle eigenstate. However, in quantum mechanics it is often easier to solve Schrodinger's equation for a single particle and ignore many body interactions. Then we approximate a many particle system as a sum of single particle systems. Thus we often speak in terms of single particle states.

Pauli Exclusion Principle

As we mentioned earlier, fermions are particles which have half–integer spin. Electrons are an example of fermions. All electrons are the same. They are indistinguishable particles. If we have a system with many electrons, as in a multielectron atom, the Pauli exclusion principle states that there can never be more than one electron in the same quantum state. In other words, a given set of quantum numbers can only be assigned to at most one electron. This is true for each type of fermion. For example, there cannot be more than one proton in a given quantum state.

Consider the quantum mechanical problem of a box with infinitely high walls. We can label the states with quantum numbers n, spin s and the z–component of spin s_z. Suppose we put 4 electrons in this box. Two electrons, one spin up and the other spin down, go into the $n = 1$ state. The quantum numbers of these two electrons is ($n = 1$, $s = 1/2$, $s_z = 1/2$) and ($n = 1$, $s = 1/2$, $s_z = -1/2$). The other two electrons go into the $n = 2$ state. They have quantum numbers ($n = 2$, $s = 1/2$, $s_z = 1/2$) and ($n = 2$, $s = 1/2$, $s_z = -1/2$).



Exchange Symmetry of Bosons and Fermions

The wavefunction of a collection of fermions is antisymmetric under the exchange of any 2 fermions. For example, if we have 2 fermions with coordinates 1 and 2, and we put them into 2 states ϕ_a and ϕ_b, an antisymmetric wavefunction for them is:

$$\psi(1, 2) = \phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1) \tag{19}$$

Notice that if we interchange 1 and 2, we get $\psi(2, 1) = -\psi(1, 2)$. This is what we mean by antisymmetry. If fermions 1 and 2 were both in the same state, say ϕ_a, then we would get

$$\phi_a(1)\phi_a(2) - \phi_a(2)\phi_a(1) = 0 \tag{20}$$

Thus antisymmetry enforces the Pauli exclusion principle. In general a wavefunction describing a collection of N fermions must be antisymmetric and satisfy

$$\psi(1, 2, ..., r, ..., s, ..., N) = -\psi(1, 2, ..., s, ..., r, ..., N) \tag{21}$$

Bosons are symmetric under exchange. For example, if we have 2 bosons with coordinates 1 and 2, and we put them into 2 states ϕ_a and ϕ_b, a symmetric wavefunction for them is:

$$\psi(1, 2) = \phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1) \tag{22}$$

If we interchange 1 and 2, we get $\psi(2,1) = \psi(1,2)$. This is what we mean by a symmetric wavefunction. If bosons 1 and 2 were both in the same state, say ϕ_a, then we would get

$$\phi_a(1)\phi_a(2) + \phi_a(2)\phi_a(1) = 2\phi_a(1)\phi_a(2) \neq 0 \tag{23}$$

Thus it's ok to put more than one boson in the same single particle state. In general a wavefunction describing a collection of N bosons must be symmetric and must satisfy

$$\psi(1,2,...,r,...,s,...,N) = +\psi(1,2,...,s,...,r,...,N) \tag{24}$$