Quantum Statistics

Our final application of quantum mechanics deals with statistical physics in the quantum domain. We'll start by considering the combined wavefunction of two identical particles, 1 and 2. By "identical" we mean that the two particles cannot be distinguished in any way. For example, if there is an interaction between identical particles, then at the end you can't tell which is which even if you knew before the interaction. Suppose we write the combined wavefunction, for particle 1 at location $\mathbf{r}_1$ and particle 2 at location $\mathbf{r}_2$, as

$$\Psi = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\ . \tag{1}$$

Now we imagine switching the places of particles 1 and 2, so that particle 1 is at $\mathbf{r}_2$ and particle 2 is at $\mathbf{r}_1$. Given that the particles are identical to each other, you might imagine that the wavefunction is unchanged, and indeed that is one possibility. However, we have to be careful! The only thing we can say with certainty is that if we switch the places of the particles, then switch them again, we *must* be back to the original wavefunction. This is possible if switching multiplies the wavefunction by -1 as well as if it multiplies the wavefunction by +1. We therefore have the two possibilities

$$\begin{aligned} &\psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) &&= +\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \\ \text{or}\quad &\psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) &&= -\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\ . \end{aligned} \tag{2}$$

Note that the probability, which is the square of the amplitude of the wavefunction, is unaffected in either case. Particles that obey the first form (with the +1 factor) are called *bosons*, and particles that obey the second form (with the -1 factor) are called *fermions*. The best-known boson is a photon. Fermions include electrons, protons, neutrons, and neutrinos. It so happens that all elementary particles have a kind of intrinsic angular momentum called "spin" (this is a purely quantum property, so don't think of electrons rotating in place). If the spin is an integral multiple of $\hbar$, the particle is a boson. If the spin is a half-integral multiple of $\hbar$, such as $\hbar/2$ or $3\hbar/2$, the particle is a fermion.

More generally, if there are any number of identical particles, then the overall wavefunction must be either completely symmetric or completely antisymmetric with respect to a swap of any two of those particles. That is,

$$\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\ldots\psi_n(\mathbf{r}_n)\ldots\psi_m(\mathbf{r}_m)\ldots = \pm\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\ldots\psi_n(\mathbf{r}_m)\ldots\psi_m(\mathbf{r}_n)\ldots \tag{3}$$

What does this mean? Let's think again about the case of just two particles. Suppose that the particles are fermions, so they have the -1 factor. **Ask class:** what is the probability of finding those two particles at the same spot, so that $\mathbf{r}_1 = \mathbf{r}_2$? It has to be zero, because the "swap" means

$$\psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) = -\psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)\ , \tag{4}$$

and the only way that can happen is if the amplitude is zero, so the probability is also zero. Now, in reality we've simplified by considering only location as part of the wavefunction. The full wavefunction also includes the state of the spin (for example, is the spin up or down?). When this is included, the general rule for fermions is the Pauli exclusion principle: no two fermions may occupy the same quantum state. **Ask class:** what is the situation for bosons? Then we have

$$\psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) = \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) \ . \tag{5}$$

This places no restrictions on the probability. In fact, if a boson occupies a state, it slightly *increases* the probability that another boson will occupy that same state. If you like, you can think of fermions being antisocial, and bosons being social!

Let's divert a bit to explain what is meant by "the same quantum state". If we have a particle with no interior structure, such as an electron, then its quantum state includes a spin state, a position, and a momentum. We'll ignore the spin for now. From the uncertainty principle we know that the position and momentum can't be known simultaneously with arbitrary precision. In fact, the uncertainty principle says

$$\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z \gtrsim h^3 \ . \tag{6}$$

This is the product of a volume in space with a "volume" in momentum. Such a product is called a "volume" in *phase space*. You can think of an element of phase space as having a "volume" of $\sim h^3$. If we now consider spin, an electron has a spin of $\hbar/2$, which can therefore be "up" ($+\hbar/2$) or "down" ($-\hbar/2$), meaning that no more than two electrons may occupy a volume in phase space less than or of order h^3. Notice that this condition has to apply jointly to position and momentum; two electrons can have almost exactly the same momentum if they are on opposite sides of the galaxy! More generally, we can say that given quantum state (including spin) cannot be occupied by more than one fermion of a given type.

With the phase space volume in mind, we can take a stab at some quantum statistics. Remember Boltzmann's law: the probability of a state of energy E in thermal equilibrium at temperature T is proportional to $\exp(-E/kT)$. What does this imply about the average number of particles in a given state (this average number is sometimes called the "occupation number")? First consider fermions. If there are n fermions in a given state, then the joint probability for this to occur is the product of n factors of $\exp(-E/kT)$, or $\exp(-nE/kT)$. Therefore, the average number of fermions at a given energy is

$$\langle N \rangle = \frac{\sum n \exp(-nE/kT)}{\sum \exp(-nE/kT)} \ . \tag{7}$$

Ask class: for fermions, what values can n take on? Just 0 or 1, from the exclusion principle. Therefore, the occupation number is

$$\langle N\rangle_F = \frac{0\cdot\exp(0) + 1\exp(-E/kT)}{1+\exp(-E/kT)} = \frac{1}{\exp(E_{\rm tot}/kT)+1}\ . \tag{8}$$

Note that $\langle N\rangle \leq 1$ for any energy, where the subscript "tot" indicates that the energy here is the total energy, including chemical potential as well as other forms of energy. **Ask class:** what does this function look like when $kT\rightarrow 0$? If $E_{\rm tot}<0$, $\langle N\rangle = 1$. If $E_{\rm tot}>0$, $\langle N\rangle = 0$. Therefore, the schematic diagram of occupation number versus energy is a step function: all states are occupied up to a certain energy, then no states are occupied. This situation ($T\rightarrow 0$) corresponds to complete degeneracy.

Ask class: what is the situation for bosons? Then n can take on any integer value from 0 to ∞, so

$$\langle N\rangle = \frac{\sum_0^\infty n\exp(-nE/kT)}{\sum_0^\infty \exp(-nE/kT)}\ . \tag{9}$$

This sum is a little trickier, but evaluation of the series leads to the simplification

$$\langle N\rangle_B = \frac{1}{\exp(E_{\rm tot}/kT)-1}\ . \tag{10}$$

Note that for a low occupation number (thus $E_{\rm tot}\gg kT$), bosons are indistinguishable from fermions. This is the realm of classical statistics.

Putting everything together, we get a distribution function (i.e., a number per phase space density) that looks like

$$n(p) = \frac{1}{h^3}\sum_{\rm states}\frac{1}{e^{E_{\rm tot}({\rm state})/{\rm kT}}\pm 1}\ . \tag{11}$$

Here $E_{\rm tot} = -\mu + E({\rm state}) + {\rm E(p)}$, where μ is the chemical potential, E(state) is the energy of the state of that species relative to some level (often the ground state energy) and $E(p)$ is the kinetic energy for momentum p. Note that the energy level relative to which one determines $E_{\rm state}$ is a free parameter, but $-\mu + E({\rm state})$ isn't, which can lead to varying definitions for μ (beware!). For degenerate energy states the distribution function is sometimes written with a g_j in the numerator, which is the number of states having the same energy E_j.

The distribution function is in (cm-momentum)$^{-3}$ units. It is usually assumed that momentum space is spherically symmetric, so that the physical number density is

$$n = \int_p n(p)4\pi p^2\,dp\ . \tag{12}$$

In general, the kinetic energy is $E(p) = (p^2c^2+m^2c^4)^{1/2} - mc^2$. The isotropic pressure is

$$P = \frac{1}{3}\int_p n(p)pv4\pi p^2\,dp \tag{13}$$

where the velocity is $\partial E/\partial p$, and the internal energy is

$$E = \int_p n(p)E(p)4\pi p^2\, dp\ . \tag{14}$$

Tell class: we are now going to concentrate for a while on "perfect" noninteracting particles, for simplicity.

Specific application: blackbody radiation. For photons, $\mu = 0$, $g = 2$ (because there are two polarizations), $E_j = 0$ (because there are no excited states), $E(p) = pc$, and minus in the denominator because photons are bosons. Put it together and what have you got? (bippity boppity boo, but never mind that). The photon number density is then

$$n_\gamma = \frac{8\pi}{h^3}\int_0^\infty \frac{p^2\, dp}{\exp(pc/kT)-1} \approx 20\, T^3\ \mathrm{cm}^{-3}\ . \tag{15}$$

The radiation pressure is $aT^4/3$ and the energy density is aT^4, where $a = 8\pi^5 k^4/15c^3h^3 = 7.6\times 10^{-15}$ erg cm^{-3} K^{-4}. If one considers this in the context of equations of state, this has the consequence that stars whose pressure and energy density are dominated by radiation are close to instability. This is one of the reasons that very high-mass stars $M > 100\, M_\odot$ are not very stable. For somewhat separate reasons having to do with cooling, accretion disks that are dominated by radiation pressure are also unstable.

From this, we can also get the spectral distribution for a blackbody.

$$u_\nu\, d\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}d\nu\ \mathrm{erg\ cm^{-3}\ Hz^{-1}\ Hz}\ . \tag{16}$$

One of the many successes of quantum theory was the ability to explain blackbody curves from fundamental physics.

Monatomic Gas: For an ideal, classical, monatomic gas, we know that the occupation number is extremely small. Therefore, the ±1 in the denominator is superfluous. Assume a nonrelativistic gas for starters, so **Ask class**: $E(p) = p^2/2m$ and $v = p/m$. Assume only one energy level, $E = E_0$; we can reference the energy to this single energy level and define $E_0 = 0$ (this simply redefines μ relative to that energy level, and different definitions exist in the literature). For an ideal gas $\mu \ll -kT$. The number density is then

$$n = \frac{4\pi}{h^3}g\int_0^\infty p^2 e^{\mu/kT}e^{-p^2/2mkT}\, dp\ . \tag{17}$$

This can be integrated to find the relation between μ and n, the total number density. This relation is

$$e^{\mu/kT} = \frac{nh^3}{g(2\pi mkT)^{3/2}}\ . \tag{18}$$

If you have a state with an energy E_j relative to the reference energy, then with this simplification the equation above would have to be multiplied by $e^{E_j/kT}$ on the right hand side. Similar integrations show that $P = nkT$ (big surprise!) and $E = \frac{3}{2}nkT$. For a fairly low-density gas, you can use these expressions along with assumptions of statistical equilibrium to derive the relative populations of atoms in different ionization states, assuming thermal ionization only (this leads to the Saha equation).

I'd like to close by considering a number of qualitative implications of quantum statistics. First, let's consider electrons. Electrons are fermions, so no more than one of them can occupy a given quantum state. **Ask class:** what effect does this have on the structure of atoms? It means that for atoms with more and more electrons, the orbitals occupied by electrons move farther and farther out. First, think about hydrogen. As we found last time, the lowest energy state that an electron can occupy has zero angular momentum, and is in the first orbital (which is said to have a principal quantum number $n = 1$). In atomic spectroscopy, zero angular momentum gets the letter "s", so we say that the electron is in the 1s state. Next, consider helium (two electrons). We put the first electron in the lowest energy level, again ($n = 1$). **Ask class:** where can we put the next electron? We can also put this one in the lowest energy level, because we can have one electron with an up spin, and one with a down spin. The electronic state is then 1s^2. **Ask class:** what about lithium, with three electrons? You can't fit any more electrons into the 1s state, and the $n = 1$ state doesn't have any angular momentum, so you have to put the electron into an $n = 2$ state. The lowest energy one turns out to be the 2s state, so the configuration is now $1\text{s}^2\ 2\text{s}^1$. The $n = 2$ state can have angular momentum, and if the angular momentum is one unit then the letter used is p. One can show that the 2s state, like the 1s state, allows two electrons (one with spin up, one with spin down), but that the 2p state allows more because it has nonzero angular momentum. The total number of electrons that can be in the 2p state is 6 (three from angular momentum, times two spin states), so the total number of electrons in the $n = 2$ state is 8 (2 in 2s, 6 in 2p). Therefore, atoms up to neon (atomic number 10) can have all their electrons in $n = 1$ or $n = 2$. For a nice website that gives ground state electronic configurations for all the elements, check out http://www.webelements.com/webelements/elements/text/periodic-table/econ.html. Note that for the heavier elements there are some apparent irregularities in the order in which orbitals are filled; these are caused by subtle interactions between the electrons that we can't model with just the Schrödinger equation. The main point here is that the periodic table, and indeed all of chemistry, stems from the Pauli exclusion principle, because otherwise all electrons would just be jammed in the 1s state!

If the electrons are in a degenerate gas, as in a white dwarf or neutron star, then Pauli exclusion plays another important role. The process of conduction transports energy by having it carried by electrons. If a typical electron can travel a long distance before it interacts, then it can carry its energy a long way and therefore be highly efficient at smoothing out temperature gradients. Now, if the electrons are degenerate, then scattering is much more difficult. Why? Because if an electron scatters, the final state it enters must not already be occupied by another electron (because of Pauli exclusion). For nondegenerate matter this is no problem; few states are occupied, so scattering happens as normal. But for degenerate electrons, scattering is much less frequent as a result of this process. Therefore, a typical electron moves a lot farther than it would otherwise. The net result is that conduction is extremely efficient in degenerate matter, so that the temperature is nearly constant throughout. Therefore, white dwarfs and neutron stars are nearly isothermal in much of their interiors.

Finally, let's talk about bosons and degeneracy. For bosons, having one boson in a state makes it *more* likely that an identical boson will also occupy that state. Take photons as an example. For two photons to occupy the same state means that their location, frequency, direction, and polarization all overlap. If you have a situation in which many photons are available, these all add up, and since they have the same direction, their intensity is tremendous. This is the principle behind lasers. In interstellar space, where densities are small and therefore collisions are infrequent, you can often find natural masers (microwave equivalents of lasers). These have great intensity, and are commonly found in places such as star forming regions. All made possible by quantum statistics!