Quantum Statistical Mechanics

Initial questions: What holds up Jupiter's core? Does the composition matter? How conductive are white dwarf and neutron star interiors?

We've talked about the interactions of photons, and (briefly) how they differ from the interactions of electrons in a fundamental way related to their quantum statistical properties. It's the difference between bosons and fermions, specifically whether particles "like" to occupy the same quantum state (bosons) or don't (fermions). In this lecture we'll explore that a bit more. To start, we need to define the concept of a chemical potential.

Chemical potential:

$$\mu_i = \left(\frac{\partial E}{\partial N_i}\right)_{S,V} \ . \tag{1}$$

Here N_i is the number density per gram of the ith species, so that $N_i = n_i/\rho$. Thermodynamic and chemical equilibrium require that if there are reactions that might change the N_i, then $\sum_i \mu_i dN_i = 0$. Photon number is not conserved, so $\mu_\gamma = 0$. Note that here we're interested in reactions that take place fairly rapidly, so things like nuclear reactions (which usually take years to billions of years) aren't included. Technically, these reactions mean that the system is *not* in equilibrium, but this is another example of how we simplify by dropping small terms. However, we should remember that it is possible to get to a lower-energy state via these reactions, and that at some point if the reactions are fast compared to chemical reactions then they must be included.

The dN_i are related to each other by particular reactions, so that means we can also write $\sum_i \mu_i \nu_i = 0$, where ν_i are the stoichiometric coefficients. From this, can see in another way that $\mu_\gamma = 0$: if a reaction of the form $A \rightarrow B + \gamma$ is allowed, so is $A \rightarrow B + \gamma + \gamma$. If μ_γ were nonzero, equilibrium would not be possible.

Before we delve into quantum statistical mechanics, let's recall classical statistical mechanics. To do this, we'll follow chapter 40 in Volume 1 of the Feynman Lectures on Physics.

Suppose that we have a gas, and we imagine two parallel planes in the gas separated by distance dx. Let there be some force F on the atoms in the gas. Suppose that the gas has a number density of n atoms per volume. We will consider an ideal gas, which has a pressure of $P = nkT$ at temperature T. In order for the system to be in equilibrium, the force due to the pressure must be balanced by the effect of the force F. However, **Ask class:** will there be any *net* force if the pressure is constant? No, it is a *change* in pressure (gradient of pressure) that can exert a net force. Therefore, the force F must balance the gradient of the pressure P.

Let's assume that the system has a constant temperature T, as it will in thermal equilibrium. Pressure (and change in pressure dP) has units of force per area. Therefore, we have

$$Fn\,dx = dP = kT\,dn\ . \tag{2}$$

Note that $-F\,dx$ is the work involved in moving a molecule from x to $x + dx$. Now suppose that the force is derived from a potential V. **Ask class:** how is the force related to the potential? We know that $F = -\nabla V = -dV/dx$ in our case. Therefore, we have

$$\begin{aligned} kT\,dn &= -n\,dV \\ dn/n &= -dV/kT \\ n &= \text{const} \times \exp(-V/kT)\ . \end{aligned} \tag{3}$$

Therefore, if the force derives from a potential, the number of molecules in a particular location depends on the negative exponential of the potential energy, divided by kT. This is called *Boltzmann's law*. It is remarkably general. *Any* force that is derived from a potential leads to Boltzmann's law, in classical physics.

But what if the force *isn't* derived from a potential? In that case, thermal equilibrium isn't possible at all! Sound bizarre? Consider the following. Suppose you have a bunch of balls in a container, and the balls have friction with each other. To be truly dissipative, the energy released in friction must leave the container entirely. Then you can see that no thermal equilibrium is possible, because energy continues to be lost from the system. In the general case, if a force isn't derived from a potential then there are closed loops in the system that lose or gain net energy, so there is no equilibrium.

We now have the distribution in space, but what about in velocity? It turns out that there is a remarkable (and not accidental) parallel with the distribution in space. Following Feynman again, let's consider a column of gas in thermal equilibrium in a uniform gravitational field. Let's say that there are no collisions between molecules. Let us consider arbitrarily some height $h = 0$ (a reference height; there could be molecules at negative h). How many molecules make it from $h = 0$ to $h = h_0 > 0$? It's not all of them, since some molecules don't have the required energy and will fall down before getting to $h = h_0$. In fact, it is exactly the molecules with enough kinetic energy that populate the higher level. We saw from before that the relative number of molecules at each height is $n(h = h_0)/n(h = 0) = \exp(-mgh_0/kT)$. Therefore, the relative fraction of molecules with enough energy to make it from $h = 0$ to $h = h_0$ must also be $\exp(-mgh_0/kT)$. By conservation of energy, the kinetic energy of those molecules must be at least $\frac{1}{2}mv_0^2$, where v_0 is the vertical speed needed to just make it to h_0 from 0. Therefore,

$$\frac{n(v > v_0)}{n(v > 0)} = \exp(-\text{kinetic energy}/kT)\ . \tag{4}$$

Adding collisions doesn't change this; we could, for example, imagine moving only a tiny height dh such that no collisions occurred in the meantime.

Combined, these two results imply something remarkable. The number of molecules in a particular state (which now includes a position, velocity, and any internal states) in thermal equilibrium is proportional to the exponential of the negative of the total energy divided by kT. Therefore, schematically, in classical physics

$$N(\text{state}) \propto \exp(-E_{\text{tot}}/kT) \; . \tag{5}$$

But what about in quantum mechanics? A lot of the interesting thermodynamic quantities can be calculated from the distribution function in 6-dimensional phase space (three coordinate, three momentum). This is also represented by the occupation number divided by h^3, where h^3 is a unit of phase-space volume. For a given species, the distribution function for a particular momentum is

$$n(p) = \frac{1}{h^3} \sum_{\text{states}} \frac{1}{e^{E_{\text{tot}}(\text{state})/\text{kT}} \pm 1} \; . \tag{6}$$

Here $E_{\text{tot}} = -\mu + E(\text{state}) + \text{E(p)}$, where $E(\text{state})$ 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_{state} is a free parameter, but $-\mu + E(\text{state})$ 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. Same deal. Of course (**ask class**) the ±1 refers to Fermi or Bose statistics. The point is that Fermi wavefunctions (for half-integral spin particles) are antisymmetric, so they avoid each other and the "occupation number" (the $1/[\exp(blah) + 1]$ bit in the distribution function) is always less than 1. Bose wavefunctions (for integral spin particles) are symmetric, and can have occupation numbers from 0 to infinity. **Ask class:** what are some examples of fermions? Electrons, protons, neutrons, for example (also neutrinos, quarks). **Ask class:** what are some examples of bosons? Photons are the best known among the elementary particles. Also, vector bosons (Z^0, $\text{W}^{\pm}$, carriers of the electroweak force), gravitons (spin 2, if they exist), and I believe gluons. Interesting that force carriers are bosons, and the "point particles" are fermions.

Ask class: under what conditions does this approach the classical distribution?

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

$$n = \int_p n(p) 4\pi p^2 \, dp \; . \tag{7}$$

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

$$P = \frac{1}{3} \int_p n(p) p v 4\pi p^2 \, dp \tag{8}$$

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

$$E = \int_p n(p)E(p)4\pi p^2\,dp\ . \tag{9}$$

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

$$n_\gamma = \frac{8\pi}{h^3}\int_0^\infty \frac{p^2\,dp}{\exp(pc/kT)-1} \approx 20\,T^3\ \mathrm{cm}^{-3}\ . \tag{10}$$

The radiation pressure is $aT^4/3$ and the energy density is aT^4, where $a = 8\pi^5k^4/15c^3h^3 = 7.6\times10^{-15}$ 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.

$$u_\nu\,d\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}d\nu\ \mathrm{erg\ cm^{-3}\ Hz^{-1}\ Hz}\ . \tag{11}$$

Monatomic Gas: The bit about $\mu \ll 0$ for an ideal gas can be derived by computing the number density and then getting μ from it; can assume it now and find that it is correct.

Given that it is, 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

$$n = \frac{4\pi}{h^3}g\int_0^\infty p^2e^{\mu/kT}e^{-p^2/2mkT}\,dp\ . \tag{12}$$

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

$$e^{\mu/kT} = \frac{nh^3}{g(2\pi mkT)^{3/2}}\ . \tag{13}$$

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 rhs.

Similar integrations show that $P = nkT$ (big surprise!) and $E = \frac{3}{2}nkT$.

Fermi-Dirac particles: Suppose we have a particle such as an electron, proton, or neutron that is spin 1/2 and therefore a fermion. Let the energy reference level be mc^2 (again, other choices are possible!). Then the degeneracy is 2, so the number density is

$$n = \frac{8\pi}{h^3} \int_0^\infty \frac{p^2\,dp}{e^{[-\mu+mc^2+E(p)]/kT}+1}\ . \tag{14}$$

In general, **Ask class**: $E(p) = mc^2\left[\sqrt{1+(p/mc)^2}-1\right]$ and the velocity is

$$v(p) = \frac{\partial E}{\partial p} = \frac{p}{m}\left[1+\left(\frac{p}{mc}\right)^2\right]^{-1/2}\ . \tag{15}$$

Ask class: how can we test whether this equation is correct? Limits for $p \rightarrow 0$, where $v = p/m$ (correct) and $p \rightarrow \infty$, where $v = c$ (correct). How about parity? v is in same direction as p, which is right. **Ask class:** from this, what is a rough boundary in momentum between relativistic and non-relativistic? When $p \approx mc$.

Completely degenerate gas: what is degeneracy? **Ask class**: it's when the density is high enough that particles start encroaching on each other's states. **Ask class:** what are the different implications for fermions and for bosons? For fermions this leads to Pauli exclusion and the fermions are forced into other energy states, whereas with bosons this leads to multiple occupation of the same state. The result is a host of phenomena, such as lasers, Bose condensation, superfluidity, and superconductivity. Some interesting properties can be derived from the fact that the particles participating in these phenomena are in a single state. For example, superfluids can't rotate because the particles would be moving with different velocities and hence would not be in the same state. Instead, any rotation in a superfluid is quantized in vortices of normal fluid.

Anyway, complete degeneracy occurs when $kT \rightarrow 0$, or more precisely when kT is much less than the numerator of the exponent above. The interesting part of the integrand is

$$F(E) = \frac{1}{e^{[E-(\mu-mc^2)]/kT]}+1}\ . \tag{16}$$

Ask class: what are the values for $kT \rightarrow 0$ when the exponent is positive and when it is negative? Clearly, either 0 or 1 for $kT \rightarrow 0$, depending on whether, respectively, $E > (\mu - mc^2)$ or $E < (\mu - mc^2)$. In this case, therefore, there is complete occupation up to the "Fermi energy" $E_F = \mu - mc^2$ and no occupation beyond that. When kT is finite, the transition between occupation and no occupation occupies a width $\sim kT$ in energy. Only these particles can interact, a fact which has great importance for things like energy transfer. Specifically, it means that only a fraction $\sim (kT/E_F)$ of particles can interact, so mean free paths are a lot longer than one would imagine and in this limit conduction can be very important. **Note:** as in our discussion of opacities, energy transfer tends to be dominated by whatever process can transport energy over a long distance rapidly. If there is a lot of scattering/absorption, this slows down the carrier particles. In degenerate matter, electrons travel a long way and hence conduction can be important; similarly, in a metal the periodicity of the potential cuts down on interactions and allows the electrons to travel far.

A simple way to remember how to get a Fermi momentum comes from the uncertainty principle. This says that $\Delta p \Delta x > \hbar$. If the number density is n, then the typical region in which a particle is confined has dimension $\Delta x \sim n^{-1/3}$. This implies that the Fermi momentum is $p_F \sim \Delta p \sim \hbar n^{1/3}$. In nonrelativistic mechanics $E \propto p^2 \propto n^{2/3}$, and in ultrarelativistic mechanics $E \propto p \propto n^{1/3}$. Note, by the way, that you can also get the energy in the nonrelativistic limit by considering an infinitely deep square well with dimension $\Delta x \sim n^{-1/3}$; the energies go as $(\Delta x)^{-2}$, as expected in the simplified treatment above. One can do the same thing in the relativistic limit.

So far we've considered completely degenerate material, but we should also mention that a rough boundary between nondegenerate and degenerate is when $E_F > kT$. This allows us to answer the burning question...

For Perspective: am I degenerate? In the old days we'd figure this out by considering my deeds and bad habits, but now we can answer it mathematically! **Ask class:** what do we need to determine? We need to figure out the Fermi energy of my constituents, then compare it to my thermal energy. **Ask class:** if there are plenty of free particles of all kinds, what kind of particle would be degenerate first? Electrons, because they have lower mass and $E_F \propto 1/m$ for nonrelativistic. **Ask class:** is the nonrelativistic limit the correct one? Yes, because 10^6 g cm^{-3} is the rough boundary, and I'm nowhere near that!

In the examples above we've discussed matter that is completely ionized, so that electrons are free to move around as they will. However, in me the electrons are mostly not free. Instead, typically there are ions. So, let's calculate first what the Fermi energy is assuming the dominant species is a molecule of some sort. What is the most common molecule? Water, of course. Water has an atomic weight 18 times that of hydrogen, or about 20 times that of the neutron, roughly speaking. The critical density at which the Fermi energy becomes relativistic goes like M^3, so for water it is about $20^3 \approx 10^4$ times that for neutrons, or about 6×10^{19} g cm^{-3}. Below this density the Fermi energy is nonrelativistic, and therefore goes like $p^2 \sim n^{2/3}$. At my density of ~ 1 g cm^{-3}, the Fermi energy is therefore $\sim 10^{-13}$ times the rest mass energy of water, or $10^{-13}\times 20$ GeV$=2 \times 10^{-3}$eV. The equivalent temperature for 1 eV is about 10^4 K, so this equates to about 20 K versus about 300 K for the temperature. Sadly, most of my mass is not degenerate! Of course, this is also true for, say, a white dwarf, where the mass is dominated by nondegenerate nucleons but the degenerate electrons provide the pressure.

But there may still be hope for me! Suppose that I have some small fraction of free electrons running around in me. In particular, suppose that there are about 10 electrons per molecule, and that about 1% of molecules have donated 1 electron to the general environment. The density of free electrons is therefore 10^{-3} times the density it would be if all atoms were completely ionized. For the purpose of this calculation, therefore, it's as if I were completely ionized but had a density of about 10^{-3} g cm^{-3}. Using the same approach as before, we know that for electrons the density at which relativistic degeneracy starts is about 10^6 g cm^{-3}, and that below this the Fermi energy scales as $p^2 \sim n^{2/3}$. Therefore, at 10^{-9} of this density the energy is 10^{-6} of the electron rest mass energy, or 0.5 eV. This equates to $\sim$5000 K, meaning that my electrons would be degenerate by a factor of more than 10! Woohoo! Unfortunately, J. Norman Hansen, professor of chemistry and biochemistry, says that in biological systems free electrons essentially don't exist, because as soon as one would be stripped off of a molecule it would go to another one, and hence electrons spend time in one orbital or another. Thus, tragically, I'm not degenerate :).