Physics 3700

Introduction to Quantum Statistical Thermodynamics

Relevant sections in text: §7.1–7.4

Quantum Statistics: Bosons and Fermions

We now consider the important physical situation in which a physical system is at a sufficiently low temperature and/or is sufficiently dense that the classical probability of two particles (or microsystems) occupying the same state is non-negligible. In this case it is mandatory to take account of the quantum nature of the particles/microsystems. In this regard there are two types of particles in the universe: *bosons* and *fermions*. Our goal in all that follows is to understand the statistical thermodynamical properties of quantum particles, that is to say, bosons and fermions. I should point out where these names come from: they are coming from the scientists who pioneered the characterization of their statistical properties. Bosons obey "Bose-Einstein statistics". Fermions obey "Fermi-Dirac statistics".

As a general rule, matter is made of fermions, *e.g.,* protons, neutrons and electrons are fermions. Bosons are particles (quanta) associated with interactions, *e.g.,* photons and the Higgs particle are bosons. The key difference between bosons and fermions concerns the behavior of identical particles — particles of the same type. The idea of identical particles, *e.g.,* electrons, is that all electrons are intrinsically the same — they all have certain immutable properties: they have the same mass, charge, spin. To be sure, the electrons can be in different states (electrons on Earth versus electrons in the sun, spin up versus spin down along some direction, high energy electrons versus low energy electrons, and so forth), but the particles are all *interchangeable* as far as their intrinsic properies (mass, charge, spin). If you've seen one electron, you've seen them all. All this talk applies to any species of particle, e.g., all photons are intrinsically the same, although they can be in different states.*

Fermions have the property that no two particles of the same type (*e.g.,* electrons) can be in the same state. You will never see two fermions all of whose measurable characteristics are the same. Bosons, on the other hand, are particles which have no such restriction — arbitrarily many bosons can be in the same state.† As we shall see, this difference between bosons and fermions leads to them having very different statistical and macroscopic behavior.

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* This distinction between "intrinsic" properties and accidental properties associated to "states" is non-trivial and is part of a proper understanding of the physics of the particle.

† This is why, for example on can get macroscopic classical electromagnetic fields from many, many photons.

A famous theorem coming from relativistic quantum field theory, the *spin-statistics theorem*, asserts that bosons have integral spin and fermions have half-integral spin. Composite systems, *e.g.,* atoms, also can exhibit bosonic or fermionic behavior. Which will it be? As it happens, if one combines an even (odd) number of half-integral spins the result is (half) integral spin. Consequently, for experiments/processes that probe the details of nuclear structure, a Helium-4 nucleus is a boson, but a Helium-3 nucleus is a fermion. For processes that don't probe atomic structure, a hydrogen atom is a boson, while deuterium is a fermion. Strictly speaking, composite systems act like bosons/fermions according to their net spin, provided one is not examining their behavior via interactions which probe the subsystems which make up the composite system. So, if you look too closely at a Helium-4 nucleus you will find it isn't really a boson, but is a collection of fermions.

When do we need to worry about quantum statistics and when will the usual classical reasoning work? The answer isn't cut and dried, but is a matter of comparing orders of magnitude and may depend upon the details of the system. Generally speaking, if densities are not too high, nor temperatures too low, then the classical probability of two particles being in the same state will usually be negligible. In this case, whether they are bosons or fermions is immaterial and their quantum behavior is likewise negligible. We just have to take care when counting states to take account of the indistinguishability of the particles. When the densities get high enough, and/or the temperatures get low enough and the classical probability of two identical particles being in the same state becomes non-negligible, we must take account of their quantum statistics.

A good illustration of this reasoning is provided by an ideal gas, so let's consider this system. To address the question for an ideal gas, I first remind you that any particle of with momentum $\vec{p}$ has a certain length associated with it — the *de Broglie wavelength* λ — given by

$$\lambda = \frac{h}{p},$$

where h is Planck's constant. As you probably know, quantum mechanical particles really don't have a precise momentum (or position for that matter) — it fluctuates statistically. But if the statistical distribution for momentum is sharply peaked around p, the wavelike behavior (in the probability distribution) for position has characteristic wavelength λ. Insofar as λ is non-negligible on the length scale of a given situation quantum effects will be important. Now, the typical momentum of a molecule in an ideal gas is determined by its kinetic energy, which is on the order of kT. So we can estimate

$$p \sim \sqrt{2mkT} \Longrightarrow \lambda \sim \frac{h}{\sqrt{2mkT}}.$$

It is conventional to define a *quantum length*:

$$l_Q = \frac{h}{\sqrt{2\pi mkT}},$$

where the factor of π is inserted for later convenience. There is a corresponding quantum area and volume:

$$a_Q \equiv l_Q^2 = \frac{h^2}{2\pi mkT}, \quad v_Q \equiv l_Q^3 = \frac{h^3}{(2\pi mkT)^{3/2}}.$$

For an ideal gas, if the volume per particle is comparable to this quantum volume, then quantum behavior — quantum statistics — will come into play. When the volume per particle is much larger than the quantum volume, then we can use the classical description. So, we have

$$\frac{V}{N} >> v_Q \quad \text{classical statistics}$$

$$\frac{V}{N} \leq v_Q \quad \text{quantum statistics}$$

Note that the quantum length scale is determined by a combination of mass and temperature, while the criterion for quantum/classical statistics depends upon the (number) density. Thus one can get quantum statistical behavior by (i) lowering the temperature (thus raising v_Q, as in liquid helium, (ii) raising the density, as in a white dwarf or neutron star, and/or (iii) reducing the mass – using light enough particles, as in the case for electrons in a (semi-) conductor.

A simple example: a gas with 2 particles

To get a feel for the statistics of bosons and fermions, let us consider a really simple situation: let the system be a gas consisting of 2 non-interacting identical particles, each of which can be in 3 distinct "single particle" states. For example, the system could consist of two identical atoms and the "single particle states" are their (first 3) energy levels. We want to enumerate the possible states of the gas in the 2 quantum statistical cases. Label the two particles as A and B and label the states as 1, 2, 3.

Bose-Einstein statistics

There are 3 distinct ways of placing the particles in the same state. There are 3 distinct ways of putting the particles in different states. It's only 3 in this case because the particles are identical. For example, putting particle A in state 1, and B in state 2, say, is the same as putting particle A in state 2, and B in state 1.* Therefore, the total number of states is 6 and the relative probability for finding two particles in the same state is 1/2. Compare with the case of two distinguishable particles where the total number of states is 9 and the relative probability for finding two particles in the same state is 1/3.

* This statement is the principal meaning of "identical particles".

Fermi-Dirac statistics

The counting is the same as in the boson case, except that the 3 states of the system where the particles are in the same single particle state are excluded. Thus there are 3 states in total. The relative probability for finding two particles in the same state is zero, of course.

You see how the statistics controls the number of states. More interestingly, you can see that the relative probability for finding particles in the same state is greatest for identical bosons and least for identical fermions, with distinguishable particles somewhere in between. Thus one can say that by their very nature, identical bosons "like" to be in the same state compared to identical fermions and other particles.

Degenerate Fermi Gas

It is easy to check that for an electron at room temperature the quantum length is about 4 nm so the quantum volume is about 64 nm^3. Consider a metal where, with about one conduction electron per atom, the volume per conduction electron is approximately 10^{-2} nm^3. Thanks to the relatively low mass of the electron and the relatively low (room) temperature, the conduction electrons in a metal must be treated quantum mechanically — the fermionic nature of the particle can be expected to be important. We will now explore the simplest possible model of a quantum electrons – the *degenerate Fermi gas*. This provides an elementary model of conduction electrons in a metal as well as an explanation for phenomena like white dwarf stars.

The degenerate Fermi gas is obtained by treating a collection of electrons as non-interacting fermions at zero temperature. As $T \to 0$ you expect the system to settle into its unique lowest energy state. If it weren't for the fact that the electrons were fermions, this lowest energy state would arise by putting all the particles in the lowest single-particle state. But we can only put 1 electron per single particle state, so we keep having to fill more and more states. Eventually we have placed all the particles, say N of them, in the lowest available energy states. The particles will have occupied all (1-particle) energies up to some value, call it ϵ_F — the *Fermi energy*. This leads to behavior with thermodynamic features — even at zero temperature!

As a simple illustration of the Fermi energy, let us return to our identical particles A and B. Let us suppose that states 1, 2, 3, have energies 1eV, 2eV, 3eV, respectively. The Fermi energy is 2eV. Can you see why?

What we'd like to do now with the degenerate Fermi gas is to compute the Fermi energy as well as a few other observables like the internal energy and pressure of the gas, all as functions of the volume and number of particles. To do this we need to get a handle on the 1-particle states. We will model the electrons as a "particle in a box". This means the following.

For a free particle in a cubic box with sides of length L, the states of a particle with a given energy ϵ have wave functions of the form

$$\Psi(x, y, z) = (const.) \sin(\frac{n_x x\pi}{L}) \sin(\frac{n_y y\pi}{L}) \sin(\frac{n_z z\pi}{L}),$$

where the n's can be any integer greater than equal to 1. Note that the wave function vanishes on the edges of the box which are taken to be at $x, y, z = 0, L$. The state is determined by the choice of the n's and the spin state of the electron, the latter can be up or down along some (arbitrarily chosen) axis. The ground state is when $n_x = n_y = n_z = 1$, irrespective of the spin state (so the ground state is doubly degenerate). The first excited states are obtained by setting 2 of the 3 n's to unity and the third n is set equal to 2, *e.g.,* $n_x = n_y = 1$, $n_z = 2$. Thus the ground state is doubly degenerate and the first excited state is 6-fold degenerate. The energy ϵ of a single partucke state determined by a given choice of the n's is

$$\epsilon = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2),$$

where m is the electron mass.

So much for the energy states of a single particle. The idea is now that, for the $T \approx 0$ ground state of the gas, each electron occupies one of the energy states such that the gas has the lowest possible energy. Actually, one can put two electrons in each energy state because there are two spin states the electron can be in for any given energy. The maximum 1-particle energy which occurs is the Fermi energy, which we write as

$$\epsilon_F = \frac{h^2}{8mL^2} n_{max}^2,$$

where n_{max}^2 is the largest value for $n_x^2 + n_y^2 + n_z^2$ which occurs. To get a handle on ϵ_F we use a geometric interpretation of this formula which arises for a macroscopic gas. Think of $\vec{n} = (n_x, n_y, n_z)$ as a position vector in 3 dimensional space. The filled 1-particle states determine a sphere of radius n_{max}. Actually, only 1/8 of a sphere is used since the vectors $\vec{n}$ have all components being non-negative. For a large enough number of particles, it is not to hard to see that the volume of this 1/8 of a sphere is approximately 1/2 the number of states which are filled, which is 1/2 the number of particles N. (The 1/2 comes because there are two particles per energy state due to the two spin states of an electron.) Thus, for $N >> 1$, we have

$$N = 2 \times \frac{1}{8} \times \frac{4\pi}{3} n_{max}^3 = \frac{\pi}{3} n_{max}^3.$$

Use this formula to eliminate n_{max} in ϵ_F and set $V = L^3$. We then get a nice formula for the Fermi energy:

$$\epsilon_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}.$$

What makes this formula "nice" is that it is built from the macroscopic observables N and V (along with a single microscopic but fixed constant m). Note that the Fermi energy is an intensive quantity.

You can check that for a typical metal the Fermi energy is on the order of an electron-volt or so. At room temperature, the average thermal energy per electron is about $kT = 1/40\, eV$. We see that the internal energy per electron is at least an order of magnitude bigger than the average thermal energy of an electron. What this means is that at room temperature the fermionic effects are dominating the thermal effects, although the latter effects aren't completely negligible. This justifies setting $T = 0$ as a first approximation. More generally, we can define a *Fermi temperature*:

$$T_F = \frac{\epsilon_F}{k} = \frac{h^2}{8mk}\left(\frac{3N}{\pi V}\right)^{2/3}.$$

The Fermi temperature is the temperature at which thermal effects are comparable to quantum effects associated with Fermi statistics. The Fermi temperature for a metal is a couple of orders of magnitude above room temperature.

We can now compute the total energy U of the gas by summing up all the single particle energies from the lowest up to ϵ_F. Once again we can get a good approximation to the total energy by taking advantage of the macroscopic nature of the gas – which then has a very large number of electrons – and replacing the sum by an integral over the Cartesian coordinates (n_x, n_y, n_z). This approximation will be valid provided we have a large enough number of fermions. We express this integral in spherical polar coordinates, integrating on the interior of the 1/8 sphere of radius m_{max}. The angular integrals are trivial and only the radial integral survives.

$$U = 2\int d^3n \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) = \frac{\pi h^2}{8mL^2}\int_0^{n_{max}} n^4 dn = \frac{3}{5}N\epsilon_F = \frac{3h^2N}{40m}\left(\frac{3N}{\pi V}\right)^{2/3}.$$

The factor of 2 in front of the integral is because there are 2 electrons/spin states for each energy level. Thus the energy of the gas is non-trivial even when thermal effects are ignored.

The degenerate Fermi gas has other thermodynamic-like properties besides internal energy. For example, we can easily compute the pressure of this gas. Recall from the thermodynamic identity that

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}.$$

We have

$$U = \frac{3}{5}N\epsilon_F = \frac{3h^2N}{40m}\left(\frac{3N}{\pi V}\right)^{2/3}$$

so that

$$P = \frac{2N\epsilon_F}{5V} = \frac{2U}{3V},$$

or

$$U = \frac{3}{2}PV.$$

Thus the relation between pressure, volume and energy is like that of a monatomic ideal gas! The analogy is not perfect; there is no formula like $U = \frac{3}{2}NkT$ — indeed, we are approximating $T = 0$. Moreover, the pressure here is not due to thermal kinetic energy, but due to the fermionic statistics only — the Pauli exclusion principle. This pressure is often called *degeneracy pressure*. There is no force *per se* which is causing the degeneracy pressure. Fermionic behavior alone means it can cost work to compress the gas. For a typical metal, this "degeneracy pressure" is on the order of $10^6 N/m^2$! But keep in mind there are some forces at play here. The electrostatic attraction of protons and electrons essentially cancels out this degeneracy pressure. But you can now begin to see how solids are, well, . . . solid.

Degeneracy pressure, white dwarves and neutron stars

The degeneracy pressure of fermions is what allows dense astrophysical objects like white dwarves and neutron stars to exist. We are now in a good position to see how this works. The basic issue is that the gravitational force tries to compress the star, while the internal energy of the fermions (electrons or neutrons) due to the Pauli exclusion principle tends to decompress the star. When these two effects balance, we get an equilibrium state. We can estimate the properties of this state using simple energy arguments and see if it matches observation.

First, the gravitational potential energy of a uniform ball of matter with mass M and radius R is given by (see any introductory physics text)

$$\mathcal{U} = -\frac{3GM^2}{5R}.$$

Next, the internal energy of a degenerate Fermi gas consisting of N fermions of mass m in a volume V is just the energy we computed above, now relabeled to avoid notational confusion:

$$K = \frac{3}{5}N\epsilon_F = \frac{3}{40}N\frac{h^2}{m}\left(\frac{3N}{\pi V}\right)^{2/3}.$$

Using $V = \frac{4}{3}\pi R^3$, we have

$$K = \frac{3}{40}N\frac{h^2}{mR^2}\left(\frac{9N}{4\pi^2}\right)^{2/3}.$$

The question we want to answer is whether there is a value for R where (stable) equilibrium is obtained. This will happen at a minimum of the energy $E = \mathcal{U} + K$. As a function of R, the energy has the form

$$E = -\frac{\alpha}{R} + \frac{\beta}{R^2}, \quad \alpha, \beta > 0.$$

If you graph the energy as a function of R you will see that it should indeed have a minimum, which can be found by setting its first derivative to zero. Taking a derivative and setting it equal zero we find

$$R = \frac{2\beta}{\alpha} = \frac{3h^2}{16GmM^2}\left(\frac{12N^5}{\pi^4}\right)^{1/3}.$$

Now, the number of fermions can be expected to be proportional to the mass of the star:

$$N = \frac{1}{\gamma}M,$$

where the choice of γ will depend upon what the star is made of. Thus the equilibrium radius is

$$R = \frac{3h^2}{16Gm}\left(\frac{12}{\gamma^5\pi^4 M}\right)^{1/3}.$$

Note that the equilibrium radius varies with mass like $M^{-1/3}$. In particular, a larger mass means a smaller radius!

For a white dwarf the fermions of interest are electrons and there is about one neutron and proton for each electron. Since the neutrons and protons provide the mass, we have

$$\gamma_{wd} = 2m_p,$$

where m_p is the proton mass. Using this value for γ, for a 1 solar mass white dwarf we then get $R_{wd} \approx 7200\ km$. For a neutron star the fermions are the neutrons, which also provide the mass. So we have

$$\gamma_{ns} = m_n$$

where m_n is the neutron mass. For a 1 solar mass neutron star we then get $R_{ns} \approx 12\ km$. Both of these estimates are pretty close to what is observed!

It is worth noting that we have ignored the temperature of the white dwarf in these considerations (neutron star temperatures are clearly low enough to be irrelevant). It is easily seen that the Fermi energy of a white dwarf is on the order of $10^5 eV$. How hot is a white dwarf? The surface temperature varies over time, but it is no higher than about $10^5 K$, so that the average thermal energy is on the order of, say, 10-100 eV. So it is not a bad approximation to ignore the temperature effect on the star's stability. Indeed, if it were not for the degeneracy pressure the white dwarf (and neutron star) could not exist!

Although it is beyond the scope of our simple discussion here, it is worth mentioning that in Einstein's (more accurate) theory of gravity there are some new effects which feature. In particular, energy of any kind (not just mass energy) creates a gravitational field and is influenced by gravitational fields. This means the attractive effect can become much stronger than was estimated above using Newtonian gravity. As it happens, if there is enough mass concentrated in a small enough volume, the effective energy function is such that no stable equilibrium can result - the body must collapse gravitationally despite the degeneracy pressure. There is no known effect which can intervene. This is how black holes are formed.

Boson gas: Photons and Blackbody Radiation

Now we turn out attention to systems composed of bosons. Unlike fermions, there is no limit to the number of bosons in a single particle state, consequently the zero temperature limit is not very exciting. We thus consider a gas of non-interacting bosons at temperature T. We will specialize our treatment to photons, which are the most familiar and important of the bosons. Like all particles, a photon is a particle-like excitation of a quantum field — the photon field — which is considered in quantum electrodynamics. Here we will use a more phenomenological description.

We want to consider a box of non-interacting photons at a given temperature (just as we considered a box of fermions at temperature zero previously). This models any situation where you have an approximate vacuum (or negligible matter) filled with electromagnetic radiation at temperature T. So, for example, this could be the inside of your oven, or it could be some region of interstellar space. The precise idea of a photon is probably a little different from what you think it is. The slogan to keep in mind is that photons are "quantum normal modes of the electromagnetic field". The idea is that the electromagnetic field can be viewed as a superposition of normal modes – the Fourier modes.† One views these normal modes – when treated quantum mechanically – as possible states of a single photon, and there is no limit to how many photons can be in a given state. Classically, each normal mode has a frequency f and wavelength $\lambda = c/f$. The quantum description of the normal modes is fairly simple: each normal mode is a quantum oscillator with natural frequency f. The possible energies of a given mode, relative to the ground state energy, are the usual oscillator energies: $0,\ hf,\ 2hf,\ 3hf,\ \ldots$. For a given normal mode, we interpret the state with energy 0 as having no photons (at that frequency); we interpret the state with energy hf as a single photon with frequency f, wavelength c/f, energy hf,

† For photons in a box, the normal modes form a discrete family of standing waves.

and momentum $h\lambda$; we interpret the state with energy $2hf$ as two photons of frequency f, and so forth.* More precisely, we re-interpret the energy quantum number of the oscillator as the photon occupation number for that mode.

Since photons will be interpreted in terms of quantum oscillators, we need to review for a moment the statistical thermodynamics of a quantum oscillator. At temperature T the partition function for an oscillator with frequency f is given by

$$Z_f = 1 + e^{-\beta hf} + e^{-2\beta hf} + \ldots = \frac{1}{1 - e^{-\beta hf}}.$$

As usual, at temperature T the oscillator can be in a variety of states, with various probabilities given by the Boltzmann formula. The average energy of the oscillator is

$$\overline{E}_f = -\frac{\partial \ln Z}{\partial \beta} = \frac{hf}{e^{hf/kT} - 1}.$$

Let us now re-interpret this result in terms of photons, since we are interested in a gas of photons at temperature T. Above, I described the scheme whereby (for a given normal mode of frequency f) each photon has energy hf. Thus, if at temperature T the average energy of an oscillator with frequency f is $\overline{E}_f$, then this can be interpreted as saying the average number of photons (in this normal mode) is

$$\overline{n}_f = \frac{\overline{E}_f}{hf} = \frac{1}{e^{hf/kT} - 1}.$$

This is a very famous formula — it is the *Planck distribution.* Note in particular that photons with energies $hf >> kT$ are exponentially suppressed. For all practical purposes, photons at such frequencies don't appear. Normal modes with lower frequencies are favored, as you can see. (Why doesn't $f = 0$ cause a problem?)

Let us now compute the internal energy of the gas of photons at temperature T and volume V, which we interpret as the average energy of the box of non-interacting photons. We do this by (1) computing the energy for each mode, (2) multiplying the energy of each mode by the average number of photons in that mode, (3) summing the result over all modes.

To compute the energy for a given normal mode, we view our volume as a cube of edge $L = V^{1/3}$, with the Cartesian axes along its edges, the normal modes of vibration are characterized by three independently specifiable integers

$$n_x = 1, 2, \ldots, \quad n_y = 1, 2, \ldots, \quad n_z = 1, 2, \ldots$$

* Note that these photon states represent quantum particles with definite momentum. Thus their position is completely uncertain, *a priori.* They are not little balls of light which are flying around in space. Indeed, a photon has just as much – if not more – in common with a something like a vibrating guitar string as it does with a particle.

The wavelength (in each direction) of this mode is

$$\lambda_x = \frac{2L}{n_x}, \quad \lambda_y = \frac{2L}{n_y}, \quad \lambda_z = \frac{2L}{n_z}.$$

Using relation between momentum and wavelength ($p = h/\lambda$) for a photon, we have for a single photon in this mode:

$$p_x = \frac{hn_x}{2L}, \quad p_y = \frac{hn_y}{2L}, \quad p_z = \frac{hn_z}{2L}.$$

The energy of a photon in terms of momentum is the familiar result $\epsilon = pc$. So, the energy of a single photon in the normal mode specified by (n_x, n_y, n_z) takes the form

$$\epsilon = hf = pc = \frac{hcn}{2L}$$

where

$$n = \sqrt{n_x^2 + n_y^2 + n_z^2}.$$

The average number of photons in a mode with frequency f is given by the Planck distribution. We can multiply by the energy hf of this mode and sum over all modes to get the average energy of the photon gas. In the thermodynamic/macroscopic limit (many photons) we can, as usual, identify this with the energy U of the photon gas.* We thus have

$$U = 2\sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} hf\overline{n}_f = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \frac{hcn}{L}\frac{1}{e^{hcn/2LkT} - 1}.$$

I inserted a factor of two here because there are two polarization states for every standing wave mode. (In this calculation, at least, this is the only place where the vector nature of the electromagnetic field comes into play.) The bulk of the sum comes from the high n values, where we can approximate the sum by an integral in the first quadrant of $\vec{n}$ space (as with the fermi gas). So, for a macroscopic gas, we have

$$\begin{aligned} U &= \int_0^\infty dn \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\phi\, (n^2 \sin\theta) \frac{hcn}{L}\frac{1}{e^{hcn/2LkT} - 1} \\ &= L^3 \int_0^\infty d\epsilon \frac{8\pi}{(hc)^3}\frac{\epsilon^3}{e^{\epsilon/kT} - 1} \end{aligned}$$

The energy density is

$$\frac{U}{V} = \frac{U}{L^3} = \int_0^\infty d\epsilon \frac{8\pi}{(hc)^3}\frac{\epsilon^3}{e^{\epsilon/kT} - 1}.$$

* Notice that we do not specify the number of photons. The number of photons is determined by the choice of temperature, since this tells how many photons per mode.

Denote by $u(\epsilon)$ the energy density per photon energy ϵ; it is just the integrand in the integral over ϵ:

$$u(\epsilon) = \frac{8\pi}{(hc)^3}\frac{\epsilon^3}{e^{\epsilon/kT} - 1}.$$

This is the celebrated Planck spectrum of photons. It tells you how much of the energy density comes from photons of various energies.

From the Planck spectrum, at a given temperature T, the energy which yields the maximum energy density is

$$\epsilon_{max} = 2.82kT.$$

This, along with the usual relation $\epsilon = hf$, gives the relation between how hot something is and what color it appears to be. It is easy enough to see that the energy density of the gas varies as T^4. To see this, just make a change of variables, $x = \epsilon/kT$, three powers of temperature come from the ϵ^3 in the integrand and one more power of temperature comes from the integration meausure $d\epsilon$.

The integral for the energy density can be computed numerically, of course. Remarkably enough, it can also be computed in closed form. It is not that easy, though. I will just tell you the answer – any decent computer algebra system can handle it:

$$\frac{U}{V} = \frac{8\pi^5(kT)^4}{15(hc)^3}.$$

Again, the energy (density) of a photon gas varies as the fourth power of the temperature. Since we expect the typical photon to have (thermally induced) energy of about kT, this means the number of photons is on the order of $(const.)T^3$. It is not hard to check that the number of photons is on the order of $10^7\,VT^3$, in SI units.

From this formula we can compute the heat capacity of the box of photons (at constant volume)

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{32\pi^5 k^4}{15(hc)^3}VT^3.$$

Notice that C_V is not constant; it vanishes as $T \to 0$ as it should – the box of photons obeys the third law.

From this formula for heat capacity we can compute the entropy of the box of photons:

$$S(T) = \int_0^T \frac{C_V(T')}{T'} = \frac{32\pi^5 k^4}{45(hc)^3}VT^3.$$

Notice that since the number of photons is proportional to T^3, the entropy is proportional to the number of photons as you might expect.

Finally, I direct you toward the text to read about some important examples of the energy-temperature relationships of a gas of photons. Of great historical importance is the idea of a "blackbody", which is an idealized emitter/absorber. It can be shown that, using our previous results, such objects radiate with a power proportional to T^4. Similarly, a point source (e.g., a small hole in the box of photons) radiates with a power proportional to T^4. An example of cosmological significance is the cosmic background radiation. Discovered in the 1960's, and predicted by cosmological models, this radiation is that of a photon gas at a temperature of $2.73K$.