1. Blackbody Radiation

"I had already been struggling with the problem of the equilibrium between matter and radiation for six years without success. I knew the formula that reproduces the energy distribution in the normal spectrum; a theoretical interpretation had to be found at any cost, no matter how high" - Max Planck

2. Molecular Absorption of Gases

Here we will examine the absorption and emission processes of molecules by first considering a gas in thermodynamic equilibrium. This will be followed by a short survey of the discrete energy levels of molecules that affect the atmospheric opacity and climate of planetary atmospheres.

2.1. Thermodynamical Equilibrium

In 1895, at the University of Berlin, Wilhelm Wien and Otto Lummer, set up an oven, punched a little hole in it, and began recording the radiation emitted from the oven at a range of frequencies. Already they knew from Jozef Stefan's experiments in 1879 that the total power per area emitted from a blackbody is proportional to the forth power of the temperature:

$$P(T) = \sigma\, T^4,$$

where $\sigma = 5.67{\times}10^{-8}$ W m^{-2} K^{-4}. In addition they knew that the wavelength, λ_{MAX}, at which most of the radiation is emitted is inversely proportional to the body's temperature:

$$\lambda_{MAX} = \frac{b}{T},$$

where $b = 2.9{\times}10^{-3}$ m K.

Now both of these laws could be explained by classical theory, the first by Ludwig Boltzmann in 1884 and the second by Wilhelm Wien in 1893. Now Wilhelm and Otto wanted to determine through this oven experiment the detailed nature of radiation emitted by an object in equilibrium. What they measured was an intensity as a function of wavelength that could not be explained through classical theory. Instead Max Planck, 5 years later, explained the measurements by postulating that matter existed only in certain energy states, quite counter to anyone's intuition, including his own.

First let's talk about black bodies. Let's consider a medium that is in chemical equilibrium, mechanical equilibrium, and radiative equilibrium. For example, there is no energy expended to change the chemistry of the medium, because the rates of all reactions are balanced by their reverse reactions. There is no energy expended to move stuff around because there are no net forces anywhere in the medium. And the amount of energy absorbed locally equals that emitted locally. Such a body is in *thermodynamic equilibrium.* It is at a constant temperature; otherwise it would either absorb or emit more radiation and heat or cool respectively. It also perfectly absorbs all radiation and emits radiation at the rate of absorption. The temperature of the body depends therefore on the radiation field that it is exposed to. In fact the intensity of the radiation emitted at each frequency depends only on the temperature.

The best blackbody is a black cavity with a tiny hole in it. This cavity is isolated from external work and thus (by the 2nd law of thermodynamics) is at a constant temperature. It absorbs all incoming radiation after it encounters (perhaps multiple times) the black surface of the wall. It emits only a tiny amount of radiation through the hole consistent with the amount absorbed.

To show that the intensity of light depends only on the temperature, consider taking two cavities A and B of the same temperature and aligning the holes. If the intensity of light I_ν exiting A and entering B exceeds that entering A and exiting B, then the temperature of the cavities will change, then B will heat up and A will cool. But that is a contradiction. Therefore the temperature depends on the intensity, and the intensity depends on the temperature The intensity is also isotropic, which can be argued in a similar way.

Kirchhoff realized (in 1860) that for such a cavity, the source function equals the intensity. That is:

$$\frac{j_\nu}{\kappa_\nu} = I_\nu.$$

Kirchhoff's law can be understood by placing a piece of material within the cavity that has the same temperature as the cavity, and a source function of S_ν. If S_ν exceeds the original intensity, B_ν, then the resultant intensity, I_ν, exceeds the original intensity,

B_ν. The converse is also true. (Recall that the source function is the intensity that is approached in an optically thick medium of constant source function.) But since the addition of the material does not change the nature of the cavity (i.e. it is still a blackbody of temperature T), I_ν should still equal B_ν. Therefore $S_\nu = B_\nu$.

A black body or enclosed radiation cavity is said to be in a state of *thermodynamic equilibrium*, shortened to "TE". Atmospheres are not in TE because, for example, they are not at one temperature and radiate from a variety of altitudes and temperature regions. Instead we find that they are in *local thermodynamic equilibrium*, where locally they behave as a blackbody such that their local source function is that of a blackbody at the local temperature, $B_\nu(T)$, but the intensity is not $B_\nu(T)$. Instead the intensity at equilibrium manifests the balance of absorption and radiation of the compositionally heterogeneous atmosphere, that results in a varied temperature field, particularly its varied temperature profile with altitude.

2.2. The Planck Function

In order to derive the intensity of radiation within the blackbody, we first derive the density of states, and then we derive the average energy of the photon states. These expressions, combined, allow us to derive the energy density per solid angle and frequency, from which we can derive the intensity, since we know that:

$$I_\nu = J_\nu = \frac{c}{4\pi}\ \mu, \qquad (1)$$

where the first equal sign follows from the isotropy of the radiation.

Density of States

To determine the density of states, we envision the radiation as consisting of standing electromagnetic waves in the cavity. Assume that the blackbody is a box of dimensions L_x=L, L_y=L, and L_z=L, and then count the number of nodes that this wave may have in the box. Each specific number of nodes represents a specific wavelength of light and therefore a specific energy state (since E=h c/λ). Consider a wave in direction $\mathbf{\hat{n}_x}$ of wave vector $\mathbf{k} = (2\pi/\lambda)\mathbf{n}$. The electromagnetic waves in the cavity must satisfy the wave equation:

$$\frac{\delta^2 E}{\delta x^2} + \frac{\delta^2 E}{\delta y^2} + \frac{\delta^2 E}{\delta z^2} = \frac{1}{c^2}\ \frac{\delta^2 E}{\delta t^2},$$

such that the electric field is zero at the walls. A metal wall can not support an electric field because the electrons would move about in such a way as to cancel the field. Furthermore, an electric field would dissipate energy at the walls and violate our assumption of equilibrium.

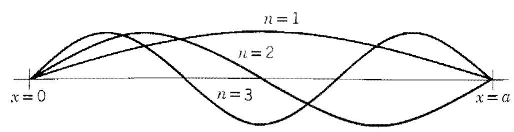

Fig. 1.— **Standing waves in a blackbody cavity with walls at x=0 & x=a. From Eisberg and Resnick.**

The solutions are standing waves (Fig. 1):

$$E = E_0\ \sin\frac{n_1 \pi x}{L} \sin\frac{n_2 \pi y}{L} \sin\frac{n_3 \pi z}{L} \sin\frac{2\pi ct}{\lambda},$$

where n_1, n_2, and n_3 are integers, and where (substituting this into the wave equation),

$$[\frac{n_1\pi}{L}]^2 + [\frac{n_2\pi}{L}]^2 + [\frac{n_3\pi}{L}]^2 =]\frac{2\pi}{\lambda}]^2$$

That is:

$$n_1^2 + n_2^2 + n_3^2 = \frac{4L^2}{\lambda^2},$$

or

$$n_1^2 + n_2^2 + n_3^2 = \frac{4L^2\nu^2}{c^2},$$

in terms of frequency ν = c/λ. These points can be viewed as making up the lattice points (projected in cartesian coordinates) of a sphere of radius r such that

$$r^2 = n_1^2 + n_2^2 + n_3^2 = \frac{4L^2\nu^2}{c^2}.$$

These lattice points also correspond to allowed frequencies.

Now the question arises as to how to count the number of allow states within a frequencies ν and $\nu + d\nu$. If we had a one dimensional cavity, which is impossible, but just as a thought experiment, we would find that the frequency is related to the state number n as:

$$\nu = \frac{nc}{2L}.$$

Therefore the number of states between ν and $\nu + d\nu$ is:

$$N(\nu) = (\frac{2L}{c})\ (\nu + d\nu)\ -\ (\frac{2L}{c})\nu = (\frac{2L}{c})\ d\nu,$$

as shown in Fig. 2, where our L is the figure's a.

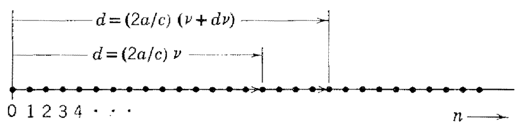

Fig. 2.— **The number of states for frequencies between ν and $\nu + d\nu$ for a 1-D model. From Eisberg and Resnick.**

Back to the real 3-D world, as you can see in figure 3, that by analogy to the 1-D case the number of states are given by the area between r and dr.

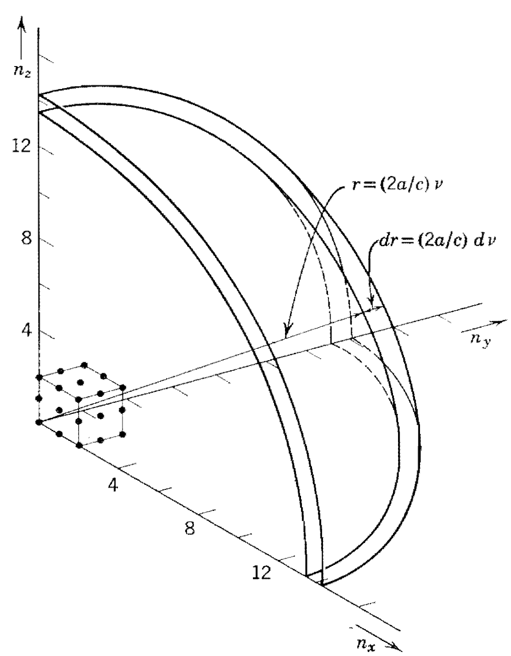

Fig. 3.— **Allowed frequencies of light in a blackbody cavity. From Eisberg and Resnick.**

That is:

$$N(r)dr = N(\nu)d\nu$$

But note that all the lattice points must be positive, so we are interested in only 1/8 of the sphere:

$$N(\nu)d\nu = N(r)dr = \frac{1}{8}\ 4\pi r^2 dr = \frac{\pi r^2 dr}{2},$$

or, writing r in terms of ν:

$$N(\nu)d\nu = \frac{\pi}{2}\ (\frac{2L}{c})^3\ \nu^2 d\nu.$$

But since light can have two states of polarization, we must multiply this by 2:

$$N(\nu)d\nu = \frac{8\pi V}{c^3}\ \nu^2 d\nu,$$

where $V = L^3$ is the volume of the cavity. Now divide this by the cavity volume to get the number of modes per wavelength and per cavity volume; that is the density of energy states:

$$D = \frac{8\pi}{c^3}\ \nu^2 \tag{2}$$

Based on the equipartition of energy, each mode (with two degrees of freedom) has an average energy of kT. Therefore, the energy density (energy per unit volume) within the frequency interval ν and $\nu\ +\ d\nu$ is

$$\mu_\nu = \frac{8\pi k_B T}{c^3}\ \nu^2. \tag{3}$$

The intensity is then (from Eq. 1):

$$B_\nu = I_\nu = \frac{c}{4\pi}\frac{8\pi\nu^2}{c^3}k_B T. \tag{4}$$

This is a classical result. It is called the Rayleigh Jeans Law. There's a problem with this: it predicts that the energy density increases to infinity as the frequency of light increases. Therefore most of the light would be emitted at infinitely high frequencies. Seems a little non-physical.

Historical Note

The intensity of the thermal emission baffled scientists in the latter part of the 19th century. The full spectrum of emitting object, that is B_ν was, in 1895, finally determined experimentally. The result was quite a puzzle. The measured intensity disagreed with the (rather unphysical) Rayleigh Jeans Law, a problem known at the time as the "ultraviolet catastrophe" (Fig. 4). For several years, no one could come

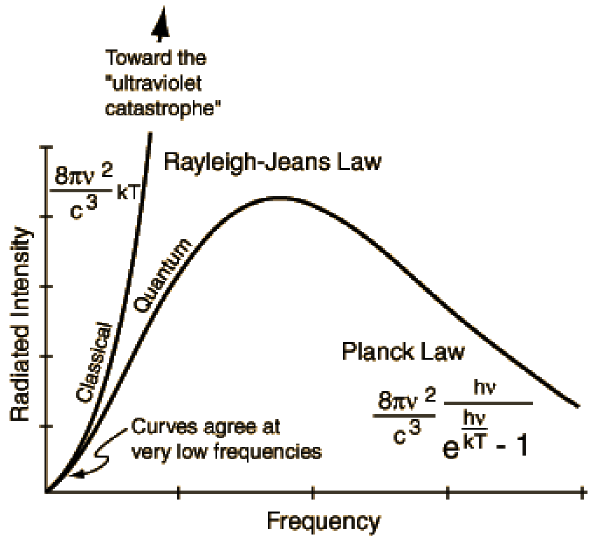

Fig. 4.— **Blackbody intensity predicted by the Rayleigh-Jeans law compared to measurements and Quantum Mechanics.**

up with a physical interpretation of the emission of a blackbody. In an "act of desperation", Planck solved this problem by deducing that only discrete energy levels were allowed.

Here's some of the logic of his argument. It's rather clever, and indeed appears a little desperate too. First of all, the Boltzmann distribution indicates that the probability of finding a state in a system with an energy E is:

$$P(E) = \frac{e^{E/k_BT}}{k_BT}$$

for a system in thermal equilibrium. The average energy of the system is then:

$$\bar{E} = \frac{\int_0^\infty EP(E)dE}{\int_0^\infty P(E)dE} = k_BT \quad (5)$$

This distribution was assumed in the derivation of the Rayleigh-Jeans law. Planck realized that if the energy states were not continuous then $\bar{E} < k_BT$. He realized that if the energy states could have only discrete values, say:

$$0, \Delta E, 2\Delta E, 3\Delta E, 4\Delta E, 5\Delta E,$$

where ΔE is the interval between the allowed energy states then he could change the Raleigh-Jean's law. Specifically, if $\Delta E << k_BT$ then $\bar{E} \sim k_BT$; if $\Delta E << k_BT$ then $\bar{E} << k_BT$, as shown in Fig. 5.

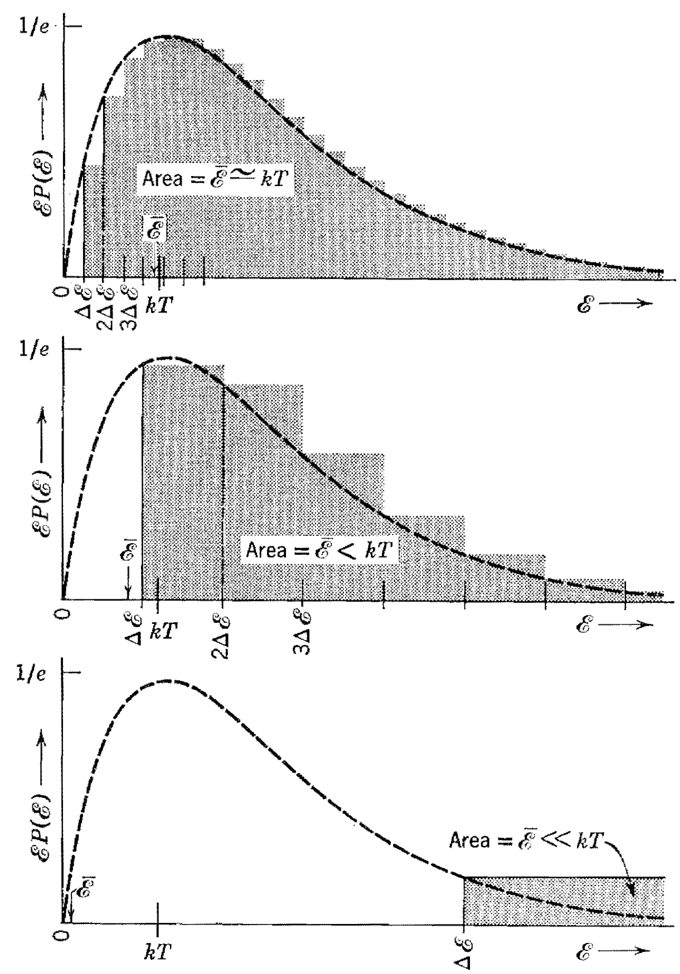

Fig. 5.— **Three figures showing qualitatively the calculation of $\bar{E}$ (Eq. 5) assuming discrete energy levels that are progressively more granular. From Eisberg and Resnick.**

Now the Raleigh-Jeans law works for low values of frequency, ν, but gives values that are too high for high frequencies. Planck thus proposed that ΔE exists and depends on frequency, and postulated the simplest relationship, i.e. that the quantum of energy states is proportional to the frequency:

$$\Delta E = h\nu,$$

where h is a constant of proportionality. If this idea were correct, then he would be able to determine h by determining the average energy of the states, and fitting the data. He did this, got a great fit, and derived a value of

$$h = 6.63 \times 10^{-34} \text{ J sec},$$

which is now known as Planck's constant. (The current value is 6.626068×10^{-34} J s.) We can see now that he found that light is quantized from the results of an oven experiment! Pretty cool.

Average Energy of the Photon States

Let's see how Planck derived the intensity of light. Consider a system in thermodynamic equilibrium with a total of N states with discrete energies E_i (i=1,2,...N). The probability for finding a state (within the system) of energy E_j, $P(E_j)$, is proportional to e^{-E_j/k_BT}, where k_B is the Boltzmann's constant.

This expression is quite general and is arrived at by realizing that the probability that the system contains such a state is proportional to the number of states having the energy E_j. This number is much smaller than the total number of states that the entire system can obtain. For this reason the number of states $N(E_j)$ accessible to the tiny subsystem A_j of the larger system A that lies near E_j can be expanded as a Taylor series. We assume that the energies of A and A_j add up to a total fixed energy E^0. That is: $E + E_j = E^0$. The probability (P_j) of finding A_j in state j such that its energy is E_j is proportional to number of states accessible to the larger system A (outside of A_j) having energy $E^0 - E_j$. That is $N(E^0 - E_j)$):

$$P_j \propto N(E^0 - E_j)$$

We must also consider the number of states for subsystem A_j with energy E_j. That is the degeneracy of the state, g_j. Let's work with the natural logarithm of N because number of states varies strongly with energy. We can expand the natural log of $N(E^0 - E_j)$ about E^0 since $E_j << E^0$ and keep only the first term:

$$P_j \propto \ln N(E^0 - E_j) = \ln N(E^0) + [\frac{d\ln N'}{dE'}]_0(-E_j)$$

Calling

$$[\frac{d\ln N'}{dE'}]_0 = \beta,$$

we have

$$\ln N(E^0 - E_j) = (\ln N(E^0)) - \beta E_j.$$

Taking the logarithm and noting that the expression in parenthesis is a constant:

$$P(E_j) = N(E^0 - E_j) = Ce^{-\beta E_j}, \qquad (5)$$

where C is a constant, independent of E_j. It turns out (with a little thermodynamics) that β is proportional to the inverse of the temperature, $\beta = 1/k_B$T, which arises through the definition of temperature.

The value of the constant of proportionality can be found by realizing that the probability that any possible energy will occur is 1. It follows that the probability for a system to have a state of energy E_j is:

$$P(E_j) = \frac{g_j e^{-\beta E_j}}{\sum_0^\infty g_i e^{-\beta E_i}} \qquad (6)$$

Note that g_i is the degeneracy of the energy state; that is the number of states that have the same energy.

Bose-Einstein Statistics

Particles can be grouped into several different groups which have different statistical properties. There are particles that obey *Maxwell-Boltzmann statistics*. These particles are all distinguishable and the state of an ensemble of these guys depends on which particle has which energy. In other words to define a state, you have to define the energy of each particle. These particles obey classical mechanics. Quantum mechanics specifies that particles act through probabilities and can not be specified exactly in time and energy or in position and momentum. These particles are indistinguishable. Particles are further grouped in terms of their spin; fermions are particles that have odd-half-integer (e.g. 1/2, 3/2...) intrinsic angular momentum spin. These particles obey the Pauli Exclusion Principal and can not co-exist in the same state. Examples of fermions are most fundamental particles, i.e. quarks, leptons (e.g. electrons), and their composites like protons and neutrons. Fermions obey *Fermi-Dirac statistics* wherein the particles are indistinguishable and there can be at most 1 particle in each state.

Bosons are particles that have integer spin (e.g. 0,1,2). All the force carrier particles are bosons, such as photons (the E&M carrier), gluons (strong force carriers), gravitons (gravity carrier), W and Z-bosons (weak force carriers), and some composites (e.g. mesons which are made up 2 quarks). These particles can exist in the same state at the same time. *Bose-Einstein statistics* describes such particles, which are indistinguishable and for which any number of particles can occupy each state. Photons obey Bose-Einstein statistics with the additional caveat that there is an unspecified number of particles.

Number of Particles in a State:

Let's say that we want to calculate the mean number of particles, $\bar{n}_s$ in a state s. We need to then sum all of possible states of n_s, weighted by the probability that a state occurs:

$$\bar{n}_s = \frac{\sum_{n_1,n_2...n_s} n_s e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+...)}}{\sum_{n_1,n_2...n_s} e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+...)}}$$

That is:

$$\bar{n}_s = \frac{\sum_{n_s} n_s e^{-\beta n_s\epsilon_s} \sum^{-s}_{n_1,n_2...} e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+...)}}{\sum_{n_s} e^{-\beta n_s\epsilon_s} \sum^{-s}_{n_1,n_2...} e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+...)}} \quad (7)$$

where the $-s$ term means that the s state is excluded in the sum. In Fermi-Dirac statistics, the values of n_R can take on only 0 and 1, since there can be only one particle in each state. In Maxwell-Boltzmann statistics the values of n_R are restricted so that they add up to the total number of particles. In addition, the energy level is associated with the particular particle. The same set of energies assigned to different particles is a different state. The expression above is in fact simplest to solve for photons, because each photon can have any possible state regardless of the occupation of photons in that state. So the $\sum^{-s}$ terms are identical and cancel, leaving:

$$\bar{n}_s = \frac{\sum_{n_s} n_s e^{-\beta n_s\epsilon_s}}{\sum_{n_s} e^{-\beta n_s\epsilon_s}}.$$

This can be written as

$$\bar{n}_s = \frac{-(1/\beta)(d/d\epsilon_s)\sum e^{-\beta n_s\epsilon_s}}{\sum e^{-\beta n_s\epsilon_s}} = -\frac{1}{\beta}\frac{d}{d\epsilon_s}\ln(\sum e^{-\beta n_s\epsilon_s})$$

This is an infinite geometric series, which can be summed:

$$\sum_{n_s=0}^{\infty} e^{-\beta n_s\epsilon_s} = 1 + e^{-\beta\epsilon_s} + e^{-2\beta\epsilon_s}.. = \frac{1}{1-e^{-\beta\epsilon_s}}$$

Therefore:

$$\bar{n}_s = \frac{1}{\beta}\frac{d}{d\epsilon_s}\ln(1-e^{-\beta\epsilon_s}) = \frac{e^{-\beta\epsilon_s}}{1-e^{-\beta\epsilon_s}}$$

(since ln(1/x) = - ln(x)), and we have what is called the Planck Distribution:

$$\bar{n}_s = \frac{1}{e^{\beta\epsilon_s}-1}. \quad (8)$$

Now let's get back to the question of the average energy of radiation of frequency ν. Let each state n be that designated by having n photons of energy $h\nu$, such that the energy of the nth state is $E_n = nh\nu$ The mean energy is then the sum of E_n weighted by the probability that this energy will occur:

$$\bar{E}(\nu) = \frac{\sum_{n=0}^{\infty} nh\nu\ e^{-\beta nh\nu}}{\sum_{n=0}^{\infty} e^{-\beta nh\nu}}.$$

Now, this is just

$$\bar{E}(\nu) = h\nu\bar{n} = \frac{h\nu}{e^{\beta h\nu}-1} \quad (9)$$

The Blackbody intensity

The energy density is the number of electromagnetic waves per unit volume times their average energy:

$$\mu = \frac{8\pi\nu^2 h\nu}{c^3(e^{h\nu/k_BT}-1)} \quad (10)$$

and the intensity of a blackbody is:

$$B_\nu = I_\nu = \frac{c}{4\pi}\mu = \frac{2h\nu^3}{c^2(e^{h\nu/k_BT}-1)}. \quad (11)$$

This is called the Planck Function. Planck's derivation of B_ν and the Planck Distribution was presented at the German Physical Society on December 14, 1900, a date now associated with the birth of quantum physics. Max Planck was awarded the nobel Prize in Physics in 1918

Summary

The difference between the classical theory and the quantum mechanical theory is occupation of states. Both theories find the same number of modes per unit volume and frequency. That is:

$$D = \frac{8\pi\nu^2}{c^3}.$$

The theories differed in the energy per mode. In classical theory the energy of a mode depends only on the temperature:

$$E_{mode} = kT.$$

Yet, quantum theory assumes that the states are quantized and finite. The occupation of states is not the same for all modes. Energy is required to jump to the higher states (of higher ν), which therefore have a low average energy because of the low occupation of states.

$$E_{mode} = \frac{h\nu}{(e^{h\nu/k_B T} - 1)}.$$

A good reference to thermodynamics and blackbody radiation is F. Rief, Fundamentals of Statistical and Thermal Physics.