A Quantum Harmonic Oscillator

The quantum harmonic oscillator (the only kind there is, really) has energy levels given by
\[ E_n = (n + 1/2)\hbar \omega, \]
where \( n \geq 0 \) is an integer and the \( E_0 = \hbar \omega/2 \) represents zero point fluctuations in the ground state. We are going to shift the origin slightly and take the energy to be
\[ E_n = n\hbar \omega. \]
That is, we are going to ignore zero point energies. The actual justification for this is a little problematic, but basically, it represents an unavailable energy, so we just leave it out of the accounting.

The partition function is then
\[ Z = \sum_{n=0}^{\infty} e^{-n\hbar \omega/\tau} = \frac{1}{1 - \exp(-\hbar \omega/\tau)} = \frac{\exp(\hbar \omega/\tau)}{\exp(\hbar \omega/\tau) - 1}. \]
(Thus is just an infinite series \( \sum x^n \) with \( x = \exp(-\hbar \omega/\tau) \).) We calculate the average energy of the oscillator
\[ \langle E \rangle = \tau^2 \frac{\partial \log Z}{\partial \tau} = \frac{\hbar \omega}{\exp(\hbar \omega/\tau) - 1}. \]
It’s instructive to consider two limiting cases. First, consider the case, that \( \hbar \omega \ll \tau \). That is, the energy level spacing of the oscillator is much less than the typical thermal energy. In this case, the denominator becomes
\[ e^{\hbar \omega/\tau} - 1 \approx 1 + \frac{\hbar \omega}{\tau} + \cdots - 1 = \frac{\hbar \omega}{\tau}. \]
If we plug this into the expression for the average energy, we get
\[ \langle E \rangle \to \tau, \quad (\hbar \omega \ll \tau), \]
just as we found for the classical case. On the other hand, if \( \hbar \omega/\tau \gg 1 \), then the exponential in the denominator is large compared to unity and the average energy becomes
\[ \langle E \rangle \to \hbar \omega e^{-\hbar \omega/\tau}, \quad (\hbar \omega \gg \tau). \]
In other words, the average energy is “exponentially killed off” for high energies. Recall that we needed a way to keep the high energy modes quiescent in order to solve our cavity radiation problem!
Quantum Cavity Radiation

Now that we have given a treatment of the quantum harmonic oscillator, we can return to the cavity radiation problem. Note that our counting of states is basically the counting of electromagnetic modes. These came out quantized because we were considering standing electromagnetic waves. That is, classical considerations gave us quantized frequencies and quantized modes. With quantum mechanics, we identify each mode as a quantum oscillator and realize that the energies (and amplitudes) of each mode are quantized as well.

In addition, with quantum mechanics, we know that particles have wave properties and vice-versa and that quantum mechanics associates an energy with a frequency according to \( E = \hbar \omega \). So given that we have a mode of frequency \( \omega \), it is populated by particles with energy \( \hbar \omega \). We can get the mode classically by considering standing waves of the electromagnetic field and we can get it quantum mechanically by considering a particle in a box. Either way we get quantized frequencies. With quantum mechanics we also find that the occupants of the modes are particles with energies \( \hbar \omega \), so we get quantized energies at each quantized frequency. When you take a course in quantum field theory, you will learn about second quantization which is what we've just been talking about!

The particles associated with the electric field are called photons. They are massless and travel at the speed of light. They carry energy \( E = h\nu = \hbar \omega \) and momentum \( p = \hbar/\lambda = h\nu/c = \hbar \omega/c \), where \( \omega \) and \( \lambda \) are the frequency and wavelength of the corresponding wave. Note that the frequency in Hertz is \( \nu = \omega/2\pi \).

When \( \hbar \omega \ll \tau \), so the thermal energy is much larger than the photon energy, we have

\[
\frac{\langle E \rangle}{\hbar \omega} \to \frac{\tau}{\hbar \omega} \gg 1, \quad (\hbar \omega \ll \tau).
\]

The average energy divided by the energy per photon is the average number of photons in the mode or the average occupancy. We see that in the limit of low energy modes, each mode has many photons. When quantum numbers are large, we expect quantum mechanics to go over to classical mechanics and sure enough this is the limit where the classical treatment gives a reasonable answer. At the other extreme, when the photon energy is high compared to the thermal energy, we have

\[
\frac{\langle E \rangle}{\hbar \omega} \to e^{-\hbar \omega/\tau} \ll 1, \quad (\hbar \omega \gg \tau).
\]

In this limit, the average occupancy is much less than 1. This means that the mode is quiescent (as needed) and also that quantum effects should be dominant. In particular, the heat bath, whose typical energies are \( \sim \tau \) has a hard time getting together an energy much larger than \( \tau \) all at once so as to excite a high energy mode.

Perhaps a bit of clarification is needed here. When discussing the ideal gas, consisting of atoms or molecules, we said that a low occupancy gas was classical and a high occupancy
gas needed to be treated with quantum mechanics—apparently just the opposite of what was said in the previous paragraph! When a large number of particles are in the same state, they can be treated as a classical field. Thus at low photon energies, with many photons in the same mode, we can speak of the electromagnetic field of the mode. At high photon energies, where the occupancy is low, the behavior is like that of a classical particle but a quantized field.

Let’s calculate the cavity radiation spectrum. The only change we need to make from our previous treatment is to substitute the quantum oscillator average energy in place of the classical result. The number of modes per unit frequency is the same whether we count the modes classically or quantum mechanically. However, since the average energy now depends on frequency, we must include it in the integral when we attempt to find the total energy. The energy per unit frequency is

\[
\frac{dU}{d\omega} = \frac{V\omega^2}{\pi^2 c^3} \frac{\hbar \omega}{\exp(\hbar \omega / \tau) - 1} d\omega,
\]

and the total energy in the cavity is,

\[
U = \int_0^{\infty} d\omega \frac{V\omega^2}{\pi^2 c^3} \frac{\hbar \omega}{\exp(\hbar \omega / \tau) - 1}.
\]

It is convenient to divide the energy per unit frequency by the volume and consider the spectral density \(u_\omega\), where

\[
u_\omega = \frac{1}{V} \frac{dU}{d\omega} = \frac{\hbar \omega^3}{\pi^2 c^3 (\exp(\hbar \omega / \tau) - 1)}.
\]

This is called the Planck radiation law. It is simply the energy per unit volume per unit frequency at frequency \(\omega\) inside a cavity at temperature \(\tau\). For convenience, let \(x = \hbar \omega / \tau\). Then \(x\) is dimensionless and we have

\[
u_\omega = \frac{\tau^3}{\pi^2 \hbar^2 c^3} \frac{x^3}{e^x - 1}.
\]

The shape of the spectrum is given by the second factor above which is plotted in the figure.
Changing the temperature shifts the curve to higher frequencies (in proportion to $\tau$) and multiplies the curve by $\tau^3$ (and constants). At low energy the spectrum is proportional to $\omega^2$ in agreement with the classical result. At high energy there is an exponential cut-off. The exponential behavior on the high energy side of the curve is known as \textit{Wien’s law}. 

To find the total energy per unit volume we have

\begin{align*}
 u &= \int_0^{+\infty} d\omega \ u_\omega , \\
 &= \int_0^{+\infty} d\omega \ \frac{h\omega^3}{\pi^2 c^3 (\exp(h\omega/\tau) - 1)} , \\
 &= \frac{\tau^4}{\pi^2 c^3} \int_0^{+\infty} \frac{x^3 \, dx}{e^x - 1} , \\
 &= \frac{\tau^4}{\pi^2 c^3} \frac{\pi^4}{15} \quad \text{(looking up the integral)} , \\
 &= \frac{\pi^2}{15 h^3 c^3} \tau^4 .
\end{align*}

The fact that radiation density is proportional to $\tau^4$ is called the \textit{Stefan-Boltzmann law}. 

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We can also calculate the entropy of radiation. We have

\[ U = Vu = \frac{\pi^2}{15h^3c^3} V \tau^4. \]

We know that \( \tau d\sigma = dU \) when the volume is constant, so

\[ d\sigma = \frac{1}{\tau} \frac{4\pi^2}{15h^3c^3} V \tau^3 d\tau = \frac{4\pi^2}{15h^3c^3} V \tau^2 d\tau. \]

We integrate this relation setting the integration constant to 0, (why?) and obtain

\[ \sigma = \frac{4\pi^2}{45h^3c^3} V \tau^3. \]

It is sometimes useful to think of blackbody radiation as a gas of photons. Some of the homework problems explore this point of view as well as other interesting facts about the blackbody radiation law.

One application of the blackbody radiation law has to do with the cosmic microwave background radiation which is believed to be thermal radiation left over from the hot big bang which started our universe. Due to the expansion of the universe, it has cooled down. This radiation has been measured very precisely by the FIRAS instrument on the COBE satellite and is shown in the accompanying figure which was put together by
Lyman Page mostly from data collected by Reach, et al., 1995, Astrophysical Journal, 451, 188. The dashed curve is the theoretical curve and the solid curve represents the measurements where the error bars are smaller than the width of the curve! Other curves on the plot represent deviations in the curve due to our motion through the background radiation (dipole), irregularities due to fluctuations that eventually gave rise to galaxies and physicists (anisotropy) and sources of interfering foreground emission. The temperature is 2.728 ± 0.002 K where the error (one standard deviation) is all systematic and reflects how well the experimenters could calibrate their thermometer and subtract the foreground sources.
More on Blackbody Radiation

Before moving on to other topics, we’ll clean up a few loose ends having to do with blackbody radiation.

In the homework you are asked to show that the pressure is given by

\[ p = \frac{\pi^2 \tau^4}{45\hbar^3 c^3}, \]

from which one obtains

\[ pV = \frac{1}{3} U, \]

for a photon gas. This is to be compared with

\[ pV = \frac{2}{3} U, \]

appropriate for a monatomic ideal gas.

In an adiabatic (isentropic—constant entropy) expansion, an ideal gas obeys the relation

\[ pV\gamma = \text{Constant}, \]

where \( \gamma = C_p/C_V \) is the ratio of heat capacity at constant pressure to heat capacity at constant volume. For a monatomic ideal gas, \( \gamma = 5/3 \). For complicated gas molecules with many internal degrees of freedom, \( \gamma \to 1 \). A monatomic gas is “stiffer” than a polyatomic gas in the sense that the pressure in a monatomic gas rises faster for a given amount of compression. What are the heat capacities of a photon gas? Since

\[ U = \frac{\pi^2}{15\hbar^3 c^3} V \tau^4, \]

\[ C_V = \left( \frac{\partial U}{\partial \tau} \right)_V = \frac{4\pi^2}{15\hbar^3 c^3} V \tau^3. \]

How about the heat capacity at constant pressure. We can’t do that! The pressure depends only on the temperature, so we can’t change the temperature without changing the pressure. We can imagine adding some heat energy to a photon gas. In order to keep the pressure constant, we must let the gas expand while we add the energy. So, we can certainly add heat at constant pressure, it just means the temperature is constant as well, so I suppose the heat capacity at constant pressure is formally infinite!

If one recalls the derivation of the adiabatic law for an ideal gas, it’s more or less an accident that the exponent turns out to be the ratio of heat capacities. This, plus the fact that we can’t calculate a constant pressure heat capacity is probably a good sign.
that we should calculate the adiabatic relation for photon gas directly. We already know \( \sigma \propto V \tau^3 \propto V p^{3/4} \), so for an adiabatic process with a photon gas,

\[
pV^{4/3} = \text{Constant},
\]

and a photon gas is “softer” than an ideal monatomic gas, but “stiffer” than polyatomic gases. Note that \( \gamma = 4/3 \) mainly depends on the fact that photons are massless. Consider a gas composed of particles of energy \( E \) and momentum \( P = E/c \), where \( c \) is the speed of light. Suppose that particles travel at speed \( c \) and that their directions of motion are isotropically distributed. Then if the energy density is \( u = nE \), where \( n \) is the number of particles per unit volume, the pressure is \( u/3 \). This can be found by the same kind of argument suggested in the homework problem. The same result holds if the particles have a distribution in energy provided they satisfy \( P = E/c \) and \( v = c \). This will be the case for ordinary matter particles if they are moving at relativistic speeds. A relativistic gas is “softer” than a similar non-relativistic gas!

On problem 3 of the homework you are asked to determine the power per unit area radiated by the surface of a blackbody or, equivalently, a small hole in a cavity. The result is \((c/4)u\) where the speed of light accounts for the speed at which energy is transported by the photons and the factor of 1/4 accounts for the efficiency with which the energy gets through the hole. The flux is

\[
J = \frac{\pi^2 x^4}{60 \hbar^3 c^2} = \frac{\pi^2 k^4}{60 \hbar^3 c^2} T^4 = \sigma_B T^4
\]

where the Stefan-Boltzmann constant is

\[
\sigma_B = \frac{\pi^2 k^4}{60 \hbar^3 c^2} = 5.6687 \times 10^{-5} \text{ erg cm}^{-2} \text{ s}^{-1} \text{ K}^{-4}.
\]

We saw that the Planck curve involved the function \( x^3/(\exp(x) - 1) \) with \( x = \hbar \omega/\tau \). Let’s find the value of \( x \) for which this curve is a maximum. We have

\[
0 = \frac{d}{dx} \frac{x^3}{e^x - 1},
\]

\[
= \frac{3x^2 e^x - x^3 e^x}{e^x - 1} - \frac{x^3 e^x}{(e^x - 1)^2},
\]

\[
= \frac{(3x^2 - x^3) e^x - 3x^2}{(e^x - 1)^2},
\]

or

\[
0 = (x - 3) e^x + 3.
\]

This transcendental equation must be solved numerically. The result is \( x = 2.82144 \). At maximum,

\[
2.82 = \frac{\hbar \omega_{\text{max}}}{\tau} = \frac{\hbar}{k} \frac{\nu_{\text{max}}}{T},
\]
or
\[ \frac{T}{\nu_{\text{max}}} = \frac{h}{2.82k} = 0.017 \text{ Kelvin per Gigahertz}. \]

So the above establishes a relation between the temperature and the frequency of the maximum energy density per unit frequency.

You will often see \( u_\nu \) which is the energy density per unit Hertz rather than the energy density per unit radians per second. This is related to \( u_\omega \) by the appropriate number of \( 2\pi \)'s. You will also see \( u_\lambda \) which is the energy density per unit wavelength. This is found from
\[ u_\lambda |d\lambda| = u_\omega |d\omega|. \]

This says that the energy density within a range of wavelengths should be same as the energy density within the corresponding range of frequencies. The absolute value signs are there because we only care about the widths of the ranges, not the signs of the ranges. We use \( \omega = 2\pi c/\lambda \) and \( d\omega = (2\pi c/\lambda^2)|d\lambda| \),
\[ u_\lambda = u_\omega \left| \frac{d\omega}{d\lambda} \right|, \]
\[ = \frac{h(2\pi c/\lambda)^3}{\pi^2 c^3 (\exp(2\pi hc/\lambda\tau) - 1)} \frac{2\pi c}{\lambda^2}, \]
\[ = \frac{8\pi hc}{\lambda^5 (\exp(hc/\lambda\tau) - 1)}, \]
\[ = \frac{8\pi\tau^5}{h^4 c^4} \frac{x^5}{e^x - 1}, \]
where \( x = hc/\lambda\tau \). At long wavelengths, \( u_\lambda \to 8\pi\tau/\lambda^4 \), and at short wavelengths \( u_\lambda \) is exponentially cut off. The maximum of \( u_\lambda \) occurs at a wavelength given by the solution of
\[ (x - 5)e^x + 5 = 0. \]
The solution is \( x = 4.96511 \ldots \) From this, we have
\[ \lambda_{\text{max}}T = \frac{hc}{4.97k} = 0.290 \text{ cm K}. \]

This is known as Wien’s displacement law. It simply says that the wavelength of the maximum in the spectrum and the temperature are inversely related. In this form, the constant is easy to remember. It’s just 3 mm Kelvin. (Note that the wavelength of the maximum in the frequency spectrum and the wavelength of the maximum in the wavelength spectrum differ by a factor of about 1.6. This is just a reflection of the fact that wavelength and frequency are inversely related.)

Let’s apply some of these formulae to the sun. First, the peak of the spectrum is in about the middle of the visible band (do you think this is a coincidence or do you suppose
there’s a reason for it?), at about $\lambda_{\text{max}} \approx 5000 \ \text{Å} = 5 \times 10^{-5} \ \text{cm}$. Using the displacement law (and assuming the sun radiates as a blackbody), we find $T_{\text{sun}} \approx 5800 \ \text{K}$. The luminosity of the sun is $L = 3.8 \times 10^{33} \ \text{erg s}^{-1}$. The radius of the sun is $r = 7.0 \times 10^{10} \ \text{cm}$. The flux emitted by the sun is $J = L/4\pi r^2 = 6.2 \times 10^{10} \ \text{erg cm}^{-2} \text{s}^{-1}$. This is about 60 Megawatts per square meter! We equate this to $\sigma_B T^4$ and find $T_{\text{sun}} \approx 5700 \ \text{K}$, very close to what we estimated from the displacement law.

Problem 17 in chapter 4 of K&K points out that the entropy of a single mode of thermal radiation depends only on the average number of photons in the mode. Let’s see if we can work this out. We will use

$$\sigma = \frac{\partial \tau \log Z}{\partial \tau},$$

where $Z$ is the partition function and the requirement of constant volume is satisfied by holding the frequency of the mode constant. We’ve already worked out the partition function for a single mode

$$Z = \frac{1}{1 - e^{-\hbar \omega / \tau}}.$$  

The average occupancy (number of photons) in the mode is

$$n = \frac{1}{e^{\hbar \omega / \tau} - 1},$$

from which we find

$$\frac{n + 1}{n} = e^{\hbar \omega / \tau}, \quad \text{or} \quad \frac{\hbar \omega}{\tau} = \log \frac{n + 1}{n}.$$  

Now let’s do the derivatives to get the entropy

$$\sigma = \frac{\partial \tau}{\partial \tau} \left( \tau \log Z \right),$$

$$= \log Z - \tau \frac{\partial}{\partial \tau} \log \left( 1 - e^{-\hbar \omega / \tau} \right),$$

$$= \log \frac{1}{1 - e^{-\hbar \omega / \tau}} - \tau \left( 1 - e^{-\hbar \omega / \tau} \right) \left( \frac{\hbar \omega}{\tau} \right) \left( -\frac{1}{\tau} \right),$$

$$= \log \frac{1}{1 - n/(n + 1)} + \frac{\hbar \omega}{\tau} \frac{e^{-\hbar \omega / \tau}}{1 - e^{-\hbar \omega / \tau}},$$

$$= \log(n + 1) + \log \left( \frac{n + 1}{n} \right) \frac{n/(n + 1)}{1 - n/(n + 1)},$$

$$= \log(n + 1) + n \log \frac{n + 1}{n},$$

$$= (n + 1) \log(n + 1) - n \log n,$$
Which is the form given in K&K. This is another way of making the point that the expansion of the universe does not change the entropy of the background radiation. The expansion redshifts each photon—stretches out its wavelength—in proportion to the expansion factor, but it does not change the number of photons that have the redshifted wavelength—the number of photons in the mode. So, the entropy doesn’t change. (This assumes that the photons don’t interact with each other or with the matter. Once the universe is cool enough (≤ 4000 K) that the hydrogen is no longer ionized, then the interactions are very small.)