**EM Radiation**

Consider an object inside a ‘skin tight’ container. Its total energy would be, as usual, just the kinetic + potential energy of its atoms. As the atoms oscillate back and forth, they will emit radiation, the backwards force of which would slow the oscillator down, causing it to lose kinetic energy, and thereby temperature. But of course, this radiation would also be absorbed by the body as well, causing it to gain kinetic energy, and preserve its temperature. So everything remains the same. But if the object is placed inside a closed container with volume greater than the object, the object will fill the container up with photons, and thereby cool down as it does. Eventually equilibrium will be established between the oscillator (object) and the radiation, so that just as much energy is being emitted as is being absorbed. Let’s define the usual quantities from E&M, concerning the radiation itself:



These are related via usual equation I = uc. And w/r to the body, let’s define the intensity, e, of radiation *emitted*, at frequency ν, called the emissivity, and the fraction, a, of incident radiation of frequency ν absorbed, called the absorptivity.



The intensity of radiation absorbed is aI. And when equilibrium is established, this must be equal to e, so aI = e. This is Kirchoff’s law.



Note that if an entity is a perfect absorber, then a = 1. But then it must also be a perfect emitter as well, at least when in equilibrium with the radiation.

**Heat capacity and equation of state for radiation**

First of all, if we have a substance at temperature T emitting radiation which fills a volume V, the energy of the said radiation should only depend on T and V. We can construct its energy and entropy as we did with the previous substances, using the heat capacity and pressure measurements. How would we take heat capacity measurements of radiation? Well we could take radiation at temperature T0 and volume V0 and place an object at temperature T΄ in the container – I’ll suppose the volume contribution to be negligible. Then the object will radiate away heat, and come to a new equilibrium temperature T. So we’ll know the change in temperature of the radiation δT = T – T0. Measurements of this sort have been taken (presumably), bringing us to the following formulas for the heat capacity and pressure:

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where α is a constant that is about α = 7.56×10-16 J/m3K4. Note that we could infer the volume dependence of the heat capacity with the equation of state, like before, since



which would of course imply that CV = 4αT3V + f(T). And there would be no way of ascertaining what f(T) is (0 obviously) without measurements or some supplemental theoretical argument. In passing let’s calculate the radiation pressure near a star. For instance our Sun has a surface temperature of about T = 5 000K. So then p ~ 0.1 N/m. Near the interior, T ~ 106K, and so p ~ 108 N/m, which is 1000 times air pressure on Earth.

**Internal energy and entropy of EM radiation**

Plugging these results into the formula for U we have:



The latter part implies U = αT4V + f(T), and the former part implies f(T) = 0. So we have:



This seems plausible since we know that the energy density of an EM wave just depends on the field strength itself u(ν) = ε0E(ν)2. And it doesn’t make sense to think that E(ν) should depend on volume itself. But E(ν) could conceivably depend on temperature since higher temperatures correspond to faster oscillations of the atoms, which is what determines the frequency of radiation emitted. So we would postulate u = ∫u(ν)dν = u(T), and so U = uV = u(T)V. And this temperature is something that we can literally measure with a thermometer. Note that since u is independent of V, the photon gas will behave much differently than an ideal particle gas. So for example if we expand the volume at constant temperature, the energy of the photon gas will increase (this energy would have to be supplied via heat). On the other hand if we do the same for an ideal gas, the energy will not increase. Also if we do a sudden expansion of the container, the temperature of a gas of photons would drop, since U would remain same, but V would increase, and so U would decrease, which means T must decrease. Note that we can write for the emissivity: *e* = *a∙*I(T) = *a*∙uc = *a*cαT4. So this is the origin of that law of thermal radiation. Let’s make note that p directly to the energy density:



where u = U/V. Now let’s consider the entropy. Expressing S as a function of T and V, and forming the total differential, we have:



and integrating this equation we find:



So this is our entropy (density) formula:



Note that for an adiabatic process, ΔS = 0, which implies. VT3 = const. We can approximate the expansion of the universe as an adiabatic process. The energy of the universe comes predominantly from radiation, and so we have a relationship that will give us the temperature of the universe as a function of its volume. Finally, we can put the energy in terms of its canonical variables now, by solving for T in terms of s. And we’ll have:



and so we have:



What is the Free Energy of the radiation? We have:



So,



Might observe that the Gibbs free energy G = E – TS + pV = 0.

**Explorations into the form of u(ν,T)**

At the end of the 19th century there was a lot of interest in determining u(ν,T). Wein used an adiabatic compression of the photon gas to characterize the functional form of u(ν,T). Wein compressed a gas of photons with a piston adiabatically, which changed the energy density accordingly. Since the compression was adiabatic he was able to deduce the new temperature at each level of compression. By analyzing the interaction between the frequency modes and the piston he was able to determine how ν shifted to ν´. So he was able to find a relationship between v’ and T. And thus he was able to postulate a scaling formula for u(T,ν)…



Secondly, it was found that at a given T, u(T,ν) reached a max at some νmax. This implied that:



This equation is a function of νmax/T only. And so the solution is νmax/T = const., where const. is some pure number. And so this implies λmaxT = const.’, which known as:

