Notes on Blackbody Radiation

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1 Plots of "experimental" data

This section refers to the series of plots shown below. Think of these as displaying experimental data (although, in truth, they are calculated – Planck would not have had data as accurate or extensive as that shown). First, note the units and scales. The vertical axis is the amount of energy radiated per unit area (that is, per 1 m^2) of an object per unit frequency interval (that is, per 1 Hz). The horizontal axis is just the frequency in Hz. Note the multiplier of the units in both cases.
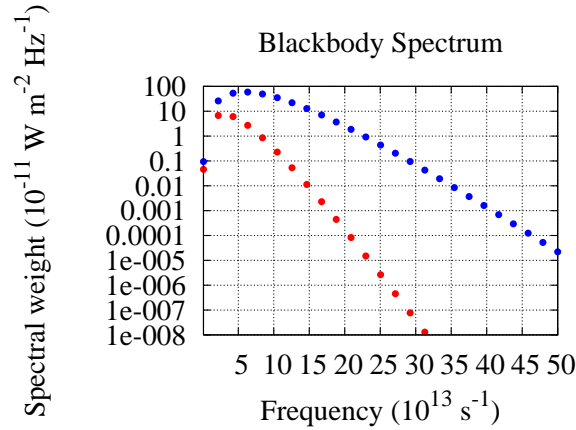
1. Linear scales
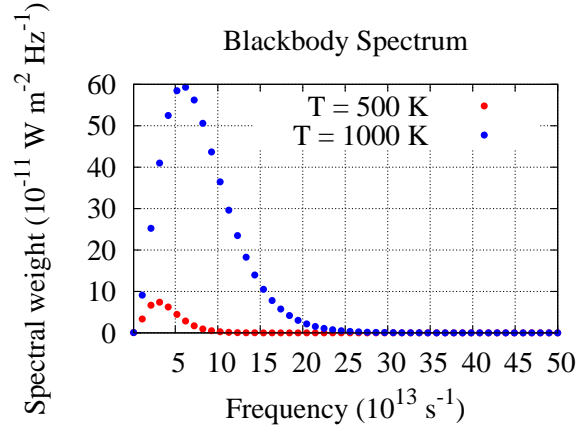
(a) Peak moves to higher frequency as T rises. In fact, doubling T doubles the frequency at which the peak occurs:

$$\nu_{max} = aT. \tag{1}$$

(b) Peak intensity goes up very rapidly: a factor of 8 for a change of T by a factor of 2.

2. Semi-log scales

Blackbody Spectrum

(a) At large frequency, intensity decays roughly exponentially: half the decay rate at twice the temperature:

$$S(\nu) \propto e^{-h\nu/k_B T} \qquad (2)$$

so that $\log(S) = -h\nu/k_B T$. Here, I've made the argument of the exponential a ratio of energies by multiplying T by Boltzmann's constant, $k_B = 1.381 \times 10^{-23}$ J/K. h is then an unknown "fitting constant" with the units of Joule-seconds – this turns out to be the fundamental quantum mechanical constant. While $h\nu$ has the units of an energy, there is no physical quantity in classical physics to which it corresponds.

3. Log-log scales

Blackbody Spectrum
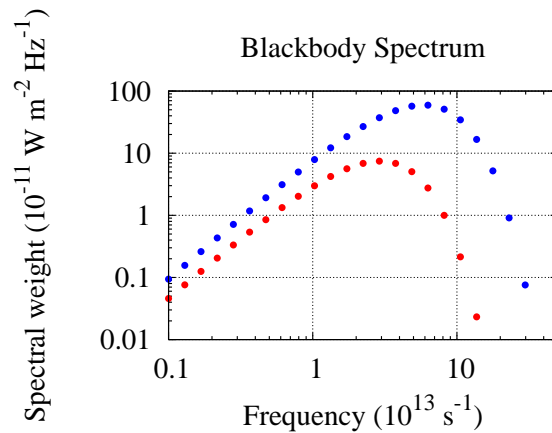
(a) Straight line at low frequency means a power law; two decades in S for one decade in ν means the power is two. Also, intensity doubles with doubling of T:

$$S(\nu) \propto T\nu^2 \qquad (3)$$

2

A good guess for the functional form of $S(\nu)$, based on the above "experimental observations", would be

$$S(\nu) \propto T \, v^2 \, e^{-h\nu/k_B T}. \tag{4}$$

However, this function doesn't quite fit the data. It misses the temperature dependence at large ν.

A function that turns out to do a perfect job was cooked up by Max Planck in 1900:

$$\boxed{S(\nu) = \frac{2\pi h}{c^2} \frac{\nu^3}{e^{h\nu/k_B T} - 1}} \tag{5}$$

Of course, h is an unknown parameter, but Planck found that he could adjust h to make this function reproduce the data – he did a "curve fit"! The parameter h is now called Planck's constant. It takes the apparently rather small value

$$\boxed{h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} = 4.136 \times 10^{-15} \text{ eV} \cdot \text{s}} \tag{6}$$

h turns out to be *the* fundamental quantum constant (more on that below)!

It might have been enough to come up with such the formula, but Planck wanted to see what the formula implied *about* blackbody radiation – what physical assumptions would go into a derivation. We turn to that below.

But first, let's take the limits we observed in the plots and see that Eq. (5) behaves correctly:

- Low frequency (long wavelength): Here, the exponential is approximately one, but since there is a -1 in the denominator, we need to keep the second term in the series expansion: $e^{h\nu/k_B T} - 1 \approx 1 + h\nu/k_B T - 1 = h\nu/k_B T$. So,

  $$\lim_{\nu \to 0} S(\nu) = \frac{2\pi}{c^2} \nu^2 k_B T, \tag{7}$$

  which is just what we expect from the log-log plot and (3). Notice that the constant, h, has canceled out in this limit and that this is precisely the classical prediction for the blackbody spectrum.

- At high frequencies (short wavelengths): The exponential is much larger than one and

  $$\lim_{\nu \to \infty} S(\nu) = \frac{2\pi h}{c^2} \nu^3 e^{-h\nu/k_B T}. \tag{8}$$

  This gives both the frequency and temperature dependence in the semi-log plot and (2). The exponential term has cut off the high frequency divergence of the classical prediction.

- The peak in the spectrum (the color with the most intensity), is found by differentiating (5) with respect to ν and setting the derivative to zero. If you work out the derivative, you should find that you have to solve an equation like

  $$1 - e^{-x} = x/3, \tag{9}$$

3

where $x \equiv h\nu/k_B T$. You can write a program or zero in on the answer with a calculator to find that the solution is $x = 2.822$. So, we find

$$h\nu_{max} = 2.822 k_B T \tag{10}$$

which is of the form of (1). Since $x = 2.822$ at the peak (independent of T), (5) implies that $S_{max} \sim \nu_{max}^3 \sim T^3$, as we observed from the data.

- If we integrate over all frequencies to compute the total power in the spectrum, we get $P(T) = \sigma T^4$, the Stefan-Boltzmann relation:

  1. $P(T) = \frac{2\pi h}{c^2} \int_0^\infty d\nu \frac{\nu^3}{e^{h\nu/k_B T} - 1}$

  2. Make the substitution $x = h\nu/k_B T$:

  $$P(T) = \frac{2\pi h}{c^2} \left(\frac{k_B T}{h}\right)^4 \int_0^\infty dx \frac{x^3}{e^x - 1} \tag{11}$$

  3. We are left with a definite integral which has the definite value $\pi^4/15$.

  4. All that's left is T^4 multiplying a bunch of constants. The constants evaluate to $\sigma = 5.67 \times 10^{-8}$ Watts/(m$^2 \cdot$ K^4), the Stefan-Boltzmann constant.

  This strong temperature dependence is just what is seen experimentally.

2 The spectrum: classical and quantum derivations

Eq. 5 fits the data, but what does it imply about the blackbody system or about radiation itself? Planck found a way to derive the equation using what amounts to the first "quantum statistical mechanics" calculation ever. He had to assume that the light is quantized into packets with energy $h\nu$ so that the energy in any of the (classically enumerated) modes could only be an integer times that energy: $E^m = n_m h\nu$, with n_m the number of packets (on average) associated with that mode. Other than that hypothesis, he used standard statistics. Planck didn't take the quantization of energy very seriously, but Einstein did! Through consideration of the photoelectric effect (which we will study shortly), he came to the conclusion that Planck's hypothesis was a fundamental property of electromagnetic waves or energy. This result was then found to be generalizable to many other types of wave phenomena.

We will see that the fact that h is small "hides" quantum phenomena in most macroscopic circumstances (recall the analogous behavior in Feynman's double slit – h will occur there too!). For example, when n_m is large (many powers of ten), which will be the case when you look at a typical light source or burning coals, etc, the discreteness of the energy content is simply not discernable because $h\nu$ is tiny.

2.1 The method

While blackbody radiation is an extremely general phenomenon, to do a calculation, we have to consider a specific physical set-up. What is seen in nature is that, with some materials-specific variations in characteristic spectral regions, all systems exhibit the same phenomena. Therefore, we are free to choose a simple, generic model for our calculation.

We want to compute the amount of energy radiated at a general frequency, ν. We start by calculating the amount of energy per unit volume, $u(\nu)$, that is contained within the box (the energy density). The amount that escapes in time dt through a hole of area, A, is $A\,S(\nu)\,d\nu\,dt = \frac{A\,c\,dt}{4}\,u(\nu)\,d\nu$, so $S(\nu) = \frac{c}{4}\,u(\nu)$. c is the speed of light or the speed with which the photons are traveling so $c\,dt$ is the distance within which photons can escape in time dt. The factor of $1/4$ is a geometrical result of summing over all photon propagation directions that are aimed toward the hole.

The calculation has two parts:

1. *How many distinguishable types of radiation are there that have frequency ν (within a differential interval, $d\nu$)?* Specifying the "type" means specifying the wavelength (hence the frequency through $\nu = c/\lambda$), the direction of propagation, and the polarization direction of the electric field (which is constrained by Maxwell's equations to point perpendicular to the direction of propagation). This part of the calculation is identical for the classical and quantum theories.

2. *How much energy does each of the modes of frequency ν possess?* This is where the classical and quantum theories diverge.

Finally, we just multiply the number of modes of frequency ν by the average energy per mode of frequency ν to get the average energy density at ν.

2.2 The model system

Consider a hollow cubic metallic box of side length, L, at temperature, T. We will compute the amount of energy in the box at each frequency (or wavelength) interval. If we punch a small hole in a wall of the box (not big enough to disrupt the uniform temperature inside), the radiation coming out will be $S(\nu) = (c/4)\,u(\nu)$, where $u(\nu)$ is the energy per unit volume in the box.

Note: the considerations below pop up in a large number of contexts. We will use the same type of logic to describe quantum waves for a confined particle. The same kind of "boundary conditions" occur in the theory of solids and many other places. It's probably worth understanding what's going on here!

The first question is, what kinds of electromagnetic waves can exist in such a box? The answer is, only waves for which the component of the electric field parallel to a wall is zero at the wall. Further, *on average*, the box will contain standing waves since there should be as much radiation going one way as the opposite way.

Just considering the x-direction, we have standing waves of the form

$$\mathbf{E}(x, t) = \mathbf{E_o}\,\sin(k_x x)\cos(\omega t) \tag{12}$$

where the boldface $\mathbf{E}$ indicates that this is a vector quantity. $\mathbf{E}$ can be resolved along two orthogonal directions, i.e., there are two independent polarizations of waves going along the x-direction ($\mathbf{E}$ must be perpendicular to the propagation direction, x – that's why there are only two independent directions or polarizations).

Not just any k_x will work in (12). The choice of using the sine function means that $\mathbf{E} = 0$ when $x = 0$ (i.e., for any point on the wall located at $x = 0$). We need an additional condition in order to assure that the same thing happens at $x = L$ (the other end of the box). Choosing the right values of k_x will do the job:

- $\sin\theta = 0$ whenever $\theta = n\pi$, with n any positive integer (negative integers also work, but do not correspond to a new mode since they amount to a 180 degree phase shift in the time factor of Eq. 12).

- We want the sine to be zero when $x = L$, so we require $k_x L = n\pi$ or

$$k_x = n\frac{\pi}{L}. \tag{13}$$

- In three dimensions,

$$\mathbf{E}(x, y, z, t) = \mathbf{E_o} \ \sin(k_x x) \ \sin(k_y y) \ \sin(k_z z) \ \cos(\omega t) \tag{14}$$

and we can specify wavevectors

$$\mathbf{k} = \frac{\pi}{L}(n_x \hat{x} + n_y \hat{y} + n_z \hat{z}), \tag{15}$$

with all n's positive integers or zero (but not all can be zero since that would make (14) zero everywhere). It is left as an exercise to show that this function again makes $\mathbf{E} = 0$ at all of the walls.

Recall that the wavelength is determined by the *magnitude* of the wavevector:

$$k = \frac{2\pi}{\lambda} = \frac{\pi}{L}(n_x^2 + n_y^2 + n_z^2)^{1/2} \tag{16}$$

and $\nu = c/\lambda$ is the frequency of oscillation of the wave.

2.3 Counting modes

1. Think of a plot where the axes are the components of $\mathbf{k}$. Each allowed $\mathbf{k}$-value corresponds to a point in this space. For our cubic box, these points form a cubic lattice with distance π/L as the length of each cube. The volume associated with each point is $(\pi/L)^3$. We do our counting in k-space just because the modes are uniformly spaced here – it's easier than the alternatives.

2. Only one octant of the $\mathbf{k}$-space is occupied since we are counting standing waves with positive n's.

6

3. For each point in **k**-space there are two modes with different polarizations.

4. How many modes are there inside a spherical shell of radius k?

   (a) The enclosed volume is $V_k = \frac{1}{8}\frac{4\pi}{3}k^3$.

   (b) The number of modes is $N_k = 2V_k/[(\pi/L)^3] = Vk^3/(3\pi^2)$, where $V = L^3$.

5. What we want is the number of modes in a shell of radial width, dk at radius k. We want this because all these modes have the same k within dk (and, therefore, the same ν within a corresponding $d\nu$).

   (a) The number in a thin spherical shell is just the change in N_k when $k \to k + dk$.

   (b) Thus,

$$D(k)dk = dN_k = \frac{dN_k}{dk}\ dk = \frac{V}{\pi^2}\ k^2\ dk. \tag{17}$$

6. Replacing k with $2\pi\nu/c$ and dk with $2\pi d\nu/c$, we get

$$D(\nu)d\nu = \frac{8\pi}{c^3}\nu^2 d\nu, \tag{18}$$

as the number of modes *per volume of box* in $d\nu$ centered at ν.

If the energy per mode at this frequency is $E(\nu)$, then the total energy content per volume (radiation energy density) is

$$u(\nu)\ d\nu = E(\nu)\ D(\nu)\ d\nu \tag{19}$$

and the emitted power at this frequency is

$$S(\nu)\ d\nu = \frac{c}{4}\ E(\nu)\ D(\nu)\ d\nu. \tag{20}$$

2.4 Energy per mode: classical calculation

Here, each radiation mode is viewed as an oscillator. Space is an "elastic" medium which gives rise to the observed dispersion relation. The classical equipartition theorem says that any oscillator should have an average energy of $E_{Cl}(\nu) = k_B T$, which of course is independent of ν.

You've probably seen the equipartition theorem before in the context of the kinetic theory of gases. The theorem assigns $\frac{1}{2}k_B T$ as the average energy associated with each *degree of freedom* that contributes to the energy. For a monatomic gas, the energy is $E = \frac{m}{2}(v_x^2 + v_y^2 + v_z^2)$, so there are three degrees of freedom and the average energy is $\frac{3}{2}k_B T$. For a one dimensional harmonic oscillator, we can write $E = \frac{m}{2}v^2 + \frac{C}{2}x^2$ (C being a spring constant), so the average energy is just $k_B T$.

The classical theory that Planck knew about is obtained by using $E(\nu) = \frac{c}{4}\ k_B T$ in (19) or (20):

$$S(\nu)d\nu = \frac{2\pi}{c^2}\ k_B T\ \nu^2 d\nu. \tag{21}$$

This formula works beautifully at low frequency (or long wavelength). Unfortunately, it fails disastrously as ν increases. There is no peak in the spectrum; instead the calculated power just continues to increase. The integral of the spectrum (the total power radiated) diverges! This situation is referred to as the "ultraviolet catastrophe".

2.5   Energy per mode: quantum calculation

The birth of the photon.   Planck found that he could "derive" the correct form of the spectrum if he took the quantity $h\nu$ that entered his exponential factor as a fundamental unit of electromagnetic energy for radiation of frequency ν (actually, he assigned this unit of energy as being characteristic of what the walls could emit – it was Einstein who generalized it to be a fundamental property of radiation). The idea is that a single radiation mode of frequency ν can only contain an integer multiple of this fundamental unit of energy: at any instant, $E(\nu) = nh\nu$ where n is some integer (positive or zero). With this single (totally bizarre for 1900) assumption, plus a more mundane statistical calculation, the complete spectrum can be calculated.

In more modern terms, we say that radiation comes in discrete quanta called photons. Each photon is characterized by a mean frequency, ν and an energy $h\nu = \hbar\omega$, where $\hbar \equiv h/(2\pi)$. But, since a photon can be emitted and absorbed at different times and places, it cannot be described by a unique frequency. To make a localized wave, we have to include a range, $\Delta\nu$, of frequencies. Therefore, we can't be sure *exactly* what the energy is! More on this later.

For the radiation in our cubic, macroscopic box, we neglect this uncertainty and say that each mode has an associated energy $E = nh\nu$ when there are n photons present.

Statistical calculation machinery.   The Boltzmann factor gives, for a system at temperature T, the ratio of probabilities for the system to be in two states, one with energy E_1, the other with E_2:

$$\frac{P(E_2)}{P(E_1)} = e^{-(E_2 - E_1)/k_B T}. \tag{22}$$

The derivation of (22) requires a bit of discussion based on entropies of systems at temperature T. The important thing is that this is a very general property of systems held at a temperature T. States with higher energy, E_2, are exponentially less likely to be occupied than lower energy states – this fits with our expectation that, at low T, a system will only be found in the lowest possible energy states.

If (22) is true, it must be that $P(E) \propto e^{-E/k_B T}$. Here, E is the energy of the particular state under consideration. To turn this proportionality into an equality requires a normalization factor:

$$P(E) = \frac{e^{-E/k_B T}}{Z}, \tag{23}$$

where

$$Z(T) = \sum_{\text{all states}} e^{-E/k_B T}. \tag{24}$$

$Z(T)$, called the *partition function*, assures that $\sum_{\text{all states}} P(E) = 1$, as it must be. In the sum in (24), $k_B T$ corresponds to some temperature and the energy, E, takes on appropriate

different values. It will turn out to be handy to use the abbreviation $\beta \equiv (k_B T)^{-1}$ and write $Z = \sum_{\text{all states}} e^{-\beta E}$.

The average energy can be computed from Z:

$$< E >= \sum_{\text{all states}} E_s P(E_s) = \sum_{\text{all states}} E_s \frac{e^{-\beta E_s}}{Z}, \tag{25}$$

where E_s labels the energies of the states. Using the definition of Z, we can come up with a nice shortcut to doing this calculation. This arises because

$$-\frac{\partial Z}{\partial \beta} = \sum_{\text{all states}} E_s \; e^{-\beta E_s}; \tag{26}$$

dividing by Z yields the formula

$$< E >= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}. \tag{27}$$

If we can manage to do the sum in (24), then we can just plug the result into (27).

Average energy in a radiation mode. What Planck did was, in effect, to use the calculational machinery given above with the assumption that $E = nh\nu$ where n is any positive integer or zero. n labels the energies of all possible states for a given mode, so the sum over "all states" becomes a sum over n. From (24), we have

$$Z = \sum_{n=0}^{\infty} e^{-nh\nu/k_B T} = \sum_{n=0}^{\infty} y^n, \tag{28}$$

where $y = e^{-h\nu/k_B T} < 1$. It's simple to prove to yourself that the sum is just $1/(1-y)$ (just multiply both sides by $(1-y)$ and see that all terms except the first '1' cancel in pairs). So, now we have

$$Z = \frac{1}{1 - e^{-h\nu/k_B T}} = \frac{1}{1 - e^{-\beta h\nu}}. \tag{29}$$

The derivative in (27) then yields (after a little algebra),

$$< E(\nu) >= \frac{h\nu}{e^{h\nu/k_B T} - 1} \tag{30}$$

for the average energy associated with a single mode of radiation.

Note that at low frequencies, $h\nu << k_B T$, (30) reduces to the classical result:

$$\lim_{\nu \to 0} < E(\nu) >= \frac{h\nu}{1 + h\nu/k_B T - 1} = k_B T \tag{31}$$

and this is just where the classical result got the correct answer! But (30) cuts off the energy in modes where $h\nu >> k_B T$ and does so exponentially fast. In this limit, there just are not very many photons allowed – this is just what we see: there are no thermally generated x-rays at room temperature (luckily enough).

The Planck formula. Finally, we just combine (30) for the energy per mode with our previous counting of the number of modes in a frequency interval (Eq. 18) to get

$$S(\nu) = \frac{2\pi h}{c^2} \frac{\nu^3}{e^{h\nu/k_B T} - 1} \tag{32}$$

As previously described, this function does everything right. It describes everything from the cosmic background radiation (at $T = 2.7$ K) to the earth's energy budget (global temperatures and global warming relevance) to glowing coals in a fire to the sun's spectrum and intensity to that of distant stars, gas clouds, and other strange objects.

While Planck did not put much credence in his derivation, it turns out that it was both correct and had implications that led to the development of quantum mechanics and to our current understanding of how the world works. Newton was right that light behaved as if composed of particles (that is, it's composed of discrete objects – photons). But, of course, Maxwell was also right that light behaves like waves (his famous equations work in an amazing variety of contexts). How can we justify these two contradictory statements?

3   A simple climate model for the earth

Blackbody radiation and its interaction with atmospheric molecules (as well as the earth's surface) is an important current topic. Here is a simple model calculation that gives an idea of the potential for average temperature changes. You might want to look at Widipedia pages on 'solar constant' and 'sunlight'; I've used these to get estimates of some parameters. The solar spectrum graph below is from the 'sunlight' page as of Sept 2009. The solid line is just the Planck formula with the temperature adjusted to fit observations; this implies that the sun's surface is at 5250 C or 5520 K.
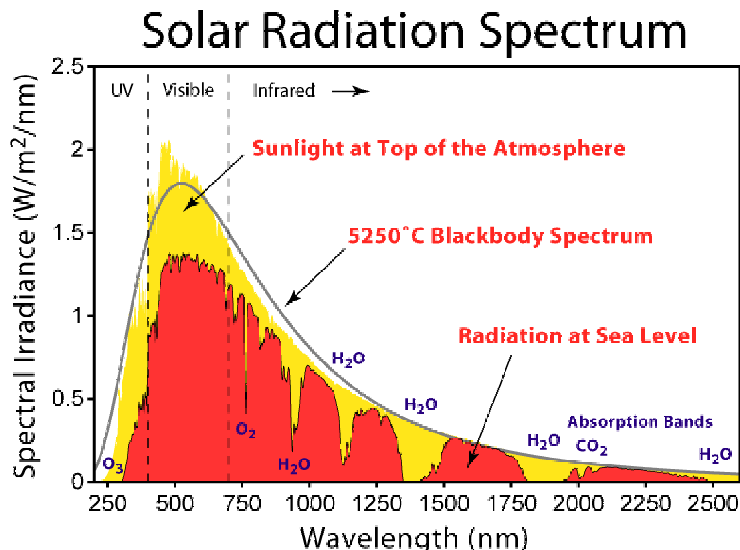
The solar constant gives the average total amount of solar energy incident on the earth's upper atmosphere. To a good approximation the number is $\gamma = 1366$ W/m^2, significantly over a kilowatt per square meter. The earth's cross-sectional area is $A_\gamma = \pi r_E^2$ with $r_E = 6.37 \times 10^6$ m. Thus, $\gamma A_\gamma = 1.74 \times 10^{17}$ Watts. This is many orders of magnitude larger than the rate of energy consumption by humans on the planet. Note that this energy is turned into heat and has to be re-radiated into space in order for the earth to stay at a constant temperature. Capturing this energy for use as "solar power" amounts to intercepting the radiation energy, using it and, as a consequence, turning it finally into heat; the effect on the earth's thermal budget is very little.

The steady state temperature of the earth's surface is determined by setting the re-radiated power equal to the input power. Treating the earth as a perfect blackbody, the radiated power is $A_E \sigma T^4$, with $A_E = 4\pi r_E^2$, so

$$\pi \ r_E^2 \ \gamma = 4\pi \ r_E^2 \ \sigma T^4. \tag{33}$$

or

$$T = \left[\frac{\gamma}{4\sigma}\right]^{1/4} = 278 \text{ K}. \tag{34}$$

Note that the radius cancels and the factor of 4 holds for any spherical object.

Now a blackbody absorbs 100% of the radiation incident on it (remember the model of a box with a small opening into which all incident light can enter and be absorbed and

thermalized by internal walls). In fact, the earth reflects radiation: blue from the oceans, many wavelengths from polar ice caps and glaciers. The 'albedo' gives the overall fraction of radiation reflected; the fraction absorbed is $f_\gamma = 1 -$ albedo. The input energy is then $\pi r_E^2 \ f_\gamma \gamma$. Currently, $f_\gamma \approx 0.7$ which yields an average temperature of 278K = 5 C whereas the current average temperature is 15 C so we know something else is going on.

The infrared radiation radiated by the earth can be absorbed by greenhouse gases in the atmosphere. Given the very different spectral ranges of the sun's and the earth's radiation, the atmosphere can be more effective in absorbing one source's radiation than the other. The absorbed energy will be re-radiated isotropically (same in all directions) with roughly half going back to the earth and half out to space. Again balancing the total input power and the total output power and assuming the atmosphere's area is about the same as the earth's,

$$A_\gamma \gamma f_\gamma + \frac{f_{IR}}{2} A_E \ \sigma T^4 = A_E \sigma T^4. \tag{35}$$

Again, $A_E = 4A_\gamma$ so

$$T = \left[\frac{\gamma f_\gamma}{4\sigma(1 - \frac{1}{2}f_{IR})} \right]^{1/4}. \tag{36}$$

f_{IR} depends on the concentration of "heat trapping," greenhouse, or IR absorbing molecules in the atmosphere. Equation 36 is our simple climate model.

The plot below shows earth temperatures as a function of f_{IR}, from no absorption to complete absorbtion for various values of f_γ (shown as f_g) or 1 - albedo. Current average earth temperature is about 15 C, and $f_\gamma \approx 0.7$, so it appears that about $\approx 80\%$ of the IR radiation is absorbed in the atmosphere and re-radiated. The worst case for this value of f_γ is obtained by raising the IR absorption to 100% where T reaches 30 C. Making things potentially worse, raising T melts ice and increases f_γ. Perhaps an improvement would be to paint *lots* of roofs white so as to reduce f_γ.
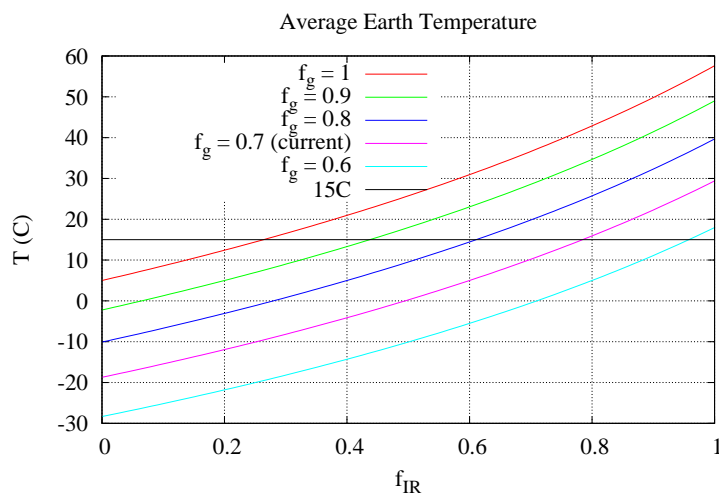
4   Thermodynamic Derivation of T^4 Law

The fact that the integrated spectral intensity scales as T^4 was derived by Boltzmann before Planck was able to calculate the actual spectrum. This thermodynamic result was a contradiction to the classically calculated spectrum which contains an infinite amount of energy at any finite temperature. So, this was another "minor annoyance" with classical physics that would up being solved by the revolutionary idea of quantum mechanics.

The thermodynamic calculation uses the "experimental observations" (?) that

$$PV = \frac{1}{3}U, \tag{37}$$

and

$$P = \frac{1}{3}\frac{U}{V} = P(T) \tag{38}$$

where the second equation says that the pressure only depends on the absolute temperature, T. The rest is the usual thermodynamic multi-variate math.

The first law of thermodynamics is

$$dU = T\ dS - P\ dV \tag{39}$$

and (37) implies that

$$dU = 3(P\ dV + V\ dP). \tag{40}$$

Combining these,

$$dS = \frac{1}{T}\ dU + \frac{P}{T}\ dV \tag{41}$$

$$= \frac{3}{T}\ (V\ dP + P\ dV) + \frac{P}{T}\ dV \tag{42}$$

$$= \frac{3}{T}V\ dP + \frac{4}{T}P\ dV. \tag{43}$$

Now we have the first partial derivatives of $S(P,V)$:

$$\left(\frac{\partial S}{\partial P}\right)_V = \frac{3V}{T}\ \text{and} \tag{44}$$

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{4P}{T}. \tag{45}$$

Equating the mixed second partials yields

$$3\left(\frac{\partial(V/T)}{\partial V}\right)_P = 4\left[\left(\frac{\partial(P/T)}{\partial P}\right)_V\right] \tag{46}$$

$$\frac{3}{T} = 4\left[\frac{1}{T} - \frac{P}{T^2}\left(\frac{\partial T}{\partial P}\right)_V\right] \tag{47}$$

where we have used (38) on the left. With a re-arrangement we get

$$\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V = \frac{4}{T} \tag{48}$$

which has the solution
$$P = AT^4 \tag{49}$$
By (37), this is equivalent to
$$\frac{U}{V} = \sigma T^4 \tag{50}$$
with σ being a (thermodynamically) unknown constant. With the integration of the Planck spectrum, σ becomes the Stefan-Boltzmann constant.