Thermal Physics

Energy density of electromagnetic waves

Consider a metallic cubic box of side L at temperature T. For standing waves to be stable, the electric field will have to be zero at each wall, so the waves are represented by the functions:

$$\mathrm{E} = E_{nx,ny,nz}\sin\left(n_x\frac{\pi x}{L}\right)\sin\left(n_y\frac{\pi y}{L}\right)\sin\left(n_z\frac{\pi z}{L}\right),$$

Where n_x, n_y *and* n_z are positive integers. The energy in this mode will be:

$$\mathrm{Energy_n} = m\frac{hcn}{2L}, \text{ where m=0, 1, 2… and } n = \sqrt{n_x{}^2 + n_y{}^2 + n_z{}^2}$$

This is the quantization hypothesis proposed by Max Plank to explain black body radiation.

Now, let us apply statistical mechanics (or thermal physics) to the energy in that mode. The Boltzmann factors corresponding to the states of mode n are:

$$Boltzmann\ factors = e^{-0\frac{hcn}{2Lk_BT}}, e^{-1\frac{hcn}{2Lk_BT}}, e^{-2\frac{hcn}{2Lk_BT}} \ldots$$

The sum of the Boltzmann factors is: $\sum Boltzmann\ factors = \frac{1}{1-e^{-\frac{hcn}{2Lk_BT}}}$, which you can demonstrate using the telescopic sum, and we know that the sum of the probabilities has to be 1, so the probabilities are:

$$\mathrm{Probabilities} = \left(1-e^{-\frac{hcn}{2Lk_BT}}\right)e^{-0\frac{hcn}{2Lk_BT}}, \left(1-e^{-\frac{hcn}{2Lk_BT}}\right)e^{-1\frac{hcn}{2Lk_BT}}, \left(1-e^{-\frac{hcn}{2Lk_BT}}\right)e^{-2\frac{hcn}{2Lk_BT}} \ldots$$

The average energy of mode *n* is calculated by multiplying each state's energy times the probability of that state and adding all the products:

$$\left\langle Energy_n \right\rangle = 0\frac{hcn}{2L}\left(1-e^{-\frac{hcn}{2Lk_BT}}\right)e^{-0\frac{hcn}{2Lk_BT}} + 1\frac{hcn}{2L}\left(1-e^{-\frac{hcn}{2Lk_BT}}\right)e^{-1\frac{hcn}{2Lk_BT}} + 2\frac{hcn}{2L}\left(1-e^{-\frac{hcn}{2Lk_BT}}\right)e^{-2\frac{hcn}{2Lk_BT}} \ldots$$

This sum can be computed recalling that $r + 2r^2 + 3r^3 \ldots = \frac{r}{(1-r)^2}$, which is another telescopic sum, so:

$$\left\langle Energy_n \right\rangle = \frac{hcn}{2L}\frac{e^{-\frac{hcn}{2Lk_BT}}}{1-e^{-\frac{hcn}{2Lk_BT}}} = \frac{hcn}{2L}\frac{1}{e^{\frac{hcn}{2Lk_BT}}-1}$$

To find the total energy we need to add all the possible energies that correspond to all possible values of n_x, n_y *and* n_z

$$\langle Energy \rangle = 2\sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty}\frac{hcn}{2L}\frac{1}{e^{\frac{hcn}{2Lk_BT}}-1}$$

Notice that we introduce a factor of 2, due to the two possible polarizations of electromagnetic waves. Instead of adding the infinite series, we can integrate over one octet of the Cartesian coordinate system:

$$\langle Energy \rangle = 2\int_0^{\infty}\frac{hcn}{2L}\frac{1}{e^{\frac{hcn}{2Lk_BT}}-1}\frac{\pi}{2}n^2 dn$$

We change variables to simplify the integral. Let $b = \frac{hcn}{2Lk_BT}$, obtaining:

$$\langle Energy \rangle = 2k_BT\left(\frac{2Lk_BT}{hc}\right)^3\int_0^{\infty}\frac{hcn}{2Lk_BT}\frac{1}{e^{\frac{hcn}{2Lk_BT}}-1}\frac{\pi}{2}\left(\frac{hcn}{2Lk_BT}\right)^2 d\left(\frac{hcn}{2Lk_BT}\right) = \pi k_BT\left(\frac{2Lk_BT}{hc}\right)^3\int_0^{\infty}\frac{b^3}{e^b-1}db$$

$$\langle Energy \rangle = \frac{8\pi k_B{}^4}{h^3c^3}L^3T^4\int_0^{\infty}\frac{b^3}{e^b-1}db$$

The volume of the box is L^3, so the density of energy in the box is:

$$\frac{\langle Energy \rangle}{L^3} = \frac{8\pi k_B{}^4}{h^3c^3}T^4\int_0^{\infty}\frac{b^3}{e^b-1}db$$

The integral has a value of $\int_0^{\infty}\frac{b^3}{e^b-1}db = \frac{\pi^4}{15}$, which you can demonstrate mathematically (see appendix), so the energy density is:

$$u = \frac{\langle Energy \rangle}{L^3} = \frac{8\pi^5 k_B{}^4}{15h^3c^3}T^4$$

The numerical factor in the energy density is:

$$\frac{8\pi^5 k_B{}^4}{15h^3c^3} = 7.56\times10^{-16}\frac{J}{m^3K^4}$$

Finally, suppose the box has a hole of area A open to the environment. If the velocities of all the modes were directed to the outside, in a time t, a volume V=Act (c is the speed of light) would move through the hole emitting radiation energy E=Actu, but the velocities are randomly distributed, so only one fourth will go through the hole. Then, E=Actu/4, and the energy radiated per unit area per unit time will be:

$$Radiation = \frac{cu}{4} = \left(\frac{8\pi^5 k_B{}^4}{15h^3c^3}\right)\frac{c}{4}T^4 = \left(\frac{2\pi^5 k_B{}^4}{15h^3c^2}\right)T^4 = 5.67\times10^{-8}T^4$$

The constant $\sigma = 5.67\times10^{-8}\,\frac{watts}{m^2K^4}$ is called Stefan-Boltzmann constant.

Black body spectrum

In the equation for the energy, we could also introduce the wavelength as the new variable, $\lambda = \frac{2L}{n}$, giving us

$$\langle Energy\rangle = 8\pi hcL^3\int_0^\infty \frac{1}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_BT}}-1}d\lambda$$

To get the total intensity of radiation per unit area we divide by the volume and multiply by the speed of light divided by 4.

$$R_{total} = 2\pi hc^2\int_0^\infty \frac{1}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_BT}}-1}d\lambda$$

Finally, since we are interested in the spectrum, we drop the integral and take only the radiation per unit wavelength, obtaining

$$R = \frac{2\pi hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_BT}}-1}$$

Appendix:

To calculate the integral $\int_0^{\infty} \frac{b^3}{e^b - 1} db = \frac{\pi^4}{15}$

Consider the periodic function $f(t) = \begin{cases} t & if \quad 0 \le t < 1 \\ 2 - t & if \quad 1 \le t < 2 \end{cases}$ with period T=2

The function is even, so it will have a Fourier representation as a sum of cosines:

$f(t) = a_o + \sum_{n=1}^{\infty} a_n \cos(n\pi t)$, where the coefficients can be calculated as follows:

$$a_o = \frac{\int_0^2 f(t)dt}{2} = 0.5 \text{ and } a_n = \int_0^2 f(t)\cos(n\pi t)dt = \int_0^1 t\cos(n\pi t)dt + \int_1^2 (2-t)\cos(n\pi t)dt$$

The integral is zero if n is even, so for n odd we get:

$$a_n = 2\int_0^1 t\cos(n\pi t)dt = \frac{2}{n\pi}\int_0^1 td\sin(n\pi t) = \frac{2}{n\pi}\left(t\sin(n\pi t) - \int_0^1 \sin(n\pi t)dt\right)$$

$$a_n = \frac{2}{n\pi}\left(-\int_0^1 \sin(n\pi t)dt\right) = \frac{2}{n^2\pi^2}\cos(n\pi t)\Big|_0^1 = \frac{4}{n^2\pi^2}$$

That means that $f(t) = \frac{1}{2} + \sum_{n=1,3,5...}^{\infty} \frac{4}{n^2\pi^2}\cos(n\pi t)$

Also, notice that the RMS value of the function f is:

$$RMS = \sqrt{\frac{\int_0^2 f^2(t)dt}{2}} = \sqrt{\int_0^1 f^2(t)dt} = \sqrt{\int_0^1 t^2 dt} = \sqrt{\frac{1}{3}}$$

Using Parseval's theorem:

$$\frac{1}{3} = \frac{1}{2^2} + \frac{1}{2}\sum_{n=1,3,5...}^{\infty} \frac{4^2}{n^4\pi^4} \rightarrow \frac{1}{3} = \frac{1}{4} + \frac{8}{\pi^4}\sum_{n=1,3,5...}^{\infty} \frac{1}{n^4} \rightarrow \sum_{n=1,3,5...}^{\infty} \frac{1}{n^4} = \frac{\pi^4}{96}$$

Also notice that: $\sum_{n=1,2,3...}^{\infty} \frac{1}{n^4} - \sum_{n=1,3,5...}^{\infty} \frac{1}{n^4} = \sum_{n=2,4,6...}^{\infty} \frac{1}{n^4} = \frac{1}{16}\sum_{n=1,2,3...}^{\infty} \frac{1}{n^4}$, so:

$$\sum_{n=1,2,3...}^{\infty} \frac{1}{n^4} = \frac{16}{15}\sum_{n=1,3,5...}^{\infty} \frac{1}{n^4} = \frac{16}{15}\frac{\pi^4}{96} = \frac{\pi^4}{90}$$

We can apply this to the integral after writing it as a series:

$$\int_0^\infty \frac{b^3}{e^b - 1} db = \int_0^\infty \frac{b^3 e^{-b}}{1 - e^{-b}} db = \int_0^\infty b^3 \left(e^{-b} + e^{-3b} + e^{-3b} \ldots\right) db$$

$$\int_0^\infty b^3 e^{-nb} db = -\frac{1}{n} \int_0^\infty b^3 de^{-nb} = -\frac{3}{n^2} \int_0^\infty b^2 de^{-nb} = -\frac{6}{n^3} \int_0^\infty b de^{-nb} = \frac{6}{n^3} \int_0^\infty e^{-nb} db = \frac{6}{n^4}$$

$$\int_0^\infty \frac{b^3}{e^b - 1} db = 6 \sum_{n=1,2,3\ldots}^{\infty} \frac{1}{n^4} = 6 \frac{\pi^4}{90} = \frac{\pi^4}{15}$$