School of Physics and Astronomy

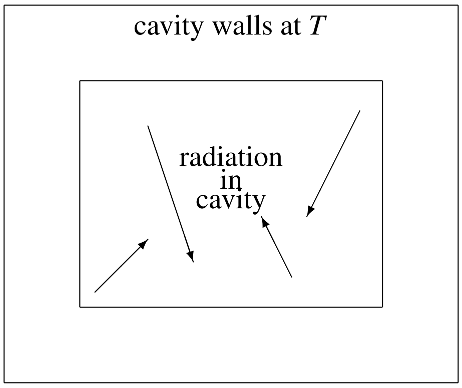
Junior Honours **Thermodynamics** GJA 2018-2019

Lecture TOPIC 12 (Finn 8.4 - 8.8)

Synopsis: Black Body Radiation and the birth of quantum mechanics

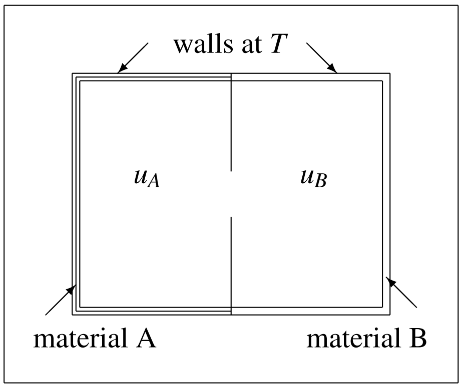
Thermal radiation as a thermodynamic system

For radiation **inside** a cavity, the cavity walls at temperature T are considered to be the surroundings and the 'empty' cavity containing the radiation as the system. In equilibrium, the radiation inside the cavity is characterised by the temperature T of its surroundings. Its volume will be the volume V of the cavity. The radiation also has an energy (U), which increases with increasing temperature (think of a domestic electric oven). Reasoning based on thermodynamics and kinetic theory lead to a value for the pressure of the radiation.



Visualised as photons in a box, the radiation in the cavity can be treated in an analogous way to the kinetic theory of molecules in a box. In particular the formula for pressure = $P = \frac{1}{3}Nmv^2_{rms}$ for N molecules **in unit volume** having mass m and root-mean-square velocity v_{rms} can be re-used replacing v_{rms} with the speed of light c and replacing mass per unit volume (Nm) by its energy equivalent u divided by c^2 where u denotes energy **density**.

This gives $P = \frac{1}{3}u$ for the pressure exerted by the radiation. For a partitioned oven having two joined compartments (A and B) made of different materials but both at the same temperature T, it is unavoidable that the radiation in the two compartments will have the same value of energy density. If $u_A > u_B$, the flow of radiation (heat) through the joining gap would make A cool and B heat up, without any work being done on the system by some external agency. A similar conclusion is reached for the case $u_B > u_A$. Thermal equilibrium requires equal energy density.



To avoid violating the Clausius version of the second law, u – summing over all wavelengths present – has to be a function of temperature only: $u = u(T)$. Inserting filters connecting the two ovens allows radiation at each wavelength to be treated as a separate system, so it can also be concluded that the energy density at a given wavelength is also a function of temperature only; $u_\lambda = u_\lambda(\lambda, T)$.

Equipartition and the ultraviolet catastrophe

In classical mechanics, the equipartition theorem said that, in thermal equilibrium, energy is shared equally among all of its various forms, e.g. rotational, translational, vibrational motion. It can be proven from Newtonian dynamics provided it is possible to exchange energy among those forms.

For black body radiation, it implied that energy should be shared equally between all frequencies. But since electromagnetism allows infinite possible frequencies, that would mean infinite energy.

Planck, and the energy spectrum of cavity radiation

In what follows, we show that classical thermodynamics allows deductions about cavity radiation, in particular resolving the so-called ultraviolet catastrophe. It is observed that $u = \int_0^\infty u_\lambda d\lambda$ ("area under the curve") is very strongly **temperature**-dependent.

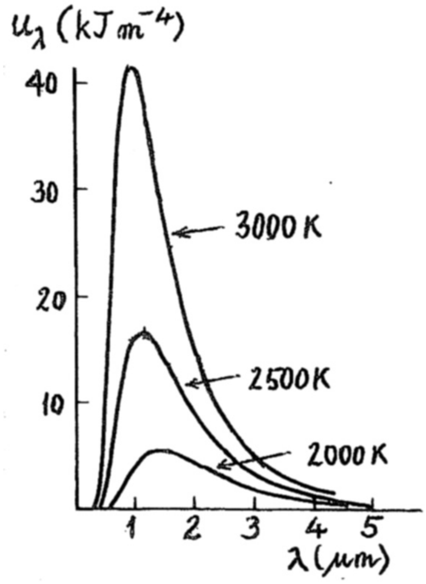
First consider the explicit dependence of u on T. From the central equation of thermodynamics, and one of the Maxwell's relations,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Using $P = \frac{1}{3}u$, $U = uV$ and $u = u(T)$ we get

$$u = \frac{1}{3}T\frac{du}{dT} - \frac{1}{3}u \implies 4\frac{dT}{T} = \frac{du}{u} \implies u = \left(\frac{4\sigma}{c}\right)T^4$$

$(4\sigma/c)$ is the constant of integration (c is the velocity of light). It is shown below that the energy radiated per unit area of surface per second by an ideal radiator is then equal to σT^4 (see below). The constant of proportionality σ is "Stefan's constant".



The full Planck distribution as a function of frequency $\nu = c/\lambda$ cannot quite be derived from Stefan's Law. However, we know it has a finite integral (no "ultraviolet catastrophe"), we know the T-dependence of that integral (Stefan's Law) and from experiment that when $u_\nu(\nu, T)$ plotted as a function of ν, it shows a single maximum, at a frequency that depends on temperature T.

It is often claimed that Planck derived his Law from quantising the radiation. This is misleading, in fact he figured it out from thermodynamics, the rederivation from postulating quantised radiation came later. Planck realised that the entropy was fundamental to the problem. From the Central equation for radiation at fixed volume we can relate the enthalpy and entropy of the subset of photons with frequency ν, and from that we can the define an independent temperature of each subset T_ν. But because all the radiation ν is in thermal contact with all other frequencies, thermodynamics equilibrium demands that these temperatures are all equal and there is a universal relationship between the entropy and the energy.

$$T_\nu = \left(\frac{\partial U_\nu}{\partial S_\nu}\right)_V = T, \forall \nu$$

Although there was no expression for the full distribution, the energy in tails of the distribution were well known. For large wavelengths Rayleigh showed that

$$U(\lambda, T) \propto T\lambda^{-4}; \qquad 1/T = c_1\lambda^5/U$$

And for short wavelengths Wein has shown that

$$U(\lambda, T) \propto \lambda^{-5}exp(-const/\lambda T); \qquad 1/T = c_2 \ln U + c_3 \ln \lambda^5$$

To help eliminate T Planck considered the quantity connecting energy and entropy

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_V = \left(\frac{\partial(1/T)}{\partial U}\right)_V \propto \lambda^4/U(LowU); \lambda^5/U^2(HighU) = \frac{c_1}{U(U+c_2)}$$

the final form being a guess which satisfied both limits. From here, he integrated wrt U to get the expression for $1/T$ in terms of U, reintroducing λ via constants of integration, and rearranged to get.

$$U_\lambda(\lambda,T) \propto \lambda^{-5}\left(\frac{1}{e^{hc/\lambda k_B T - 1}}\right)$$

where I wrote Planck's "arbitrary constant" in its now-known form hc/k_B

To derive a distribution, rather than fit it to observations, Planck still needed an expression for the entropy, and one which gave lower entropy at higher ν. He turned (reluctantly) to Boltzmann's idea $S = k\ln W$, writing

"If E is considered to be a continuously divisible quantity, this distribution is possible in infinitely many ways. We consider, however - this is the most essential point of the whole calculation - E to be composed of a well-defined number of equal parts."

The assumption that energy is *quantised* meant that the formula for the energy distribution law, expressing energy density as a function of frequency ν, and temperature T, is constrained to be the Planck Law, or something very similar.

$$u_{tot} = \int_0^\infty u_\nu(\nu,T)du_\nu = \frac{4\sigma T^4}{c} = \int_0^\infty constant \times \nu^3\left(\frac{1}{e^{h\nu/k_B T} - 1}\right)d\nu$$

The exact form required some assumptions about the quantum of energy (counting of what we now call photons). The simplest guess, that the photon energy is proportional to frequency via "Planck's constant", enabled Planck to derive the full expression, and its veracity is proved by the accurate match to experiments.

Free Energy

Planck's calculation of the Entropy involved quanta, but we can get it from continuum thermodynamics via the specific heat capacity.

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = 4\sigma_o V T^3$$

with $\sigma_o = 4\sigma/c$, remembering that we've been using energy density, so total internal energy $U = uV$. Then, taking $S(T=0) = 0$, which we'll later see is the third Law,

$$S = \int \frac{C_v dT}{T} = \frac{4}{3}\sigma_o V T^3$$

and the enthalpy is:

$$H = U + PV = \frac{4}{3}\sigma_o V T^4 = TS$$

which we already knew was true for every frequency independently.

Now if we calculate the Gibbs Free Energy for black body radiation,

$$G = uV - TS + PV = \sigma_o V T^4 - \frac{4}{3}\sigma_o V T^4 + \frac{1}{3}\sigma_o V T^4 = 0$$

Which looks a bit weird. Microscopically, it means that the second law of thermodynamics allows a black body to spontaneously create or destroy photons.

It is possible to reverse this whole chain of logic, starting with the observation that a black body to spontaneous creates and destroys photons, which requires $G = 0$, and thus $TS = H$ for photons.

Stefan's Law

For a perfect black body we consider all incident radiation is absorbed. Consider a sphere containing radiation at number density n_ν moving isotropically at speed c. The rate of photons striking a small fraction of the surface defined by solid angle $d\Omega/4\pi$ depends on the normal velocity $c\cos\theta$

$$\text{flux} = \text{particles sec}^{-1}\text{area}^{-1} = \int n_\nu c\ \cos(\theta)\frac{d\Omega}{4\pi} = \int_{\phi=0}^{\phi=2\pi}\int_{\theta=0}^{\theta=\pi/2} n_\nu\ c\ \cos(\theta)\frac{\sin(\theta)d\theta d\phi}{4\pi} = \frac{1}{4}n_\nu\ c$$

This equation can be applied to a subset of photons with frequency between ν and $\nu + d\nu$; The total radiation flux from a body at temperature T is then $\varepsilon(T)$, and is obtained by integrating over all frequencies

Then,

$$\begin{aligned} \varepsilon(T) &= \frac{c}{4}\int u_\nu d\nu = \frac{cuT^4}{4} = \frac{c\left(\frac{4\sigma}{c}\right)T^4}{4} \\ \Rightarrow \varepsilon(T) &= \sigma T^4 \end{aligned}$$

This is Stefan's Radiation Law, σ is a universal constant (Stefan's constant), $\sigma = 56.7nWm^{-2}K^{-4}$.

Radiation flux

The flux of particles through a small orifice can be found by integrating the flux incident from the side of interest over all incident directions. Suppose the density of particles with velocity v is $n(v)$ is assumed isotropic, the fraction moving in a particular solid angle is just $d\Omega/4\pi$. Those incident at an angle θ to the normal to the surface in which the orifice is located and with velocity v arrive at rate per unit area $n(v)cos(\theta)$ at the orifice. The flux of particles with velocity v per unit area of the orifice is then given by:

$$\text{flux} = \text{particles sec}^{-1}\text{area}^{-1} = \int \frac{d\Omega}{4\pi} n(v)\ v\ cos(\theta)$$

$$\text{flux} = \int_{\theta=0}^{\theta=\pi/2}\int_{\phi=0}^{\phi=2\pi} \frac{d\phi d\theta sin(\theta)}{4\pi} n(v)\ v\ cos(\theta)$$

The integral over θ is easily done by substituting $x = cos(\theta)$ and noting that $dx = -sin(\theta)d\theta$ giving: flux $= \frac{1}{2}\int_1^0 -x\ n(v)\ v\ dx$

$$\boxed{(\text{flux with velocity } \ v) = \frac{1}{4} n(v)\ v}$$

This equation can be applied to a subset of photons with frequency between ν and $\nu + d\nu$; The total radiation flux is then obtained by integrating over all frequencies

$$(\text{Energy flux})_\lambda d\lambda = \frac{c}{4} u_\lambda d\lambda; \qquad \text{(i.e. the energy flux depends only on the energy density)}_\lambda$$

Considering two equal-temperature cavities as before connected by a filter. The Second law of thermodynamics tells us cannot have a net energy flow from one side to the other (no work is done) so that $\frac{c}{4}u_\lambda d\lambda$ and therefore u_λ (in a vacuum) must be a universal function and depend on temperature only (independent of cavity walls etc).

Cavity walls - emissivity - Kirchoff's Law

Consider a small section of the wall of a cavity as the system. Consider this to be in equilibrium with radiation at temperature T. From the second law we must conclude that the energy radiated per unit surface over a small range of wavelengths $\varepsilon_\lambda(T)$ must be equal to that absorbed. Suppose that a fraction α_λ of the incident energy is absorbed, then:

$$\varepsilon_\lambda(T) = \frac{\alpha_\lambda c u_\lambda(\lambda, T)}{4}$$

This is Kirchoff's law relating emissivity to the absorption coefficient of a surface. Notice that $u_\lambda(\lambda, T)$ is a universal function.

Radiation from a surface not in equilibrium

The above formula for the radiation from a surface was derived assuming thermal equilibrium between the wall and thermal radiation. However changing the radiation bathing the surface cannot change the emission which is determined only by the properties of the surface itself (notably its temperature). Therefore the surface continues to emit radiation at the same rate per unit surface (determined by $\alpha_\lambda(T)$ and T) even when not in equilibrium. This is the usual context in which the above radiation formula is used.