Thermodynamics of radiation

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Abstract Classical thermodynamics is combined with elementary electro-magnetic theory to analyse black-body radiant energy. This leads quickly to the Stefan–Boltzmann fourth-power radiation law and then to Wien's laws, including the 'foundryman's law'. The student is warned, however, about certain fallacies arising from misapplying equilibrium theory to non-equilibrium situations and invited to consider some of the cosmological implications following from this re-enactment of the initiation of modern quantum theory. Points for examples or examination questions are indicated.

Keywords thermodynamics; electro-magnetic theory; black-body radiant energy; Stefan–Boltzmann law; Wien's laws

A second course in thermodynamics for engineers benefits from examples drawn more widely than from fluids in one and two phases. One such topic is the thermodynamics of radiation, which has a practical engineering link to radiative heat transfer. Much of this thermodynamics was developed in the transition from the nineteenth to the twentieth century but few writers for engineers, with the notable exception of Bejan, bring the matter up to the twenty-first century. Although some of these further developments are more suited to physicists than engineers, I have found that a limited amount of speculation in the realms of cosmology interests engineering students and may motivate a deeper study. The following material represents about one lecture, with opportunities for reading in depth and examples or examination questions. Inherent in the thermodynamics is the concept of radiation pressure,[1] that is, light and other radiation exerts a pressure. This might be anticipated from the Maxwell relation:

$$\left.\frac{\partial S}{\partial V}\right)_T = \left.\frac{\partial P}{\partial T}\right)_V$$

so that, since entropy is positive, we might expect energy to exert a pressure which increases with temperature.

The most immediate result and motivation for the development is to provide a theoretical basis for the Stefan–Boltzmann fourth-power radiation law, which then leads to Wien's 'foundryman's' law. The remaining discussion is to give the lecturer some background from which to deal with some of the deeper questions that the topic can engender in a good class discussion.

1 The first reference seems to be A. Bartoli, *Sopra i movimenti prodotti dalla luce e dal calore* (Le Mounier, Florence, 1876).

Electro-magnetic theory

Some electrical theory is necessary before embarking on the thermodynamics. Students will be familiar, perhaps, with the photon, the quantised element of electromagnetic (e-m) theory. A photon of frequency ν and wavelength $\lambda = c/\nu$ has zero rest mass but carries, at speed c, both energy, $h\nu$, and momentum of magnitude $h\nu/c$, where h is Planck's constant of action introduced originally by him in the treatment of thermal radiation. This momentum, a vector, gives rise therefore to radiation pressure. Photons in empty space do not interact with each other, a consequence of the linearity of the underlying Maxwell e-m equations. The simplest way of determining the relationship between energy density, e, and the pressure, p, is from a consideration of photons directed along, say, the x-axis in a cylinder of unit area cross-section between two perfect normal plane mirrors a distance L apart. Then the change of magnitude of momentum on each reflection is $2h\nu/c$ and the frequency of impacts is $c/2L$, so that the pressure (rate of change of momentum) is $h\nu/L = e$ on the end faces, but zero on the sides. Hence if the photons were uniformly distributed in all directions, as they are in an equilibrium, then the pressure on each face would by only $p = \frac{1}{3}e$. This is the significant result[2] that must be established to make thermodynamics progress, the equation of state for radiation analogous to $pV = nRT$. If photons are thought of as a gas, the pressure[3] is only half that of the equivalent perfect gas due to the factor of $\frac{1}{2}$ in the expression for the gas kinetic energy $\frac{1}{2}mv^2$.

Alternatively, a more formal geometric exercise is possible that can usefully be compared to the analogous development for a point-mass perfect gas model. Consider again reflections from the end faces of a cube of side $L = 1$ with perfect optical surfaces and having unit area end faces. For a photon at angle θ to the x-axis, the momentum in the axial direction and the rate of impacts upon one face are given by $(h\nu/c)\cos\theta$ and $(c/2L)\cos\theta$, respectively. Then the pressure exerted by this one photon on the x-faces is given by the rate of change of momentum as $p_1 = (h\nu/L)\cos^2\theta = e_1\cos^2\theta$, where e_1 is the corresponding energy density. The total pressure will be given by an integral over an isotropically, i.e. uniformly, distributed radiation field:

$$p = \frac{e}{2\pi}\int_{2\pi}\cos^2\theta d\Omega = \frac{e}{2\pi}\int_0^{\frac{\pi}{2}}\int_0^{2\pi}\cos^2\theta 2\pi\sin\theta d\psi d\theta = \frac{e}{3} \quad (1)$$

2 A concise derivation is given in D. Elwell and A. J. Pointon, *Classical Thermodynamics* (Penguin, Harmondsworth, 1972; reprinted Cambridge University Press). A longer but easily understood derivation is given in F. H. Crawford, *Heat, Thermodynamics and Statistical Physics* (Harcourt, Brace and World, New York, 1963).

3 Care is needed in discussing the radiometer or light windmill. This consists of four small paddle wheels that rotate on a vertical axis in sunlight. One side of a paddle is blackened and the other reflective. The direction of spin is the opposite of what might be expected of *radiation* pressure (twice the change of momentum when reflected as when absorbed) and is due to the warming action on incident molecules on the black and therefore hotter side, which therefore trails. Typical explanations on commercial samples are not accurate or clear.

The use of the cosine weighting of the momentum is equivalent to Lambert's law for the cosine weighting of the normal component of radiation from an emitting black surface to determine the off-normal intensity.

Engineering students are less likely to be familiar with the concepts of e-m field theory but may know that in a magnetic field of constant strength B, the magnetic energy density (per unit volume) is $\frac{1}{2\mu}B^2$ (with μ the permeability) and the pressure exerted by the field has the same *magnitude*, $\frac{1}{2\mu}B^2$. The direction of propagation of energy for crossed electric and magnetic fields, that is the direction of the corresponding photons, is in the direction normal to both, i.e. as given by the Poynting vector $\boldsymbol{P} = \boldsymbol{E} \times \boldsymbol{H}$. But it is important to note that such a field has a direction and that the 'pressure' is a tension, i.e., negative, in the direction of the field, but is a compression, i.e. positive, in the other two normal directions. Thus when we come to consider an equilibrium state with many photons isotropically distributed, in which there is no preferred direction in the e-m field, one-third of the effect (the axial component) cancels with one of the two-thirds of the transverse effects, leaving one-third. Similar arguments pertain to the electric field also, so that, overall, in an equilibrium uniform distribution, having no preferred direction, the pressure exerted on the walls of a container is again one-third of the energy density: $p = \frac{1}{3}e$.

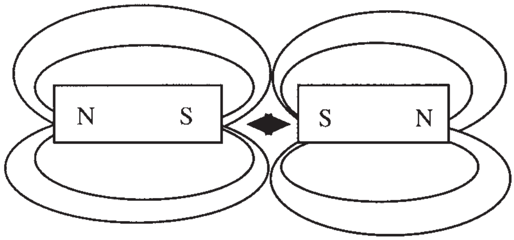
For those entirely unfamiliar with e-m theory, a diagram (Fig. 1a) of two magnets with Faraday's 'elastic' lines of force can be used to demonstrate the tension along lines and the repulsion between lines. Fig. 1b is a simple electro-magnet showing a consequence important in their mechanical engineering design: that failure may come by collapse in the axial direction or by bursting radially. This may be enough to justify the factor of one-third in the pressure versus energy density relation.

Thermodynamic theory: Stefan–Boltzmann radiation law

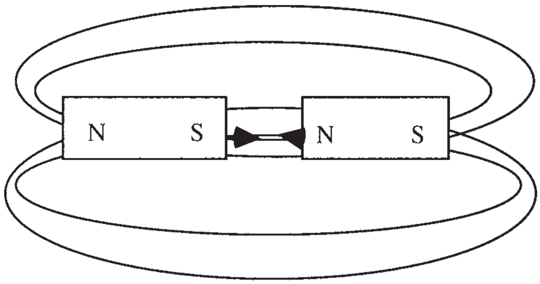
It is not obvious that e-m radiation can be subject to thermodynamics, the classical thermodynamics of the closed system. Clearly, a burst of radiation travelling through space is not an equilibrium system. It was Kirchhoff who saw the way forward, by analysing a cavity whose walls would re-radiate the energy impinging on them and whose contents could properly be described as coming into equilibrium.

Consider then a cavity of volume V, free of material but filled with e-m radiation. The opaque physical walls are maintained at a uniform temperature, T. The system is called in German a *Hohlraum*, literally empty space (Fig. 2). The walls absorb and then emit radiation in several directions, rather than reflect under optical conditions.

Kirchhoff went on to deduce some basic properties of surfaces. By considering a Hohlraum with two parts (at the same temperature) connected by a narrow tube, we can argue that just as much energy will be transmitted left as right, to maintain the dynamic energy balance – otherwise one side would accumulate more energy and get hotter. Then as much energy is re-emitted as is absorbed. Extending the argument to include a 'window' transmitting a narrow-wavelength band, the equality of absorption and emission is valid at every wavelength. Similarly there can be no bias in polarisation or else a polarising filter would act as a one-way valve. In the

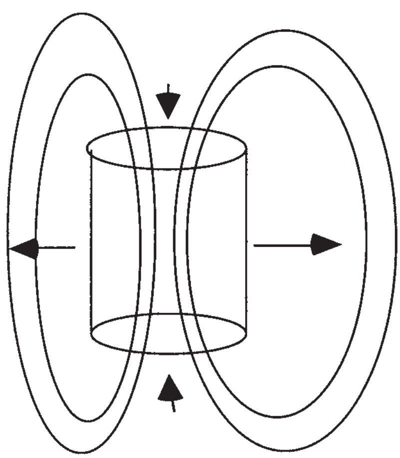


Repulsion between magnetic lines of force



Attraction along magnetic lines of force

Fig. 1a *Compression and tension associated with magnetic fields.*



Radial bursting and axial crushing forces on an electro-magnet

Fig. 1b *Mechanical forces on an electro-magnet.*

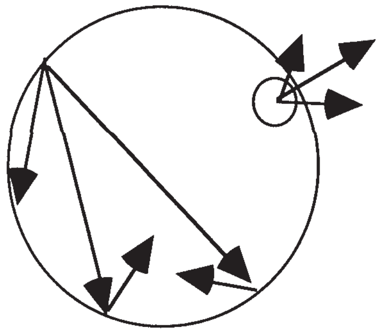


Fig. 2 *The Hohlraum.*

Hohlraum, there is no one-way effect when the temperatures and spectral distributions are the same either side.

In the Hohlraum, the energy impinging on the surface is, in general, part reflected and in part absorbed and then re-emitted, leading to the equality of absorption and emission coefficients. Whatever the nature of the surface, the repeated interactions in the closed Hohlraum ensure that at equilibrium all directions within the radiation are equally favoured; equilibrium radiation is randomised and isotropic.[4] Kirchhoff used similar arguments to obtain the law of view factors,

$$F_{12}dA_1 = F_{21}dA_2 \tag{2}$$

from the dynamic equilibrium that must obtain between any two elementary surfaces of area dA at the same temperature exchanging radiation, where F_{12}, the geometric view factor, is that fraction of the radiation leaving surface A_1 that is intercepted by surface A_2. Thus, although derived in terms of equal temperatures and black-body surfaces, this geometric fraction is a more general concept satisfying the reciprocity relation of equation (2).

In the equilibrium Hohlraum, therefore, surface shape or nature, and direction are immaterial; the intensive properties of the radiation are determined by the surface temperature only, so that we ascribe the temperature of the walls to the radiation itself. This step and this only allows us to talk of the temperature of radiation, when it is in equilibrium with a Hohlraum whose walls have that temperature. Correspondingly, nothing can be determined by an observer within the Hohlraum at equilibrium about the nature of the contents other than the equilibrium radiation itself; no distinction is possible between 'black' and 'white' surfaces, so you cannot, for example, read a book in the Hohlraum.

4 We can reasonably assume that the walls are not perfect reflectors and the original radiation not so aligned as to favour some directions over others. Were this the case, a small speck of black material could be inserted to bring the radiation into directional equilibrium. But there are no real perfect reflectors.

Now we can provide a small opening for the escape or admission of radiation.[5] Not only will the radiation leaving the Hohlraum be in the same energy distribution over wavelength and angle as within (isotropic within becomes Lambert's distribution at the surface), but radiation entering the Hohlraum through the window will be multiply reflected and finally absorbed; the opening is *black* to radiation falling on it. If an isolated surface outside the Hohlraum condition behaves in the same way, absorbing all radiation falling on it and re-emitting to give uniform distribution in solid angle or Lambert's cosine equivalent, it is called black. If the thermal radiation has the same *relative* distribution in energy at that temperature, it is called grey, and otherwise coloured according to the part of the spectrum most favoured.

We can now claim that the contents constitute a system having entropy S, energy E with volume V at temperature T. The symbol E is used rather than U (for internal energy), since internal energy should be independent of a Galileian transformation, a moving observer, and this proves not to be the case with e-m energy, which suffers Doppler effects.

The first three of these properties are *extensive* in nature, the sum of their parts. The temperature of course is *intensive* and the pressure p provides a second but not necessarily independent intensive property, the same in all parts of the system. These properties are independent of the shape and surface nature of the Hohlraum and depend only on the volume and temperature.

Since photons have zero rest mass, it is preferable to express the thermodynamic relations in terms of volume-specific properties rather than mass-specific ones, as we have done already with the energy density, $e = E/V$. Thus we write $s = S/V$ for the volume-specific entropy density.

The fundamental thermodynamics is expressed by the first master equation that relates reversible heat transfer and reversible work transfer to the corresponding change in energy:

$$dE = TdS - pdV$$

and hence

$$Vde + edV = TVds + TsdV - \frac{1}{3}edV \tag{3}$$

Then we have

$$\left[\frac{4}{3}e - Ts\right]dV = V[Tds - de] \tag{4}$$

Let the temperature and volume be our independent variables. If the extensive system variables are indeed extensive, both the volume-specific entropy (or entropy density) and the energy density will be functions of temperature only:

5 Small means that the cube of the hole area shall be much less than the square of the Hohlraum volume. But note that the area itself must be large compared with the wavelength to allow energy of such frequency to escape. There is therefore a degree of approximation in this conceptual step.

$$s = s(T), \quad e = e(T), \quad p = p(e) = p(T)$$

Thus an isothermal process changing volume, but leaving the temperature unchanged, leaves zero on the right-hand side of equation (4). It follows from the left-hand side that we have the relationship

$$\frac{4}{3}e = Ts \tag{5}$$

While this has been derived for an isothermal process, it is more generally true at any given temperature. And for an isochoric process, leaving the volume unchanged, we have the ordinary differential equation (in the single independent variable of temperature)

$$\frac{de}{ds} = T = \frac{4e}{3s} \tag{6}$$

This has the solution, in terms of arbitrary constants of integration C, and assuming zero energy density at zero temperature,

$$e^3 = C's^4 = C''\left(\frac{e}{T}\right)^4$$

$$\text{or} \quad e = CT^4 \tag{7}$$

Finally an isentropic (reversible and adiabatic) process satisfies

$$d(eV) = -pdV$$

$$\text{and} \quad e^3V^4 = \text{const.} \quad \text{or} \quad pV^{4/3} = \text{const.} \tag{8}$$

for the photon gas, in contrast with the perfect gas law, $pV^\gamma = \text{const.}$

The result at equation (7) is evidently close to the Stefan–Boltzmann law but it is not quite there yet. The law refers to the energy current density $\dot{q}''$ or energy radiated per unit of time and area from a perfect 'black' surface, here the inside surface of the Hohlraum. The volumetric energy density, e, times a speed of light, c, however, refers to the energy current density crossing normal to a unit surface drawn arbitrarily within the Hohlraum itself. What we want is not the net current, which is zero in equilibrium, but the one-way current of energy density, which will be the same for the emitting surface as an imaginary surface in the interior. The rate of crossing is cu. This is spread over all directions and so there is a factor to account for the energy striking and re-emitted from the physical surface at directions other than the normal. It is a straightforward if tedious geometrical calculation along the lines of equation (1) to show that this factor is one-quarter. As a matter of hand waving, one-half comes from the observation that we want the energy crossing one way rather than both ways, and the other factor of a half from the spread of directions from tangential to normal. The formal derivation again makes a useful exercise.

Then, overall, we have, within an unknown constant still (the Stefan–Boltzmann constant, σ), the radiation law for the rate of emission of radiation from a 'black' surface or a Hohlraum at uniform temperature:

$$\dot{q}'' = \frac{e}{4c} = \frac{C}{4c}T^4 = \sigma T^4 \tag{9}$$

with units such as watts per square metre. In these units, $\sigma = 0.567032 \times 10^{-9}$ W/m^{2}K^4 from experiment and quantum theory, or $\sigma = 5.67 \times 10^{-8}$ W/m^{2}K^4 in a slightly non-SI but memorable numerical form (from equations 5–8).

For completeness, since temperature and volume have been taken as the independent variables, it is appropriate to write down the Helmholtz function for the photon gas as:

$$F(T,V) = E - TS = -\frac{4\sigma}{3c}VT^4 \tag{10}$$

It is a useful exercise to carry through all these operations for a perfect gas and realise that there is a substantial difference. Molecules of the gas are conserved upon compression, whereas photons are not conserved; they simply appear or disappear to fill the space available.

A further exercise is to analyse a Carnot cycle in the Hohlraum, processes at constant temperature and constant entropy in succession, to show the net work from a reversible cycle satisfies conventional Carnot theory.

Wien's displacement law and distribution law

A further development of nineteenth-century thermodynamics was achieved by Wien. His law describes how the perceived colour at the peak of the radiation spectral distribution shifts with temperature, describing the transition from a dull red-glow at 1000 K to the intense light of the sun, say 5800 K, at a wavelength where the eye developed its greatest sensitivity and we see white light. The full distribution law of the Hohlraum required the work of Planck, but Wien was able to discuss in thermodynamic terms how the peak of the distribution, as yet to be discovered theoretically, shifts with this change of temperature and how the energy distribution depends on wavelength. It is worth observing that the same argument can be used in an exercise with the Boltzmann distribution of particles, as in thermalised matter or thermal neutron transport theory [2]. I follow Adkins' development for photons [3].

For this development, the Hohlraum with black-body surfaces is replaced by a chamber whose walls are perfect reflectors. Thus the photons do not interact, either within the chamber or at its walls, where they are perfectly reflected. It may be shown, by introducing temporarily an insignificant, mobile, speck of black-body material, that at the relevant times the radiation *once in equilibrium* will indeed

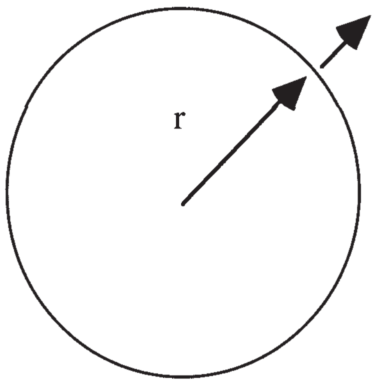


Fig. 3 *The expanding chamber.*

remain in an equilibrium distribution.[6] By this argument, during an isentropic expansion the radiation in a narrow range of wavelengths and precise direction may be treated as an optical beam with no interaction of photons of different frequency and different direction. During the expansion,[7] the moving walls will reflect the photons with a Doppler-decreased frequency and increased wavelength, the 'red shift'. Fig. 3 shows a spherical chamber with an expanding surface moving at speed $dr/dt = v$. The standard non-relativistic Doppler shift expression for the change in frequency of light from a moving reflector, with allowance for the normal component of the ray, at angle θ, is given by $d\lambda = 2\lambda v/c \cos\theta$. The photon has a reflection rate $c/2r\cos\theta$, so that assuming the wavelength must be zero at zero radius,

$$\frac{d\lambda}{dt} = \frac{\lambda v}{r}$$

$$\text{or} \quad \lambda \approx r \tag{11}$$

This result, that the wavelength increase with the radius, is consistent with a simple wave-mechanic view (Fig. 4), where, during an isentropic expansion, the Schrödinger wave retains the same wave number.

We have, from the analysis of *all* the radiation previously given, that during this expansion

6 In the original development of the Hohlraum in thermal equilibrium, it was said that the wall surface properties were somewhat arbitrary and the surface not necessarily black; the equilibrium balance was due rather to the repeated reflections within the closed cavity. We see now that a perfect specular reflector should be ruled out; such a surface does not absorb radiation and therefore does not emit, only reflect. Correspondingly, it would not necessarily lead to an isotropic distribution in a too-regular cavity.

7 The expansion within the perfectly reflecting walls may be considered isentropic as well as adiabatic only because the spectrum starts in the equilibrium distribution and remains there.

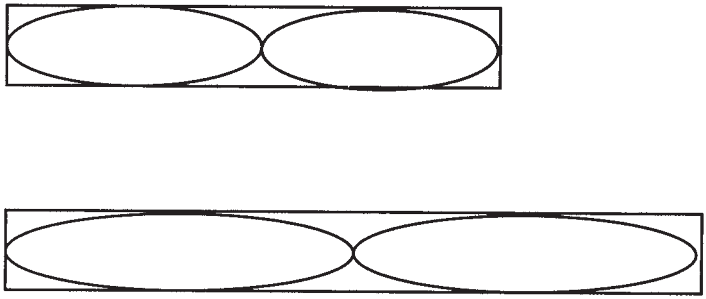


Fig. 4 *The variation of wavelength with linear size in isentropic expansion.*

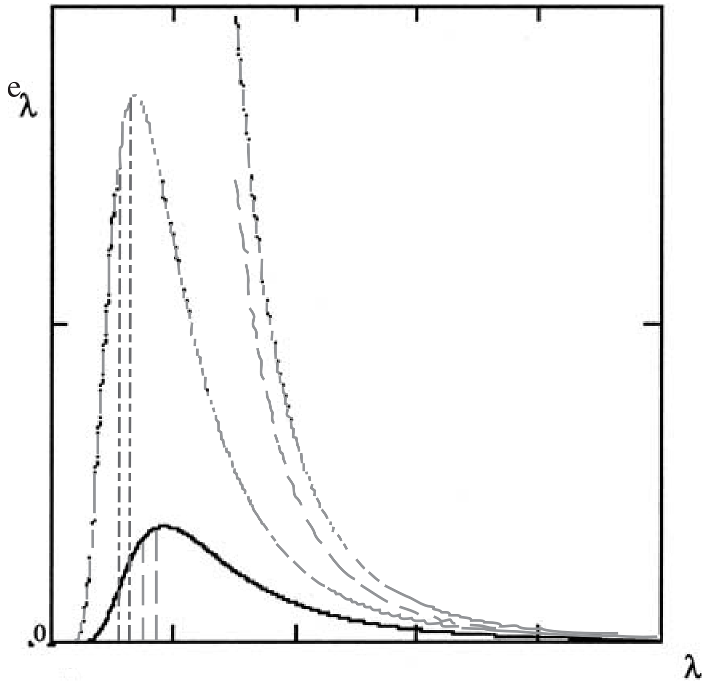


Fig. 5 *Squeezing of wavelength band with temperature change against wavelength, Planck formula with Rayleigh–Jeans approximation.*

$$eV^{\frac{4}{3}} = \text{const.}$$

$$\text{or} \quad er^4 = \text{const.}$$

$$\text{hence} \quad e\lambda^4 = \text{const.} \tag{12}$$

Combining this with Stefan–Boltzmann's fourth-power law, we have, along an isentrope, Wien's displacement law:

$$\lambda T = \text{const.} \tag{13}$$

That is, each packet of radiation in the wavelength band of black-body radiation at temperature T will change during an isentropic process to a packet at a different wavelength (and a different width band) as the temperature changes, such that λT is constant (Fig. 5). Because the expansion is spherical, all directions are affected equally and the distribution remains uniform over angle. Were we to reintroduce the black speck, there would be no change from the equilibrium conditions, so the expanded radiation is still black body but at the new temperature.

Now the displacement law, λT = const., is not as yet a statement for the change of peak wavelength with temperature; it describes the shift that any wavelength has in isentropic compression. One peak might not remain a peak when shifted. Nevertheless, it will be shown to be true, and that the peak remains a peak, by deriving Wien's second, or distribution, law. Meanwhile, from experiment or from more advanced quantum theory, we may find that at the maximum of the energy distribution, at a wavelength that will dominate the other components, $\lambda_{\max}T = 0.0029$ mK. So the surface of the sun, at about 6000 K, has a maximum at a wavelength of some 0.5 μm, i.e. in the visible portion of the spectrum (in accordance with elementary notions of biological development theory), while room temperature material has a maximum at about 10 μm, in the far infra-red. This then is the 'foundryman's law', in which the temperature is judged by the colour seen through a small aperture leading to the furnace.

The further step that can be taken in classical thermodynamics, Wien's displacement law, is to integrate the energy component in the narrow wavelength band over all wavelengths. Suppose we have an element of energy $dE_\lambda d\lambda$ in this band. Then, for the pressure exerted by this band only, we have:

$$d(E_\lambda d\lambda) = d(Ve_\lambda d\lambda) = d(e_\lambda d\lambda)V + e_\lambda d\lambda dV = -p_\lambda dV = -\frac{1}{3}e_\lambda d\lambda\, dV \tag{14}$$

or $$\frac{d(e_\lambda d\lambda)}{e_\lambda d\lambda} = -\frac{4}{3}\frac{dV}{V} = -4\frac{dr}{r}$$

or $$e_\lambda(d\lambda)r^4 = \text{const.} \tag{15}$$

But both the wavelength and the size of the wave packet are proportional to the radius so that:

$$e_\lambda r^5 = \text{const.}$$

and $$e_\lambda \approx T^5$$

whence $$e_\lambda = T^5 f(\lambda T)$$

or $$e_\lambda = \lambda^{-5} g(\lambda T) \tag{16}$$

where f and g are as yet unknown functions, differing by a constant. Thus $e_\lambda \lambda^5$ (and its integral, the energy up to wavelength λ) can be plotted as a universal curve against

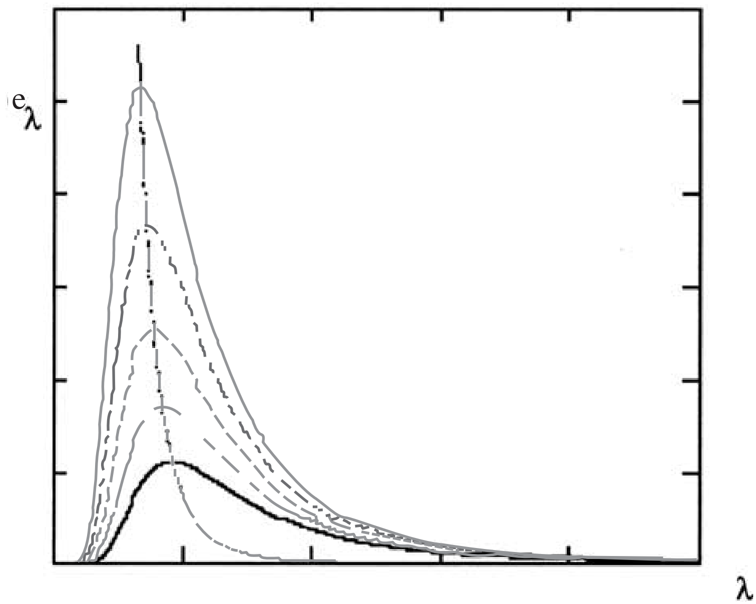


Fig. 6 *The Planck distribution of energy density, eλ, as a function of wavelength, λ, with peaks satisfying λT = const.*

λT. Now we may investigate the maximum by putting the differential to zero and for any function g we have:

$$g(\lambda_{\max}T)/(\lambda_{\max}T)^5 = \text{const.}$$

$$\text{or} \quad e_{\lambda_{\max}} = \lambda_{\max}^{-5} g(\lambda_{\max}T) = C\lambda_{\max}^{-5} \tag{17}$$

so that the peak indeed satisfies $\lambda_{\max}T$, as shown in Fig. 6 using equation (17). A discussion point for work outside the lecture might be to ask if a displacement law could be found for any other factor than one-third in the expression for the radiation pressure. Task: plot the universal curve for the energy content up to wavelength λ.

However, after the success of Boltzmann in putting the fourth-power law on a theoretical basis, it was disturbing that the new statistical science of Boltzmann and Maxwell was unable to provide the missing unknown function. The continuous theory used led to functions which did not converge on integration, due to the effect at very short wavelengths and high frequencies – the ultraviolet catastrophe. For example, the Rayleigh–Jeans approximation of 1905 describes a classical oscillator[8]

8 Such an oscillator can be thought of as an electron behaving like a mass on a spring and vibrating. Classical e-m theory then requires the accelerated–decelerated charge to radiate energy.

with equipartition of a continuous energy spectrum. This leads to a fifth-power law by putting the function g to unity, which matches, in Fig. 6, the long wavelength distribution but clearly does not converge when integrated over the short, ultra-violet wavelengths. Wien put forward a better approximation of the form[9] $g(\lambda T) = C\mathrm{e}^{-\frac{C'}{\lambda T}}$ or $e_\lambda = C\lambda^{-5}\mathrm{e}^{-\frac{C'}{\lambda T}}$. This may readily be integrated if converted to frequencies instead of wavelengths and is related to the factorial of 3. It matches observation quite well, but not exactly and lacks a rigorous basis.[10] This lack of accuracy at long wavelengths troubled Planck.

This was about as far as classical thermodynamics based on the continuum could go. The rigorous form for the unknown function of λT awaited a new physics, the quantum assumption of Planck [8], who showed that:

$$g(\lambda T) = \frac{8\pi hc}{e^{hc/k\lambda T} - 1}$$

$$\text{or} \quad e_\lambda = \frac{8\pi hc\lambda^{-5}}{e^{hc/k\lambda T} - 1} \tag{18}$$

Here k is the Boltzmann constant or the universal gas constant per molecule, entity, photon, etc. In principle, both h and k may be measured by determining the radiation intensity at a peak wavelength at a known temperature; indeed, this was the first estimate of h. But it is a great result of Planck's theory to relate radiation to the two fundamental constants widely found in nature. This exact result matches Wien's distribution at high frequencies, short wavelengths (series expansion of the denominator), where radiation may be treated as a continuum. The difference shows up at long wavelengths. In deriving these results (see Appendix) from a treatment of radiation as a photon gas, it has to be considered that for every (vector) momentum there are in fact two photons to account for the different polarisations, leading to eight rather than four in the formulae of equation (18). The Planck distribution (Fig. 6) may again be integrated (numerically – show that instead of 3! = 6 we obtain 6.494 . . .) and also differentiated to determine the dependence of the peak wavelength upon temperature, yielding, as a further numerical exercise (an expansion solution is insufficient):

$$\frac{hc}{k\lambda T} \approx 4.965 \tag{19}$$

The development here is for the intensity as a function of wavelength. It can also be developed as a function of frequency, of course, and it is a good exercise to see

9 Here e in the formula is the exponential, not the energy density. It makes Wien's distribution analogous to the Maxwell–Boltzmann distribution, although the fifth-power law is unique to radiation.

10 Pippard [9] derives Nyquist's equation for Johnson noise for electrical engineers from thermodynamics using the Rayleigh–Jeans formula. A full discussion is available in *Problems in Thermodynamics and Statistical Physics*, P. T. Landsberg, ed. (Pion, London, 1971).

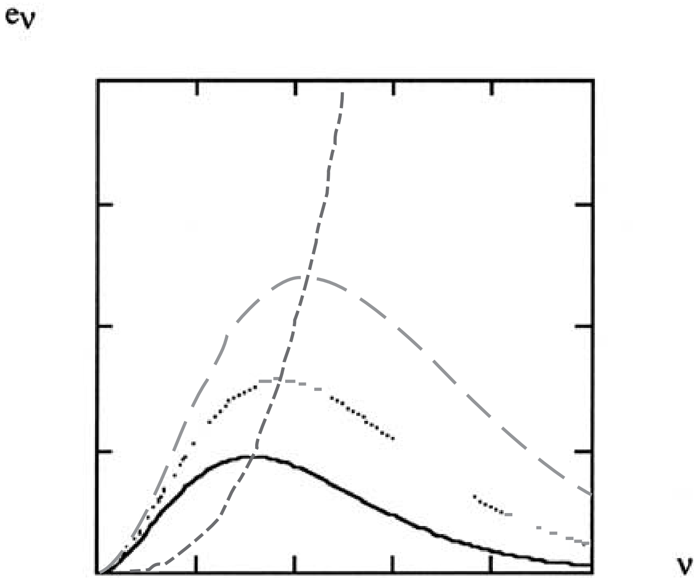


Fig. 7 *Radiation density as a function of frequency, showing the peak relationship.*

what the relationship is in frequency at a peak intensity (Fig. 7). In the frequency distribution, $h\nu \approx 2.82\,kT$ at a maximum. Planck's distribution may be outside the interests of engineers but they have at least studied some aspects of the problem that brought about the quantum revolution, the resolution of the ultraviolet catastrophe.[11]

Fig. 8 shows the observed insolation falling on the earth. It looks convincing. However, it should be said that if, instead of frequencies at or near the visible, we look at radio waves around 5 m in length, then the sun appears much larger in the sky and considerably hotter, around 1 MK instead of 6 kK. Equally, at very high frequency, the sun looks small and cooler. One explanation is that the high-frequency rays in the magnetically dominated corona of the sun, visible to the naked eye only during a total eclipse, interact to produce the observed temperature and size of the radio-frequency source.

It is worth commenting that the Hohlraum spectrum derived is for a stationary observer. A moving observer will see Doppler effects, which will give a red shift to those components moving away and a blue shift for those components moving towards the observer. Thus the observed spectrum close to the source may be smeared out for the moving observer and its peak alone will not uniquely identify the temperature. However, the integral of the observed distribution will remain proportional to the fourth power of the temperature. It is for this reason we do not

11 A fuller development is available in Elwell and Pointon, *op. cit.*

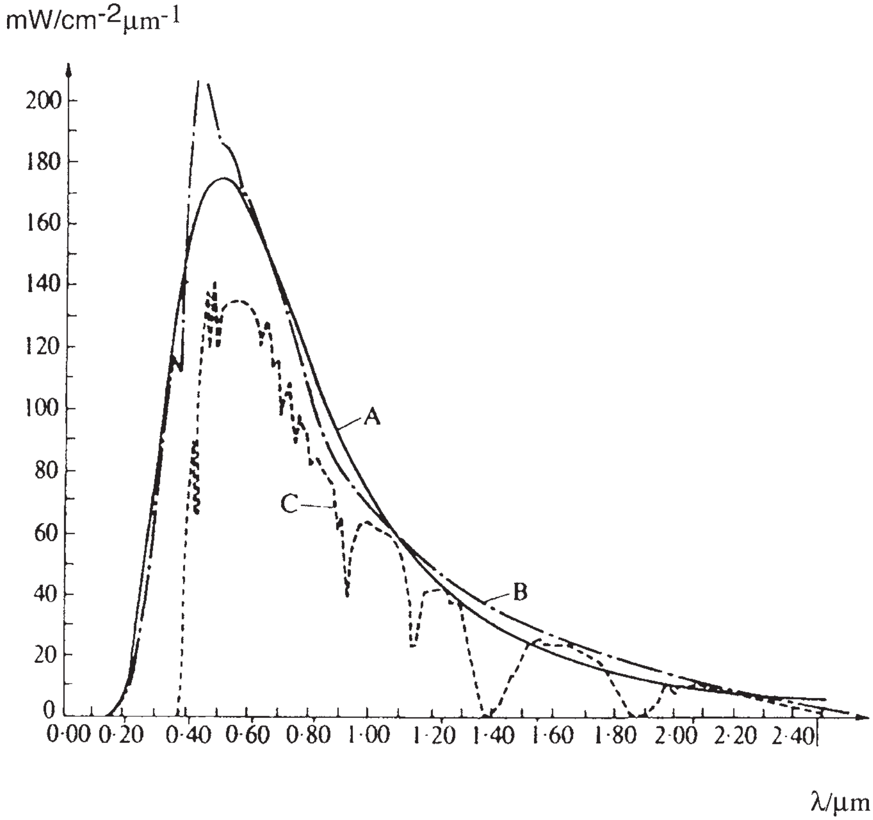


Fig. 8 *The energy of sunlight falling on the earth distributed over wavelength. A: Black-body radiation at 5760 K. B: Direct solar radiation above the atmosphere (note the shortfall at extreme wavelengths). C: Direct solar radiation on earth's surface with the sun vertically overhead on a clear day (note ozone absorption in the ultra-violet range then oxygen, water and finally carbon dioxide in the infra-red range at long wavelengths).*

express the analysis as internal energy, since what is observed about radiation depends in part upon the external observer.

The photon as a chemical constituent

A modern view of e-m fields is to say that the photon mediates the field and that all properties of a field, 'action at a distance', are effected by the photon. A similar view is applied to strong nuclear forces involving the muon, gravitational fields involving gravitons, etc. When the Hohlraum expands at constant temperature, requiring energy to be introduced through the surface, then more photons appear. If these are thought to be introduced through the surface, then one should enquire as to the free energy being introduced or the chemical potential of the photon. It will be recollected that, in conventional chemistry, the chemical potential of the elements is taken as zero and compounds have a higher chemical potential by virtue of the work done at the corresponding pressure and temperature to form the compound.

Reverting to the molar-specific view of conventional thermodynamics, the Gibbs chemical potential μ_i of species i is defined as:

$$\mu_i = \left.\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j\neq i}} \tag{20}$$

where $G = E + pV - TS$ in the present context is the Gibbs function for the system consisting of n_j moles of constituent species. We also have the Gibbs–Duhem relationship, which, for a single species as here, is

$$n\mu = G = E + pV - TS = V\left[e + \frac{1}{3}e - Ts\right] = 0 \tag{21}$$

This result is arrived at by summing $dG(p,T) = \mu(p,T)dn$ over the extensive variables at constant pressure and temperature. From equation (5) we see that the photon has zero chemical potential. The molecular mass of the photon is also zero, so that moles of photons are perhaps undefinable, but the development could equally well have been made in terms of a number of photons, n, and the chemical potential of a single photon is then indeed zero.

In this view, therefore, it is the photon that is the fundamental constituent or chemical species. A zero-mass photon of sufficient energy, greater than 1.02 MeV, is known to be capable of creating massive particles, say an electron and its antimatter equivalent, the positron. With greater energy, it might create protons and neutrons and hence the chemical elements. These ‘elements’ are no longer the independent building blocks of chemistry and they can be given a chemical potential based on the free energy needed to create them out of e-m radiation. There is then no value in ‘opening’ the closed system to view photons as transferring energy by passing through the system boundaries; the photons have no chemical potential.

Fallacies in thermodynamics of radiation

There are a number of fallacies about radiation which are amusing and instructive. Furthermore, the topic of how much sunlight can, in principle, be converted to work is poorly treated in many texts and some clarification is offered here. We may start with the observation that sunlight reaching the earth carries a ‘signature’, the peak wavelength, of the surface temperature of the sun, but of course this is not the temperature of the arriving radiation itself. One approach to the question of how much work can be obtained from sunlight is to ask what maximum temperature might be achieved when the sunlight falls on a surface which might then be used as a thermal source to drive a heat engine.

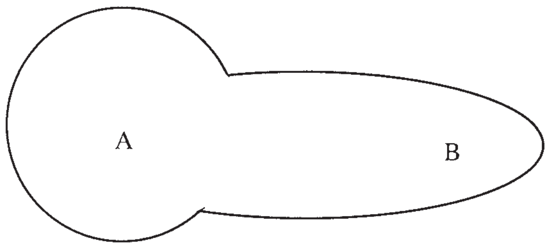


Fig. 9 *An ellipsoidal–spherical body with sources at the foci, A and B.*

The sunlight is not at the temperature of the sun because although its *relative* energy spectrum corresponds closely to the sun's temperature, the absolute magnitude is decreased by the expansion the rays have undergone; in addition, the direction is not either that of a Hohlraum or that emitted from a Hohlraum, i.e., it is nearly plane parallel. The dilution factor is the square of the distance, r, from the centre of the sun in units of the radius of the sun $(r/r_0)^2$. Since the temperature goes as the quarter-power of this energy density, the temperature that could be achieved by the sunlight falling on a black surface, insulated at its back, would be such that the energy re-emitted would sustain a system in equilibrium with the energy received and hence:

$$T/T_0 = (r_0/r)^{1/2} \approx 0.00465^{1/2} = 1/14.7 \tag{22}$$

In the absence of the earth's own heat source and consequent temperature, this would suggest that a maximum temperature 'in the sun' would be some 410 K. Since this is low to generate work, practical systems use optics to concentrate the sunlight. Practical proposals include an approximation to a hemi-spherical mirror to concentrate the sunlight. One series of fallacies[12] supposes that it is possible to design such optical systems so as to produce a temperature higher than that of the sun itself. Note that the image of the sun cannot be concentrated to a point. If this concentration were onto a window in a Hohlraum we can see that the maximum temperature inside cannot be greater than that of the sun or more radiation would leave the aperture than would be received from the mirror. More realistically, the receiver would radiate from all sides and hence the temperature will be lower than that of the sun.[13]

(1) An illustration of one such fallacy is given in Fig. 9. Here an ellipsoid body has perfect, specular reflecting walls with point sources at its foci, A and B. The complete body would therefore radiate all the energy from one focus to the other. Equilibrium would demand the two point sources had the same temperature. However, the ellipsoid is truncated where it meets a spherical specular reflector with

12 Discussed also by L. D. Landau and J. M. Lifschitz, *Statistical Physics* (Pergamon, London, 1958).
13 And the Hohlraum itself would obscure part of the mirror, thus decreasing the potential temperature.

focus at A. All energy from A reaching the sphere returns to A and it is seen that only a small part is directed via the ellipsoid to B. However, nearly all the energy from B reaches A. It would seem that there is a paradox, that A accumulates energy from B and must therefore get hotter. But the argument is fallacious; such a point source has no area and at finite temperature can emit no energy. If real, finite-area sources are substituted, then the actual images must be considered. Simply use Kirchhoff's laws for view factors, equation (2), to establish what proportion of the energy from A reaches B and vice versa.

(2) It might similarly be asked how a 'one-way mirror', i.e. a half-silvered mirror, accords with the view that transmission must be equal in both directions. But of course such a mirror in practice is used to separate a bright room from a dark room; the reflection of bright light obscures the image transmitted from the darkened room but allows the transmission from the bright room to be visible in the dark room. In the Hohlraum, the transmission is the same in both directions for the same spectrum either side, while what is not reflected in absorbed and re-radiated.

(3) Consider again a cubic container with perfect reflecting walls and introduce photons, in a Planck distribution of wavelength but aligned solely with the x-axis. The end walls then feel a pressure but there is no pressure on the remaining walls. No photons impact the side walls; correspondingly, the Poynting vector is along the x-axis and so the electric field is, say, in the y-direction and has a tension which is exactly cancelled by the compression from the magnetic field, which will then be in the z-direction. Expand the x-axis adiabatically to deliver work. The Kirchhoff argument applied to this system leads to a relationship:

$$dE = Vde + edV = \theta[Vd\sigma + \sigma dV] - edV$$

or $$[2e - \theta\sigma]dV = V[\theta d\sigma - de]; \quad \theta = 2\frac{e}{\sigma}; \quad e = C\theta^2 \tag{23}$$

The result is not the fourth-power Stefan–Boltzmann law and the concept θ is not a temperature nor σ the entropy density. The system was not in equilibrium and indeed the result depends upon the direction of expansion.

(4) Similarly, when radiation in a container is not isotropically distributed, it is not in equilibrium. Temporarily add a speck of black matter. The radiation will then become isotropic but this is an irreversible process which cannot be returned to the original state without the expenditure of work and removal of heat. For discussion: is it possible to calculate the increase of entropy produced, recollecting the definition of entropy as a change during a reversible process? The mistake is typical of specifying speed when velocity, implying direction, is more appropriate. There is a similar effect in molecular distribution theory, where the Maxwell–Boltzmann distribution in *velocity* is Gaussian, greatest around small velocities and falling to zero at the tails of large magnitude speeds in the positive or negative direction. As a distribution in speed, however, it has a more conventional shape, falling to zero at zero speed, since the right- and left-going components cancel (Fig. 11, left and right).

A further group of misunderstandings, rather than paradoxes or fallacies, concern the maximum utilisation of sunlight to produce work. Bejan [1] gives an excellent detailed account of the thermodynamics of the conversion of sunlight, which might

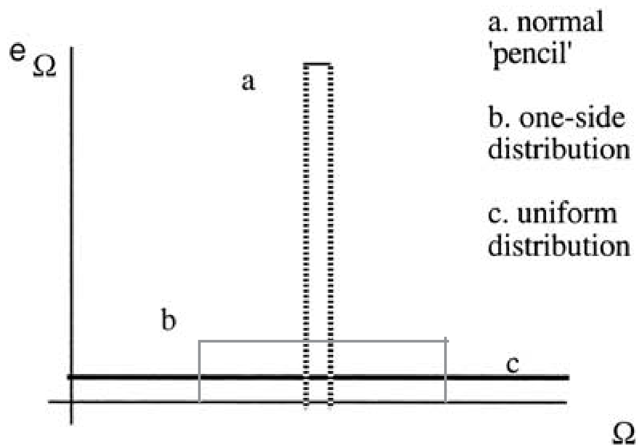


Fig. 10 *The Planck distribution in thermal equilibrium (solid) and the distribution over a narrow beam (dotted) or over the external surface of a Hohlraum window (dotted) versus angle.*

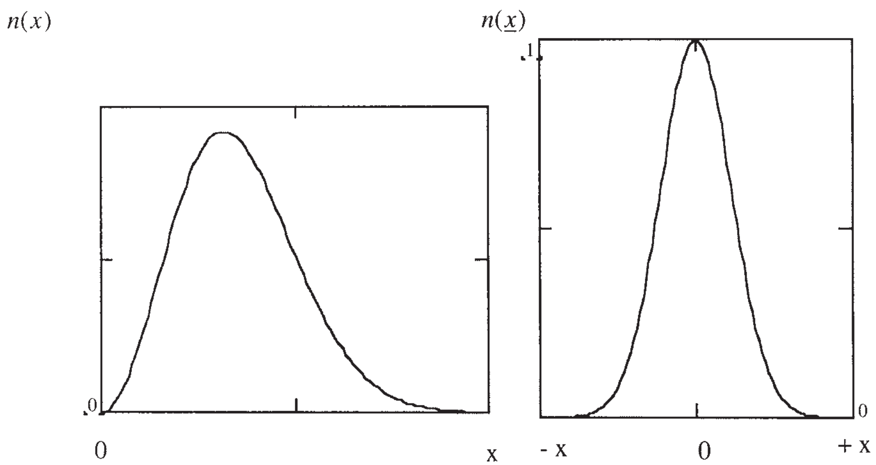


Fig. 11 *The Maxwell–Boltzmann distribution of thermal molecular density. Left: as a function of speed; right: as a function of velocity.*

form a substantial course component in its own right. In discussing these problems Bejan rightly draws attention to a number of points that are often overlooked. These include:

- Thermal radiation from a source at long distance is not *exactly* parallel and exists in a waveband and solid angle band. Indeed, the energy associated with this band, $e_\lambda d\lambda d\Omega$ per unit area, would be zero if $d\Omega = 0$. Equally, the radiation cannot be focused down to a point.

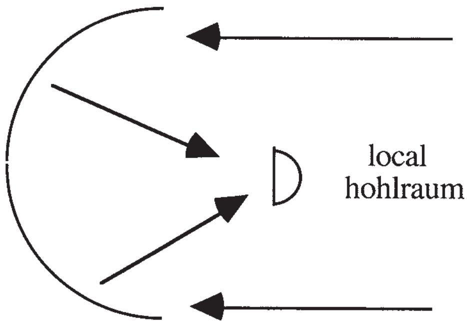


Fig. 12 *Focusing sunlight.*

- The full analysis must cover every stage from the sun's emission to the production of power.
- The sun emits radiation continuously and so the engineer's problem is one of maximising the *power* obtainable from radiation rather than static Carnot theory, maximising work obtained from the exchange of heat between two thermal reservoirs.

It is a misunderstanding to deal only with the maximum temperature driven by the source of sunlight, with Carnot theory to give the maximum conversion efficiency. We need instead to optimise the combination of the rate of heat taken (recollecting that some will be re-radiated anyway) and the temperature of the hot source to maximise the power provided, not the thermal efficiency. In other words, the problem is not that of maximum efficiency (with no heat taken and no work produced) but maximum power from the insolation. If the aim is to create a hot source of heat from sunlight, then this cannot be hotter than the (equilibrium) source driving it, because it will re-radiate as much energy as it receives at such a temperature. This maximised temperature in itself will not provide any work at all since no heat will be available to drive a thermal engine. The hot source is better at some intermediate temperature to drive a thermal engine subject to Carnot's limitations.

Suppose the surface of the sun provides radiation at temperature T_s. If this could drive a reversible heat engine to the earth as a cold source at T_o, the thermal efficiency would be $\eta = 1 - T_o/T_s$. But consider the more practical model that sunlight (Fig. 12) is the source of a Hohlraum on the earth at the focus of a parabolic mirror, thus converting the nearly plane parallel radiation to a semi-equilibrium distribution, to be maintained at some intermediate temperature, T (Fig. 13). This in turn is used to drive a reversible Carnot engine. Then allowing for the re-radiation from the Holhlraum proportional to the fourth power of the temperature as well as the input from the sun at the fourth power, we have the fraction of incident sunlight that is converted to work reversibly by the engine driven from this intermediate temperature as:

$$\frac{\dot{W}}{\dot{Q}_s} = \left(1 - \frac{T_0}{T}\right)\left(1 - \frac{T^4}{T_s^4}\right) \tag{24}$$

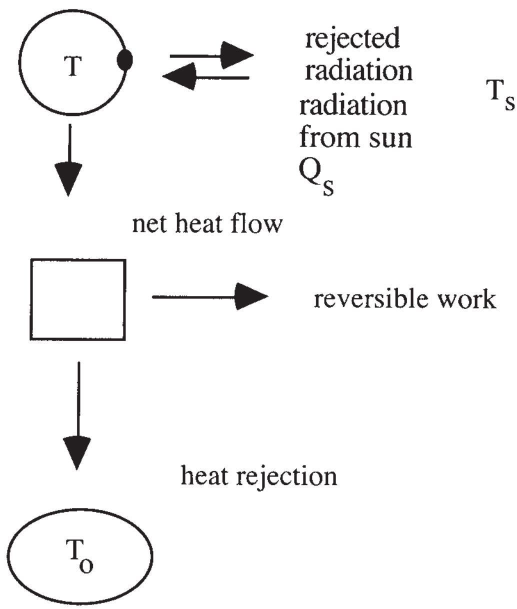


Fig. 13 *Maximising the power from sunlight.*

This may now be optimised over the intermediate temperature, T, to obtain an equation for the optimum temperature maximising the power output:

$$\left(\frac{T_s}{T}\right)^5 + 3\left(\frac{T_s}{T}\right) = 4\frac{T_s}{T_o} \qquad (25)$$

Thus although the maxmum efficiency between the sun at say 6000 K and the earth as a sink at 300 K is 95%, it can be shown by solving equation (25) that the efficiency of the intermediate engine at maximum power is only some 87%. The assumption of a reversible engine is itself too simple but the analysis shows the consequence of posing the appropriate question. Problem: show that, if the re-radiation from the Holhlraum is wasted, the overall efficiency at maximum power is about 78%.

(5) One approach supposes that the earth itself is a cold source. But another supposes that radiation not turned into work can be rejected by radiating to outer space at a temperature of only a fraction of a kelvin. This in itself needs clarification; is there an equilibrium situation in the cold sink? But, overall, establishing the maximum Carnot efficiency is not the issue, but rather finding the maximum power available from the continuous flow of sunlight.

But why limit the discussion to this intermediate heat source? What, if any, are the thermodynamic limits on converting the radiant energy of the sun directly?

(6) It might be supposed that a photo-electric effect could convert all (or more than the Carnot limit) of the sunlight to work. But in a steady state, the photo-

electric material would have its temperature and corresponding thermal motion, which would reduce the photo-electric effect, leading to conventional Carnot limitations on conversion efficiency.

(7) One might appeal to the science-fiction stand-by of the 'photon' drive. Caught in a sail, the 'almost plane parallel' sunlight exerts pressure and can add mechanical energy to the device with only mechanical and e-m, not thermodynamic, limits to efficiency.[14] But this is not now an equilibrium device subject to the thermodynamic laws of the cyclic system.

Now suppose we could surround the sun, a black-body radiator, with a perfect reflecting spherical envelope at the radius of the earth. Neglecting all other radiation, the pressure exerted on the envelope (which is allowed to expand) can do work. The reflected radiation will return to the sun and be absorbed in the black body. In addition to supplying work, however, the increased volume will have to be filled with radiation, both going outward and reflected back. Thus the proportion of the radiant energy supplied turned to work is not 100%. The paradox would be to say that this efficiency is independent of the temperature of any sink and hence might be supposed to outwit the Second Law. Project: try to find a way to use expanding and contracting spherical shells around the sun, which may be turned opaque or transparent at will, to form a theoretical *cyclic* engine to extract work from the radiation. Can this avoid the limits of conventional thermodynamics and the Second Law?

Indeed, the procedure lies outside the Second Law because this is not a cyclical process restoring the system; there is no rejection to a sink so Carnot theory and the Second Law are not relevant. Note that if the excess radiation filling the volume increase were allowed to escape, we must still postulate a cold sink appropriate to absorb it, which would then re-radiate a back-pressure on the expanding and contracting envelope of a cyclic system.

While the proposition is solely a 'thought experiment', it shows there is no thermodynamic limitation to the conversion of radiant energy, other than in the equilibrium Hohlraum; radiant energy outside the Hohlraum does not have a true temperature.

Discussion

The thermodynamics of radiation has practical import and should be better understood, not just for conventional heat transfer purposes but in the light of proposals for converting the sun's energy to work. The immediate result of classical thermodynamics allied with optical or e-m theory is the fourth-power radiation law and the foundryman's law.

Going further perhaps than most engineers require, radiation thermodynamics has significance in cosmology that might appeal to some students and motivate further

14. It is also worth relating this to the theory of rocket travel, that the best form for the matter rejected in a rocket gaining thrust from any available mass and energy, is with the smallest molecular weight. The smallest possible molecular mass is given by the photon, of zero rest mass.

study. According to special relativity, photons moving in free space do so at the speed of light such that their own 'local' time, as measured by a clock travelling with them, is reduced to zero; the local clock indeed stops. Thus the photon arrives at its destination simultaneously with its departure. The e-m field, unlike the strong nuclear field, has indefinite range, so that the whole of space can be traversed by a photon in zero local time. This has some profound implications for thermodynamics, where entropy characterises the supposed one-wayness of time, 'time's arrow' in Eddington's phrase. If the photon is emitted, lowering the energy of the system it leaves, it will 'simultaneously' be absorbed somewhere in the universe, raising the energy. Modern cosmology relates this externally observed natural increase of entropy to the expanding universe, which cools and hence makes the absorption likely, as opposed to a contracting universe, which would presumably see a restoration of order and a decrease in entropy.[15]

It is hoped this outline will encourage a wider view of thermodynamics. I have found the coverage of Kondepudi and Prigogine [2] stimulating.[16] A more formal account of statistical mechanics covering radiation can be found, for example, in Kestin and Dorfman [4]. For a speculation into cosmology, see, for example, *In Search of Schrödinger's Cat* [5], available in paperback editions through Black Swan. Reference [6] has a number of articles of a more rigorous nature. Thomas Kuhn [10] has a philosophical account of the development of quantum theory from radiation thermodynamics. I add a brief biography in the hope of encouraging students to a historical study of their discipline, together with, in an appendix, a development of Planck's distribution function.

Acknowledgement

I am happy to acknowledge the support of the Leverhulme Trust for this work. I am grateful to Brian Pippard for discussion and correspondence with Adrian Bejan.

References

[1] A. Bejan, *Advanced Engineering Thermodynamics* (Wiley, New York, 1988).

[2] D. Kondepudi and I. Prigogine, *Modern Thermodynamics: From Heat Engines to Dissipative Structures* (Wiley, New York, 1998) (but see 2nd edn, when available, for corrections).

[3] C. J. Adkins, *Equilibrium Thermodynamics* (McGraw-Hill, New York, 1968).

[4] J. Kestin and J. R. Dorfman, *A Course in Statistical Thermodynamics* (Academic Press, New York, 1971).

15. Further cosmology is discussed in, for example: H. Reeves, *Observational and Physical Cosmology* (Cambridge University Press, Cambridge, 1992); D. V. Schroeder, *Introduction to Thermal Physics* (Addison-Wesley Longman, London, 2000); J. V. Narlikar *et al.*, 'Standard cosmology,' *Ann. Rev. Astron. Astrophys.*, **39** (2001), 211–248.

16. There are, however, egregious errors in the first edition in dealing with conventional thermodynamics.

[5] J. Gribben, *In Search of Schrödinger's Cat; Quantum Physics and Reality* (Wildwood House, London, 1984).
[6] B. Gal-Ov, ed., *Modern Developments in Thermodynamics* (Wiley, New York, 1974) especially T. Gold, 'The world map and the apparent flow of time', and J. V. Narlikar, 'Thermodynamics and cosmology'.
[7] P. M. Morse, *Thermal Physics*, 2nd edn (Benjamin/Cummings, London, 1969).
[8] M. Planck, *Theory of Radiation* (Verlag, Leipzig, 1913).
[9] A. B. Pippard, *Elements of Classical Thermodynamics* (Cambridge University Press, Cambridge, 1966).
[10] T. S. Kuhn, *Black Body Theory and the Quantum Discontinuity: 1894–1912* (Clarendon Press, Oxford, 1978).

Appendix. Thermal radiation as a boson ensemble

Several textbooks [2, 7] give the statistical properties of a Bose–Einstein ensemble. Like fermions, bosons enter a degenerate state at low energy, where quantum effects outweigh the classical effects governing a Maxwell–Boltzmann distribution. Photons are bosons but have no chemical potential. Their statistical behaviour consequently simplifies in the grand canonical ensemble function Λ, the distributions available at any given energy, etc., whose logarithm is proportional to the entropy. Here the distribution function describes the probability of finding a number of photons in a given quantum state when the system is in contact with a thermal reservoir which, in this case, acts as a photon reservoir also.

$$\Lambda = \sum_{N=0}^{\infty} \sum_{\{N_j\}_N} \exp\left(-\frac{1}{kT} \sum_j \varepsilon_j N_j \right) = \sum_{\{N_j\}_N} \exp\left(-\frac{1}{kT} \sum_j \varepsilon_j N_j \right) \tag{A1}$$

Here, subscript j denotes the quantum state or level, N is a total number of photons, N_j the number in the quantum state and $\{N_j\}_N$ denotes summation over the N_j adding up to N. This in turn can be written:

$$\Lambda = \sum_{N_i} \exp\left(-\frac{\varepsilon_1 N_1}{kT} \right) \sum_{N_2} \exp\left(-\frac{\varepsilon_2 N_2}{kT} \right) \sum_{N_3} \exp\left(-\frac{\varepsilon_3 N_3}{kT} \right) \ldots \tag{A2}$$

where the sequence is taken to infinity since in any reasonably sized system with finite numbers, the probability of seeing anything beyond this maximum is vanishingly small. Bosons can occupy a quantum state without limit and hence $N_j = 0, 1, 2, \ldots$. Then taking logarithms and noting how the exponential term can now be summed,

$$\psi = \ln(\Lambda) = \sum_j \ln\left(\sum_{N_j} \exp - \left(\frac{\varepsilon_j N_j}{kT} \right) \right) = \sum_j \ln\left[1 - e^{-\varepsilon_j/kT}\right] \tag{A3}$$

The final sum can be replaced by an integral to give:

$$\psi = -\frac{2V}{h^3} \int \ln\left[1 - e^{-\varepsilon_p/kT}\right] d^3\boldsymbol{p} \tag{A4}$$

The factor of two comes from the two polarisations of photons. Coming out of momentum space we have, for the energy density:

$$e = \frac{E}{V} = -\frac{\partial \psi}{\partial 1/kT}\bigg)_V = \frac{2}{h^3}\int \frac{cp}{e^{cp/kT}-1} d^3 p = \frac{8\pi h}{c^3}\int_0^\infty \frac{\nu^3}{e^{h\nu/kT}-1} d\nu \tag{A5}$$

From this it follows directly that in the frequency space, which may then be converted to the wavelength form,

$$e_\nu = \frac{8\pi h}{c^3} = \frac{\nu^3}{e^{h\nu/kT}-1} \tag{A6}$$

This brief account may give the student some idea at least where the Planck function [8] comes from and the role of the denominator $e^{h\nu/kT} - 1$.

Biography

Robert Wilhelm Bunsen (1811–99)

Born in Göttingen, he became Professor of Chemistry at Heidelberg, where he collaborated with Kirchhoff. Best known for his invention of the Bunsen burner in furtherance of spectroscopic theory, his experimental work left him partially blinded in one eye.

Ludwig Boltzmann (1844–1906)

Professor of Physics at Vienna 1895, his work in statistical and kinetic theory led to him formulating statistical thermodynamics. Disproof of his *H*-theorem by the Frenchman Jules Henri Poincaré (1854–1912) and attacks by Ernst Friedrich Ferdinand Zermelo (1871–1953), Planck's mathematical assistant, is said to have contributed to Boltzmann's suicide. Boltzmann's gravestone in Vienna bears the inscription $S = k \ln W$, the formula for statistical entropy.

Nicholas Léonard Sadi de Carnot (1796–1832)

Originally a military engineer, he formulated the significant concept of reversibility in thermodynamics, published in 1824 as *Rèflexions sur la puissance motrice du feu et sur les machines proposes à développer cette puissance*, but for some time ignored, until re-issued 1834 by Benoit Paul Emile Clapyron (1799–1864), the civil and railway engineer with interests in steam engines.

(Sir) Arthur Stanley Eddington (1882–1944)

Astronomer who established the validity of Einstein's general relativity theory by observation. Author of *The Expanding Universe* (1933). As a student, Eddington came top of the final mathematics examination (First Wrangler) in only his second year of studies.

Michael Faraday (1791–1867)

The newspaper boy and bookbinder's apprentice who rose to be Professor of Chemistry at the Royal Institution, London, but whose great success as an experimentalist was to found the science of electro-magnetism. His ‘lines of force’ gave rise to the formalism of field theory.

Herman von Helmholtz (1821–94)

Originally a military doctor, he was appointed Professor in Berlin in 1871. He had a wide range of interests in physiology and physics.

Gustav Robert Kirchhoff (1824–87)

Professor of Physics at Heidelberg and then Berlin. In collaboration with Bunsen, at Heidelberg, developed spectrum analysis as part of his studies of thermal radiation.

James Clerk Maxwell (1831–79)

A Scot (his father was born a Clerk but added the Maxwell name), Maxwell, nicknamed ‘Dafty’ at school, made the experimental laws of Faraday sound on a mathematical basis, and developed with Boltzmann statistical and kinetic theory, leading to the distribution law for molecules in thermal equilibrium that bears their names. The success of this law led to the fruitless search for a continuum law in radiation. Maxwell resigned in 1865 from his Professorship at King’s College, London, where it was said he was an unsatisfactory lecturer, subsequently becoming the first Cavendish Professor at Cambridge and bringing that university great glory.

Max Karl Ernst Planck (1858–1947)

Professor of Physics at Berlin from 1889, following Helmholtz. First formulated Boltzmann’s equation. Resolved the discrepancy in Wien’s empirical distribution in 1900 by supposing the oscillators in the emitting walls of the Hohlraum were quantised and could not give out continuous spectra. Is said never to have believed that quantisation was inherent in the spectrum of light itself, even when developed by Albert Einstein (1879–1955) as the theory of MASERS and LASERS in 1905 for optics and Erwin Schrödinger in wave mechanics. Nobel Laureate, 1918, for work in thermodynamics of radiation leading to quantum theory.

Erwin Schrödinger (1887–1961)

Artillery officer in the First World War. Initiated wave mechanics on the basis of quantum theory. Noble Laureate, 1931.

Joseph Stefan (1835–93)

Professor at Vienna, 1863. First estimated the apparent (surface) temperature of the sun from the observation of Tyndal of radiation from known temperatures, suggesting a fourth-power law. His work was developed more rigorously by both Maxwell and Wien.

John Tyndall (1820–93)

Irish physicist and railway engineer. He studied under Bunsen at Heidelberg, collaborator with Kirchhoff, and became Professor at the Royal Institution. In 1859 he embarked upon Alpine studies of glaciers, the scattering of light from the sky and thermal radiation, studies which included the first ascent of the Weisshorn. Tyndall died from accidental poisoning with chloral.

Wilhelm Carl Werner Otto Fritz Franz Wien (1864–1928)

Student of Helmholtz and then Professor at Munich from 1920. Nobel Laureate, 1911, for his work on black-body radiation following up Stefan's empirical laws.