THERMAL RADIATION

Why study thermal ("blackbody") radiation? Where's the relevance?

Consider:



1. All objects emit electromagnetic energy as thermal radiation, a fundamental (but often overlooked) property of matter. This kind of radiation has important applications related to radiant heating and cooling, industrial design, remote sensing, infrared thermometers, and climate change and the "greenhouse" effect.





2. Megaton-TNT-equivalent thermonuclear weapons for WW III are powered by the fusion of hydrogen and lithium isotopes detonated by the intense thermal radiation pressure (proportional to the temperature raised to the *fourth power*) produced by kiloton-scale nuclear fission explosions using uranium or plutonium.

1. The "Primary" High Explosive Lens Two-point, hollow-Two lenses drive pit, fusion-boosted primary implosion high explosive weight 350 kg implosion Plutonium-239 Pit Beryllium-reflected hollow pit 2. The "Secondary" length 2.0 m Spherical, all-fissile, Tritium & Deuterium fusion-boosted Booster gas, fusion radiation implosion width 0.5 m makes neutrons Lithium-6 Deuteride 3. Radiation Case Lithium becomes tritium, Peanut-shaped. 500 kiloton yield fusion makes neutrons channels x-rays from primary to secondary Uranium-235 "Sparkplug" (about 0.6 cubic Starts tritium generation and 4. Channel Filler fusion in the secondary Plastic foam football fields plasma generator Uranium-235 "Pusher" of TNT) Heat shield, tamper, and fission 5. Booster Gas fuel (fission by all neutrons) Cannister Periodic replace-Uranium-238 Case ment as tritium Fission by fusion

gas decays

W88 Warhead for Trident D-5 Ballistic Missile

application ...

neutrons only

Ohio-Class Ballistic Missile Submarines

("Boomers")

The USN operates 14 Ohio-class boomers. Each boat can launch 24 intercontinental ballistic missiles (ICBMs). Each missile carries 8 thermonuclear warheads to hit 8 different targets.



3. Multi-billion-dollar international research projects are being funded to develop controlled thermonuclear fusion reactions $(e.g., {}^{1}\text{H} + {}^{3}\text{H} \rightarrow {}^{4}\text{He})$ to provide virtually unlimited energy for humankind. The same nuclear fusion reaction that power the sun. Star power on Earth!

National Ignition Facility (in California)

196 high-power laser beams are used to "blast" and implode metal capsules containing deuterium and tritium thermonuclear fuel.

The laser radiation vaporizes and heats the metal capsule, generating intense thermal radiation (called cavity or holhraum radiation) to compress and heat the fuel for controlled fusion.



4. Stellar evolution depends crucially on thermal radiation. Radiation pressure keeps large stars from collapsing under their own weight, until they eventually run out of nuclear fuel and implode or explode, scattering huge amounts of heavy elements throughout the universe.



5. The universe is filled with cosmic microwave background radiation (CMB), equivalent to the thermal radiation emitted by an object at 2.8 K.

This radiation is the cooled and expanded remnant of the primordial fireball at the "big bang" birth of the universe, billions of years ago.

CMB radiation was discovered when microwave antennas for communication applications detected a faint "hiss" (first thought to be amplifier noise) coming from all directions in the sky.



6. Max Planck's analysis of thermal radiation won a Nobel Prize and helped lead to the discovery of energy quantization and Planck's constant, the foundation of quantum mechanics and modern physics. 7. Absorption and emission spectra for atoms and molecules are not always discrete "line" spectra from transitions between well-defined energy levels! **Thermal radiation** is quantized, but the differences in the energy levels are so small that thermal radiation *appears* to be continuous, illustrating a connection between classical and quantum physics.

8. The analysis of thermal radiation, in addition to demonstrating energy quantization and a failure of classical physics, illustrates an application of the **Boltzmann distribution over energy levels**, one of the most important laws of nature, for classical or quantum mechanical systems.

9. One of the first problems traditionally analyzed by students of quantum chemistry is the "**particle in a box**". The analysis of thermal radiation is simpler because it does not require Schrodinger's equation, quantum mechanical wave functions and concepts of "wave-particle duality". Classical wave equations and quantization are combined by matching the wavelengths of electromagnetic radiation to the cavity size.

10. Thermal radiation calculations illustrate how we can use a "**distribution function**" to calculate the amount of radiation energy in a particular frequency or wavelength range.

11. The thermodynamic analysis of thermal radiation illustrates the breadth of **thermodynamics**. It applies not only to gases, liquids and solids, but also to non-material systems, such as electromagnetic radiation consisting of a "photon gas".

Thermal Radiation – Background



Electric current passing through the tungsten filament of an incandescent light bulb provides a good example of thermal radiation from a heated object. The electrons flowing through the metal meet resistance and are scattered by the vibrating metal atoms. As the electric current and the heating increase, the filament glows red, yellow, and then

white hot, illustrating that the average frequency of the emitted thermal radiation increases with temperature.

"Cold" objects emit radiation too. At room-temperature, thermal radiation is mostly infrared, as revealed by thermal imaging cameras. The radiation from "ultra-cold" objects at a few degrees K peaks at microwave frequencies.

The thermal radiation emitted by objects as a function of temperature and frequency was a major unsolved problem for classical physics.

The mechanism for radiation emission and absorption seemed to be well understood: accelerating electric charges emit radiation. Heating an object causes the negatively-charged electrons and the positively-charged nuclei and vibrate more strongly, emitting more radiation, just like **microscopic antennas**. The spectrum of the emitted radiation can be predicted for macroscopic objects using Maxwell' theory of electromagnetic radiation.

What is "Thermal" Radiation?

The radiation absorbed and emitted by a heated object usually depends in a complicated way on the composition of the body and its size, shape, surface area and reflectivity. Some materials, such as glass, absorb very little light. Visible light (but not all radiation) appears to pass right through glass. For a shiny metallic surface, light is reflected and not strongly absorbed at all.

"Black" materials, such as soot or fine metal powders, absorb light and heat radiation almost completely and get warm. <u>A true</u> "blackbody", by definition, absorbs all incident radiation (at all frequencies) and reflects none.

This behavior can be understood in terms of the interaction of electromagnetic waves with charged particles, especially electrons, in the material, causing the charges to oscillate and absorb energy from the incident radiation. For glass, visible light is absorbed very weakly. A complete understanding of how this works needs quantum mechanics, but the general idea is as follows. The electrons in glass are able to oscillate in response to external oscillating electric fields, but these charges are tightly bound to atoms (glass is an insulator) and can only oscillate at certain frequencies. For ordinary glass, none of these frequencies correspond to those of visible light, so there is no resonance with a light wave, and almost no visible light energy is absorbed.

In contrast, electrons in metals are free to move through the entire solid. This is why **metals are good electronic conductors**. It also explains why **metals are shiny**. Free electrons at the surface of a metal object oscillate in response to the electrical field of an incoming light wave and then re-radiate the wave. The radiation from the oscillating electrons is the reflected light. Little of the incoming radiant energy is absorbed. Most of it is reflected. **Soot** (tiny particles of graphite or related carbonaceous materials), like metals, also conduct electric current, though less efficiently. Fee electrons move through soot particles, but have short mean free paths because of the small particle sizes, and pores and crevices. When soot electrons hit an obstruction, they cause vibrations of the atoms and release energy as heat (thermal motion on the atomic scale). Soot particles and other powders are therefore very good at absorbing radiation and converting it to heat.

Absorption and Emission of Radiation

Heated bodies radiate by processes analogous to absorption, but operating in reverse. Added heat causes the soot lattice to vibrate more vigorously, giving more energy to the electrons. The accelerating electrons convert kinetic energy to electromagnetic radiation, just like electrons in a transmitting antenna. Electrons in metals have very long mean free paths. Because they are less sensitive to lattice vibrations, they are less effective in emitting radiation. <u>So good absorbers of radiation are also good emitters</u>.

At sufficiently high temperatures, all objects become good radiators. Different material heated until they glow red-hot in a fire look much more similar than they do at room temperature. For a metal, this is a result of the shorter mean free path of the electrons caused by interference from the more strongly vibrating lattice.

Emissivity e(v,T)

The emissivity of an object, e(v,T)dv, is defined as the amount of radiation energy emitted per unit area per unit time at frequencies in the range from v to v + dv. The emissivity of a blackbody at a given frequency depends only on the temperature, and is completely independent of its chemical composition. This important point can be demonstrated by considering a cavity in material A (*e.g.*, brick) connected by a small hole with a cavity in a second material B (*e.g.*, copper). At thermal equilibrium, the amount of radiation leaving A and entering B must equal the amount of radiation leaving B and entering A at all frequencies, $e_A(v,T) = e_B(v,T) = e(v,T)$, otherwise one part of an isolated system at equilibrium would spontaneously cool and another part would spontaneously heat up. The transfer of heat from one body to another at the same temperature would violate the Second Law of thermodynamics, and has never been observed.



Reflectivity r(v,T) What about objects that are not black, such as "graybodies"? For unit area of material A in thermal equilibrium with unit area of material B behaving as a blackbody, the total radiation $\int e(v,T) dv$ emitted by the black wall is incident on A. Of this radiation, the amount $\int r_A(v,T)e_T(v,T)dv$ is reflected, where the fraction $r_A(v,T)$ is defined as the reflectivity of A at frequency v. At equilibrium, the energy $\int [1 - r_A(v,T)]e(v,T)dv$ absorbed by A must equal the amount $\int e_A(v,T)dv$ radiated by A, otherwise the Second Law would be violated. And this relation between the emissivity and the reflectivity must hold over any frequency interval

$e_{\mathrm{A}}(v,T) = [1-r_{\mathrm{A}}(v,T)]e(v,T)$

This general relation between reflectivity and emissivity is known as **Kirchoff's Law**.

Measuring Thermal Radiation Spectra

Any object emits electromagnetic radiation. The intensity and frequency distribution of the radiation depend in a complicated way on the structure, composition and reflectivity of the body.

Drastic simplification is obtained for objects which are perfect absorbers ("black bodies") and therefore the best possible emitters.

An excellent approximation to a blackbody can be constructed by drilling a small hole in the wall of a hollow object (hohlraum). Radiation entering the hole from outside is scattered around inside and eventually absorbed. None of the incident radiation is reflected back through the hole, so the hole behaves as a perfect blackbody.

At thermal equilibrium, from Second Law considerations given above, a small hole in wall of a hollow object must also be a perfect blackbody radiation emitter, at all frequencies.

Experiments indicate that the intensity of blackbody radiation emitted at any frequency depends only on the temperature, and is independent of the composition of the walls, as noted above, and also independent of the size or shape of the internal cavity.

At low frequencies, the blackbody emissivity e(T,v) is proportional to v^2 , a parabolic frequency dependence, predicted using classical physics and Maxwell's laws of electromagnetic radiation.

But at increasing frequencies, measured emissivities fall well below the initial parabola v^2 , peak at v_{max} , then decay quite rapidly – almost exponentially – to zero as the frequency v increases.

The measured spectrum of thermal radiation could not be explained using classical physics.

Stefan's Law

What happens to the spectrum of thermal radiation if the temperature is changed?

Stefan's Law The total energy radiated per unit area per unit time from a black surface at temperature *T* is

$\int e(v,T) \mathrm{d}v = \sigma T^4$

Stefan's constant σ is 5.67051 × 10⁻⁸ J s⁻¹ m⁻² K⁻⁴. Typical units of $\int e(v,T) dv$ are Joules per second per square meter (watts per square meter). At room temperature (≈ 300 K), one square meter of a black surface has a radiant power of about 460 watts. This power increases very steeply with increasing temperature, reaching 60 megawatts at 5700 K, the temperature of the surface of the sun.



This graph plots the **emissivity** e(v,T) (energy emitted per unit surface area per unit time per unit frequency range) as a function of frequency. For a cavity with a small hole, radiation inside the cavity is pumped out at speed of light, c (2.997924 × 10⁸ m s⁻¹). When allowance is made for the fact that an opening of unit area is effectively less than unit area for radiation coming in at an angle, and half the energy is in waves moving in directions away from the hole, the actual rate of emission of energy through a hole of unit area is equal to c/4 times the energy density (*i.e.*, energy per unit volume) in the cavity.

The blue curve in the graph above is for 300 K and the red curve is for 600 K. To find the radiation energy density $\rho(T, v)$ in a given frequency range, we multiply the emissivity e(v,T) by 4/c.

 $\rho(T, v) = (4/c) e(v,T)$

Similar calculations are used in the kinetic theory of gases to calculate the leak rate of molecules through small holes (effusion).

The upward shift in v_{max} with *T* is familiar. When an iron object is heated in a fire, the first visible radiation (at around 900 K) is deep red, corresponding to the lowest frequency visible light. Further increase in *T* causes the color to change to orange, yellow, and then white at a very high temperature, indicating that the intensity of the emitted light is roughly identical at of all the visible frequencies.

The change in v_{max} is proportional to the absolute temperature:

$v_{\rm max} \propto T$ <u>Wein's Displacement Law</u>

The sun's surface temperature, for example, is about 5700 K. At that temperature, much of the energy is radiated as visible light. This is no accident. Evolution has adapted us to see most efficiently in the light most readily available.

The shift with temperature in the frequency at which radiant power is a maximum is very important. For example, to harness solar energy in a greenhouse, the glass needs to allow the solar radiation in, but not let the heat radiation out. This is feasible because the two radiations are in very different frequency ranges: ≈ 5700 K for average solar radiation and ≈ 300 K for infrared radiation. Many materials are transparent to light but opaque to infrared radiation. This is only possible because in v_{max} varies with temperature.

Understanding BlackBody Radiation: Thermodynamics and the Photon Gas Analogy

Experimental investigations of the radiation intensity as a function of temperature and frequency gave well-defined reproducible results, independent of the wall material of the oven, *etc*. For a small hole, the radiation emitted is representative of the radiation bouncing around inside the box, in equilibrium with the wall.

The general shape of the function e(T,v) resembles the kinetic energy distribution in a gas in thermal equilibrium, as analyzed by Maxwell and Boltzmann. But in contrast to the molecules in a gas, the different wavelengths of radiation do not collide with each other in the middle of the oven. Nevertheless, energy can shift from one mode to another by being absorbed by a wall, converted to heat, and then re-emitted at another frequency, allowing the different frequencies of radiation inside the oven to rapidly reach thermal equilibrium.

The speed of light, though relatively large, is not infinite. At any given instant, a quantity of radiation emitted by the walls of a cavity will be "in transit". The radiation in the cavity can be pictured as a "**photon gas**" in equilibrium with the walls.

Thermodynamics, usually applied to material systems, can also be used to explore the properties of blackbody relation in equilibrium with the walls of a cavity. The differential expression for the Helmholtz function (A = U - TS, where U is the internal energy, T is the temperature and S the entropy) is

$$dA = -SdT - pdV$$

Because $-S = (\partial A/\partial T)_V$, $-p = (\partial A/\partial V)_T$ and $(\partial^2 A/\partial V \partial T) = (\partial^2 A/\partial T \partial V)$, thermodynamics tells us that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Expanding the size of a cavity isothermally creates a larger volume of the radiation gas at the same temperature, so the entropy must increase. It follows that the **radiation exerts a pressure** on the walls of the cavity, which increases with temperature.

To develop the thermodynamic equation of state for thermal radiation, consider a cubic box of unit volume filled with radiation. Let N(v) be the number of photons of frequency v at equilibrium. The momentum of each photon is hv/c. In this case the pressure exerted by radiation on the walls of the box is caused by collisions of the photons. Each collision imparts the momentum change hv/c (initial) – [-hv/c (final)] = 2hv/c to a wall upon reflection. Because the motion of the photons is completely random, 1/6 of the photons are moving toward a given wall at any instant. The number of photons colliding per unit area of wall in one second is therefore N(v)c/6. The pressure is the total momentum imparted to the wall per unit time

$$p(v) = \frac{N(v)c}{6} \frac{2hv}{c} = \frac{N(v)hv}{3}$$

The energy density a frequency v is u(v) = U(v)/V = N(v)hv, so we arrive at the result

$$p(T,v) = \frac{1}{3} \frac{U(T,v)}{V} = \frac{u(T,v)}{3}$$

Integrating over all frequencies

$$p(T) = \int_{0}^{\infty} p(T, v) dv = \frac{1}{3} \int_{0}^{\infty} u(T, v) dv$$

shows that the radiation pressure equals one third of the energy density.

$$p(T) = \frac{U(T)}{3V} = \frac{u(T)}{3}$$
 thermal radiation pressure

(Interestingly, a similar derivation for an ideal gas with average kinetic energy $3kT/2 = mv^2/2$ per molecule gives

$$p = NkT/V = 2u/3$$
 ideal gas pressure

Applying the thermodynamic equation of state dU = TdS - pdV

$$\left(\frac{\partial U}{\partial V}\right)_{T} = T\left(\frac{\partial S}{\partial V}\right)_{T} - p = T\left(\frac{\partial p}{\partial T}\right)_{V} - p$$

to blackbody radiation gives

$$u(T) = \frac{T}{3} \left(\frac{\partial u(T)}{\partial T} \right)_{v} - \frac{u(T)}{3}$$

Rewriting this result

$$4u(T) = T\left(\frac{\partial u(T)}{\partial T}\right)_{V}$$

and integrating gives

$$u(T) = \beta T^4$$
$$p(T) = \beta T^4/3$$

The constant β is 7.56 × 10⁻¹⁶ J m⁻³ K⁻⁴. At room temperature, the pressure exerted by blackbody radiation is negligible, about 0.000006 Pa or 10 trillionths of an atmosphere. In nuclear explosions and the interior of some stars ($T \approx 10^7$ K), however, the radiation pressure can reach hundreds of millions of atmospheres!

Combining the identity $(\partial S/\partial V)_T = (\partial p/\partial T)_V$ and $p(T) = \beta T^4/3$ gives $S = 4\beta VT^3/3$ for the entropy of blackbody radiation. For a reversible adiabatic expansion (constant entropy), the volume *V* increases, so the temperature drops and the radiation cools. The expansion of the universe, as mentioned above, has cooled the radiation leftover from the Big Bang to about 2.8 K.

For an ideal gas at a density of *N* molecules per unit volume traveling at average speed v, the number of molecules colliding per

unit area of wall per unit time is Nv/4. Applying this result to a photon gas traveling at speed c provides the relation

$$e(T,v)\mathrm{d}v = (c/4)\rho(v,T)\mathrm{d}v$$

between the radiant energy emitted per unit time per unit surface area and the density of radiant energy in the frequency interval from v to v + dv. Stefan's constant σ for the law giving the total blackbody radiation energy radiated emitted per unit time per unit surface area $\int e(v,T)dv = \sigma T^4$ on and the equation $u(T) = \beta T^4$ for the radiation energy per unit volume are therefore related by $\beta = 4\sigma/c$.

Counting the Degrees of Freedom

To make any quantitative progress in analyzing blackbody radiation, a clear picture of the number of degrees of freedom is required: how many oscillators have frequencies in a given energy range? These oscillations are standing electromagnetic waves. The waves are contained in the oven because the electric field intensity drops rapidly to zero on approaching and going into the walls. Inside the walls electric energy is rapidly dissipated by currents or polarization. In fact, the boundary condition at the walls is analogous to the boundary condition for standing waves on an oscillating string fixed at both ends where the wave amplitude is zero.

Consider the frequency distribution function of the possible different modes of vibration (that is, the different degrees of freedom) of a string stretched between two points a distance *a* apart. Possible values of the wavelength are

 $\lambda = 2a, 2a/2, 2a/3, 2a/4, \dots$

so the allowed frequencies (frequency = wave speed *c* divided by wavelength λ)

$$v = c/\lambda = c/2a, c/a, 3c/2a, 2c/a, ...$$

are equally spaced and c/2a apart. The *spectral density*, defined as the number of modes between v and $v + \Delta v$, is $N(v)\Delta v$ for small values of Δv compared with the range of frequencies in the system, but large compared with the spacing between successive allowed frequencies. In this one-dimensional case, N(v) is a constant equal to 2a/c.

The amplitude of oscillation as a function of time for the standing waves has the form

 $E(x,t) = A \sin(2\pi x/\lambda) \sin(2\pi v t)$

which is more conveniently written as

$$E(x,t) = A \sin(k\lambda) \sin(2\omega t)$$

where

$$\omega = 2\pi v$$
$$k = 2\pi/\lambda$$



SO

$$\omega = ck$$

Here $\omega = 2\pi v$ is the *radial* frequency, the number of *radians* per second (rather than cycles per second) the time dependent component of the wave moves through. *k* is called the *wave number* because it counts the radians of spatial change in unit length ($k = \omega/c = 2\pi v/v\lambda = 2\pi/\lambda$).

Now the more complicated problem of three-dimensional standing electromagnetic waves in a cubical oven. The first guess, just generalizing the expression above, would be

 $E(x, y, z, t) = E_0 \sin(k_x x) \sin(k_y y) \sin(k_z z) \sin(\omega t)$

This will clearly satisfy the wave equation

$$\frac{\partial E(x, y, z; t)}{\partial t} = c^2 \nabla^2 E(x, y, z; t)$$

if

 $\omega^2 = c^2 (k_x^2 + k_y^2 + k_z^2)$

The electric field will be zero at all the walls (required for standing waves) if we choose the *k*'s appropriately, that is: $sink_x a = 0$, *etc*.

For standing electromagnetic waves in a cavity, just as for propagating waves, the electric field is perpendicular to the direction in which the wave is moving. In other words, it is a transverse wave. The fact that there are two independent polarizations (*e.g.*, *x* and *y* polarization for a wave moving in the *z* direction) which we must remember to count when we find the total number of degrees of freedom.

It remains to find the allowed frequencies of vibration - the normal modes - of the electromagnetic radiation in the oven. The first step is to find the allowed values of the wave numbers k_x , k_y and k_z . These are fixed by the boundary conditions $\sin k_x a = 0$, etc., so

$$k_x = \pi/a, 2\pi/a, 3\pi/a, ...$$

 $k_y = \pi/a, 2\pi/a, 3\pi/a, ...$
 $k_z = \pi/a, 2\pi/a, 3\pi/a, ...$

so the wave vector \vec{k} is

$$\vec{k} = (k_x, k_y, k_z) = \frac{\pi}{a}(l, m, n)$$

Where *l*, *m* and *n* are positive integers, such as (1, 1, 1) or (5, 13, 4). In other words, each possible standing electromagnetic wave in the cavity corresponds to a point in the (k_x, k_y, k_z) space labeled by three positive integers. These are the *intersection points of a cubic lattice* in the integer space $k_x > 0$, $k_y > 0$, $k_z > 0$.

Each such point can be associated with a lattice element cube of volume π^3/a^3 for which the point in question is the furthest corner of the cube from the *k*-space origin. The little cubes stack together to fill all that part of *k*-space having $k_x > 0$, $k_y > 0$ and $k_z > 0$.

The frequency of vibration of the wave having wave numbers (k_x, k_y, k_z) is

$$\omega^2 = c_{\sqrt{k_x^2 + k_y^2 + k_z^2}}$$

Recall that the experimental measurement of black body radiation from the oven detects the intensity of radiation in a given frequency range. It does not tell us the wave numbers of the radiating modes. To compare with these experimental results, we must choose a small frequency range and find how many possible sets of wave numbers correspond to modes of vibration having frequencies within that range.

Notice that a fixed value of the frequency corresponds to a surface in *k*-space, in this case a sphere of radius ω/c .

$$\frac{\omega^2}{c^2} = k_x^2 + k_y^2 + k_z^2$$

The number of possible modes of radiation in the oven having frequencies in the range ω to $\omega + \Delta \omega$ is therefore equal to the number of lattice-point wave number values (k_x, k_y, k_z) between two spherical surfaces centered at the origin and having radii between ω/c and $(\omega + \Delta \omega)/c$, and only counting in the octant corresponding to $k_x > 0$, $k_y > 0$ and $k_z > 0$.

Now, as argued above, each lattice point can be associated with a small cube of volume π^3/a^3 . Assuming we choose $\Delta \omega >> a$, there will be many of these small cubes between the spherical surfaces, and the total number of lattice points between the spheres in the positive octant will be just the volume of the space between the spheres divided by the volume of one of these cubes.

So the number of possible modes of radiation in the oven having frequencies in the range ω to $\omega + \Delta \omega$ is

$$\frac{\frac{1}{8} \times 4\pi \frac{\omega^2}{c^2} \frac{\Delta \omega}{c}}{\frac{\pi^3}{a^3}} = \frac{1}{2} a^3 \frac{\omega^2 \Delta \omega}{c^3 \pi^2}$$

Putting this in terms of the frequency v in cycles per second, $\omega = 2\pi v$ and inserting an extra factor of two for the two independent polarizations of the wave (discussed above) we find the distribution function for the number of modes in frequency range v to v + dv is given by

$$N(v)\mathrm{d}v = \frac{8V\pi v^2}{c^3}\mathrm{d}v$$

where $V = a^3$ is the volume of the oven cavity.

Equipartition of Energy

The point of the rather tedious calculation above (finding how many different modes of vibration, or degrees of freedom, there are in an oven full of radiation) was to construct an argument parallel to that applied successfully to understand the properties of gases. The first conclusion would be that there is kT of energy, on average in each wave mode (not $\frac{1}{2}kT$, because the standing wave is like an oscillator with both kinetic and potential energy).

Using kT per mode, the radiant energy per unit volume (the energy density) between frequencies v and v + dv density predicted by classical physics is

$$\rho(v)\mathrm{d}v = \frac{8\pi v^2 kT}{c^3}\mathrm{d}v$$

This result is known as the *Rayleigh-Jeans Law*.

The Rayleigh-Jeans expression for the emissivity is $e(T,v)dv = (2\pi v^2 kT/c^2)dv$. For low frequencies (v << kT/h or hv/kT << 1), this is exactly what is observed. The amount of radiation shining out of the oven at low frequencies is correctly predicted by counting modes, as above, and allocating kT of energy to each mode.



The <u>Ultraviolet Catastrophe</u>

The problem is that as we go to higher frequencies, there are more and more possible degrees of freedom. According to classical physics, the oven should be radiating huge amounts of energy in the blue and ultraviolet. But it isn't. For this system, *the theorem of equipartition of energy doesn't appear to be working*!

The graph shows the prediction of radiation intensity from the classical equipartition compared (dashed curves) with the experimental result. It is evident that the higher frequency modes are not getting their "fair share" kT of energy. They are getting "frozen out", evidently those at really high frequencies are getting almost no share in the energy at all.

It is important at this point to go back to the curves for two different temperatures, and ask the question: *how is the sharing of energy among the modes affected by raising the temperature*? For the lowest frequencies, doubling the temperature does indeed double the intensity of the radiation, exactly what we expect if the radiation is proportional to kT, the energy in each mode. (T = 300 K here, by the way.) We can also see, though, that at the higher temperature, the observed radiation intensity stays closer to the classical prediction as we go to higher frequencies. *This means the higher modes are less locked out of the energy sharing when we go to higher temperatures*. For any given temperature, though, if we go to high enough frequencies, the intensity drops exponentially with further increase in frequency.

Planck's Suggestion

Planck suggested that the blackbody radiation curves could be understood if the oscillators in the walls of the oven were somehow constrained so that they could not emit arbitrary amounts of radiation, as Maxwell's equations would predict, but could only emit it in chunks - called *quanta* - of definite magnitudes. For the higher frequencies, he suggested, the radiation had to be emitted in bigger chunks. This would explain the lack of radiation in the oven at these higher frequencies - assuming the oscillators in the walls had on average energy kT, it would be very unlikely that one oscillating charge would by random excitation have an energy of, say, 5kT, so if its frequency of oscillation were high enough, it would almost never have enough energy to emit one quantum, so by Planck's theory, it would not emit any radiation at all and be "frozen" out. On the other hand, if the temperature were increased fivefold, it would often have enough energy to emit a quantum. Given that bigger chunks of energy are emitted at the higher frequencies, just how does the size of a chunk depend on the frequency of the radiation? The clue is given by the Wein displacement formula $v_{\text{max}} \propto T$. v_{max} is the frequency at which the curve "turns over" and begins to descend, moving far from the classically predicted parabola, which of course continues upwards. Thus, doubling the temperature doubles the frequency range over which the curve approximates the classically predicted parabola. (If we stiffen the requirements for approximating the classical curve, for example by requiring it to be within 5%, say, then we can see from the graph of low energy modes above that doubling the temperature still doubles the range over which the curves remain close.

In other words, doubling the temperature apparently doubles the frequency range in which oscillators get approximately their full share kT of thermal energy. But doubling the temperature doubles the size of a chunk of energy that can be easily moved. This leads to the conclusion that if two oscillators have frequencies v and 2v, the one at 2v must emit energy in quanta just twice the size of those emitted by the one at v. The size of the energy quantum therefore depends linearly on the frequency

E = hv

where *h* is Planck's constant (6.62608×10^{-34} J s).

The way this evolved historically was that at first the higher frequency part of the black body radiation curve was mapped out by experimentalists in Berlin, and Wien showed that it was well approximated by the formula

$$e_W(v) dv \propto v^3 e^{-Av} dv$$

with A a constant. This was reminiscent of the Maxwell distribution for gas molecules, but with v^3 in place of v^2 . It soon

became evident, though, that the formula was not accurate at low frequencies, where in fact it appeared that the distribution went as v^2 , as discussed above. Planck then wrote down a formula having the right behavior for both high and low frequencies

$$\rho(T,v)\mathrm{d}v = \frac{8\pi h v^3}{c^3 (e^{hv/kT} - 1)} \mathrm{d}v$$

He did not at first have any theoretical justification for this formula, but it was a very accurate fit to some very precise experiments.

It is easy to see how Wien's Displacement Law follows from this formula. The maximum radiation per unit frequency range is at the frequency v for which the function $v^3/(e^{hv/kT}-1)$ is a maximum. Solving $d\rho(T, v)/dT = 0$ numerically to locate the maximum gives $hv_{\text{max}}/kT = 2.82$. This is the frequency range at which the radiation *per unit frequency range* is a maximum.

The blackbody radiation distribution law can also be written in terms of wavelengths. Using $c = \lambda v$ and the expression for $\rho(T, v)dv$ gives

$$\rho(T,\lambda)\mathrm{d}\lambda = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)}\mathrm{d}\lambda$$

Solving $d\rho(T, \lambda)/dT = 0$ numerically to locate the maximum and gives the *wavelength* at which the *radiation per unit wavelength range* is maximum: $hc/\lambda_{max}kT = 4.96$. Because the wavelength and frequency are not linearly related, but in fact are inversely related, these two maxima are not at the same frequency or wavelength.



Interpreting Planck's Radiation Formula

Factoring out $N(v) = (8\pi v^2/c^3)$, the number of modes of oscillation in the frequency range dv, Planck's formula tells us that the average energy per mode is

$$\frac{hv}{e^{hv/kT}-1}$$

At low frequencies, $hv \ll kT$ and $e^{hv/kT} \approx 1 + (hv/kT)$, this gives kT per mode, in agreement with the predictions of classical physics. The formula follows if we assume the oscillator can only have discrete (not continuous) quanta of energy: 0, hv, 2hv, 3hv, ... If we further assume, using Boltzmann's distribution law, that the probability of an oscillator at temperature *T* having energy *E* is proportional to $e^{-E/kT}$, then the probabilities of having energy 0, *hv*, 2*hv*, ... are proportional to 1, $e^{-hv/kT}$, $e^{-2hv/kT}$, The actual probabilities are given by dividing these relative probabilities by the sum of all of them. They are the terms of a geometric series

$$1 + e^{-hv/kT} + e^{-2hv/kT} + \dots = 1/(1 - e^{-hv/kT})$$

and their sum is $1/(1 - e^{-hv/kT})$. So, to find the average energy in the oscillator, we take the possible energies 0, hv, 2hv, 3hv, ... and weight each of them with their probability of occurring, that is, we must find $0 + hve^{-hv/kT} + 2hve^{-2hv/kT} + ...$ and divide the sum by $1/(1 - e^{-hv/kT})$. (Done in detail in Tutorial #1!) Planck gave a more complete and elegant discussion, applying Boltzmann's ideas about entropy to simple harmonic oscillators having only certain energies allowed. In fact, he effectively derived the Boltzmann distribution for this system.

A note on blackbody spectrum calculations

e(T, v) and $e(T, \lambda)$ are *distribution functions*. They give the radiation energy emitted per unit area per unit time *per unit frequency or wavelength range*. The *total* radiation emitted per unit area per unit time is calculated by integration over all possible frequencies

$$e(T) = \int_{0}^{\infty} e(v,T) dv = \int_{0}^{\infty} \frac{2\pi h v^{3}}{c^{2} (e^{hv/kT} - 1)} dv = \sigma T^{4}$$

where σ is Stefan's constant.

How is the integration performed? It is convenient to define the dimensionless variable y = hv/kT. Changing to this variable gives

$$\int_{0}^{\infty} e(T, v) dv = \frac{2\pi (kT)^4}{h^3 c^2} \int_{0}^{\infty} \frac{y^3}{e^y - 1} dy$$

A table of definite integrals may be used to evaluate

$$\int_{0}^{\infty} \frac{y^{3}}{e^{y} - 1} \, \mathrm{d}y = \frac{\pi^{4}}{15}$$

It follows that

$$e(T) = \int_{0}^{\infty} e(v,T) dv = \frac{2\pi^{5}}{15} \frac{(kT)^{4}}{h^{3}c^{2}} = \sigma T^{4}$$

where $\sigma = 2\pi^5 k^4 / 15h^3 c^2 = 5.67051 \times 10^{-8} \text{ J s}^{-1} \text{ m}^{-2} \text{ K}^{-4}$ is Stefan's constant.

For some applications it is useful to know the amount of radiation emitted in a frequency range v_1 to v_2

$$\int_{\nu_1}^{\nu_2} e(\nu,T) \mathrm{d}\nu$$

which can be interpreted as the "area" under the e(T, v) curve from v_1 to v_2 . The radiation emitted in the corresponding wavelength range from λ_1 to λ_2

$$\int_{\lambda_1}^{\lambda_2} e(\lambda,T) \mathrm{d}\lambda$$

is simply the equivalent "area" under the $e(T, \lambda)$ curve from λ_1 to λ_2 . To evaluate this area, we calculate $y_1 = hv_1/kT = hc/\lambda_1kT$ and $y_2 = hv_2/kT = hc/\lambda_2kT$ and integrate over this range.

Analytic expressions for the integration of $y^3/(e^y - 1)$ are not available, so we must resort to numerical methods, such as the trapezoid rule or Simpon's rule. The area under the $y^3/(e^y - 1)$ curve divided by the total area $\pi^4/15$ gives the fraction of the total energy emitted: (σT^4) and therefore



To use the trapezoid rule to estimate the area under the $y^3/(e^y - 1)$ curve from y_1 to y_2 , the interval in question is divided into N rectangles of width $\Delta y = (y_1 - y_2)/N$ and heights $(y_1 + \Delta y/2)^3/(e^{y_1 + \Delta y/2} - 1)$, $(y_1 + 3\Delta y/2)^3/(e^{y_1 + 3\Delta y/2} - 1)$, $(y_1 + 5\Delta y/2)^3/(e^{y_1 + 5\Delta y/2} - 1)$, ..., $(y_1 + (2N-1)\Delta y/2)^3/(e^{y_1 + (2N-1)\Delta y/2} - 1)$.

Measuring the energy emitted by an object in a certain spectral range, for example, allows the temperature of the object to be estimated. In the design of electric light bulbs, it is important to maximize the energy emitted in the visible portion of the spectrum.