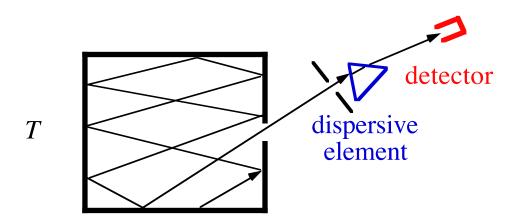
BLACK-BODY RADIATION AND PLANCK'S QUANTUM LEAP

- (1) What is a black body and what does it tell us about radiation?
- (2) Kirchhoff's, Wien's, Stefan's, and Paschen's laws
- (3) Electromagnetic cavity modes, the law of Rayleigh & Jeans, and the ultraviolet catastrophe
- (4) Planck's act of desperation and the birth of the quantum

1. What is a black body - and what does it tell us about radiation?

- the heat carried by light first studied by William Herschel (an English astronomer of German descent, discoverer of Uranus and numerous nebulae) started wondering, in 1800, about the temperature of the glowing stars such as the Sun; with a blackened Hg-thermometer and a prism, he found that the temperature of Sun's radiation increases from to blue to the red; moreover, that in the invisible range beyond the red there's radiation (infrared) that carries even more heat than the red (i.e., the intensity of sun's radiation was found to increase with increasing wavelength)
- Johann Seebeck (a German private scholar) discovered, in 1822, the thermoelectric effect: a junction of two different metals produces a voltage that depends on the junction's temperature; such a junction (a 'thermocouple') can be used as a sensitive thermometer
- John Tyndall (at the Royal Institution, German educated) measured, in 1863, the temperature due to different spectral regions of a glow (e.g., from an electric arc or from an incandescent filament) with a thermocouple thermometer; found that the maximum temperature (in the range between 500 and 1500 K) arises for the infrared portion of the spectrum (i.e., at wavelengths greater than roughly 800 nm)

- Gustav Kirchhoff (1824-1877, active in Heidelberg and Berlin) concluded, in 1860 that "[h]eat rays are, by their nature, the same as light rays ... Invisible heat rays differ from light rays only in their ... wavelength."
- coined the notion of a black body for a body at thermal equilibrium which receives exactly as much radiative energy as it emits (otherwise the temperature of the black body would change); such a body is in a thermal equilibrium with radiation
- a black body is best realized inside a cavity whose walls absorb exactly as much radiant energy as they emit and have the same temperature as the black body;
- actually, just the insides of a cavity well approximate a black body
- as for a black body's geometry, think of a furnace or Wedgewood's kiln which made glow red everything in the same way as the kiln's walls, independent of size, shape or material



2. Kirchhoff's, Wien's, Stefan's, and Paschen's laws

- Kirchhoff's law: at any wavelength λ and temperature T, the energy, $\varepsilon_e(\lambda,T)$, emitted by a cavity wall per unit area and unit time is equal to the energy, $\varepsilon_a(\lambda,T)$, absorbed by it
- this is a statement of the energy conservation law for a system consisting of radiation and matter at thermal equilibrium; the wavelength dependence is empirical
- note that we can write

$$\varepsilon_a(\lambda, T) = \alpha(\lambda, T)I(\lambda, T)$$

where $\alpha(\lambda, T)$ is the absorbed fraction of the radiant energy – a property of a given material

• the spectral intensity

$$I(\lambda, T) = \frac{\varepsilon_e(\lambda, T)}{\alpha(\lambda, T)}$$
 [W/m²/m = W/m³]

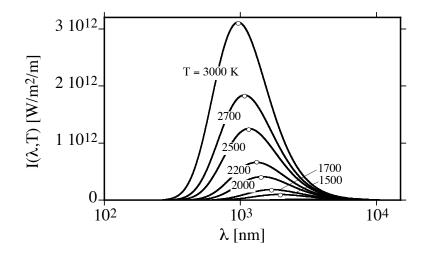
is then a universal function independent of any other properties of the body (such as composition, shape, etc.) other than the wavelength and temperature; it's called the black body spectral distribution function

• for a black body, $\alpha(\lambda, T) = 1$ by definition, and so

$$I(\lambda,T) = \varepsilon_{\rho}(\lambda,T)$$

i.e., the spectral distribution function of a black body can be determined by measuring its emission, $\varepsilon_e(\lambda, T)$

- the emission of any glowing body of any geometry resembles that of a black body as long as it's in a thermal equilibrium at *T*
- Samuel Langley (at the Smithsonian Institution) developed, by 1880, the bolometer (a device based on the steep dependence of resistance of metals on temperature) and obtained a first quantitative measurement of the shift with increasing temperature of the black-body radiation intensity towards the blue
- Hermann von Helmholtz (1821-1894) and his circle (including O. Lummer, E. Pringsheim, W. Wien, H. Rubens, F. Paschen, and others) at the Physikalisch-Technische Reichsanstalt (PTR) in Berlin (and elsewhere) developed (a) high-intensity sources of radiation that well approximated a black body and whose temperature could be accurately controlled; (b) techniques to accurately measure temperatures above 1000 K; (c) techniques to spectrally analyze the radiation from the UV to IR; (d) techniques to precisely measure the light intensity
- as a result, by the late 1890s, the black body spectral distribution function became accurately known



- Josef Stefan (in Vienna) noticed, in one of Tyndall's papers, that the reported total intensity emitted by a Pt-filament at 800 K was 11.5 times less than at 1470 K and realized that $11.5 \approx (1470/800)^4$ and concluded that the total radiated intensity is proportional to T^4 (Stefan's law); based on this law, Stefan estimated the temperature of the Sun's surface at 6100 K
- Willy Wien (in 1893) noticed that the black-body spectral distribution curves exhibit a pattern: the positions of the maxima, $\lambda_{\max}(T)$, of the $I(\lambda,T)$ curves shift with T according to

$$\lambda_{\max}(T)T = const. \& I(\lambda_{\max}, T) \propto T^5$$

which is known as Wien's law

• Friedrich Paschen (also in 1893) took up V. Michelson's idea of treating light using Boltzmann's statistical mechanics and "derived," essentially by fitting the data, a formula

$$I(\lambda, T) \propto \lambda^a \exp\left(-\frac{b}{\lambda T}\right)$$

• this could have been the last word in black body radiation theory (with the discrepancies between experiment and the formula swept under the carpet) - but it wasn't, because the careful experimentalists at the PTR have found that the formula fails at large wavelengths (where it predicts more spectral intensity than observed); also the physical meaning of a and b was unclear

3. Electromagnetic cavity modes, the law of Rayleigh and Jeans, and the ultraviolet catastrophe

- a rigorous attempt to derive the black-body distribution function (from what we call today, classical physics) was made by Lord Rayleigh and by James Jeans (between 1899 and 1900)
- two similar counter-propagating waves interfere (add up) and give rise to a standing wave; let

$$E_y^+ = E_{0y} \sin[k(x - ct)]$$
 & $E_y^- = E_{0y} \sin[k(x + ct)]$

be such counterpropagating waves (along the + and - x-axis); then their superposition (which is automatically a solution of the wave equation) is

$$E_{y} = E_{y}^{+} + E_{y}^{-} = 2E_{0y}\sin\frac{2\pi x}{\lambda}\cos\frac{2\pi ct}{\lambda} = 2E_{0y}\sin\frac{2\pi x}{\lambda}\cos\omega t$$

i.e., the electric field vanishes everywhere for

$$\frac{2ct}{\lambda} = \pm (N + 1/2)$$
 N is an integer

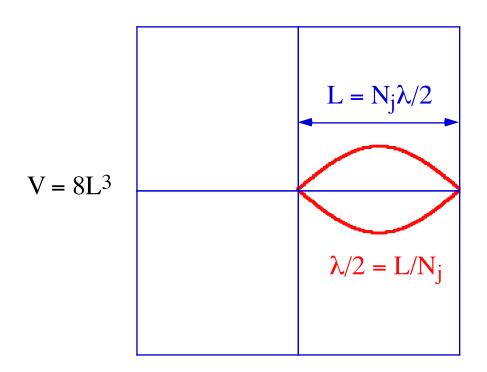
and is always zero for

$$\frac{2x}{\lambda} = \pm N$$

• the electric field E_y is said to have nodes at

$$x = \pm N \frac{\lambda}{2}$$

- a 1-D cavity (along the *x*-axis) obtains when walls are installed at the nodes of the wave
- or vice versa, two walls will select waves whose nodes are integer multiples of $\lambda/2$ and a thermal equilibrium between the waves and the walls will be established; this is because the electric field must be zero at the walls or else currents would be induced and energy dissipated, which would tip the thermal equilibrium
- the electromagnetic field in a cubic cavity of side L ($L >> \lambda$ or the molecular dimension) consists of standing waves in 3-D which fulfill the conditions (here j stands for x, y, or z)



hence

$$N_j = \frac{2L}{\lambda_j} = \frac{2Lk_j}{2\pi} = \frac{2L\omega_j}{2\pi c} = \frac{L\omega_j}{\pi c}$$

is the number of modes along the *j*-axis

- each set of integers (N_x, N_y, N_z) defines a cavity mode
- the number of modes with frequencies between ω_j and $\omega_j + d\omega_j$ is $dN_j = \frac{Ld\omega_j}{\pi c}$

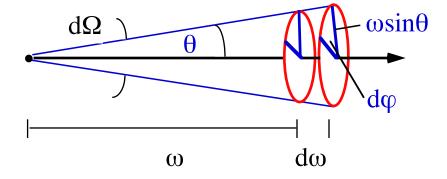
and so

$$d^{3}N = dN_{x}dN_{y}dN_{z} = \left(\frac{L}{\pi c}\right)^{3}d\omega_{x}d\omega_{y}d\omega_{z}$$

is the number of modes with frequencies between ω_x and $\omega_x + d\omega_x$, ω_y and $\omega_y + d\omega_y$, and ω_z and $\omega_z + d\omega_z$

on transforming to spherical coordinates

$$dV = (\omega d\omega)(\omega \sin\theta d\theta)(d\varphi)$$
$$= \omega^2 d\omega \sin\theta d\theta d\varphi = \omega^2 d\omega d\Omega$$



$$d^3N \to dN = \left(\frac{L}{\pi c}\right)^3 \omega^2 d\omega d\Omega$$

where $d\Omega$ is a solid angle element

• integrating over the solid angle (i.e., over the whole cavity) under the assumption of a spherical symmetry yields

$$\int d\Omega = \int_{0}^{\pi} \sin \theta d\theta \int_{0}^{2\pi} d\varphi = 4\pi$$

and so the number of cavity modes with frequencies between ω and $\omega + d\omega$ becomes

$$dN = \frac{4L^3}{\pi^2 c^3} \omega^2 d\omega$$

• as a result, the number of cavity modes per $d\omega$ over the cavity volume $V = 8L^3$ is

$$\frac{dN}{Vd\omega} = \frac{\omega^2}{2\pi^2 c^3}$$
 spectral mode density (per polarization)

• spectral energy density, U, obtains by applying the equipartition theorem to the spectral mode density: each polarization carries kT of energy and there are two polarizations per spectral mode; hence

$$U(\omega,T) = 2\frac{dN}{Vd\omega}kT = \frac{\omega^2 kT}{\pi^2 c^3}$$

since

$$|U(\omega,T)d\omega| = |U(\nu,T)d\nu|$$
 & $|U(\nu,T)d\nu| = |U(\lambda,T)d\lambda|$

where

$$d\omega = 2\pi dv$$
 & $|dv| = |(c/\lambda^2)d\lambda|$

have

$$U(v,T) = \frac{8\pi v^2 kT}{c^3} \& U(\lambda,T) = \frac{8\pi kT}{\lambda^4}$$

note that

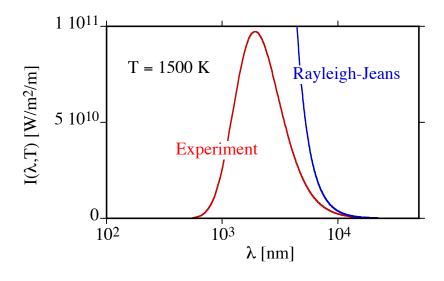
$$U(\omega,T)d\omega$$
 & $U(v,T)dv$ & $U(\lambda,T)d\lambda$ in $\left[\frac{J}{m^3}\right]$

• spectral intensity obtained as

$$I(\lambda, T) = \frac{cU(\lambda, T)}{4} = \frac{2\pi ckT}{\lambda^4} = I_{R-J}(\lambda, T) \quad [J/s/m^3 = W/m^2/m]$$

which is the Rayleigh-Jeans law

• let's compare $I_{R-J}(\lambda,T)$ with experiment:



• this discrepancy is known as the ultraviolet catastrophe

4. Planck's act of desperation and the birth of the quantum

"Those [scientists] who dislike entertaining contradictory thoughts are unlikely to enrich their science with new ideas."

- Max Planck (1858-1947) excelled in music, languages and math; studied in Berlin under Kirchhoff and Helmholtz; became successor to Kirchhoff after the first two choices, Hertz and Boltzmann, declined
- in his attempt to explain the black-body spectral distribution function, Planck relinquished the idea that energy is a continuous variable
- classically, if a system can have energies E_1 and E_2 then it can also have all energies E such that $E_1 < E < E_2$ (for $E_1 < E_2$)
- according to Planck, only discreet values of energy are possible; if these are, say, E_1 and E_2 then

$$E_2 - E_1 = h v$$

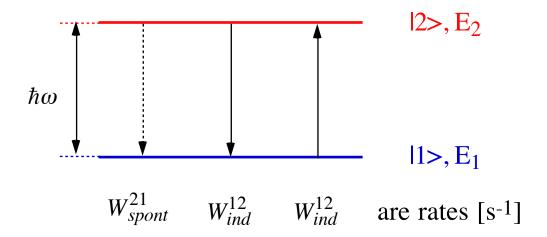
where hv is Planck's quantum of energy, v is a characteristic oscillation frequency of the system (say of the atoms that make up the black body), and h is an elementary quantum of action (Planck's constant), $h = 6.6262 \times 10^{-34}$ Js

• Planck was leaning on the statistical thermodynamics of Boltzmann (which, while under Mach's spell, Planck disapproved of, then adopted); the introduction of the quantum of energy made it possible to actually count "how many energies" there are in a given energy interval (there are always infinitely many for a continuously changing variable)

"In a word, I could call the whole procedure an act of despairation. For I am, by nature, peaceable and not inclined to dubious adventures. But I had been struggling with the problem of equilibrium between radiation and matter for six years, without success. I knew that this problem was of fundamental importance to Physics, I knew the [black-body spectral distribution] formula; hence a theoretical interpretation had to be found at any price, no matter how high that might be."

- there was no justification for the procedure other than that it enabled Planck to get an exact fit of the black-body radiation data
 - "I tried immediately to weld the elementary quantum of action somehow in the framework of classical theory. But in the face of all such attempts this constant showed itself to be obdurate ... My futile attempts to put the elementary quantum of action into the classical theory continued for a number of years and they cost me a great deal of effort."
- in his Nobel lecture (1920): "When I look back at the time, already twenty years hence, when the idea and importance of the physical quantum of action first began to emerge ... it appears to me as one more illustration of Goethe's wise words: man errs as long as he strives."

- let's consider Einstein's derivation of the black-body radiation law (from a 1917 paper)
- assume a two-level molecular system



- this implements Planck's desperate assumption of a discrete energy $E_2 E_1 = hv = \hbar\omega$
- transition rates in a two-level system exposed to radiation of aspectral energy density *U*: spontaneous emission, induced emission, and induced absorption
- spontaneous emission

$$W_{spont}^{21} = A_{21} = \frac{1}{\tau} \equiv A$$

where A_{21} (or A) is Einstein's coefficient of spontaneous emission, τ is the lifetime of state $|2\rangle$

induced emission

$$W_{ind}^{21} = B_{21}U$$

where B_{21} is Einstein's coefficient of induced emission

induced absorption

$$W_{ind}^{12} = W_{absorp} = B_{12}U$$

where B_{12} is Einstein's coefficient of (induced) absorption; there's no spontaneous absorption

• if levels |1> and |2> are nondegenerate

$$B_{12} = B_{21}$$

and so

$$W_{ind}^{12} = W_{ind}^{21}$$

- note that Einstein's coefficients are independent of temperature
- at equilibrium, the system, molecules + radiative field, is in a stationary state, i.e., the rates for absorption and emission are the same:

$$N_1 W_{ind}^{12} = N_2 (W_{ind}^{21} + W_{spont}^{21})$$

where N_1 and N_2 are the populations, i.e., numbers or number densities of molecules, in states $|1\rangle$ and $|2\rangle$ at equilibrium

• in terms of Einstein's coefficients

$$N_1 B_{12} U^{eq} = N_2 (B_{21} U^{eq} + A_{21})$$

where U^{eq} is the equilibrium spectral energy density

• since, according to Boltzmann statistics,

$$N \propto \exp\left[-\frac{E}{kT}\right]$$

we have

$$\frac{N_1}{N_2} = \exp\left[\frac{E_2 - E_1}{kT}\right] = \exp\left[\frac{\hbar\omega}{kT}\right] = \frac{B_{21}U^{eq} + A_{21}}{B_{12}U^{eq}}$$

• the last equation can be solved for U^{eq} with the result

$$U^{eq} = \frac{\frac{A_{21}}{B_{21}}}{\frac{B_{12}}{B_{21}} \exp\left[\frac{\hbar\omega}{kT}\right] - 1} = \frac{A}{B} \frac{1}{\exp\left[\frac{\hbar\omega}{kT}\right] - 1} = U^{eq}(\omega, T)$$

since

$$\frac{A}{B} = \frac{\hbar \omega^3}{\pi^2 c^3}$$
 (trust me ...)

$$U^{eq}(\omega,T) = \frac{\hbar\omega^3}{\pi^2c^3} \frac{1}{\exp\left[\frac{\hbar\omega}{kT}\right] - 1}$$

or

$$U^{eq}(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{\exp\left[\frac{hc}{\lambda kT}\right] - 1}$$

and so

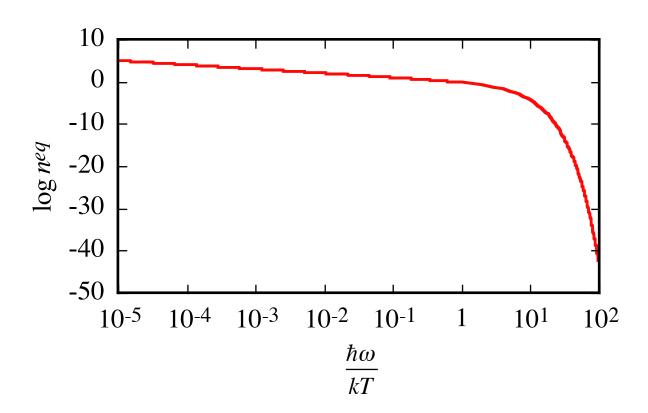
$$I(\omega,T) = \frac{cU^{eq}(\omega,T)}{4} = \frac{\hbar\omega^3}{4\pi^2c^2} \frac{1}{\exp\left[\frac{\hbar\omega}{kT}\right] - 1}$$

or

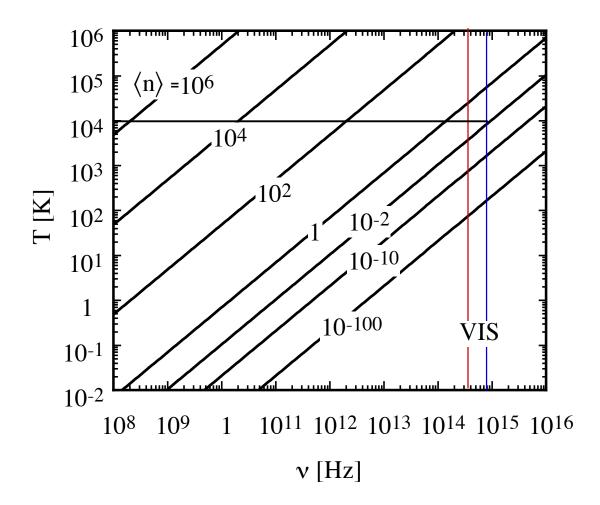
$$I(\lambda, T) = \frac{cU^{eq}(\lambda, T)}{4} = \frac{2\pi hc^2}{\lambda^5} \frac{1}{\exp\left[\frac{hc}{\lambda kT}\right] - 1}$$

• the equilibrium number of the light quanta per mode is

$$n^{eq} = \frac{1}{\exp\left[\frac{\hbar\omega}{kT}\right] - 1}$$



• in the visible range (VIS) at $T < 10^4$ K, very few photons per mode (e.g., at T = 10000 K, there are just 0.02 light quanta per mode in the blue)



• note that the total intensity, I(T), of the black body radiation at a temperature T obtained by integration of the spectral intensity distribution function:

$$I(T) = \int_{0}^{\infty} \frac{2\pi hc^{2}}{\lambda^{5}} \frac{1}{\exp\left[\frac{hc}{\lambda kT}\right] - 1} = \frac{2k^{4}\pi^{5}}{15c^{2}h^{3}} T^{4}$$
 [W/m²]

which is Stefan's law, with

$$\frac{2k^4\pi^5}{15c^2h^3} = 5.65 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}$$