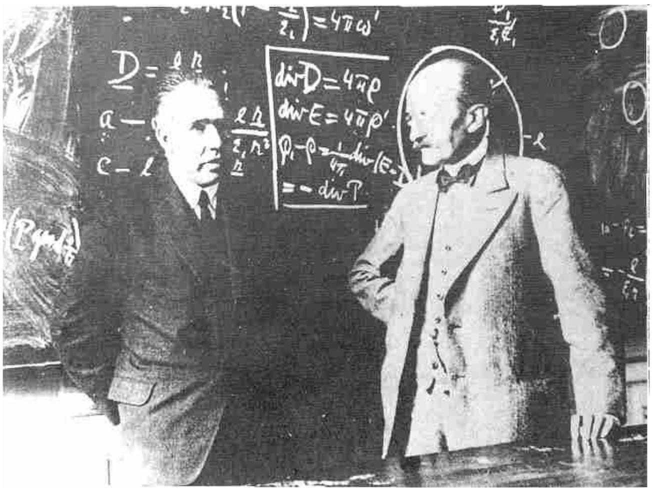
Thermodynamics of Radiation



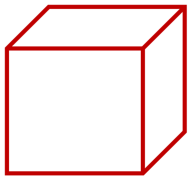
Niels Bohr & Max Planck

Chapter 7

Thermodynamics of Radiation

7.1 Thermodynamics of Radiation

- Consider an evacuated box at temperature T. It contains electromagnetic radiation (“equilibrium radiation” or “**black-body radiation**”).



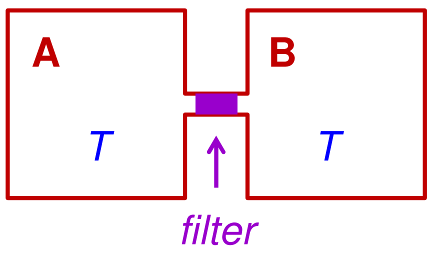
- From a QM point of view, this is a gas of photons and the walls continually **emit, absorb, & reflect** photons.
- From a classical perspective, regard it as a superposition of many standing electromagnetic (EM) waves in a cavity.
- In thermodynamics we can treat this like a gas. But there are some important differences:
  - Number N of particles (photons) is not fixed.
  - All photons have the same speed c (though not the same energy).

Energy Density

- Introduce the spectral energy density, u_λ, i.e. the energy per unit volume in the range $d\lambda$ is $u_\lambda d\lambda$. It depends only on λ and T. It does not depend on the nature of walls.

Integrated energy density $$u(T) = \int u_\lambda(\lambda, T) d\lambda$$

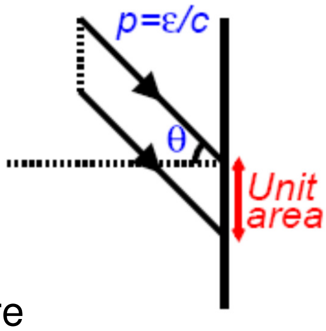
- To show this, imagine two boxes, **A** and **B**, both at temperature T, connected through a filter which passes only the range $[\lambda, \lambda + d\lambda]$.



- If $u^A_\lambda > u^B_\lambda$ there would be a net flow of energy from A $\rightarrow$ B. Impossible if $T_A = T_B$.
- **If we expand a cavity at fixed T, the total energy will increase by creating more photons, not by changing their spectrum or density.**

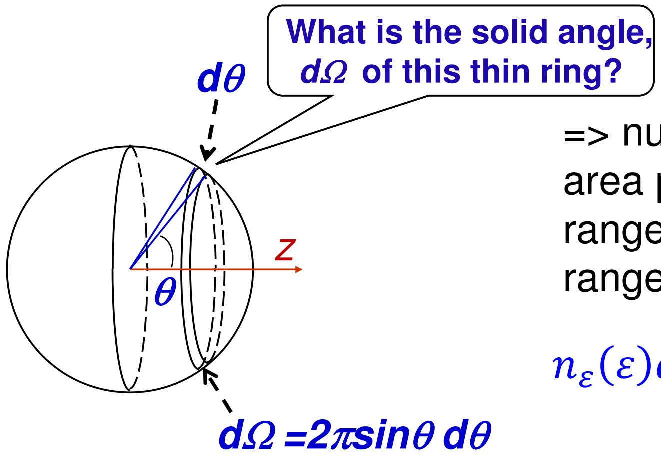
Radiation Pressure

- Suppose the number of photons per unit volume with an energy in the range $[\varepsilon, \varepsilon+d\varepsilon]$ is $n_\varepsilon(\varepsilon)d\varepsilon$.



Consider photons approaching the surface at an angle θ to the normal: in unit time, photons in volume $c \cos\theta \times 1$ will hit a unit area.

But what fraction of the total number of photons are approaching the surface at angles between θ and θ+dθ?



=> number of photons hitting a unit area per unit time with energy in the range $[\varepsilon, \varepsilon+d\varepsilon]$ and angles in the range $[\theta, \theta+d\theta]$ is

$$n_\varepsilon(\varepsilon)d\varepsilon \cdot c\cos\theta \cdot \underbrace{\frac{1}{2}\sin\theta d\theta}_{= d\Omega/4\pi}$$

Pressure of Radiation

- For a photon $\frac{\omega}{k} = c \;\Rightarrow\; \hbar k = \frac{\hbar\omega}{c} \;\Rightarrow\; p = \frac{\varepsilon}{c}$, so each photon carries a momentum component orthogonal to the surface $\varepsilon\cos\theta/c$.

  For perfectly reflecting surfaces its momentum change is $2\varepsilon\cos\theta/c$ and the pressure is:

$$p = \int_{\varepsilon=0}^{\infty}\int_{\theta=0}^{\pi/2} 2\varepsilon n_\varepsilon(\varepsilon)d\varepsilon\cos^2\theta\,\frac{1}{2}\sin\theta\,d\theta$$

$$= \int_{\varepsilon=0}^{\infty} u_\varepsilon(\varepsilon)d\varepsilon\left[-\frac{1}{3}\cos^3\theta\right]_0^{\pi/2} = \frac{1}{3}u$$

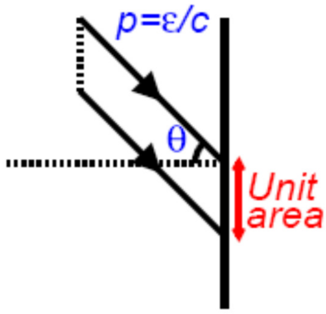
- For a perfectly absorbing surface (‘black’) in equilibrium, **the surface must be radiating the same energy as it absorbs**, ⇒ the extra (recoil) pressure is equal to this. Net pressure $p = (1/3)u$ again.

- A similar argument applies for partially absorbing surfaces.

7.2 Kirchhoff's Law

- A surface is in equilibrium with radiation ⇒ there must be an energy **balance between emitted, absorbed and reflected radiation**.
- Consider flux of photons from a gas of number density *n* hitting a surface:

  In unit time, photons in volume $c \cos\theta \times 1$ will hit a unit area.



$$\Rightarrow \text{Flux} = \int c\cos\theta \cdot n \cdot \frac{d\Omega}{4\pi}$$

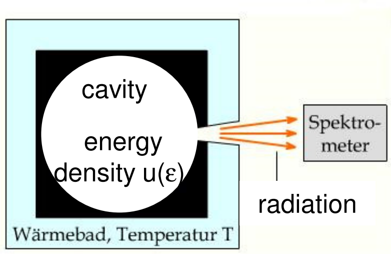
$$= \int c\cos\theta \cdot n \cdot \frac{1}{2}\sin\theta d\theta = \frac{1}{4}nc$$

…just like kinetic theory.

- Replace *n* by $n_\varepsilon(\varepsilon)d\varepsilon$ above if we are looking in a restricted spectral range. Or $n_\lambda(\lambda)d\lambda$

Kirchhoff's Law

- Consider a body in equilibrium with radiation inside a cavity at temperature *T*.
- Energy hitting a unit area of the surface per unit time for an energy interval $d\varepsilon$



$$= \frac{1}{4}n_\varepsilon(\varepsilon)c\, d\varepsilon \cdot \varepsilon$$

$$= \frac{1}{4}u_\varepsilon(\varepsilon)c\, d\varepsilon = \frac{1}{4}u_\lambda(\lambda)c\, d\lambda$$

- Define "Spectral absorptivity" = $\alpha_\lambda(\lambda)$ as the fraction absorbed.
- Define "Spectral radiant exitance" = $e_\lambda(\lambda, T)d\lambda$ as the energy per unit area emitted in the wavelength range $[\lambda, \lambda + d\lambda]$
- **Energy out = energy in**. ⇒ $e_\lambda d\lambda = \frac{1}{4}u_\lambda\, c\, d\lambda\alpha_\lambda$

Kirchhoff's Law

$$e_\lambda d\lambda = \frac{1}{4} u_\lambda \, c \, d\lambda \alpha_\lambda$$

- This gives us Kirchhoff's law: $\boxed{\dfrac{e_\lambda}{\alpha_\lambda} = \dfrac{1}{4} u_\lambda(\lambda, T) c}$
- The r.h.s. is a universal function of λ and T only; it applies for any body.
- Specifically, for a 'Black Body' which absorbs perfectly at all wavelengths, $\alpha^{BB}{}_\lambda = 1$, and hence
$$e_\lambda^{BB} = \frac{1}{4} u_\lambda(\lambda, T) c$$
- This demonstrates that black-body radiation is equivalent to equilibrium radiation in a cavity (i.e. same spectrum and temperature dependence).
- For a 'non black' body the "Spectral radiant exitance" = $e_\lambda(\lambda, T)$ is then given by:
$$e_\lambda(\lambda, T) = \varepsilon_\lambda e_\lambda^{BB}(\lambda, T)$$

where, by Kirchhoff's law the emissivity of the surface (fraction of the black body intensity that a surface emits at a particular wavelength) is equal to the spectral absorptivity: $\boxed{\varepsilon_\lambda(\lambda) = \alpha_\lambda(\lambda)}$

7.3 Stefan-Boltzmann Law

- For Radiation we have internal energy (U) and internal energy density (u) related by $U = u(T)V$, and $\left(\dfrac{\partial u}{\partial V}\right)_T = 0$
- First Law: $dU = TdS - pdV$; divide by dV at constant T:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p \quad \Rightarrow \quad u = T\underbrace{\left(\frac{\partial p}{\partial T}\right)_V}_{\text{Maxwell}} - p$$

- Recalling that $p = (1/3)u$, this gives

$$u = \frac{1}{3}\left(T\frac{du}{dT} - u\right) \quad \Rightarrow \quad \frac{du}{u} = 4\frac{dT}{T} \quad \Rightarrow \quad u = AT^4$$

where A is a constant of integration.

Stefan-Boltzmann Law

- We can relate $u = AT^4$ to the emission from a black body.

  Energy emitted per unit area per unit time =

$$\int e_\lambda d\lambda = \int \frac{1}{4} u_\lambda(\lambda, T) c d\lambda = \frac{1}{4} u(T) c = \frac{1}{4} A c T^4 = \sigma T^4$$

- σ is the Stefan-Boltzmann constant. We need quantum theory + statistical mechanics to calculate it (see later) . In fact:

$$\sigma = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} = 5.67 \times 10^{-8} \text{ W m}^2 \text{ K}^{-4}$$

- [Note: from $u = AT^4$ we have $p = (1/3) AT^4$. This is in effect the equation of state for the photon gas (and doesn't involve V).]

- *(at 300K corresponds to ≈50mW/cm² – compare sunlight – 1kW/m² at Earth's surface, or 0.1W/cm²)*

7.4 Entropy and Gibbs free energy of a photon gas

- The Gibbs free energy of a photon gas will be given by:

$$G = U + PV - TS$$

  and per unit volume: $g = u + p - Ts$ (where *g* and *s* are the Gibbs free energy and entropy per unit volume)

- To evaluate *s* we need to integrate dq/T as the photon gas is heated from absolute zero. Since we are working at constant volume, heat transferred for a change in temperature is:

$$dq = du = 4AT^3 dT$$

  and so the entropy of the photon gas is given by:

$$s = \int_0^T \frac{dq}{T} = \int_0^T 4AT^2 dT = \frac{4}{3} AT^3$$

Giving a Gibbs free energy per volume:

$$g = AT^4 + \frac{1}{3} AT^4 - T.\frac{4}{3} AT^3 = 0$$

This means that the Gibbs free energy per photon, (the chemical potential, μ), is also zero.

$\mu = 0$ *for a photons : photons are different*

- Recall at the start of the course we pointed out that the state of a system is defined by specifying the number of particles (*i.e*. contents), the energy and volume of a box. But photons are clearly different from 'normal' particles in a number of ways – not least that they can be created and annihilated seeming at will on the walls of the box.
- Recall the expression for entropy change from the master equation is:

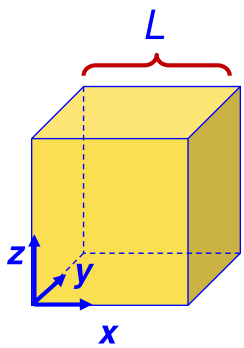
$$dS = \frac{dU}{T} + \frac{p}{T}dV + \frac{\mu}{T}dN$$

So the fact that *dN* can be seemingly changed with no penalty (other than the need to find the energy, *dU*, from somewhere) is consistent with the fact that the chemical potential, μ, is zero – so there is no effect on *S* when these photons are created and annihilated (other than the associated transfer of energy to the box).

- The point is you cannot separate the existence of the 'particle' that is a photon from the transfer of energy to a mode of the electromagnetic waves in the box – so worryinig about the effect on the entropy of transferring a particle (*dN*) as well as the energy transfer (*dU*) be double counting the effect of the change in state.

Permitted states: 'Waves in a box"

- In order to use statistical thermodynamics to gain information about the spectrum of black body radiation need to know what the photon states are.
- Consider electromagnetic standing waves in a box. Take a cubic box, of side *L* so that the electric field $\underline{\mathcal{E}}_{\|} = 0$ at $x = 0, L$ etc. Standard boundary conditions give:



$$\underline{\mathcal{E}} = \underline{\mathcal{E}}_0 \sin(k_x x)\sin(k_y y)\sin(k_z z)$$

where

$$k_x L = n_x \pi; \quad k_y L = n_y \pi; \quad k_z L = n_z \pi$$

i.e. the photons must have wave vectors:

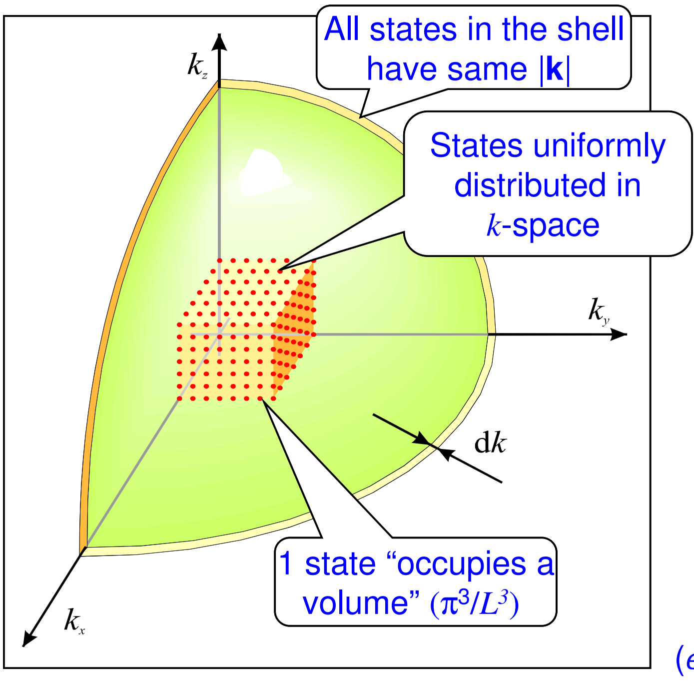
$$\mathbf{k} = \frac{\pi}{L}(n_x \quad n_y \quad n_z)$$

Where n_x, n_y and n_z are all positive

Note: momentum states are uniformly distributed in *p* space

"Waves in a box": density of states

- Since the photon energy depends on $|\mathbf{k}|$ we want to know how many states (δN) lie between $|\mathbf{k}|=k$ and $|\mathbf{k}|=k+\delta k$, *i.e.* **what is the density of states $g(k)$ ($=\frac{dN}{dk}$) since $\delta N = g(k)\,\delta k$.**



2 Polarisations/*k* state

Volume of shell

Vol. of one state

$$\delta N = g(k)\delta k = 2\,\frac{4\pi k^2 \delta k}{8} \Big/ \frac{\pi^3}{L^3}$$

$$= \frac{Vk^2}{\pi^2}\delta k \quad \Rightarrow \quad g(k) = \frac{Vk^2}{\pi^2}$$

And the energy density of states:

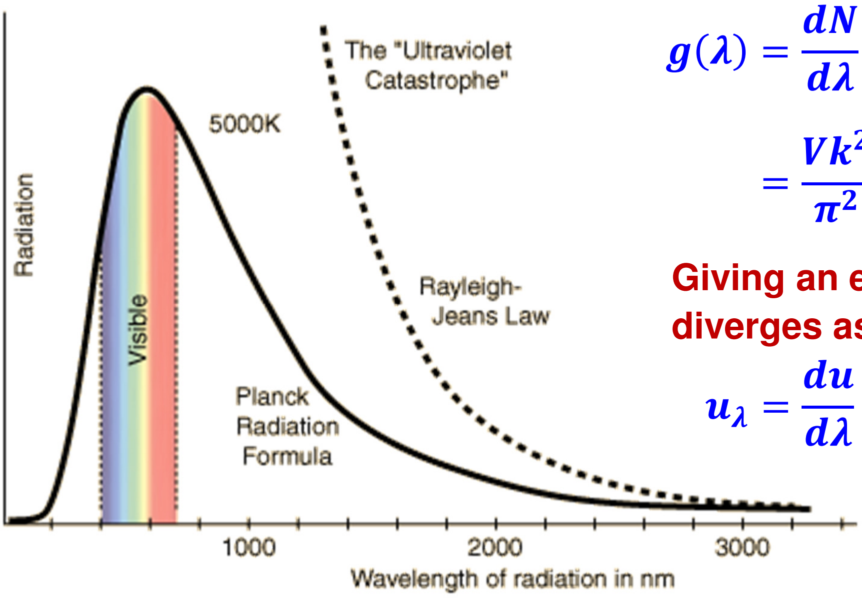
$$g(\epsilon) = \frac{dN}{d\varepsilon} = \frac{dN}{dk}\frac{dk}{d\varepsilon} = g(k)\frac{dk}{d\varepsilon}$$

$$g(\epsilon) = \frac{V\epsilon^2}{\hbar^3 c^3 \pi^2}$$

($\epsilon = \hbar\omega = \hbar ck$ and $V=L^3$=volume of box)

"Ultraviolet Catastrophe"

- In classical thermodynamics, each way of storing energy which is a quadratic function of a coordinate takes ½$k_B T$ of energy – here we have energy stored in E and B fields (½$\varepsilon_0 E^2$ and ½B^2/μ_0 per unit volume) – so each k state gets $k_B T$ of energy. Working with λ gives:



$$g(\lambda) = \frac{dN}{d\lambda} = \frac{dN}{dk}\frac{dk}{d\lambda} = g(k)\frac{dk}{d\lambda}$$

$$= \frac{Vk^2}{\pi^2}\frac{2\pi}{\lambda^2} = \frac{8\pi V}{\lambda^4} \qquad (k = \tfrac{2\pi}{\lambda})$$

Giving an energy density that diverges as $\lambda \to 0$:

$$u_\lambda = \frac{du}{d\lambda} = k_B T\frac{dN}{d\lambda} = \frac{k_B T 8\pi V}{\lambda^4}$$

(Rayleigh-Jeans Law)

7.5 Planck's Law

- Planck proposed that energy was transferred in quanta of $\hbar\omega$. Since we can have an integer *n* photons in each mode, each mode can have energies 0, $\hbar\omega$, $2\hbar\omega$ … and the mean energy per mode is exactly as for the simple harmonic oscillator – the 'Planck' formula.

$$\bar{U} = -\frac{1}{Z}\frac{dZ}{d\beta} = \frac{\hbar\omega e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})} = \frac{\hbar\omega}{(e^{\beta\hbar\omega} - 1)} = \frac{\hbar\omega}{\left(e^{\frac{\hbar\omega}{kT}} - 1\right)}$$

- To get the spectral energy density, we need to multiply this energy per photon mode (*i.e.* per *k* state) by the density of states w.r.t. ω.

$$g(\omega) = \frac{dN}{d\epsilon}\frac{d\epsilon}{d\omega} = g(\epsilon)\frac{d\epsilon}{d\omega} = \frac{V\epsilon^2}{\hbar^3 c^3 \pi^2}\frac{d\epsilon}{d\omega} = \frac{V(\hbar\omega)^2}{\hbar^3 c^3 \pi^2}\hbar = \frac{V\omega^2}{c^3\pi^2}$$

Planck's Law (contd.)

- Hence

$$g(\omega) = \frac{V\omega^2}{c^3\pi^2}$$

- Energy density: $u(\omega, T)d\omega$ is the energy/unit volume between ω and $\omega + d\omega$:

$$u(\omega, T) = g(\omega)\bar{U}/V = \frac{\omega^2}{c^3\pi^2}\frac{\hbar\omega}{\left(e^{\frac{\hbar\omega}{kT}} - 1\right)}$$

- This yields the Planck black body spectrum:

$$\boxed{u(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\hbar\omega/kT} - 1)}}$$

Planck's Law (contd.)

- Integrate $u(\omega, T)$ to obtain the total energy density, substituting $x = \beta\hbar\omega$:

$$u(T) = \frac{\hbar}{\pi^2 c^3}\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega}-1}d\omega$$

$$= \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^4 \underbrace{\int_0^\infty \frac{x^3 dx}{e^x - 1}}_{=\pi^4/15}$$

$$\boxed{u(T) = \frac{k^4 T^4 \pi^2}{15\hbar^3 c^3}}$$

Stefan-Boltzmann law

Planck's Law (contd.)

- Can rewrite the Planck distribution in terms of wavelength λ (this was actually Planck's first form of the law, proposed as an empirical fit to data.).

$$u_\lambda(T) = \frac{8\pi ch}{\lambda^5(e^{hc/\lambda kT}-1)}$$

- The basic dependence on λ – namely $u_\lambda(T) = \lambda^{-5} f(\lambda T)$ is called **Wien's Distribution Law**.

- By differentiating w.r.t. λ one obtains **Wien's Displacement Law**

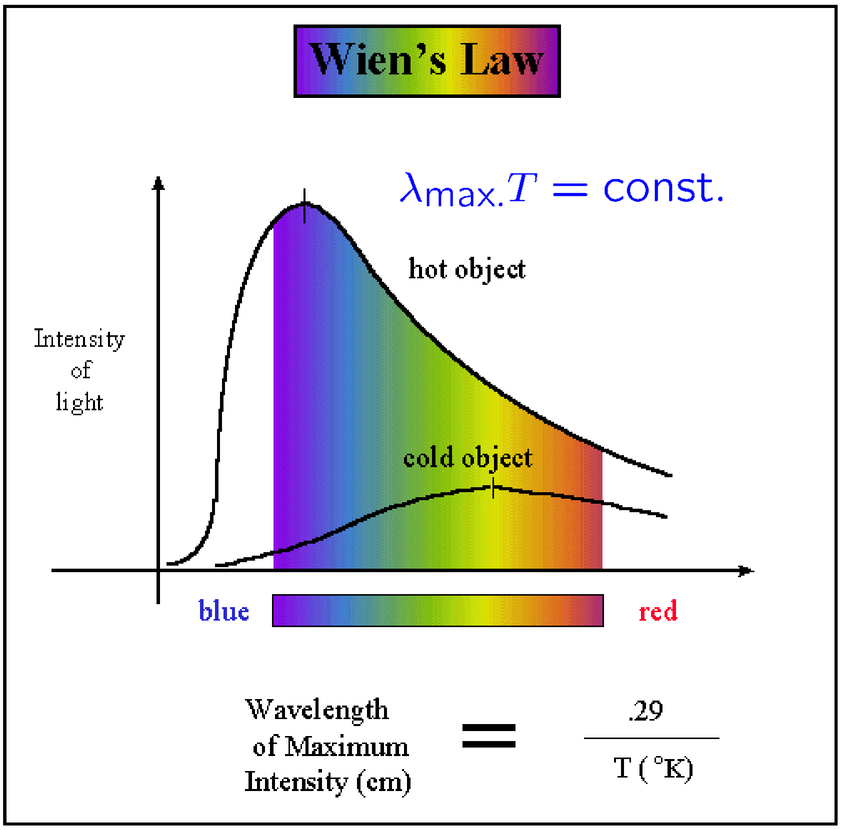
$$\frac{du_\lambda}{d\lambda} = f'(\lambda T)T\lambda^{-5} - 5\lambda^{-6}f(\lambda T) = \frac{f'(\lambda T)\lambda T - 5f(\lambda T)}{\lambda^6}$$

$$f'(\lambda_{\max}T)\lambda_{\max}T - 5f(\lambda_{\max}T) = 0$$

$$\lambda_{\text{max.}}T = \text{const.}$$

$\lambda_{\text{max.}}$ is the wavelength at which the distribution peaks. Numerically, $\lambda_{\text{max.}}T = 2.9$ mm K, inserting constants from Planck distribution.

Wien's Displacement Law



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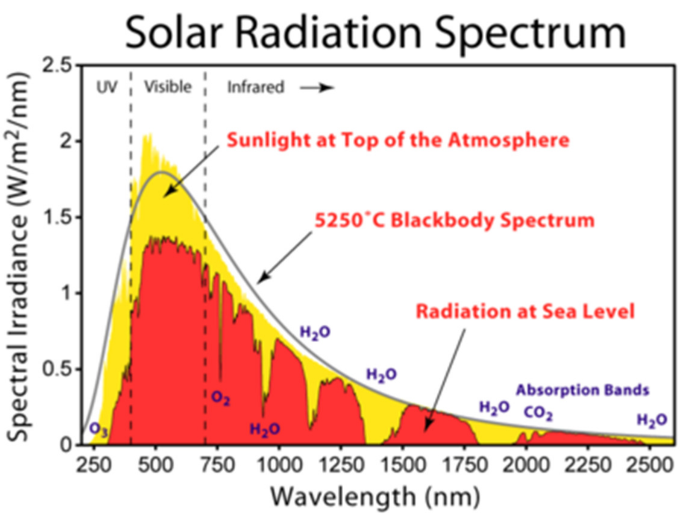
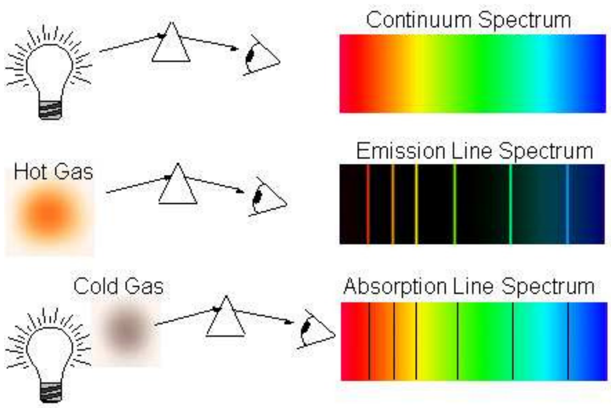
http://www.astro.cornell.edu/academics/courses/astro201/wiens_law.htm

Examples



http://ockhams-axe.com/global_warming



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http://www.astro.cornell.edu/academics/courses/astro101/herter/lectures/lec09.htm

Section 7- Summary

- Consider cavity or black-body radiation as a gas of photons.
- pressure $p = \frac{1}{3}u$
- Kirchhoff's Law

$$\boxed{\frac{e_\lambda}{\alpha_\lambda} = \frac{1}{4}u_\lambda(T)c}$$

- Stefan-Boltzmann Law: $u = AT^4$; power emitted per unit area = σT^4.
- Planck distribution for Black Body radiation:

$$\boxed{u(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\hbar\omega/kT} - 1)}}$$