

CHEM 26100 (Quantum Mechanics) Notes

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Chapter 1

From Classical to Quantum Mechanics

1.1 Blackbody Radiation

9/27: • The surface of a hot body emits energy in the form of EM radiation.

• Changes that occur with temperature:

- If less than 500 °C, we have IR Radiation (heat).
- If 500 °C to 600 °C, we have visible radiation (a glowing body).
- If 5 000 °C, we have a “white hot” body (short wavelength).

• As a body gets hotter, it emits shorter wavelength radiation.

• **Stefan-Boltzmann law:** The the total emissive power R (recall that power is en / time) of a blackbody (BB) is given by

$$R(T) = \sigma T^4$$

where $\sigma \approx 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ is **Stefan’s constant**.

- Work done by Stefan and Boltzmann (c. 1870 / 1884, respectively).

• **Wien’s 1st Law:** The wavelength for maximum emissive power obeys the equation

$$\lambda_{\text{max}} T = b$$

where $b = 2.808 \times 10^{-3} \text{ m K}$ is **Wein’s displacement constant**.

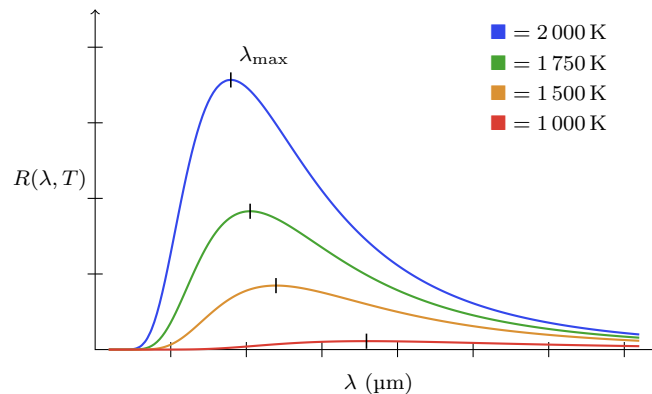


Figure 1.1: Wein’s 1st Law.

- Area under the curve (found with integration) is the total emissive power.
- We now change variables from emissive power R to energy density ρ in the BB cavity.

$$\rho(\lambda, T) = \frac{4}{c} R(\lambda, T)$$

- Wien's 2nd Law (1893): The energy density must have a functional relationship with the following form.

$$\rho(\lambda, T) = \frac{f(\lambda T)}{\lambda^5}$$

– $f(\lambda T)$ cannot be determined from thermodynamics. Thus, something else is needed!

- Lord Rayleigh and his graduate student Jeans (1899) propose a solution.
 - EM: The thermal radiation within a cavity must exist in the form of standing waves.
 - RJ showed that the number n of standing waves per unit volume, per wavelength has the following form.

$$n(\lambda) = \frac{8\pi}{\lambda^4}$$

– If $\bar{\epsilon}$ is the average energy in the mode with wavelength λ , then

$$\rho(\lambda, T) = \frac{8\pi}{\lambda^4} \bar{\epsilon}$$

- Waves come from atoms in the walls of the BB cavity, which act as linear harmonic oscillators at a frequency $\nu = c/\lambda$.
- Assuming thermal equilibrium, we obtain

$$\begin{aligned} \bar{\epsilon} &= \frac{\int_0^\infty \epsilon e^{-\epsilon/kT} d\epsilon}{\int_0^\infty e^{-\epsilon/kT} d\epsilon} \\ &= -\frac{\partial}{\partial \beta} \ln \left(\int_0^\infty e^{-\beta \epsilon} d\epsilon \right) \\ &= \frac{1}{\beta} \\ &= kT \end{aligned}$$

where k is the Boltzmann constant.

- Basically, we sum all energies ϵ , weighted by the probability $e^{-\epsilon/kT}$ of the energy existing, and divided by the total energy.
- The first equation is equivalent to the second with $\beta = 1/kT$.
- Therefore,

$$\rho(\lambda, T) = \frac{8\pi kT}{\lambda^4}$$

- UV catastrophe: Rayleigh's formula diverges from the experimental data for short wavelength.
 - The above formula diverges to $+\infty$, driven by the λ^4 term in the denominator, as $\lambda \rightarrow 0$. However, the amount of radiation of shorter wavelengths should decrease past a point, as seen in Figure 1.1.
- Max Planck comes in, proposes an idea to the German academy that's so radical, they think he's insane, but he's actually right and it lays a key idea for quantum mechanics.
- Planck's key insight: The energy levels of the oscillators are not continuous, but are quantized.

- So we can't actually take an integral as Rayleigh did; we have to take an infinite series.
- In reality,

$$\begin{aligned}\bar{\epsilon} &= \frac{\sum_{n=0}^{\infty} n\epsilon_0 e^{-\beta n\epsilon_0}}{\sum_{n=0}^{\infty} e^{-\beta n\epsilon_0}} \\ &= \frac{\epsilon_0}{e^{\beta\epsilon_0} - 1}\end{aligned}$$

- Thus,

$$\rho(\lambda, T) = \frac{8\pi\epsilon_0}{\lambda^4(e^{\epsilon/kT} - 1)}$$

- But to satisfy Wien's 2nd law, we must let $\epsilon_0 \propto 1/\lambda$. More specifically, $\epsilon_0 = hc/\lambda = h\nu$, where h is Planck's constant.
 - This setup allowed us to get an accurate value for Planck's constant for the first time in history.
- Planck's theory predicts the data of Figure 1.
- A perfect blackbody absorbs and emits radiation at all frequencies.
 - A star is pretty close to a blackbody. The graphite in a pencil is 97% a blackbody. We are all blackbodies.
 - The entire universe can be viewed as a blackbody.
- Princeton and Bell Labs telescopes find **Cosmic Background Radiation** (A. A. Penzias and R. W. Wilson, 1964).
 - Background radiation from the universe itself.
 - $\lambda_{\max} = 7.35$ cm.
 - Isotropic radio signal, that comes from everywhere.
 - From this, you can work out the temperature of the universe from Wein's first law.
 - Thus, the whole universe is a blackbody with a temperature of approximately 3 K.