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 $\sigma \approx 5.67 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}}$ 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

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

  where $b = 2.898 \times 10^{-3}\,\mathrm{m\,K}$ is **Wein's displacement constant**. *Also known as* **Wien's displacement law**.

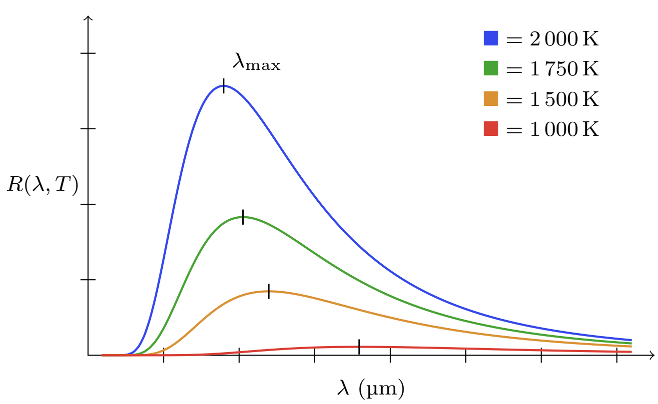

Figure 1.1: Wein's 1st Law.

- 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

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

    where k is the Boltzmann constant.
    - Basically, we sum all energies ϵ, weighted by the probability $\mathrm{e}^{-\epsilon/kT}$ 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 $\lambda \to 0$. 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 acacdemy 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,

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

- Thus,

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

- 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.
  - $\lambda_{\text{max}} = 7.35\,\text{cm}$.
  - Isotropic radio signal, that comes form everywhere.
  - From this, you can workout the temperature of the universe from Wein's first law.
  - Thus, the whole universe is a blackbody with a temperature of approximately $3\,\text{K}$.

1.2 Chapter 1: The Dawn of the Quantum Theory

From McQuarrie and Simon (1997).

9/28:

- **Blackbody**: A body which absorbs and emits all frequencies. *Also known as* **ideal body**.
- "Many theoretical physicists tried to derive expressions consistent with these experimental curves of intensity versus frequency [see Figure 1.1], but they were all unsuccessful. In fact, the expression that is derived according to the laws of nineteenth century physics is" as follows (McQuarrie & Simon, 1997, p. 3).
- **Rayleigh-Jeans law**: The equation

$$\mathrm{d}\rho(\nu, T) = \rho_\nu(T)\,\mathrm{d}\nu = \frac{8\pi k_B T}{c^3}\nu^2\,\mathrm{d}\nu$$

  where $\rho_\nu(T)\,\mathrm{d}\nu$ is the "radiant energy density between the frequencies ν and $\nu + \mathrm{d}\nu$" (McQuarrie & Simon, 1997, p. 3).
- The ultraviolet catastrophe is so named because the frequency increases as the radiation enters the ultraviolet region.
- Planck's solution:

  - Rayleigh and Jeans assumed (as does classical physics) that the energies of the electronic oscillators responsible for the emission of the radiation could have any value whatsoever.
  - However, Planck assumed discrete oscillator energies proportional to an integral multiple of the frequency: $E = nh\nu$, where $n \in \mathbb{Z}$.
  - Using this quantization energy and ideas from statistical thermodynamics (see Chapter 17), Planck derived the **Planck distribution law for blackbody radiation**.
  - The only undetermined constant in the above equation was h, and Planck showed that if we let $h = 6.626 \times 10^{-34}\,\mathrm{J\,s}$, then this equation gives excellent agreement with the experimental data for all frequencies and temperatures.

- **Planck distribution law for blackbody radiation**: The equation

$$\mathrm{d}\rho(\nu, T) = \rho_\nu(T)\,\mathrm{d}\nu = \frac{8\pi h}{c^3}\frac{\nu^3\,\mathrm{d}\nu}{\mathrm{e}^{h\nu/k_BT} - 1}$$

  - Note that for small frequencies, the Planck distribution law and Rayleigh-Jeans law converge, but they diverge for large frequencies, as expected.
  - Because ν and λ are related by $\lambda\nu = c$ (and subsequently by $\mathrm{d}\nu = -c/\lambda^2\,\mathrm{d}\lambda$), we can write the Planck distribution law in terms of wavelength, as well.

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

- Differentiating $\rho_\lambda(T)$ with respect to λ gives an alternate formulation for b:

$$\lambda_{\max}T = \frac{hc}{4.965k_B}$$

- Astronomers use the theory of blackbody radiation to estimate the surface temperatures of stars.
  - We can measure the electromagnetic spectrum of a star (which will follow a curve similar to one of the ones in Figure 1.1).
  - Then we can find $\lambda_{\max}$. From here, all that's necessary is to plug into Wien's displacement law:

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