Blackbody radiation

In his theory of blackbody radiation, energy density at frequency ν inside cavity with temperature T is given by

$$\mathcal{U}(\nu, T) = \rho u$$

where ρ is the number of radiation modes per unit volume and u is the average energy at said frequency. Both quantity respectively are given by

$$\rho = \frac{8\pi\nu^2}{c^3}, \quad u = \frac{h\nu}{\exp(h\nu/kT) - 1}$$

Hence

$$\mathcal{U}(\nu, T) = \frac{8\pi h}{c^3}\frac{\nu^3}{\exp(h\nu/kT) - 1}$$

or, we can write it in terms of λ

$$\mathcal{U}(\lambda, T) = \frac{8\pi hc}{\lambda^5}\frac{1}{\exp(hc/\lambda kT) - 1}$$

The particle density as function of wavelength

$$n(\lambda, T) = \frac{8\pi}{\lambda^4}\frac{1}{\exp(hc/\lambda kT) - 1}$$

And the relation with energy density

$$\mathcal{U}(\lambda) = n(\lambda)E(\lambda)$$

with $E = hc/\lambda$.

Planck's Derivation

In his work, Planck assumes that the walls of the cavity act as oscillator with energy of integer multiple ϵ. This has some similarity with Boltzmann discrete model. We denote n_k as the number particle with $k\epsilon$ energy, with maximum energy of $P\epsilon$. Therefore, we have the following constraints.

$$\sum_{k=0}^{P} n_k = N, \quad \sum_{k=0}^{P} kn_k = P$$

Planck he defined entropy as

$$S_P = k\ln(W) + C$$

where

$$W = \frac{\mathcal{R}}{\mathcal{J}}$$

is the probability of the N atoms have $p\epsilon$ energy. In other hand, $\mathcal{R}$ denotes the number of said configuration and $\mathcal{J}$ denotes the total configuration. It then may be written as

$$S_P = k\ln\mathcal{R}$$

where $\mathcal{R}$ is given by

$$\mathcal{R} = \frac{(L+N-1)!}{L!(N-1)!}$$

The logarithm of $\mathcal{R}$ can be evaluated as

$$\begin{aligned}\ln \mathcal{R} = (N+L-1)[\ln(N+L-1)-1] - L[\ln(L)-1] \\ - (N-1)[\ln(N-1)-1]\end{aligned}$$

and then

$$\ln \mathcal{R} = (N+L-1)\ln(N+L-1) - L\ln L - (N-1)\ln(N-1)$$

and then

$$\begin{aligned}\ln \mathcal{R} = (N+L)\ln(N+L-1) - \ln(N+L-1) - L\ln L \\ - N\ln(N-L) + \ln(N-1)\end{aligned}$$

and then

$$\begin{aligned}\ln \mathcal{R} = (N+L)\left[\ln\left(\frac{N+L-1}{N+L}\right) + \ln\left(N+L\right)\right] - L\ln L \\ - N\left[\ln\left(\frac{N-1}{N}\right) + \ln(N)\right] - \ln\left(\frac{N+L-1}{N+L}\right)\end{aligned}$$

then finally we rewrite it as

$$\begin{aligned}\ln \mathcal{R} = (N+L)\ln(N+L) - L\ln L - N\ln N \\ - N\ln\left(\frac{N-1}{N}\right) + (N+L-1)\ln\left(\frac{N+L-1}{N+L}\right)\end{aligned}$$

For large N, L; those last two terms will approach zero. Hence,

$$\ln \mathcal{R} = (N+L)\ln(N+L) - L\ln L - N\ln N$$

This equation give the same result for $\ln(\mathcal{P}_{\max})$ in the case of Boltzmann discrete model. Therefore, we write

$$S_P = Nk\left[\left(1+\frac{u}{\epsilon}\right)\ln\left(1+\frac{u}{\epsilon}\right) - \frac{u}{\epsilon}\ln\left(\frac{u}{\epsilon}\right)\right]$$

Based on empirical data, Planck concludes that entropy is a function of energy and frequency

$$S_P = f\left(\frac{u}{\nu}\right)$$

On comparing those two equation, it can be seen that energy ϵ is proportional to frequency ν. To show this relationship, we then write $\epsilon = h\nu$. By solving the equation of entropy S_P for average energy u we will have the desired result.

To do so, we use the thermodynamics relationship

$$\left.\frac{\partial S}{\partial U}\right|_{V,N_i} = \frac{1}{T}$$

Change the variable we are differentiating against to average energy

$$\frac{\partial S_P}{\partial U} = \frac{1}{N}\frac{\partial S_P}{\partial u}$$

Then

$$\frac{1}{T} = k\left[\frac{1}{\epsilon}\ln\left(1+\frac{u}{\epsilon}\right) + \left(1+\frac{u}{\epsilon}\right)\left(1+\frac{u}{\epsilon}\right)^{-1}\frac{1}{\epsilon} - \frac{1}{\epsilon}\ln\left(\frac{u}{\epsilon}\right) - \frac{u}{\epsilon}\frac{\epsilon}{u}\frac{1}{\epsilon}\right]$$

Moreover

$$\frac{1}{T} = \frac{k}{\epsilon}\left[\ln\left(1+\frac{u}{\epsilon}\right) - \ln\left(\frac{u}{\epsilon}\right)\right] = \frac{k}{\epsilon}\ln\left(\frac{\epsilon}{u}+1\right)$$

Furthermore

$$\frac{\epsilon}{u} + 1 = \exp\left(\frac{\epsilon}{kT}\right)$$

Hence

$$u = \frac{\epsilon}{\exp(\epsilon/kT) - 1}$$

Substituting $\epsilon = h\nu$ from our empirical observation, we obtain

$$u = \frac{hv}{\exp(hv/kT) - 1} \quad \blacksquare$$

Bose's Derivation

Bose derived Planck's law independent of classical electrodynamics to obtain coefficient $8\pi\nu^2/c^3$. He defined the cell $\mathcal{P}_v$ as a box which photon are distributed. Let $n_{k\nu}$ defined as the number of boxes that contain k photon of frequency ν. We have then the following constraints.

$$P_\nu = \sum_{k=0}^{\infty} n_{k\nu}, \quad U_\nu = hv\sum_{k=0}^{\infty} kn_{k\nu}$$

or simply

$$P_\nu = \sum_{k=0}^{\infty} n_{k\nu}, \quad N_\nu = \sum_{k=0}^{\infty} kn_{k\nu}$$

where N_ν is the number of photon with frequency ν. The number of configuration is given by

$$\mathcal{P}_\nu = P_\nu!\left(\prod_{k=0}^{\infty} n_{k\nu}\right)^{-1}$$

All of those equations applies for distinct frequency ν, what we what however distribution over all frequency $(0, \infty)$. The expression for constraints is

$$P_\nu = \sum_{k=0}^{\infty} n_{k\nu}, \quad U = h\sum_{k=0}^{\infty} v\sum_{k=0}^{\infty} kn_{k\nu}$$

and the expression for the number of configuration is

$$\mathcal{P} = \sum_{\nu=0}^{\infty} \mathcal{P}_\nu$$

As usual, the equation that we want to maximize not the configuration $\mathcal{P}$ itself, but rather its logarithm; which may be written as

$$\ln \mathcal{P} = \sum_{\nu=0}^{\infty} \ln \left[\mathcal{P}_v! \left(\prod_{k=0}^{\infty} n_{k\nu} \right)^{-1} \right]$$

On using Stirling's approximation

$$\ln \mathcal{P} = \sum_{\nu}^{\infty} \left[\mathcal{P}_\nu \ln (\mathcal{P}_\nu) - \mathcal{P}_\nu - \sum_{k}^{\infty} \{ n_{k\nu} \ln (n_{k\nu}) - n_{k\nu} \} \right]$$
$$\ln \mathcal{P} = \sum_{\nu}^{\infty} \left[\mathcal{P}_\nu \ln (\mathcal{P}_\nu) - \sum_{k}^{\infty} n_{k\nu} \ln (n_{k\nu}) \right]$$

Since we want to maximize said logarithm with respect to $n_{k\nu}$, we construct the following function using Lagrange's method.

$$F(n_{k\nu}) = \sum_{\nu} \left[\mathcal{P} \ln \mathcal{P}_\nu - \sum_{k} n_{k\nu} \ln n_{k\nu} \right] + \lambda_1 \sum_{k} n_{k\nu} + \lambda_2 h \sum_{v,k} vk n_{k\nu}$$

Setting its derivative to zero

$$\frac{dF}{dn_{k\nu}} = -\ln(n_{k\nu}) - 1 + \lambda_1 + \lambda_2 hk\nu = 0$$

which implies

$$n_{k\nu} = \exp(1 - \lambda_1 - \lambda_2 hk\nu) = C \exp(-\lambda_2 hk\nu)$$

Substituting the result into $\mathcal{P}_\nu$ constraints

$$\mathcal{P}_\nu = C \sum_{k} \exp(-\lambda_2 hk\nu) \implies C = \mathcal{P}_\nu \left[\sum_{k} \exp(-\lambda_2 hk\nu) \right]^{-1}$$

The term inside parenthesis is a geometric series with ratio of $\exp(-\lambda_2 h\nu)$. The constant then can be simply evaluated into

$$C = \mathcal{P}_\nu \left[\frac{1}{1 - \exp(-\lambda_2 h\nu)} \right]^{-1} = \mathcal{P}_\nu \left[1 - \exp(-\lambda_2 h\nu) \right]$$

Hence the $n_{k\nu}$ assumes the form

$$n_{k\nu} = \mathcal{P}_\nu \left[1 - \exp(-\lambda_2 h\nu) \right] \exp(-\lambda_2 hk\nu)$$

On using this to the expression for logarithm of $\mathcal{P}$, we obtain

$$\ln \mathcal{P}_{\max} = \sum_{\nu} \Big[\mathcal{P}_\nu \ln (\mathcal{P}_\nu) - \sum_{k} n_{k\nu} \ln\{ \mathcal{P}_\nu \left[1 - \exp(-\lambda_2 h\nu) \right] \exp(-\lambda_2 hk\nu) \} \Big]$$

Then by definition of Boltzmann entropy, we have

$$S_B = k\ln\mathcal{P}_{\max} = \sum_\nu k\Bigg[\mathcal{P}_\nu \ln(\mathcal{P}_\nu)$$
$$- \sum_k n_{k\nu}\ln\{\mathcal{P}_\nu[1-\exp(-\lambda_2 h\nu)]\exp(-\lambda_2 hk\nu)\}\Bigg]$$

We then write it as such

$$S_B = \sum_\nu k\Bigg[\mathcal{P}_\nu \ln(\mathcal{P}_\nu)$$
$$- \sum_k n_{k\nu}\{\ln(\mathcal{P}_\nu) + \ln(1-\exp\{-\lambda_2 h\nu\}) - \lambda_2 vkh\}\Bigg]$$

additionally

$$S_B = \sum_\nu k\left[\lambda_2 hv\sum_k kn_{k\nu} - \sum_k n_{k\nu}\ln(1-\exp\{-\lambda_2 h\nu\})\right]$$

Recall the $\mathcal{P}_\nu$ and U_ν constraints

$$S_B = k\left[\lambda_2 U - \sum_\nu \mathcal{P}_\nu \ln(1-\exp\{-\lambda_2 h\nu\})\right]$$

Using the following relationship

$$\frac{1}{T} = \frac{\partial S}{\partial U}$$

we have

$$\frac{1}{T} = k\lambda_2 \implies \lambda_2 = \frac{1}{kT}$$

At last, we have

$$n_{k\nu} = \mathcal{P}_\nu\left[1-\exp\left(-\frac{h\nu}{kT}\right)\right]\exp\left(-\frac{hk\nu}{kT}\right)$$

and

$$S_B = \frac{U}{T} - \sum_\nu k\mathcal{P}_\nu \ln\left[1-\exp\left(-\frac{h\nu}{kT}\right)\right]$$

Henceforward, we use these result to evaluate the following quantity. First we evaluate the number of quanta of frequency ν denoted as N_ν

$$N_\nu = \sum_k^\infty kn_{k\nu}$$

Substituting the known value of $n_{k\nu}$, we get

$$N_\nu = \sum_k k\mathcal{P}_\nu\left[1-\exp\left(-\frac{h\nu}{kT}\right)\right]\exp\left(-\frac{hk\nu}{kT}\right)$$
$$= \mathcal{P}_\nu\left[1-\exp\left(-\frac{h\nu}{kT}\right)\right]\sum_k^\infty k\exp\left(-\frac{hk\nu}{kT}\right)$$

To evaluate such sum we consider the geometric series

$$\sum_{k=0}^\infty r^k = \frac{1}{1-r}$$

for $r < 1$. Taking a derivative of both sides to get

$$\sum_{k=0}^{\infty} kr^{k-1} = \frac{1}{(1-r)^2}$$

Then shift the index down by one

$$\sum_{k=-1}^{\infty} (k+1)r^k = \sum_{k=0}^{\infty} (k+1)r^k$$

where the left side is allowed since the series is zero at $k = -1$. Then subtract this series with the first series

$$\sum_{k=0}^{\infty} (k+1)r^k - r^k = \sum_{k=0}^{\infty} kr^k = \frac{1-(1-r)}{(1-r)^2} = \frac{r}{(1-r)^2}$$

Using the formula above, with

$$r = \exp\left(-\frac{h\nu}{kT}\right)$$

we can now evaluate the number of quanta

$$\begin{aligned}
N_\nu &= \mathcal{P}_\nu \left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right] \exp\left(-\frac{h\nu}{kT}\right) \left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right]^{-2} \\
&= \mathcal{P}_\nu \exp\left(-\frac{h\nu}{kT}\right) \left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right]^{-1} \\
&= \mathcal{P}_\nu \left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^{-1}
\end{aligned}$$

$$N_\nu = \sum_k k n_{k\nu} = \frac{\nu^2}{c^3} \frac{8\pi V}{\exp(h\nu/kT) - 1}\, d\nu$$

The second is energy within the same frequency

$$U_\nu = h\nu N_\nu = \frac{\nu^3}{c^3} \frac{8\pi h V}{\exp(h\nu/kT) - 1}\, d\nu$$

To obtain the average energy per unit frequency, we divide U_ν by spatial volume (since we derived it from phase space volume) V and by unit frequency $d\nu$

$$\mathcal{U}(\nu, T) = \frac{U_\nu}{V\, d\nu} = \frac{\nu^3}{c^3} \frac{8\pi h}{\exp(h\nu/kT) - 1}$$

Einstein's Method

Suppose we use Einstein method to rederive Planck's law, just like Bose did. In his method, he distributed the number of identical quanta N_ν within distinct P_ν cells. The number of configuration in this case is given by

$$\mathcal{P}_\nu = \frac{(N_\nu + P_\nu - 1)}{N_\nu!(P_\nu - 1)!}$$

The logarithm for total frequency reads

$$\ln \mathcal{P} = \sum_{\nu} (N_\nu + P_\nu) \ln(N_\nu + P_\nu) - N_\nu \ln(N_\nu) - P_\nu \ln(P_\nu)$$

We want to maximize this logarithm constrained by

$$U = h \sum_{\nu=0}^{\infty} \nu N_\nu$$

The constraints on number of quanta simply does not exist since the quanta continuously created and destroyed by the cavity walls. To maximize the said logarithm, we then construct

$$F = \ln \mathcal{P} + \lambda_1 h \sum_{\nu} \nu N_\nu$$

We then set its derivative to zero

$$\ln(N_\nu + P_\nu) + 1 - \ln(N_\nu) - 1 + \lambda h\nu = 0$$

Hence

$$\frac{N_\nu + P_\nu}{N_\nu} \exp(-\lambda_1 h\nu)$$
$$N_\nu = \frac{P_\nu}{\exp(-\lambda_1 h\nu) - 1}$$

Substituting this into the logarithm of $\mathcal{P}$ to obtain

$$\ln \mathcal{P}_{\max} = \sum_{\nu} \left[N_\nu \left(-\lambda_1 - \lambda_1 E\right) + P_\nu \ln\left(\frac{\exp(-\lambda_1 E)}{\exp(-\lambda_1 E) - 1}\right)\right]$$

The entropy reads

$$S = \sum_{\nu} k_B P_E \ln\left(\frac{\exp(-\lambda_1 E)}{\exp(-\lambda_1 E) - 1}\right) - k_B \lambda_1 U$$

Hence

$$\frac{1}{T} = \frac{\partial S}{\partial U} = -k_B \lambda \implies \lambda_1 = \frac{1}{T}$$

Substituting this constant back, we have

$$N_\nu = \frac{\nu^3}{c^3} \frac{8\pi hV}{\exp(h\nu/k_B T) - 1}\, d\nu, \quad U_\nu = \frac{\nu^3}{c^3} \frac{8\pi hV}{\exp(h\nu/k_B T) - 1}\, d\nu$$

and

$$\mathcal{U}(\nu, T) = \frac{\nu^3}{c^3} \frac{8\pi h}{\exp(h\nu/k_B T) - 1}$$

which is the same as Bose's result.

Rayleigh-Jeans Model

This model is only accurate for large λ or small ν. The energy density described by this model is

$$\mathcal{U}(\lambda, T) = \frac{8\pi}{\lambda^4} kT \quad \text{or} \quad \mathcal{U}(\nu, T) = \frac{8\pi\nu^2}{c^3} kT$$

Derivation. For large λ, the exponential term approaches zero, so it can be approximated with

$$\exp\left(\frac{hc}{\lambda kT}\right) \approx \frac{hc}{\lambda kT} - 1$$

Hence, the energy density as function of wavelength is

$$\mathcal{U}(\lambda, T) \approx \frac{8\pi hc}{\lambda^5} \frac{1}{(hc/\lambda kT)} = \frac{8\pi}{\lambda^4} kT \quad \blacksquare$$

Wien's Law

In other hand, this model only accurate for small λ or large ν. The energy density based this model is

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

Wien's model is able to obtain the fact that the product maximum wavelength and temperature is constant, in particular

$$\lambda_m T = 2.897 \text{ mmK}$$

Derivation. For small λ, the exponential term approach infinity, so the denominator term of the Plack distribution can be approximated with

$$\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1\right]^{-1} \approx \exp\left(-\frac{hc}{\lambda kT}\right)$$

Hence

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

To find the maximum wavelength given by Wien's distribution, we set

$$\frac{du}{d\lambda} = 8\pi hc \left[-\frac{5}{\lambda^6} \exp\left(-\frac{hc}{\lambda kT} +\right) \frac{1}{\lambda^5} \frac{hc}{\lambda^2 kT} \exp\left(-\frac{hc}{\lambda kT} +\right)\right]$$

into zero to obtain

$$\frac{5}{\lambda_m^6} = \frac{hc}{\lambda_m^7 kT}$$

$$\lambda_m T = \frac{hc}{5k} = 2.897 \text{ mmK}$$

Stefan's Law

$$u = \alpha T^4$$

where $\alpha = 1.65 \cdot 10^{-16}$ J/K^{4}m^3.

Derivation. Integrating $\mathcal{U}(\lambda)$ over all possible wavelength to obtain

$$u = \int_0^\infty \frac{8\pi hc}{\lambda^5} \frac{1}{\exp(hc/\lambda kT) - 1} d\lambda$$

Substituting $x = hc/\lambda kT$, we have $1/\lambda = xkT/hc$ and $d\lambda = -hc/x^2kT\ dx$. Thus,

$$\begin{aligned} u &= \int_0^\infty 8\pi hc \left(\frac{xkT}{hc}\right)^5 \frac{1}{e^x - 1} \left(-\frac{hc}{x^2kT}\right) dx \\ &= \frac{8\pi(kT)^4}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1} dx \\ u &= \frac{8\pi(kT)^4}{(hc)^3} 6 \frac{\pi^2}{90} \end{aligned}$$

Evaluating the constant, we finally have

$$u = 7.65 \cdot 10^{-16} T^4 \quad \blacksquare$$

Stefan-Boltzman's Law

$$I = \sigma T^4$$

where $\sigma = 5.57 \cdot 10^{-8}$ J/K^{4}m^2.

Derivation. Based on MB distribution, the flux of a gas is

$$\Gamma = \frac{1}{4} \rho \langle v \rangle$$

On using this to gas of photon we have

$$\Gamma = \frac{1}{4} nc$$

By using the relation

$$\mathcal{U}(\lambda) = n(\lambda) E(\lambda)$$

we have our intensity as

$$I = \frac{1}{4} uc = \frac{1}{4} 7.65 \cdot 10^{-16} T^4 c = 5.57 \cdot 10^{-8}\ T^4$$