

**Blackbody radiation** In his theory of blackbody radiation, energy density at frequency  $\nu$  inside cavity with temperature  $T$  is given by

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

where  $\rho$  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

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

or, we can write it in terms of  $\lambda$

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

## Planck's Derivation

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In his work, Planck assumes that the walls of the cavity act as oscillator with energy of integer multiple  $\epsilon$ . 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.

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

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

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

and then

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

then finally we rewrite it as

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

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  $\epsilon$  is proportional to frequency  $\nu$ . 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

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

Moreover

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

Futhermore

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

Hence

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

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

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

## Bose's Derivation

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

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

or simply

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

where  $N_\nu$  is the number of photon with frequency  $\nu$ . 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  $\nu$ , what we what however distribution over all frequency  $(0, \infty)$ . The expression for constraints is

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

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

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

On using Stirling's approximation

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

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

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

Setting its derivative to zero

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

which implies

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

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

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

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

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

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

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

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

$$\begin{aligned} \ln \mathcal{P}_{\max} = \sum_{\nu} & \left[ \mathcal{P}_{\nu} \ln(\mathcal{P}_{\nu}) \right. \\ & \left. - \sum_k n_{k\nu} \ln\{\mathcal{P}_{\nu} [1 - \exp(-\lambda_2 h \nu)] \exp(-\lambda_2 h k \nu)\} \right] \end{aligned}$$

Then by definition of Boltzmann entropy, we have

$$\begin{aligned} S_B = k \ln \mathcal{P}_{\max} = \sum_{\nu} & k \left[ \mathcal{P}_{\nu} \ln(\mathcal{P}_{\nu}) \right. \\ & \left. - \sum_k n_{k\nu} \ln\{\mathcal{P}_{\nu} [1 - \exp(-\lambda_2 h \nu)] \exp(-\lambda_2 h k \nu)\} \right] \end{aligned}$$

We then write it as such

$$\begin{aligned} S_B = \sum_{\nu} & k \left[ \mathcal{P}_{\nu} \ln(\mathcal{P}_{\nu}) \right. \\ & \left. - \sum_k n_{k\nu} \{\ln(\mathcal{P}_{\nu}) + \ln(1 - \exp\{-\lambda_2 h \nu\}) - \lambda_2 v k h\} \right] \end{aligned}$$

additionally

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

Recall the  $\mathcal{P}_\nu$  and  $U_\nu$  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  $\nu$  denoted as  $N_\nu$

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

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

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

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

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

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

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

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  $U_\nu$  by spatial volume (since we derived it from phase space volume)  $V$  and by unit frequency  $d\nu$

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