Distribution for Boson

The distribution for indistinguishable ideal quantum gas also called the Bose-Einstein distribution. The number particle per unit energy interval is given by

$$n_E = \frac{2\pi}{h^3} \frac{V(2m)^{3/2}\sqrt{E}}{\exp\left[(E - \mu)/k_B T\right] - 1}$$

Energy and Frequency Cells

Quintessential step in Einstein's method is to distribute state of particle into certain cells. There are two kinds of cells, one for distributing particle in terms of their energy P_E and another in terms of their frequency P_ν. For energy, we write

$$P_E = \frac{2\pi}{h^3} V(2m)^{3/2}\sqrt{E} \, dE$$

and for frequency

$$P_\nu = \frac{8\pi V \nu^2}{c^3} \, d\nu$$

Energy Cells derivation. He first considers the energy of non-relativistic particle, which is

$$E = \frac{p^2}{2m}$$

This implies

$$p = \sqrt{2mE}, \quad dp = \frac{m}{p} dE = \frac{m}{\sqrt{2mE}} dE$$

This will be used to determine the volume of $(\mathbf{r}, \mathbf{p} + d\mathbf{p})$ phase space

$$dw = V\frac{4}{3}\pi\left[(p + dp)^3 - p^3\right] = \frac{4}{3}\pi V\left[3p^2 \, dp + 3p \, d^2p + d^3p\right]$$
$$= 4\pi V p^2 \, dp = 4\pi V \, 2mE \, \frac{m}{\sqrt{2mE}} dE = 2\pi(2m)^{3/2}\sqrt{E} \, dE$$

The said volume then divided into cells of h^3 volume. Let this number of distinct cells as

$$P_E = \frac{dw}{h^3} = \frac{2\pi}{h^3} V(2m)^{3/2}\sqrt{E} \, dE$$

Frequency Cells derivation. He considered gas of photon with energy of $E = h\nu$ and momentum $p = h\nu/c$. He assumed that quantum state is described by space and momentum phase space. Next he determined the volume of phase space within interval $(\nu, \nu + d\nu)$, which is

$$dw = V \, d\mathcal{V}$$

where V is the spatial volume and $d\mathcal{V}$ is the momentum volume of the shell within radii $h(\nu + d\nu)/c, h\nu$. The said shell volume is given by

$$
\begin{aligned}
d\mathcal{V} = (\mathcal{V} + d\mathcal{V}) - \mathcal{V} &= \frac{4\pi h^3}{3c^3}\left[(\nu + d\nu)^3 - \nu^3\right] \\
&= \frac{4\pi h^3}{3c^3}\left[3\nu^2\,d\nu + 3\nu\,d^2\nu + d^3\nu\right] = \frac{4\pi h^3}{c^3}\nu^2\,d\nu
\end{aligned}
$$

The resulting volume of phase space $d\omega$ is

$$
d\omega = \frac{4\pi V h^3}{c^3}\nu^2\,d\nu
$$

This volume then divided by Bose into cells of volume h^3. The number P_ν as phase space cells available to the photon within $(\nu, \nu + d\nu)$ expressed by

$$
P_\nu = \frac{2}{c^3}d\omega = \frac{8\pi V \nu^2}{c^3}\,d\nu
$$

where the factor of 2 comes after taking account the two direction of polarization.

Bose's Derivation

The number of configuration $\mathcal{P}_E$ for distributing N_E indistinguishable particle in P_E boxes is given by

$$
\mathcal{P}_E = \frac{(N_E + P_E - 1)}{N_E!(P_E - 1)!}
$$

This gives configuration for particle within $(E, E + dE)$, conversely the total configuration is given by

$$
\mathcal{P} = \prod_{E=0}^{\infty} \mathcal{P}_E
$$

We then move to determining the entropy $S = k_B \ln \mathcal{P}_{\max}$ by maximizing the logarithm of $\mathcal{P}$ with respect to N_E subjected to the following constraints.

$$
N = \sum_{E=0}^{\infty} N_E, \quad U = \sum_{E=0}^{\infty} E N_E
$$

Using Stirling's approximation on said logarithm, we have

$$
\ln \mathcal{P} = \sum_E \ln \frac{(N_E + P_E - 1)}{N_E!(P_E - 1)!}
$$

$$
\ln \mathcal{P} = \sum_E (N_E + P_E)\ln(N_E + P_E) - N_E \ln(N_E) - P_E \ln(P_E)
$$

By Lagrange's method

$$
F = \ln \mathcal{P} + \lambda_1 \sum_E N_E + \lambda_2 \sum_E E N_E
$$

Setting its derivative to zero

$$
\ln(N_E + P_E) + 1 - \ln(N_E) - 1 + \lambda_1 + \lambda_2 E = 0
$$

Taking the exponential and solving for N_E

$$\frac{N_E + P_E}{N_E} = \exp(-\lambda_1 - \lambda_2 E)$$

$$N_E = \frac{P_E}{\exp(-\lambda_1 - \lambda_2 E) - 1}$$

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

$$\ln \mathcal{P}_{\max} = \sum_E \left[(N_E + P_E) \left[\ln(P_E) + \ln \left(\frac{\exp(-\lambda_1 - \lambda_2 E)}{\exp(-\lambda_1 - \lambda_2 E) - 1} \right) \right] \right.$$
$$\left. - P_E \ln(P_E) - N_E \left[\ln(P_E) - \ln \left(\exp\{-\lambda_1 - \lambda_2 E\} - 1 \right) \right] \right]$$

then

$$\ln \mathcal{P}_{\max} = \sum_E \left[(N_E + P_E) \ln \left(\frac{\exp(-\lambda_1 - \lambda_2 E)}{\exp(-\lambda_1 - \lambda_2 E) - 1} \right) \right.$$
$$\left. + N_E \ln \left(\exp\{-\lambda_1 - \lambda_2 E\} - 1 \right) \right]$$

moreover

$$\ln \mathcal{P}_{\max} = \sum_E \left[N_E \left(-\lambda_1 - \lambda_2 E \right) + P_E \ln \left(\frac{\exp(-\lambda_1 - \lambda_2 E)}{\exp(-\lambda_1 - \lambda_2 E) - 1} \right) \right]$$

Hence

$$S = \sum_E k_B P_E \ln \left(\frac{\exp(-\lambda_1 - \lambda_2 E)}{\exp(-\lambda_1 - \lambda_2 E) - 1} \right) - k_B (N \lambda_1 + U \lambda_2)$$

On using the following relations

$$\frac{1}{T} = \left. \frac{\partial S}{\partial U} \right|_{V,N}, \quad -\frac{\mu}{T} = \left. \frac{\partial S}{\partial N} \right|_{U,V}$$

we have

$$\frac{1}{T} = -\lambda_2 k_B \implies \lambda_2 = -\frac{1}{k_B T}$$

and

$$-\frac{\mu}{T} = \lambda_1 k_B \implies \lambda_1 = \frac{\mu}{k_B T}$$

Thus

$$N_E = \frac{2\pi}{h^3} \frac{V (2m)^{3/2} \sqrt{E}}{\exp\left[(E - \mu)/k_B T \right] - 1} \, dE$$

The quantity n_E is defined as the number of molecules per unit energy interval

$$n_E = \frac{N_E}{dE} = \frac{2\pi}{h^3} \frac{V (2m)^{3/2} \sqrt{E}}{\exp\left[(E - \mu)/k_B T \right] - 1} \qquad \blacksquare$$

Distribution for Distinguishable Particle

The distribution function is given by

$$n_E = \left(\frac{\sqrt[3]{4} N^{2/3}}{\sqrt{\pi} k_B T} \right)^{3/2} \sqrt{E} \exp \left(-\frac{E}{k_B T} \right)$$

Derivation. The number of way to distribute N_E distinct particle into P_E distinct cells is

$$\mathcal{P}_e = P_E^{N_E}$$

where

$$P_E = \frac{2\pi}{h^3} V (2m)^{3/2} \sqrt{E} \; dE$$

Hence the number of distribution for all energy interval is

$$\mathcal{P}_E = \prod_{E=0}^{\infty} P_E^{N_E}$$

The total number of configuration is obtained by multiplying the number of configuration for distinct case $\mathcal{P}_E$ by the number of ways to distribute N_E particle from N

$$\mathcal{P} = \prod_E P_E^{N_E} N! \left(\prod_E N_E! \right)^{-1}$$

By applying Stirling's approximation, the logarithm reads

$$\ln \mathcal{P} = \sum_E N_E \ln P_E + N \ln N - N - \sum_E N_E \ln N_E + N_E$$

$$\ln \mathcal{P} = \sum_E N_E \ln \left(\frac{P_E}{N_E} \right) + N \ln(N)$$

Then define the following function according to Lagrange's method

$$F = \sum_E N_E \ln \left(\frac{P_E}{N_E} \right) + N \ln(N) + \lambda_1 \sum_E N_E + \lambda_2 \sum_E E N_E$$

where we have used the N and U constraints. Then set its derivative to zero

$$\ln \left(\frac{P_E}{N_E} \right) - 1 + \lambda_1 + \lambda_2 E = 0$$

Solving for N_E

$$\frac{P_E}{N_E} = C_1 \exp \left(-\lambda_2 E \right)$$

$$N_E = P_E C_2 \exp \left(-\beta E \right)$$

Inserting this into N constraint

$$N = \sum_E P_E C_2 e^{-\beta E} = \frac{2\pi}{h^3} V (2m)^{3/2} C_2 \int_0^{\infty} \sqrt{E} e^{-\beta E} \; dE$$

The integral is solved as follows. Consider

$$I = \int_0^\infty \sqrt{x}\, e^{-ax}\, dx$$

Make change of variable $u = -ax$. We have then $d\alpha = -a\,dx$ and $\sqrt{x} = i\sqrt{\alpha/a}$. The integral then reads

$$I = -\frac{i}{a^{3/2}} \int_0^{-\infty} \sqrt{\alpha}\, e^\alpha\, d\alpha$$

By choosing $u = \sqrt{\alpha}$ and $dv = e^\alpha$, consequently we have $du = 1/2\sqrt{\alpha}$ and $v = e^\alpha$. Using method of integral by parts,

$$I = -\frac{i}{a^{3/2}} \left[e^\alpha \sqrt{\alpha} \Big|_0^{-\infty} - \int_0^{-\infty} \frac{e^\alpha}{2\sqrt{\alpha}}\, d\alpha \right] = \frac{i}{2a^{3/2}} \int_0^{-\infty} \frac{e^\alpha}{\sqrt{\alpha}}\, d\alpha$$

We again make the change of variable $t^2 = \alpha$; which implies $d\alpha = 2t\,dt$. Although in this case, the lower limit remains the same, namely zero, the upper limit has two possible value due to quadratic nature of our variable

$$t^2 = -\infty \implies t = \pm\infty i$$

The value we pick is the negative one; this is due to the nature of logarithm. Recalling the definition of imaginary error function. The integral above can be recast as

$$I = \frac{i}{a^{3/2}} \int_0^{-\infty i} e^{t^2}\, dt = \frac{i\pi}{2a^{3/2}} \operatorname{erfi}(-\infty i)$$

Hence, the result is

$$I = \frac{\pi}{2a^{3/2}}$$

a positive value. For positive value $t = -\infty i$, the resulting integral will be negative instead. We want the positive value of the integral since we will be taking the logarithm. Positive argument will ensure the value of our logarithm is real, since it represent the logarithm of number a configuration, which is positive real.

Now plugging the result of previous integral, we have

$$N = \frac{2\pi}{h^3} V (2m)^{3/2} C_2 \frac{\sqrt{\pi}}{2\beta^{3/2}} = C_2 V \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2}$$

or by solving of C_2,

$$C_2 = \frac{N}{V} \left(\frac{h^2 \beta}{2\pi m} \right)^{3/2}$$

And by plugging this into N_E, we also have

$$N_E = \frac{N}{V} P_E \exp(-\beta E) \left(\frac{h^2 \beta}{2\pi m} \right)^{3/2}$$

The logarithm of maximum configuration then

$$\ln \mathcal{P}_{\max} = \sum_E N_E \ln \left[\frac{V}{N} \exp(\beta E) \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} \right] + N \ln(N)$$

$$\ln \mathcal{P}_{\max} = N \ln(V) + \frac{3}{2} N \ln \left(\frac{2\pi m}{h^2 \beta} \right) + \beta U$$

As for the entropy

$$S = Nk_B \ln(V) + \frac{3}{2} Nk_B \ln\left(\frac{2\pi m}{h^2\beta}\right) + k_B\beta U$$

Using the thermodynamics relationship of

$$\frac{1}{T} = \frac{\partial S}{\partial U}\bigg|_{V,N} = k_B U \implies \beta = \frac{1}{T}$$

Now the number of particle within $(\nu, \nu + d\nu)$ can be evaluated as

$$N_E = \frac{N}{V}\frac{2\pi}{h^3} V (2m)^{3/2} \sqrt{E} \exp\left(-\frac{E}{k_B T}\right) \left(\frac{h^2}{2\pi k_B Tm}\right)^{3/2} dE$$

$$N_E = \left(\frac{\sqrt[3]{4} N^{2/3}}{\sqrt{\pi} k_B T}\right)^{3/2} \sqrt{E} \exp\left(-\frac{E}{k_B T}\right) dE$$

and the distribution function as

$$n_E = \left(\frac{\sqrt[3]{4} N^{2/3}}{\sqrt{\pi} k_B T}\right)^{3/2} \sqrt{E} \exp\left(-\frac{E}{k_B T}\right)$$

We can also recover the ideal gas law using the thermodynamics relationship

$$\frac{P}{T} = \frac{\partial S}{\partial V}\bigg|_{S,N} = \frac{Nk_B}{V} \implies PV = Nk_B T$$