

## Distribution for Boson

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The distribution for indistinguishable ideal quantum gas—also called boson—the Bose-Einstein distribution. In general, the number of particle per unit energy interval is given by

$$n(E) = \frac{g(E)}{\exp[(E - \mu)/k_B T] - 1}$$

For a free bosonic gas, the density state is

$$g(E) = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$

then the distribution function simply evaluate into

$$n(E) = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \frac{E^{1/2}}{\exp[(E - \mu)/k_B T] - 1}$$

## Energy and Frequency Cells

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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  $P_\nu$ . 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

$$\begin{aligned} d\omega &= V \frac{4}{3} \pi [(p + dp)^3 - p^3] = \frac{4}{3} \pi V [3p^2 dp + 3p d^2 p + d^3 p] \\ &= 4\pi V p^2 dp = 4\pi V 2mE \frac{m}{\sqrt{2mE}} dE = 2\pi (2m)^{3/2} \sqrt{E} dE \end{aligned}$$

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

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

**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

$$d\omega = V d\mathcal{V}$$

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

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

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  $P_\nu$  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

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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

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

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  $N_E$

$$\begin{aligned} \frac{N_E + P_E}{N_E} &= \exp(-\lambda_1 - \lambda_2 E) \\ N_E &= \frac{P_E}{\exp(-\lambda_1 - \lambda_2 E) - 1} \end{aligned}$$

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

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

then

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

moreover

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

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

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

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

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

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

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

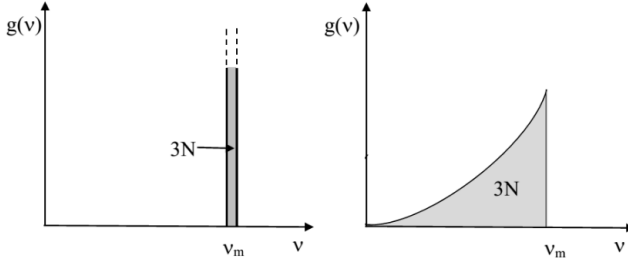


Figure: Density of state based on Einstein's and Debye's model.

## Phonon

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A phonon is a quantum mechanical quantization of the modes of vibrations for elastic structures of interacting particles. Phonons behave as a quasi particle that carries energy and momentum.

As quantized lattice vibrations, phonons can have three polarization directions: one direction of longitudinal and two for transversal, all with respect to the direction of propagation. Thus, for  $N$  phonons, the total state of frequency is  $3N$ . Two of the popular model for the frequency density of state is Einstein's and Debye.

**Einstein's model.** Here, he assumed that all the  $3N$  oscillator oscillate with the same frequency. Thus, all the  $3N$  state is equal to  $\nu_m$

$$g(\nu) = 3N\delta(\nu - \nu_m)$$

**Debye's model.** Unlike Einstein, he assumed that the density of state is quadratic up to maximum frequency  $\nu_m$ . The said density of state is given by

$$g(\nu) = \begin{cases} \frac{9N}{\nu_m^3} \nu^2, & \nu \leq \nu_m \\ 0, & \nu_m < \nu \end{cases}$$

To derive said DoS, recall that it is proportional to the square of frequency. Hence, the DoS assumes the form of

$$g(\nu) = A\nu^2$$

On integrating this within all allowed frequency  $(0, \nu_m)$ , we have

$$3N = \int_0^{\nu_m} A\nu^2 d\nu = A\frac{1}{3}\nu_m^3$$

Then simply solve for the constant

$$A = \frac{9N}{\nu_m^3}$$

## Einstein' Solid

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Einstein's theory on solid is only accurate for large  $T$ , experimental data disagree with his theory for small  $T$ . On using the DoS given by

Einstein's model, the phonon density reads

$$n(\nu) = \frac{3N\delta(\nu - \nu_m)}{\exp(h\nu/kT) - 1}$$

We determine the total energy of given phonon as

$$E = \int_0^\infty E(\nu)n(\nu) d\nu$$

Using said distribution

$$E = \int_0^{\nu_m} h\nu \frac{3N\delta(\nu - \nu_m)}{\exp(h\nu/kT) - 1} d\nu$$

$$E = \frac{3Nh\nu_m}{\exp(h\nu_m/kT) - 1}$$

The experimental data that was mentioned prior takes the form of heat capacitance, hence Einstein's theory should give the heat capacitance by using the definition

$$C_V = \left. \frac{\partial E}{\partial T} \right|_{V, N=N_A}$$

**Large temperature.**

**Small temperature.**

## Debye's Solid

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Unlike Einstein's theory, Debye's theory agree with experimental data for both low and high  $T$ . Let us consider the phonon density

$$n(\nu) = \frac{9N}{\nu_m^3} \frac{\nu^2}{\exp(h\nu/kT) - 1} \quad \nu \leq \nu_m$$

Then the total energy

$$E = \int_0^{\nu_m} \frac{9Nh}{\nu_m^3} \frac{\nu^3}{\exp(h\nu/kT) - 1} d\nu$$

Since the integral is expressed as incomplete Riemann-Zeta function, we need some simplification. In other word, we make assumption.

**Large temperature.** For this case, the exponential term is small, hence it can be approximated with

$$\exp\left(\frac{h\nu}{kT}\right) = 1 + \frac{h\nu}{kT}$$

Thus the integral simplifies into

$$E = \frac{9Nh}{\nu_m^3} \int_0^{\nu_m} \frac{\nu^3}{h\nu/kT} d\nu = \frac{9N}{\nu_m^3} kT \frac{1}{3} \nu_m^3 = 3NkT = 3RT$$

And we also have the heat capacitance of

$$C_V = 3R$$

**Small temperature.**