Zero Point Energy: Thermodynamic Equilibrium and Planck Radiation Law

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Abstract: In a recent paper, we proved that Planck's radiation law with zero point energy is equivalent to the combined assumptions of zero point energy hypothesis, the quantum law and the approximated Boson statistics.

Here, we apply the principle of maximal entropy to show that Planck's radiation law with zero point energy represents a state of thermodynamic equilibrium.

Introduction In a recent paper [1], we proved that Planck's radiation law with zero point energy [2] is equivalent to the combined assumptions of the zero point energy hypothesis, the quantum law and the approximated Boson statistics.

Planck applied the principle of maximal entropy to a volume in space, to obtain the state of thermodynamic equilibrium for ideal mono-atomic gases [3].

Bose, in a 1924 paper, translated and published by Einstein [4], applied the principle of maximal entropy to a volume in phase space to obtain Planck's radiation law at a state of thermodynamic equilibrium.

We apply the principle of maximal entropy in phase space to show that Planck's radiation law with zero point energy is obtained at a state of thermodynamic equilibrium.

Here, the maximal entropy principle is only a tool, that does not replace any of the three combined assumptions that we proved equivalent to the radiation law with zero point energy. Under the three assumptions, the principle of maximal entropy implies that the radiation law with zero point energy is obtained at a state of thermodynamic equilibrium.

Maximal Entropy and ZPE radiation law:

Following Bose approach in [4], elaborated by Einstein in [5], the momentum of a radiation quantum is

$$p = \left| \overrightarrow{p} \right| = \frac{hv}{c} \,.$$

That is, radiation quanta with the same momentum are on the surface of the sphere

$$p_x^2 + p_y^2 + p_z^2 = \frac{h^2 v^2}{c^2}.$$

Then, for each of its two polarizations, the momentum of the radiation per volume element, in the spherical shell between v, and v + dv, is

$$4\pi p^2 dp = 4\pi \frac{h^2 v^2}{c^2} \frac{h}{c} dv = 4\pi \frac{v^2 dv}{c^3} h^3.$$

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Therefore, for both polarizations, there are $8\pi \frac{v^2 dv}{c^3}$ momentum cells of size h^3 per volume element in the spherical shell between v, and v + dv.

For the possible frequencies v_l , l = 0, 1, 2, ... there are

$$n_l = 8\pi \frac{v_l^2 dv_l}{c^3}$$

momentum cells of size h^3 , per volume element, in the spherical shell between v_i , and $v_i + dv_i$.

Then,

$$n_{l} = n_{l}^{(0)} + n_{l}^{(1)} + n_{l}^{(2)} + \dots = \sum_{j=0}^{\infty} n_{l}^{(j)}, \quad (1)_{l}$$

where

 $n_l^{(0)}$ is the number of cells that have no quanta,

 $n_l^{(1)}$ is the number of cells that have one quanta,

 $n_t^{(2)}$ is the number of cells that have two quanta,

•••••

The n_i momentum cells of size h^3 , per volume element, in the spherical shell between v_i and $v_i + dv_i$, can be arranged in

$$\frac{n_l!}{n_l^{(0)}!n_l^{(1)}!n_l^{(2)}!...} = n_l!\prod_{j=0}^{\infty}\frac{1}{n_l^{(j)}!}$$

ways.

Thus, all the momentum cells of size h^3 , per volume element, can be arranged in

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$$w = \prod_{l=0}^{\infty} n_l ! \prod_{j=0}^{\infty} \frac{1}{n_l^{(j)} !}$$

ways.

The entropy per volume element is

$$s = k_B \log w = k_B \sum_{l=0}^{\infty} \log(n_l !) - k_B \sum_{l=0}^{\infty} \sum_{j=0}^{\infty} \log(n_l^{(j)} !),$$

where k_B is Boltzman constant.

By Sterling's formula $\ln M! \approx M \ln M - M$,

$$s \approx k_{B} \sum_{l=0}^{\infty} (n_{l} \log n_{l} - n_{l}) - k_{B} \sum_{l=0}^{\infty} \sum_{j=0}^{\infty} (n_{l}^{(j)} \log n_{l}^{(j)} - n_{l}^{(j)})$$
$$= k_{B} \sum_{l=0}^{\infty} n_{l} \log n_{l} - k_{B} \sum_{l=0}^{\infty} \sum_{j=0}^{\infty} n_{l}^{(j)} \log n_{l}^{(j)}.$$

The number of radiation quanta hv_l between v_l , and $v_l + dv_l$ is

$$n_l^{(1)} + 2n_l^{(2)} + 3n_l^{(3)} + \dots = \sum_{j=0}^{\infty} jn_l^{(j)}$$

Following Planck's assumption of Zero Point Energy [2], we assume zero point energy of $\frac{1}{2}hv_i$ in each of the n_i momentum cells of size h^3 , per volume element, between v_i and $v_i + dv_i$, Therefore, the radiation energy per volume element is

$$u = \sum_{l=0}^{\infty} h v_l \sum_{j=0}^{\infty} j n_l^{(j)} + \sum_{l=0}^{\infty} \frac{1}{2} h v_l n_l = \sum_{l=0}^{\infty} h v_l \left(\sum_{j=0}^{\infty} j n_l^{(j)} + \frac{1}{2} n_l \right).$$
(2)

At thermal equilibrium, the entropy has a maximum under the constraints $(1)_l \ l = 0, 1, 2, ...$, on the number of momentum cells, and the constraint (2), on the radiation energy.

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To find that maximum, we apply the Lagrange multiplier method with multipliers λ_l , l = 0, 1, 2, ..., for the constraints $(1)_l$ l = 0, 1, 2, ..., and $\beta > 0$, for the constraint (2), to the auxiliary function

$$F(n_{l}^{(j)},\lambda_{l},\beta) = \sum_{l=0}^{\infty} n_{l} \log n_{l} - \sum_{l=0}^{\infty} \sum_{j=0}^{\infty} n_{l}^{(j)} \log n_{l}^{(j)} + \sum_{l=0}^{\infty} \lambda_{l} (n_{l} - \sum_{j=0}^{\infty} n_{l}^{(j)}) + \beta (u - \sum_{l=0}^{\infty} hv_{l} \sum_{j=0}^{\infty} (j + \frac{1}{2}) n_{l}^{(j)}).$$

The critical points are at

$$0 = \frac{\partial F}{\partial n_l^{(j)}} = -\log n_l^{(j)} - 1 - \lambda_l - \beta (j + \frac{1}{2}) h v_l, \quad (3)$$
$$0 = \frac{\partial F}{\partial \lambda_l} = n_l - \sum_{j=0}^{\infty} n_l^{(j)}, \quad (4)$$
$$0 = \frac{\partial F}{\partial \beta} = u - \sum_{l=0}^{\infty} h v_l \sum_{j=0}^{\infty} (j + \frac{1}{2}) n_l^{(j)}. \quad (5)$$

From (3),

$$\log n_{l}^{(j)} = -1 - \lambda_{l} - \beta (j + \frac{1}{2}) h v_{l}, (6)$$

or,

$$n_{l}^{(j)} = e^{-1 - \lambda_{l} - \frac{1}{2}\beta h v_{l}} e^{-j\beta h v_{l}} .$$
 (7)

By (5), and (6),

$$n_{l} = \sum_{j=0}^{\infty} n_{l}^{(j)} = e^{-1-\lambda_{l} - \frac{1}{2}\beta hv_{l}} \sum_{j=0}^{\infty} e^{-j\beta hv_{l}} = \frac{e^{-1-\lambda_{l} - \frac{1}{2}\beta hv_{l}}}{1 - e^{-\beta hv_{l}}} = \frac{e^{-1-\lambda_{l} + \frac{1}{2}\beta hv_{l}}}{e^{\beta hv_{l}} - 1} .$$
(8)

Therefore,

$$1 + \lambda_{l} + \log n_{l} = \log \frac{e^{\frac{1}{2}\beta hv_{l}}}{e^{\beta hv_{l}} - 1}.$$
 (9)

The quotient

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$$\frac{n_l^{(j)}}{\sum_{j=0}^{\infty} n_l^{(j)}} = e^{-(j+1)\beta h v_l} \frac{1}{e^{\beta h v_l} - 1}$$

is the Bose-Einstein distribution function.

By (8),

$$\sum_{j=0}^{\infty} j n_l^{(j)} = e^{-1-\lambda_l - \frac{1}{2}\beta h v_l} \sum_{j=0}^{\infty} j e^{-j\beta h v_l} = n_l (1 - e^{-\beta h v_l}) \sum_{j=1}^{\infty} (-\frac{d}{d(\beta h v_l)} e^{-j\beta h v_l}).$$

The series $\sum_{j=1}^{\infty} e^{-j\beta hv_l}$ converges uniformly to $\frac{1}{1-e^{-\beta hv_l}}$, and can be

differentiated term by term with respect to $\xi \equiv \beta h v_i$. Thus,

$$\sum_{j=1}^{\infty} \left(-\frac{d}{d(\beta h v_l)} e^{-j\beta h v_l} \right) = -\frac{d}{d\xi} \sum_{j=0}^{\infty} e^{-j\xi} = -\frac{d}{d\xi} \frac{1}{1 - e^{-\xi}} = \frac{e^{-\xi}}{\left(1 - e^{-\xi}\right)^2}.$$

Therefore,

$$\sum_{j=0}^{\infty} j n_l^{(j)} = n_l (1 - e^{-\beta h v_l}) \frac{e^{-\beta h v_l}}{(1 - e^{-\beta h v_l})^2} = \frac{n_l}{e^{\beta h v_l} - 1}.$$
 (10)

By (5), and (4), and (10),

$$u = \sum_{l=0}^{\infty} hv_l \sum_{j=0}^{\infty} (j + \frac{1}{2}) n_l^{(j)} = \sum_{l=0}^{\infty} n_l hv_l (\frac{1}{e^{\beta hv_l} - 1} + \frac{1}{2}).$$
(11)

By (6),

$$s \approx k_B \sum_{l=0}^{\infty} n_l \log n_l - k_B \sum_{l=0}^{\infty} \sum_{j=0}^{\infty} n_l^{(j)} \left(-1 - \lambda_l - \beta (j + \frac{1}{2}) h v_l \right)$$
$$= k_B \sum_{l=0}^{\infty} n_l \left(1 + \lambda_l + \log n_l \right) + k_B \beta \sum_{l=0}^{\infty} h v_l \sum_{j=0}^{\infty} (j + \frac{1}{2}) n_l^{(j)} .$$

Substituting (9), and (10), and (4),

$$s(\beta) = k_B \sum_{l=0}^{\infty} n_l \log \frac{e^{\frac{1}{2}\beta l N_l}}{e^{\beta l N_l} - 1} + k_B \beta \sum_{l=0}^{\infty} n_l h v_l (\frac{1}{e^{\beta l N_l} - 1} + \frac{1}{2})$$

Using (11),

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$$s(\beta) = k_B \sum_{l=0}^{\infty} n_l \log \frac{e^{\frac{1}{2}\beta h v_l}}{e^{\beta h v_l} - 1} + k_B \beta u .$$
(12)

Hence,

$$\frac{1}{T} = \frac{\partial s}{\partial u} = k_B \beta \; .$$

That is,

$$\beta_{\max} = \frac{1}{k_B T},$$

and β_{max} is positive as required. Then,

$$s(\beta_{\max}) = k_B \sum_{l=0}^{\infty} n_l \log \frac{e^{\frac{1}{2}l\nu_l/k_B T}}{e^{l\nu_l/k_B T} - 1} + \frac{u}{T}$$
(13)

is the maximal entropy.

To confirm that the entropy is maximal, we recall that the Lagrange multiplier method produces either a maximum or a minimum for the function in question, which here is the entropy. Thus, to confirm a maximum, it is enough to check the value of the entropy at any other point. For instance, take

$$\beta = 1$$
.

Then,

$$\frac{e^{hv_l/2}}{e^{hv_l}-1} < \frac{e^{hv_l/2k_BT}}{e^{hv_l/k_BT}-1},$$

and for $k_B T < 1$,

$$s(1) = k_B \sum_{l=0}^{\infty} n_l \log \frac{e^{\frac{1}{2}hv_l}}{e^{hv_l} - 1} + k_B u < k_B \sum_{l=0}^{\infty} n_l \log \frac{e^{\frac{1}{2}hv_l/k_B T}}{e^{hv_l/k_B T} - 1} + \frac{u}{T} = s(\beta_{\max}).$$

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Therefore, at $\beta = \beta_{max}$, the entropy is maximal, and at the attained thermodynamic equilibrium

$$u(\beta_{\max}) = \sum_{l=0}^{\infty} n_l h v_l \left(\frac{1}{e^{h v_l / k_B T} - 1} + \frac{1}{2}\right) = \sum_{l=0}^{\infty} n_l \overline{\varepsilon_v}.$$

Then,

$$\overline{\varepsilon_{v}} = hv_{l}\left(\frac{1}{e^{hv_{l}/k_{B}T} - 1} + \frac{1}{2}\right)$$

is Planck's radiation law with zero point energy.

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