Chemical potential of photon gas (zero)

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The chemical potential of photon gas is zero. Here I collected several proofs from references. I like #1 (thermodynamics) and #8 (by Robertson). I understand that so many people try to explain using a variety of methods why the chemical potential of photon gas is zero.

1. Chemical potential of photon (thermodynamics)

We show that the chemical potential of photon is zero;

$$\mu = 0.$$

We know that

$$PV = \frac{1}{3}U$$

where $U = \alpha T^4$ and α is constant.

$$G = \mu N = F + PV = U - ST + \frac{1}{3}U = \frac{4}{3}U - ST$$

The entropy S is

$$dS = \frac{dU}{T} = \frac{4\alpha T^3}{T}dT = 4\alpha T^2 dT$$

So we get

$$S = \int dS = \int 4\alpha T^2 dT = \frac{4\alpha}{3}T^3 = \frac{4U}{3T}$$

The Helmholtz free energy is

$$F = U - ST = U - \frac{4}{3}U = -\frac{1}{3}U$$

The substitution of S to the expression of G is

$$G = \mu N = \frac{4}{3}U - \frac{4}{3}U = 0$$

The chemical potential is zero.

2. Discussion by Kubo

The equilibrium value of the total number of photons can be determined by the condition of minimizing the Helmholtz free energy $F(T,V,N)$, if one uses a method which allows an approximate calculation of the canonical partition function by its maximum term,

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = 0$$

This is merely the relation $\mu = 0$.

3. Method of Lagrange multiplier (Kubo)

The number of photons in a container is not a constant but only its average value is determined as a function of container volume *V* and the temperature *T*. This is because the photons (light) are emitted and absorbed by the matter inside or by the surface of the walls of the container. Hence one should omit the condition that the total number *N* = constant in the procedure for the derivation of the Bose-Einstein distribution (Lagrange undetermined multiplier method) . Accordingly, the chemical potential which is to be introduced as a Lagrange multiplier drops out from the Bose-Einstein distribution. This is equivalent to putting $\mu = 0$.

4. Planck's distribution function

We consider a system consists of *f* harmonic oscillators (with the same ω)

For each oscillator, the energy is quantized as

$$\hat{H}|n\rangle = \hbar\omega n|n\rangle = \varepsilon_n|n\rangle$$

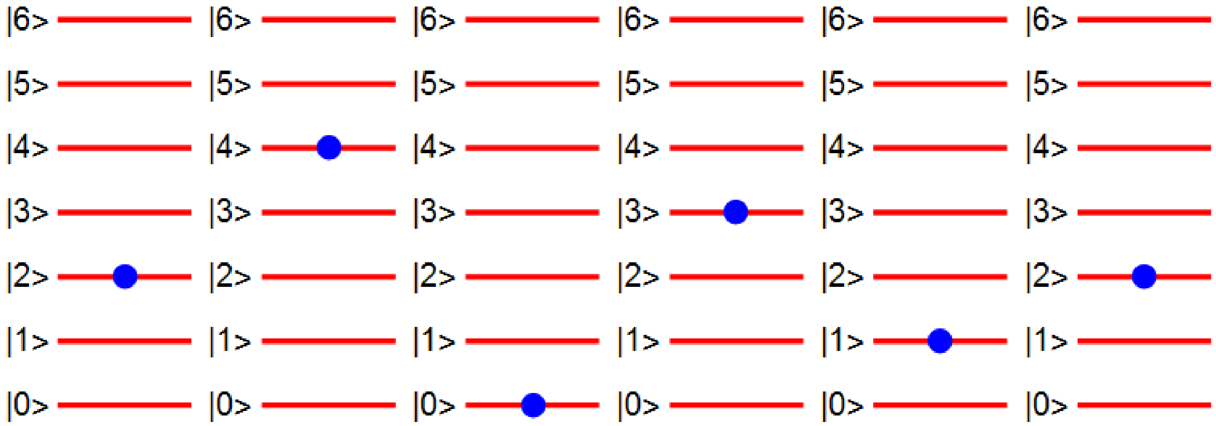
where $|n\rangle$ is the eigenstate of the Hamiltonian with the energy eigenvalue $\varepsilon_n = n\hbar\omega$. *n* is the integer; *n* = 0, 1, 2, ….

Suppose that m_i is the number of oscillators with the energy ε_i.

The total number of simple harmonic oscillators is

$$f = m_0 + m_1 + m_2 + \dots,$$

State $\left|\varepsilon_0\right\rangle$ with energy ε_0 level m_0 oscillators
State $\left|\varepsilon_1\right\rangle$ with energy ε_1 level m_1 oscillators
……………………………………..



The total energy for this configuration is

$$E = \varepsilon_0 m_0 + \varepsilon_1 m_1 + \varepsilon_2 m_2 + \dots\dots$$

The way to choose m_i oscillators in the same state $\left|\varepsilon_i\right\rangle$ is evaluated as

$$\frac{f!}{m_0! m_1! m_2! \dots} \delta_{m_0 + m_1 + m_2 + \dots +, f}$$

where these oscillators are distinguishable. Then the partition function for the simple harmonics can be obtained as

$$\begin{aligned}
Z_C(\beta) &= \sum_{m_0} \sum_{m_1} \dots \sum_{m_s} \frac{f!}{m_0! m_1! \dots} \exp[-\beta(\varepsilon_0 m_0 + \varepsilon_1 m_1 + \varepsilon_2 m_2 + \dots\dots)] \delta_{m_0 + m_1 + m_2 + \dots +, f} \\
&= \sum_{m_0} \sum_{m_1} \dots \sum_{n_s} \frac{f!}{m_0! m_1! \dots} [\left(e^{-\beta\varepsilon_0}\right)^{m_0} \left(e^{-\beta\varepsilon_1}\right)^{m_1} ..] \delta_{m_0 + m_1 + m_2 + \dots +, f} \\
&= \left(e^{-\beta\varepsilon_0} + e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + \dots\right)^f \\
&= [Z_{C1}(\beta)]^f
\end{aligned}$$

where $\beta = \frac{1}{k_B T}$. $\delta_{m_0+m_1+m_2+...+,f}$ means the condition of total oscillator number being kept constant. We note that $Z_{C1}(\beta)$ is the partition function for the one-oscillator system.

$$\begin{aligned} Z_{C1}(\beta) &= \sum_n e^{-\beta\varepsilon_n} \\ &= \sum_n e^{-n\beta\hbar\omega} \\ &= (1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + ...) \\ &= \frac{1}{1 - e^{-\beta\hbar\omega}} \end{aligned}$$

or

$$Z_{C1}(\beta) = \frac{e^{\beta\hbar\omega}}{e^{\beta\hbar\omega} - 1}$$

and

$$Z_C(\beta) = \left(\frac{e^{\beta\hbar\omega}}{e^{\beta\hbar\omega} - 1} \right)^f$$

The internal energy is

$$\frac{U}{f} = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} = \hbar\omega\langle n \rangle$$

with

$$\langle n \rangle = \frac{1}{e^{\beta\hbar\omega} - 1}$$

which is the distribution function for an ideal gas with $\mu = 0$.

5. Discussion by Schroeder

We consider the Helmholtz free energy *F*, which must attain the minimum possible value at equilibrium with *T* and *V* held fixed. In a system of photons, the number *N* of photons is not constrained, but rather takes whatever value will minimize *F*. If *N* then changes infinitesimally, *F* should be unchanged:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = 0 \qquad \text{(at equilibrium)}$$

This partial derivative is precisely equal to the chemical potential.

A second argument makes use of the condition for chemical equilibrium. Consider a typical reaction in which a photon (γ) is created or absorbed by an electron;

$$e \leftrightarrow e + \gamma \qquad \text{(reaction)}$$

The equilibrium condition for such a reaction is the same as the reaction equation, with the name of each species replaced by its chemical potential. In this case

$$\mu_e = \mu_e + \mu_\gamma \qquad \text{(equilibrium)}$$

In other words, the chemical potential for photons is zero.

By either argument, the chemical potential for a gas of photon inside a box at fixed temperature is zero, so the Bose-Einstein distribution reduces to the Planck's distribution, as required.

6. Discussion by Landau and Lifshitz

It should be mentioned that at least a small amount of matter must be present if thermal equilibrium is to be reached in the radiation, since the interaction between the photons themselves may be regarded as completely absent. The mechanics by which equilibrium can be established consists in absorption and emission of photons by matter. This result in an important specific property of the photon gas: the number of photons N in it is variable, and not a given constant as in an ordinary gas. Thus N itself must be determined from the conditions of thermal equilibrium. From the condition that the free energy of the gas should be minimum (for given T and V), we obtain as one of the necessary conditions,

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu = 0$$

This gives $\mu = 0$, i.e. the chemical of the photon gas is zero.

The distribution of photons among the various quantum states with definite values of the momentum $\hbar \boldsymbol{k}$ and energy $\varepsilon = \hbar\omega_{\boldsymbol{k}}$ (and definite polarization) is therefore given by the formula with $\mu = 0$

$$\langle n_{\boldsymbol{k}} \rangle = \frac{1}{e^{\beta\hbar\omega_{\boldsymbol{k}}} - 1} \qquad \text{(Planck's distribution function)}$$

6. Discussion by Baierlein

The key insight is that photons are not subject to a conservation law for number. The atoms in a container wall readily absorb and emit photons. Even if one invoked energy conservation, an atom could absorp one photon of high energy and emit two photons, each of lower energy. In the calculation of photon gas, we consider all conceivable numbers of photons in each possible mode and weighted the corresponding states by the probability of occurrence according to the canonical probability distribution. The calculation presumes that we know the volume *V* of the container and the temperature *T*, a temperature common to both walls and photon gas. At thermal equilibrium, everything about a photon gas is determined by *T* and *V*. Given this information, we can readily compute the chemic al potential for a photon gas. In general, for a gas consisting of a single species of particle, the Helmholtz free energy is a function of the set {*T*, *V*, *N*}. Because everything about a photon gas is determined by *T* and *V*, its Helmholtz free energy must be a function of *T* and *V* only.

$$F_{photon\ \mathrm{gas}} = F(T,V)$$

The chemical potential now follows from

$$\mu = \left(\frac{\partial F_{photon\ \mathrm{gas}}}{\partial N} \right)_{T,V} = 0$$

because $F_{photon\ \mathrm{gas}}$ does not depend on *N*.

8. Discussion by Robertson

In general, even without good input data for $\langle N \rangle$, it is possible to use the grand canonical formalism as if $\langle N \rangle$ were a valid number. But after the formal results, the required step is the minimization of the Helmholtz free energy at constant volume and constant temperature, in order to find the equilibrium value of *z* or *μ*, since, in the absence of a valid input constraint for $\langle N \rangle$, the correct equilibrium state is the one that minimizes *F*.

In the Grand canonical ensemble, we have

$$G = F + PV = \mu\langle N \rangle$$

The Helmholtz free energy is

$$
\begin{aligned}
F &= -PV + \mu\langle N\rangle \\
&= k_B T[\langle N\rangle \ln z - \ln Z_G]
\end{aligned}
$$

From this expression, the derivative gives

$$
\begin{aligned}
\left(\frac{\partial F}{\partial\langle N\rangle}\right)_{T,V} &= \left(\frac{\partial F}{\partial\langle N\rangle}\right)_{\alpha} \\
&= \frac{\partial(F,\alpha)}{\partial(\langle N\rangle,\alpha)} \\
&= \frac{\dfrac{\partial(F,\alpha)}{\partial(z,\alpha)}}{\dfrac{\partial(\langle N\rangle,\alpha)}{\partial(z,\alpha)}}
\end{aligned}
$$

or

$$
\begin{aligned}
\left(\frac{\partial F}{\partial\langle N\rangle}\right)_{\alpha} &= \frac{\left(\dfrac{\partial F}{\partial z}\right)_{\alpha}}{\left(\dfrac{\partial\langle N\rangle}{\partial z}\right)_{\alpha}} \\
&= \frac{k_B T}{\left(\dfrac{\partial\langle N\rangle}{\partial z}\right)_{\alpha}}[\left(\frac{\partial}{\partial z}\right)_{\alpha}[\langle N\rangle \ln z - \ln Z_G] \\
&= \frac{k_B T}{\left(\dfrac{\partial\langle N\rangle}{\partial z}\right)_{\alpha}}[\frac{1}{z}\langle N\rangle + \left(\frac{\partial\langle N\rangle}{\partial z}\right)_{\alpha}\ln z - \left(\frac{\partial \ln Z_G}{\partial z}\right)_{\alpha}
\end{aligned}
$$

where $\alpha = T, V$. We note that

$$
\langle N\rangle = z\left(\frac{\partial \ln Z_G}{\partial z}\right)_{T,V}]
$$

The requirement for minimum *F* at constant *T* and *V*,

$$\left(\frac{\partial F}{\partial \langle N\rangle}\right)_{T,V} = \frac{k_B T}{\left(\frac{\partial \langle N\rangle}{\partial z}\right)_{T,V}} \left(\frac{\partial \langle N\rangle}{\partial z}\right)_{T,V} \ln z = k_B T \ln z = \mu$$

As a consequence, the choice $z = 1$ or $\mu = 0$, is necessary in order to minimize the Helmholtz free energy at constant *V* and constant *T*, in the absence of a valid physical constraint on $\langle N\rangle$. When this choice is made, the Helmholtz free energy and the grand potential becomes equal, as do the canonical and grand partition functions.

9. Discussion by Sturge

We cannot use the usual expression

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

for μ, since one cannot increase *N* (that is, add photons to the system) at constant volume *V* and at the same time keep the temperature *T* constant; $\left(\frac{\partial F}{\partial N}\right)_{T,V}$ does not exist for a photon gas. Instead, we use the free Gibbs free energy. Hence

$$G = \mu N = F + PV = U - ST + \frac{1}{3}U = \frac{4}{3}U - \frac{4}{3}U = 0$$

Thus, photons in equilibrium have zero chemical potential, even though their free energy *F* is nonzero. This result can be obtained in a more intuitively appealing way by considering what happens if the volume of the cavity increases by dV, the temperature and hence the pressure remaining constant. This expansion increases the number of photons by an amount proportional to dV. For a change at constant pressure, *G* takes a minimum in equilibrium, so that $dG = 0$. hence we have

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = 0$$

((**Note**))

$$G = F + PV, \qquad dG = -SdT + VdP + \mu dN$$

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