

Chemical Potential of Photons: a Babylonian Approach*

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Abstract: In the paper we present several notes which may be useful for all who want to teach undergraduate students about photons at a phenomenological level, in particular to explain the black body radiation as a photon gas.

1. Introduction

In the undergraduate courses of fundamentals of physics and of introductory statistical physics students get familiar with the notion of photons on a phenomenological level well before the advanced course of quantum electrodynamics. Photons are for the first time mentioned in context of photoeffect, Compton scattering and black body radiation. Explaining black body radiation in terms of a grand canonical photon gas in a box the lecturer has to justify the fact that the chemical potential of photons is zero. In this paper we shall try to present several ways of argumentation, not starting with any fundamental principles (or axioms). We shall rather present a set of non-hierarchical interrelated facts which all together make the statement “chemical potential of photons is zero” plausible.

This is a Babylonian way of reasoning as described by Feynman [1]: “What I have called the Babylonian idea is to say, I happen to know this, and I happen to know that, and maybe I know that; and I work everything out from there. Tomorrow I may forget that this is true, but remember that something else is true, so I can reconstruct it all again. I am never quite sure of where I am supposed to begin or where I am supposed to end. I just remember enough all the time so that as the memory fades and some of the pieces fall out I can put the thing back together again every day.”

2. Radiation as a photon gas

Maybe the fastest way how to derive the black body radiation formula is to consider the grand canonical distribution for a photon gas in a cubic box with the edge a . The one-particle states are given by wave vectors

$$\vec{k}_{mnl} = \frac{m}{a}, \frac{n}{a}, \frac{l}{a}$$

and the corresponding frequencies are

*Dedicated to Professor Peter Prešnajder on the occasion of his 70th birthday

$$c|\vec{k}_{mnl}| = \frac{c}{a} \sqrt{m^2 \pi^2 + n^2 \pi^2 + l^2 \pi^2}$$

Thus the energy spectrum is

$$E_{mnl} = \frac{c\hbar}{a} \sqrt{m^2 \pi^2 + n^2 \pi^2 + l^2 \pi^2}$$

The number of states with the energy less than E is given by the 1/8 of the volume of a sphere in the (m, n, l) space

$$N(E) \approx \frac{1}{8} \frac{4}{3} \pi r^3 = \frac{1}{6} \frac{4}{3} \pi \left(\frac{aE}{c\hbar} \right)^3$$

The prefactor 2 is for the two photon polarizations. The density of states is then given by the derivative of

$$g(E) = V \frac{1}{c^3 \pi^2 \hbar^3} E^2$$

To calculate the total energy of photons in the box we just take the mean occupation number of each one-particle state which is given by the Bose Einstein distribution formula, multiply by the energy of the state and sum over all the states:

$$E = \int_0^\infty E g(E) \frac{1}{\exp(\frac{E}{kT}) - 1} dE$$

Now comes the crucial moment: what is the correct value for the chemical potential of photons at temperature T . We can say: it is to be determined experimentally. We compare the final formula with the experimental radiation spectrum and fit the correct value of μ .

The result of such a fit would give $\mu = 0$ independently of the temperature.

Taking $\mu = 0$ we get

$$E = V \int_0^\infty dE \frac{\hbar^3 E^3}{\exp(\frac{E}{kT}) - 1} \frac{1}{c^3 \hbar^3}$$

$$E = V \int_0^\infty dE \frac{1}{\exp(\frac{E}{kT}) - 1} \frac{\hbar^3 E^3}{c^3}$$

The function below the integral is just the Planck formula for the frequency spectrum of the black body radiation. To get this agreement with experiment it was essential to put $\mu = 0$. At this level of reasoning the zero value of the photon chemical potential is just an experimental fit. There is nothing wrong about it a priori. There are many situations like this in physics. In electrodynamics we have a parameter, the charge of the electron. We are (currently) not able to determine its value from "first principles". We have to fit its value using data from some particular experiment and then to use that fitted value to get "pure predictions" for other experiments.

It is the value zero for the chemical potential of photons which makes us a bit uneasy to accept it as a fitted value without some "theoretical reasoning". Zero is too special a value. In what follows we shall try to make this value plausible in the context of other pieces of theoretical physics knowledge within the Babylonian approach. We shall not attempt to present any hierarchical axiomatic "first principle approach".

Let us start first with repetition of how the notion of chemical potential is defined for “ordinary” particles like atoms, protons, electrons etc. and then explain what makes the photons different.

3. Chemical potential for ordinary particles

We consider two isolated systems, each of them being individually in equilibrium. Their energies, volumes and particle numbers are $E_1, E_2, V_1, V_2, N_1, N_2$. We bring them into a contact enabling to redistribute particles between them through some hole. Of course redistributing particles also redistributes energy. The new energies will be E'_1, E'_2 , the new particle numbers will be N'_1, N'_2 . The volumes will be unchanged. We shall consider a case when the total number of particles is fixed (no chemical reactions), so $N_1 + N_2 = N'_1 + N'_2$.

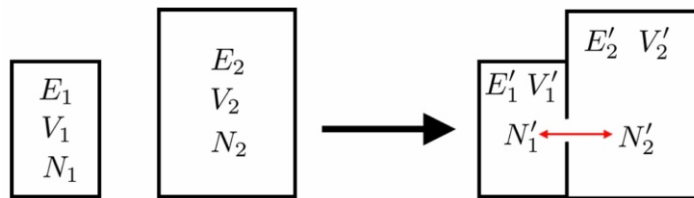


Fig. 1. Redistributing particles in equilibrium.

After the final common equilibrium is established the total entropy will be

$$S = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$$

The final values of energies will be the same as in the case when we have considered just a thermal contact. The only unknown value in this relation is N'_1 , since N'_2 is given by the total number of particles conservation. We get the final value N'_1 by maximizing the entropy.

$$\frac{dS(N'_1)}{dN'_1} = \left. \frac{S_1}{N} \right|_{N_1} = \left. \frac{S_2}{N} \right|_{N_2} = 0$$

$$\left. \frac{S_1}{N} \right|_{N_1} = \left. \frac{S_2}{N} \right|_{N_2}$$

What is the physical meaning of this equation? Entropy function $S(E, V, N)$ when differentiated with respect to N gives some other function of the (macro)state variables E, V, N . So it is some state function of the macrostate, it is some physical quantity characterizing the macrostate. The equation says that this state variable has the same value for the two systems in contact. The problem is that in cases of energy and volume redistributions we have an intuitive feeling what are the relevant physical quantities which emerge to be the same after reaching common equilibrium (temperature and pressure). Here we normally do not have everyday experience what is the particle redistribution-controlling quantity. In lectures on statistical physics we just define the relevant quantity, the chemical potential μ , by the formula

$$\mu = - \left. \frac{S}{N} \right|_{E, V}$$

This definition of chemical potential requires that the total number of particles is conserved. It means, that the number of particles N is “a good external quantity”. Practically it means, that preparing a macrostate we start with an empty box and have a store of particles. We take N particles out of the store, put them into the box and wait until the equilibrium is established. During the relaxation process the number of particles in the box is constant: it is one of the external quantities defining the macrostate and its value can be chosen at will.

It has to be stressed that the grand canonical ensemble machinery also requires that the number of particles is conserved. A macrostate with given μ is achieved by bringing the system considered to a contact with a very big reservoir of particles which keeps the chemical potential constant. For the derivation see for example Reif [2].

4. Chemical potential of photons

Photons differ from “ordinary particles” by the fact that their number is not a conserved quantity and cannot be chosen at will as an independent external parameter. We cannot prepare a box with electromagnetic radiation by starting with an empty box and put N photons into it taken out from a “photon store”. Even if we were able to start with the box containing N photons, this number will not be conserved during some relaxation process and a different equilibrium number of photons will be established during the relaxation. So “a photon gas in a box” has just two free parameters T, V while ordinary particle gas has three T, V, N . For example in our derivation of the Planck black body radiation formula in Section 2 we did not fix the number of photons as some chosen parameter. Still the number of photons in the equilibrium macrostate is a well defined quantity established during the relaxation to equilibrium and can be calculated from the Planck formula as

$$N = V d \frac{1}{\exp(\frac{h\nu}{kT}) - 1} \frac{\nu^2}{c^3 h^2}$$

When we start with an empty box and heat it to temperature T the photons appear inside. How is it possible? It is because the box is not just a “space limiting passive boundary” as we consider it to be for a gas of ordinary particles. The photons just do not “emerge of nothing” in an empty box. The photons are continuously emitted and absorbed by the walls (by charged particles in the walls). So the box is an “active player” in the game. The statement “radiation is a gas of photons in a box” is just not true. Such a statement has an ontological character, describing what the radiation **is**. It is much safer to limit ourselves tognoseological statements like “we can consider radiation **as if** it were a gas of photons in a box” and **as if** photons were able to appear or disappear inside the volume of the box until the equilibrium is established. So we can completely abstract from the complicated radiation and absorption processes in the walls assuming some magic property of photons to appear or disappear in the internal volume of the box. More comments about **as ifs** in physics see in the last section.

Since the number of photons is not conserved (it is not an independent external parameter) it is debatable what the notion of chemical potential means for photons. Or whether the grand canonical ensemble has a well defined meaning for photon gas at all. Still, if one is prudent enough, one can use that machinery with $\mu = 0$ **as if** everything was well defined.

5. Number of photons as a parameter of nonequilibrium

Let us investigate a non-equilibrium photon gas in a box. We can imagine for example that we start with an equilibrium macrostate at some temperature and then very quickly double the temperature of the walls. For such a rapid change of external conditions the number of photons will be the same as in the original equilibrium, but different from the number of photons that will be established in the new equilibrium.

During the relaxation the number of photons in the box will be at any time instance a well defined number. Let us denote it as N_{neq} . We can consider the number N_{neq} as an additional external parameter characterizing the level of non-equilibrium. Let us stress that a non-equilibrium macrostate must be characterized by a larger number of parameters than the equilibrium macrostate. So for example the equilibrium free energy of photon gas in a box is given by just two parameters T, V . The non-equilibrium free energy can be characterized for example by three parameters T, V, N_{neq} . For given external T, V the non-equilibrium free energy $F_{neq}(T, V, N_{neq})$ will be decreasing during the relaxation until it finally reaches its minimum for N_{neq} equal to its equilibrium value N_{eq} . So the equilibrium free energy $F_{eq}(T, V)$ is equal to the non-equilibrium free energy evaluated for $N_{neq} = N_{eq}$.

$$F_{neq}(T, V, N_{neq}) \Big|_{N_{neq} = N_{eq}} = F_{eq}(T, V)$$

So the following relation is true

$$\frac{\partial F_{neq}(T, V, N_{neq})}{\partial N_{neq}} \Big|_{N_{neq} = N_{eq}} = 0$$

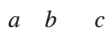
For ordinary particles the equilibrium free energy is a function of three independent parameters T, V, N and the following relation holds

$$\frac{\partial F(T, V, N)}{\partial N}$$

Comparing the last two relations and assuming that we can calculate with the chemical potential of photons as if for ordinary particles we can deduce that the chemical potential of photons is zero. This is roughly the argument of Landau [3] why $\mu = 0$ for photons.

6. Photons as if created in a dummy chemical reaction

Even for ordinary particles their number is not always conserved if there are chemical reactions. For example let us consider the reaction



If we initially put into an empty box N_a, N_b, N_c particles then after some relaxation time the number of particles will be N_a, N_b, N_c . The final particle concentrations can be calculated by minimizing the Gibbs potential. The equilibrium condition can be expressed through the chemical potentials (see for example a simple introductory discussion in Kittel [4])

$$\mu_a + \mu_b = \mu_c$$

Now let us treat the equilibrium number of photons in a box **as if** it was an equilibrium for a miraculous (dummy) chemical reaction taking place inside the volume of the box (no role for walls here)

nothing \rightleftharpoons photon

The equilibrium condition for such a miraculous reaction would be

From there we obviously get $\frac{\text{nothing}}{\text{photon}} = 0$.

7. Derivation of the Planck formula not mentioning photons

We shall do here the statistical physics of a free electromagnetic field in a box. We have to learn how to write the canonical ensemble for a free electromagnetic field in a box. To do that we have to learn how to write quantum microstates of the electromagnetic field in a box. The proper way how to do that would be doing quantum electromagnetic field theory. But we can guess the correct results just writing the stationary electromagnetic waves in a box, observe that the system is mathematically equivalent to a set of harmonic oscillators then use the formula for the mean energy of a quantum harmonic oscillator and perform a summation over the full set of field-equivalent oscillators.

The free electromagnetic field in a box has to satisfy the wave equation. For the electric component it reads

$$\vec{\nabla}^2 \vec{E}(x, y, z, t) - \frac{1}{c^2} \frac{\partial^2 \vec{E}(x, y, z, t)}{\partial t^2} = 0$$

A partial differential equation needs also boundary conditions. Skipping derivation details we just write the result, that the electric field in a box with perfectly conducting walls can be expressed through its Fourier components as

$$E_x(x, y, z, t) = \sum_{mnl} E_{x; mnl}(t) \cos \frac{m x}{a} \sin \frac{n y}{a} \sin \frac{l z}{a} \quad (1)$$

$$E_y(x, y, z, t) = \sum_{mnl} E_{y; mnl}(t) \sin \frac{m x}{a} \cos \frac{n y}{a} \sin \frac{l z}{a} \quad (2)$$

$$E_z(x, y, z, t) = \sum_{mnl} E_{z; mnl}(t) \sin \frac{m x}{a} \sin \frac{n y}{a} \cos \frac{l z}{a} \quad (3)$$

The Fourier coefficient functions are not independent, they have to satisfy the condition of zero divergence of the electric field and we get

$$\frac{m}{a} E_{x; mnl}(t) - \frac{n}{a} E_{y; mnl}(t) + \frac{l}{a} E_{z; mnl}(t) = 0$$

So only two coefficient functions are arbitrary, the third one can be expressed through the other two. This corresponds to the fact that the electromagnetic wave has two independent polarizations.

Inserting the expressions (1), (2), (3) into the wave equation we get for the two independent coefficient functions equations

$$\frac{d^2}{dt^2} E_{x; mnl}(t) + \omega_{mnl}^2 E_{x; mnl}(t) = 0$$

$$\frac{d^2}{dt^2} E_{y,mnl}(t) = -\omega_{mnl}^2 E_{y,mnl}(t)$$

where

$$\omega_{mnl}^2 = \frac{c^2}{a^2} (m^2 + n^2 + l^2)$$

Thus the electric field in a box is mathematically equivalent to two sets of independent harmonic oscillators, labeled by integer triplets m, n, l with frequencies ω_{mnl} . More detailed discussion shows that these two sets of independent oscillators fully describe the magnetic field as well, so the two sets of oscillators describe a state of electromagnetic field in a box completely.

We can now do the statistical physics of electromagnetic field in a box as if the statistical physics of two sets of independent harmonic oscillators. The mean energy of just one quantum harmonic oscillator at temperature T reads

$$\bar{E} = \frac{\hbar \omega_{mnl}}{\exp(\frac{\hbar \omega_{mnl}}{kT}) - 1} = \frac{1}{2} \hbar \omega_{mnl}$$

In what follows we shall omit the contribution from zero oscillations which would just add a physically irrelevant additive constant to the total energy. (Well, the additive constant will be infinite, but we cannot dwell here on problems of infinities in quantum field theory.)

Now we do a standard trick: we approximate the sum by an integral over ω . To do this we have to know how many oscillators have the frequency less than some value ω . We see that the oscillators correspond to points in the abstract m, n, l space with integer coordinates. The trick is the same as we used when calculating the number of one-particle states for photons. So we get (the factor 2 is for two states polarization states).

$$g(\omega) = 2 \frac{4}{8} \frac{a}{c} \omega^3$$

The total energy of the field we get by summation over all the oscillators

$$E = V \int_0^\infty d\omega \frac{1}{\exp(\frac{\hbar \omega}{kT}) - 1} \frac{\hbar \omega^3}{2c^3}$$

This is exactly the Planck formula.

We have not used any photons here, we just did the canonical distribution for the harmonic oscillators. But now we understand why a grand canonical distribution of photons lead to the same result. Just by lucky coincidence the mean energy of a harmonic oscillator

$$\bar{E} = \frac{\hbar \omega_{mnl}}{\exp(\frac{\hbar \omega_{mnl}}{kT}) - 1}$$

is given by the same formula as the Bose Einstein mean occupation number with $\mu = 0$. There is one-to-one correspondence between the language of harmonic oscillators and the language of photons if we put $\mu = 0$ for photons. In both cases the states are given by a triplet of integers m, n, l the frequency ω_{mnl} is given by the same formula in both cases. Even if we never heard about photons we could arrive at a conclusion that there are two equivalent ways to do statistical physics either as if the electromagnetic field were sets of

harmonic oscillators or **as if** the electromagnetic field were a gas of photons. So we have invented here photons without the quantum field theory. Well, **as if**.

8. Babylonian “as if” physics

During our discussions we have used several times an “**as if**” approach. This may sound strange for many people who consider physics to be a rigorous science. Well, physics is certainly more rigorous than many other branches of science, but still we are not preaching “absolute truth”. We often find in popular text statements like “modern science has proved that energy is conserved and cannot be destroyed or created”. Nobody really proved that without any assumed unproved “first principles”. We do not say in physics that our statements correspond to absolute truth, we say they are currently our best advice we can give you to be able to survive in the jungle of the world.

We have all learned in school that “light **is** waves” since it was proved by interference experiments. This statement is of ontological character. Anybody formulating such statements must be prepared to be “disproved” by photoelectric effect. It is much safer to say “in interference experiments we can handle light **as if** light were waves”.

We have all learned at school that everything around us is made of molecules, which **are** composed of atoms which are composed of protons, neutrons and electrons. Another ontological statement. What would an average teacher say if some pupil complains: “I can easily prove that this cannot be true. I learned on Internet that neutrons are unstable particles and decay within (statistically) a quarter of an hour. You are speaking here already for longer time without any observable decay.” There are stories that young Einstein and Mileva Marić (his future first wife), used to irritate their professors by pointing to inconsistencies between the taught knowledge and newer scientific findings. My answer to the complaining pupil will be something like “very often we can consider the neutrons bound in atomic nucleus **as if** they were stable particles. Who knows how many the today’s “absolutely true scientific statements” will be formulated as “**as if**” statements in future.

Galileo refused to accept the **as if** game (proposed to him by the Inquisition) insisting “Eppur si mouve”. Actually the Copernicus book was published (half a century before the Galileo process) with an over-prudent **as if** preface added by Osiander. This was criticized by many. In fact no side of the heliocentrism against geocentrism quarrel was rigorously technically right even though psychologically the Copernicus theory was of absolute importance. Just technically it is closer to truth to say that the Sun and the Earth both rotate around their common center of mass. Even this I would prefer to formulate as an “**as if**” statement.

9. Acknowledgements

This paper is dedicated to Peter Prešnajder on the occasion of his 70th birthday. He was at first my teacher, later a collaborator and friend. I greatly acknowledge his contribution to the friendly working atmosphere at our department.

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