Chemical potential of equilibrium electromagnetic radiation and the means for electromagnetic waves to propagate in free space

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(Dated: January 31, 2011)

The article shows that in case if the photon is viewed as a particle moving in empty space the zero value of chemical potential of equilibrium electromagnetic radiation cannot be explained basing only on first principles of statistical physics. On the contrary, to explain the chemical potential of equilibrium electromagnetic radiation being equal to zero is rather simple if the photon is considered as a quasi-particle that is the way to describe collective motion of a system consisting of particles whose number is a fixed value. Collective motions of the particles of mentioned system are interpreted in the article as oscillations of an electromagnetic field that corresponds to observation data of modern astronomy, according to which the space, that fills the gaps, both between massive objects and between massive particles forming them, should be attributed to characteristics of a continuous medium.

As is known, the equilibrium (black-body) electromagnetic radiation is electromagnetic radiation being in a state of thermal equilibrium. Thus, the electromagnetic radiation with temperature T, filling the closed cavity in the material, is equilibrium if the walls of this cavity have the same temperature T as the temperature of the radiation. For example, in some metrological measurements platinum is used as the substance forming walls of the cavity in question. In this case measurements are carried out through the narrow channel connecting a cavity in platinum with outer space. It was found that when the walls of the cavity are at room temperature, the bulk of the equilibrium radiation will be concentrated in the infrared part of the spectrum, but if the walls of the cavity are heated to high temperatures, when the spectral maximum of the radiation observed is shifted to greater energies of visible range.

The study of the energy spectrum of the equilibrium radiation, made at the turn of the nineteenth and twentieth centuries, has enriched physics by the Planck's constant h (in modern designations $\hbar = 1,054 \cdot 10^{27}\mathrm{erg}\cdot\mathrm{sec}$), which should be introduced in order to avoid so-called "ultraviolet catastrophe" in the spectrum of equilibrium radiation. Thus, this contribution became the first step on a way to create the future quantum physics. However, the analysis made by authors of the current work, has shown that the "ultraviolet catastrophe" is not the only inherent question of the physics of equilibrium radiation needed to be clarified. There is one more aspect of this problem which is beyond attention of researchers, namely, a question concerning chemical potential of equilibrium electromagnetic radiation.

As is known, the chemical potential μ (the Gibbs free energy per one particle) of any thermodynamic system, consisting of N identical particles, is defined as the increment dE of the energy of this system due to one more particle added to the system (i.e. when $dN = 1$; in case of equilibrium radiation $-$ when one more photon is added), the V volume and entropy S of the system remaining constant. So, according to the definition, $\mu = (\partial E/\partial N)_{V,S}$.

All the expertise gained from the history of physics indicates that in the equilibrium electromagnetic radiation $\mu = 0$. However, existing theoretical arguments in favor of zero value of the chemical potential of the equilibrium electromagnetic radiation, basing on first principles and not resorting to those or other model representations, cannot be recognized as satisfactory ones. So, when substantiating the equality $\mu = 0$, the authors [1] presume the relation $\mu = (\partial F/\partial N)_{V,S}$, where F is the free energy (Helmholtz free energy) of the equilibrium radiation. It is postulated in [1], that free energy F of black-body radiation in the state of equilibrium is minimal. Then in this state the derivative must be zero i.e. the equality $\mu = 0$ holds by all means. But in order for the free energy F of the equilibrium radiation to be minimal at the equilibrium, the second law of thermodynamics for the nonequilibrium processes occurring in this system should look as

$$0 > (dF)_{V,T}, \tag{1}$$

i.e. it is necessary that the free energy in nonequilibrium processes be always decreasing, tending to minimum in the equilibrium.

However, the statement of the second law of thermodynamics for nonequilibrium processes in the form of (1) is valid only for systems in which the number of particles N is constant, i.e. for systems in which equality $dN = 0$ holds. Meanwhile, photon gas is (for nonequilibrium processes) a system with variable number of photons, thus, for it the value dN (in nonequilibrium processes) is not altogether equal to zero. In the latter case (when N is not constant)

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the second law of thermodynamics for nonequilibrium processes is written as

$$\mu \cdot dN > (dF)_{V,T}. \tag{2}$$

Supposing, for example, that the chemical potential of black-body radiation is strictly negative (i.e. if $\mu < 0$) provided that also $dN < 0$, we obtain from the inequality (2), that the change $(dF)_{V,T}$ of free energy in this case will be less than a certain positive number − but not less than zero as it takes place in the inequality (1). This means that here the change of free energy may be positive, and in some nonequilibrium processes the free energy itself will grow in this case. Consequently, the system with variable number of particles (and nonzero chemical potential) will not possess in the state of equilibrium a minimum of free energy (the same result is obtained from the assumption, that $\mu > 0$, at $dN > 0$).

The zero in the left part of the inequality (2), necessary for the due decrease of free energy in nonequilibrium processes, will appear only in the event of $\mu = 0$. Thus, we conclude, that postulating in [1] minimality of free energy of a system with variable number of particles in it, is as a matter of fact equivalent to the assumption, that the chemical potential of this system is equal to zero. Thus, in [1] the equality $\mu = 0$ does not follow as an objective consequence of first principles, but is introduced by a voluntaristic assumption that the value μ is equal to zero!

Similar to [1], a looseness in the derivation of $\mu = 0$ for equilibrium electromagnetic radiation occurs in [2] as well, with only difference that in [2] not the free energy, but entropy of a system with variable number of particles is considered. And other authors, regarding one or another model of the interaction of electromagnetic radiation with matter, directly or implicitly use the above assumption $\mu = 0$. So, it was not demonstrated in a correct way till now, basing only on first principles and not using any model representations, that chemical potential of the equilibrium electromagnetic radiation is equal to zero. Therefore, the equality $\mu = 0$ for a Bose gas with a variable number of particles is actually an implicitly introduced postulate, rather than an objective consequence of the first principles of modern statistical physics. Meanwhile, it will be shown below, that a similar question for physics of the quantum continuum − namely, what is the magnitude of chemical potential of the gas of quasi-particles in this medium − has very simple decision.

As is known [3], under quasi-particle is understood a way to describe collective phenomena in the quantum continuum (in the quantum physics of solids or in physics of quantum liquids). So, the description of collective thermal motion in a solid medium at low temperatures is carried out introducing a gas of quasi-particles − phonons; and in superfluid helium (so-called helium II) thermal motion at low temperatures is described introducing a gas consisting of quasi-particles − phonons and quasi-particles − rotons.

In connection with studying the gas of quasi-particles in helium II, L. Landau considered the question of chemical potential of this gas. The calculation of μ was made separately for the gas of phonons and for the gas of rotons [3]. In this event the proof itself of equality $\mu = 0$ differed in no way from the above mentioned proof that chemical potential of equilibrium electromagnetic radiation equals zero. However, we have just shown that this proof is not always valid.

The correct solution to the question of chemical potential of the gas of quasi-particles in helium II becomes possible if we will consider the problem of calculating the chemical potential of the whole ensemble of the quasi-particles of the medium. Thus, in helium II it is necessary to solve the problem of calculating the chemical potential of a gas formed by all phonons and rotons. Since the gas consisting of all the phonons and rotons is only a way to describe the collective thermal motion in helium II, therefore we have:

$$F_q = F_p, \tag{3}$$

where: F_q is free energy of the gas of all quasi-particles in helium II (i.e. all phonons and rotons available in helium II), F_p free energy of all particles comprising helium II (i.e. all atoms of helium II).

Insofar as the number of atoms that make up helium II is taken to be fixed, the change dF_p of free energy F_p of all atoms of helium II will (in nonequilibrium processes) meet inequality (1), instead of inequality (2). Thereof, according to inequality (1), the quantity F_p will have a minimum in a state of equilibrium. But then the minimum in the state of balance, according to (3), there will also have F_q − the total free energy of the gas of quasi-particles. Thus, we come to the simple demonstration of the chemical potential under consideration being equal zero. Since for the proof of equality $\mu = 0$ in the gas of all quasi-particles in helium II there were not used any features specific of the superfluid helium, the proof in question can be extended also to the case of a gas of phonons existing in a solid body at low temperatures.

Concerning the photon gas which comprises the equilibrium electromagnetic radiation, we may arrive at a following conclusion. Were the photon a traditionally understood particle, moving in empty space [4], we could not explain the vanishing of the chemical potential of equilibrium electromagnetic radiation basing only on first principles of statistical physics. But if the photon is a quasi-particle, that is a way to describe the collective motion of primary elements of a system whose number is a fixed quantity, the equality $\mu = 0$ can be explained very simply just as described above.

Certainly, within the bounds of the thermodynamic approach stated above we cannot operate by any microscopic models of the system mentioned whose collective motions we interpreted as oscillations of the electromagnetic field.

However the reasoning developed in this article is yet another argument in favor of the following point of view. The space, which fills intervals between massive objects as well as between massive particles, that form these objects, should be attributed to characteristics of a continuous medium. Lately, such a view is increasingly used in the interpretation of some astronomical [5–7] and laboratory [8] observations carried out in the second half of the twentieth and early twenty-first century

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