

# A stochastic treatment for radiation in equilibrium with a thermal reservoir

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## Abstract

A stochastic equation is described for the evolution of the probability distribution of a simplified model of photons in contact with a thermal reservoir or heat bath made of two level atoms at a temperature  $T$ . The basic transition probabilities for the emission and absorption of photons was given by Einstein in 1916, and is in accordance with modern quantum electrodynamics. It is shown that, without invoking the principles of statistical mechanics, the stationary solution of this equation is the Bose Einstein distribution, and the level occupation of the atoms in the heat bath is given by the canonical Gibbs distribution. The derivation for a similar model given in B. Lavenda's book on statistical physics [4] is shown to be incorrect.

Recently, a one step Markovian stochastic equation has been applied to illustrate the approach to equilibrium of a model with two level atoms which emit and absorb monochromatic photons[1]. This treatment is based on an extension of Einstein's 1916 detailed balance derivation of the Planck blackbody distribution for thermal photons[2]. In Einstein's derivation, the energy levels of the atoms are *assumed* to be occupied in accordance with Gibb's canonical distribution, but in the stochastic treatment in reference [1] this distribution and the Bose-Einstein distribution for the photons is *derived* by correlating the atomic transitions with the emission and absorption of photons. Thus,

this stochastic treatment provides an elementary example that illustrates the foundations of equilibrium thermodynamics and statistical mechanics on the principles of quantum mechanics.

It is of interest, however, to consider also this stochastic approach when the fluctuations associated with the atomic transitions are neglected, as was done originally in Einstein's treatment. In this case the atoms can be considered to constitute a thermal heat bath that determines the temperature  $T$  of the photons at equilibrium, and the basic transition probabilities for the emission and absorption of photons will depend on this temperature. The question then arises whether by applying the stochastic equation to the photons only, this temperature dependence can be determined directly from the second law of thermodynamic, or whether an appeal has to be made to Gibb's canonical distribution for the atoms, as was originally made by Einstein.

Let  $p_n(t)$  be the probability at time  $t$  for having  $n$  monochromatic photons with frequency  $\nu$  in an enclosure in contact with a heat bath at temperature  $T$ . Then the time evolution of  $p_n(t)$  is determined by the differential equation for a one step Markovian stochastic process [3], [4]

$$\dot{p}_n(t) = r_{n+1}p_{n+1}(t) + g_{n-1}p_{n-1}(t) - (r_n + g_n)p_n(t) \quad (1)$$

where  $r_n$  is the transition probability per unit time ( $n \rightarrow n - 1$ ) for the absorption of a photon in an enclosure containing  $n$  photons with the same frequency, and  $g_n$  is the corresponding probability ( $n \rightarrow n + 1$ ) for the emission of a photon. We have

$$r_n = Bn_g n, \quad g_n = Bn_e(g + n), \quad (2)$$

where  $B$  is the coefficient for the rate of induced emission and absorption of radiation introduced by Einstein and later determined from quantum electrodynamics,  $g = A/B$  is associated with Einstein's  $A$  coefficient for spontaneous radiation which depends also on the frequency  $\nu$  of the photons, and  $n_e$  and  $n_g$  are the number atoms in an excited state and in the ground state, respectively with energy difference  $\epsilon = h\nu$ . In thermal equilibrium, Einstein model accounts for the lack of photon number conservation for thermal photons by the continuous creation and annihilation of photons interacting with the atoms constituting the heat bath. The stationary or equilibrium solution

of Eqs. 1 and 2, is obtained by setting  $\dot{p}_n = 0$  together with the boundary condition  $p_{-1} = 0$ , and yields the recurrence relation

$$nn_g p_n = (g + n - 1)n_e p_{n-1}, \quad (3)$$

This is the stochastic generalization of Einstein's well known detailed balance condition for the *mean* number  $\bar{n}$  of photons, [2],

$$\bar{n}n_g = (g + \bar{n} - 1)n_e \quad (4)$$

which is obtained here by summing over  $n$  both sides of Eq. 3 (for  $1 \ll g + \bar{n}$  the term  $-1$  in brackets can be neglected). Solving Eq. 3 with the normalization condition  $\sum p_n = 1$  yields [5],

$$p_n = \Omega(n) \left(\frac{n_e}{n_g}\right)^n \left(1 - \frac{n_e}{n_g}\right)^{-g}, \quad (5)$$

where

$$\Omega(n) = \frac{(g + n - 1)!}{n!(g - 1)!} \quad (6)$$

is the celebrated *Bose – Einstein* distribution. As in our earlier treatment [1], this equilibrium distribution has been derived without making the standard assumptions of equilibrium statistical mechanics about equal a priori probabilities and indistinguishability of photons in phase space.

The most probable number  $n_p$  of photons is determined at the maximum of  $p_n$ , and for large  $n$  this value is obtained by evaluating the maximum of  $\ln(p_n)$  in the Stirling approximation. According to Eq. 5,

$$\ln(p_n) = (g + n)\ln(g + n) - n\ln(n) - g\ln(g) + n\ln\left(\frac{n_e}{n_g}\right) + \text{constant}, \quad (7)$$

and  $n_p$  is obtained by setting  $d\ln(p_s(n))/dn = 0$ . This condition yields the relation

$$\frac{g}{n_p} + 1 = \frac{n_g}{n_e}. \quad (8)$$

which corresponds to Einstein's detailed balance relation, Eq. 4 with  $n_p = \bar{n}$ . In statistical mechanics, the thermodynamic entropy  $S_n$  is associated with the probability  $p_n$  according to Boltzmann's relation

$$S_n = k_B \ln(p_n), \quad (9)$$

where  $k_B$  is Boltzmann's constant, and the the thermodynamic condition of maximum entropy for the equilibrium state of an isolated system (photons and heat bath atoms),  $dS_n/dn = 0$ , correspond to the condition for the maximum of the probability  $p_n$ . This entropy is the sum of the entropy  $S_a$  associated with the heat bath

$$S_a = S_o + k_B n_p \ln\left(\frac{n_e}{n_g}\right), \quad (10)$$

where  $S_o$  is a constant, and the entropy  $S_p$  of the photons

$$S_p = k_B \ln \Omega(n_p). \quad (11)$$

At first sight, it is strange that the entropy of the heat bath,  $S_a$ , depends not only on the ratio  $n_e/n_g$  of the number of atoms in the excited and in the ground state, but also on the equilibrium number  $n_p$  of photons. In our model, however, the creation of  $n_p$  photons is due to the decay of an equal number of excited states in the heat bath, and the corresponding transfer of an amount of energy (heat)  $E = n_p \epsilon$  to the photons. Indeed, Eq. 10 is the first order term in an expansion in powers of  $n_p$  of the expression in statistical mechanics of the entropy of a system consisting of two level atoms

$$S^a = k_B [n_a \ln(n_a) - n_e \ln(n_e) - n_g \ln(n_g)] \quad (12)$$

where  $n_a = n_e + n_g$  is the total number of atoms,  $n_e = n_e^o - n_p$ , and  $n_g = n_g^o + n_p$  are the number of atoms in the excited and ground state respectively, and  $n_e^o$  and  $n_g^o$  are the corresponding values when the electromagnetic interaction between atoms and photons is "switched off". [6]. Therefore, the temperature  $T$  of the heat bath is determined by the relation

$$\frac{dS_a}{dn_p} = -\frac{\epsilon}{T}, \quad (13)$$

where a minus sign is introduced because  $E = n_p \epsilon$  is the amount of energy transferred from the heat bath to the photons, i.e.  $dn_e = -dn_p$ . Hence, we obtain the canonical Gibbs distribution

$$\frac{n_e}{n_g} = e^{-\epsilon/k_B T}. \quad (14)$$

Likewise, a temperature  $T_p$  for the photons is determined by the relation

$$\frac{dS_p}{dn_p} = \frac{h\nu}{T_p}, \quad (15)$$

The condition for thermal equilibrium,  $T_p = T$  corresponds to the maximum entropy condition which leads to Eq. 8, and we obtain the Planck blackbody distribution for the equilibrium number of photons

$$n_p = \frac{g}{e^{h\nu/kT} - 1}, \quad (16)$$

with  $h\nu = \epsilon$ .

It is tempting to think that in our model, which requires the conservation condition  $n_p + n_e = \text{constant}$ , the photon distribution should have a finite chemical potential, i.e. that it is not a thermal distribution [7]. However, since  $h\nu = \epsilon$ , this number conservation is identically the same as the conservation of total energy of the photons and the atoms,  $E = n_p h\nu + n_e \epsilon$ . and therefore it does not give rise to a finite chemical potential. In his book on statistical physics [4], B. Lavenda discussed also the stochastic equation, Eq. 1, and applied it to describe the thermal equilibrium of an ideal gas of Bose-Einstein or Fermi-Dirac particles. He introduced similar expressions for the basic transition probabilities in the form  $r_n = \alpha n$  and  $g_n = \beta(m - \eta n)$ , where  $\alpha$  and  $\beta$  are parameters, and  $\eta = 1$  for Fermi Dirac,  $\eta = -1$  for Bose Einstein statistics respectively, but he did not provide any justification for these expressions based on quantum mechanics. Instead, he imposed the requirement that the Bose-Einstein or Fermi-Dirac distributions emerge as a stationary solution of the stochastic equation, Eq. 1, and found the transition probabilities that would achieve this result. Moreover, Lavenda argued that this treatment could be applied when the number of particles is conserved. But this claim is manifestly incorrect, because at each transition the stochastic process *changes* the number  $n$  of particle. Such a change is possible only with a generalized heat bath as described by the grand canonical ensemble for equilibrium statistical mechanics, which allows for the exchange of particles between a thermal reservoir and the system under consideration. However, in a stochastic treatment, this requires the introduction at least of a second variable to account for the change of both the energy and of the number of particles of the ideal gas [8]. To reach his erroneous conclusion, in Eq. 3.24 Lavenda gave an incorrect expansion for  $\ln(p_n)$  in powers of  $n - \bar{n}$ , where

$\bar{n} = n_p$ , and in Eq. 3.26 he introduced improper partial derivatives of the entropy function  $S(\bar{n})$  which is a function of the *single* variable  $\bar{n}$  [8].

In conclusion, it has been shown that the canonical results for equilibrium thermal radiation obtained from the principles of statistical mechanics, can also be derived without invoking these principles, from a stochastic treatment based on the fundamental laws of emission and absorption of photon first discussed by Einstein in 1916. Another stochastic treatment of this problem given in B. Lavenda's book[4] has been shown to be flawed.

## References

- [1] M. Nauenberg, *The evolution of radiation towards thermal equilibrium: A soluble model that illustrates the foundations of statistical mechanics*, American Journal of Physics 72, 313 (2004)
- [2] A. Einstein *On the Quantum theory of Radiation*, Phys. Zeitschrift 18 (1917) 121. First printed in Mitteilugender Physikalischen Gesellschaft Zurich. No 18, 1916. Translated into English in Van der Waerden "Sources of Quantum Mechanics (North Holland 1967)pp. 63-77.
- [3] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North Holland 1981)
- [4] B. Lavenda, *Statistical Physics: A probabilistic approach* (Wiley, 1991) This book contains identically the same treatment and notation of the one step Markovian process found in the book of van Kampen, [3].
- [5] This stationary solution of Eq. 1 was given in a note added in proof in reference [1], and corresponds to Eq. 3.2 in [4] with  $\beta/\alpha=n_e/n_g$  and  $g = m$ .
- [6] There is a dependence on  $n$  in the values  $n_e = n_e^o - n$  and  $n_g = n_g + n$  appearing in Eq. 2 for the transition probabilities  $r(n)$  and  $g(n)$  which was neglected in Eq. 1. Previously, it was taken into account in reference [1]. The approximation made here is justified by the assumption that the two level atoms constitute a heat bath for the photons, which requires that that  $n \ll n_e^o$  and  $n \ll n_g^o$ .

[7] F. Hermann and P. Würfel, *Light with nonzero chemical potential*, American Journal of Physics **73** (2005) 717

[8] Equation 3.6 in reference [4] has the form

$$\left(\frac{\partial S(\bar{n})}{\partial \bar{n}}\right)_V = \left(\frac{\partial S(\bar{n})}{\partial \bar{n}}\right)_{V, \bar{U}} + \left(\frac{\partial S(\bar{n})}{\partial \bar{U}}\right)_{V, \bar{n}} \frac{d\bar{U}}{d\bar{n}} = \frac{-\mu + \epsilon}{T} \quad (17)$$

where  $S(\bar{n})$  is the Bose Einstein entropy,  $\bar{U} = \epsilon \bar{n}$ ,  $\mu$  is a chemical potential, and  $V$  is presumably the volume of the system. However, since the variable  $\bar{U}$  is proportional to  $\bar{n}$  the partial derivatives

$$\left(\frac{\partial S(\bar{n})}{\partial \bar{n}}\right)_{V, \bar{U}}, \text{ and } \left(\frac{\partial S(\bar{n})}{\partial \bar{U}}\right)_{V, \bar{n}} \quad (18)$$

do not make any mathematical sense. In order to introduce a chemical potential there must be *at least* two different states with energies  $\epsilon_1$  and  $\epsilon_2$  that can be occupied by the Bose particles, where  $n_1$  and  $n_2$  are the occupation numbers. Then the entropy of the bosons can depend on two *independent* variables  $\bar{n}$  and  $\bar{U}$ , namely,  $\bar{n} = \bar{n}_1 + \bar{n}_2$  and  $\bar{U} = \bar{n}_1 \epsilon_1 + \bar{n}_2 \epsilon_2$ .