The evolution of radiation toward thermal equilibrium: A soluble model that illustrates the foundations of statistical mechanics

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Abstract

In 1916 Einstein introduced the first rules for a quantum theory of electromagnetic radiation and applied them to a model of matter in thermal equilibrium with radiation to derive Planck's black-body formula. Einstein's treatment is extended here to time-dependent stochastic variables, which leads to a master equation for the probability distribution that describes the irreversible approach of his model to thermal equilibrium and elucidates aspects of the foundations of statistical mechanics. An analytic solution of the master equation is obtained in the Fokker-Planck approximation, which is in excellent agreement with numerical results. It is shown that the equilibrium probability distribution is proportional to the total number of microstates for a given configuration, in accordance with Boltzmann's fundamental postulate of equal a priori probabilities. Although the counting of these configurations depends on the particle statistics, the corresponding probability is determined here by the dynamics which are embodied in Einstein's quantum transition probabilities for the emission and absorption of radiation. In a special limit, it is shown that the photons in Einstein's model can act as a thermal bath for the evolution of the atoms toward the canonical equilibrium distribution. In this limit, the present model is mathematically equivalent to an extended version of the Ehrenfests's "dog-flea" model.

1 Introduction

In a seminal paper written in 1877, Boltzmann[1] formulated the basic principle of statistical mechanics: in equilibrium all the microstates of an isolated system that have the same total energy occur with equal *a priori* probability. As a consequence, the probability for a given macroscopic configuration is proportional to the accessible number of microscopic states that comprise it. Boltzmann demonstrated that the thermodynamic entropy is proportional to the logarithm of the maximum value of this number of configurations. Boltzmann's principle often is regarded as a necessary postulate from which other concepts of statistical mechanics and their relationship to thermodynamics can be deduced.[2]

In 1900 Planck made a fundamental application of this postulate to derive his famous black-body radiation formula.[3] Planck considered the source of the radiation to be Hertzian electromagnetic oscillators of frequency ν, but introduced the radical assumption that the energies of these oscillators were quantized in units of $\epsilon = h\nu$, where h is Planck's constant. This assumption yields a finite and countable number of microscopic configurations of fixed energy for which Boltzmann's statistical postulate could be readily applied.[4]

In 1916 Einstein developed a different approach to describe the condition for the thermal equilibrium of radiation and matter, which lead him also to a derivation of Planck's black-body radiation formula.[5] Following Bohr's quantum rules for the atom, Einstein proposed a quantum theory for the emission and absorption of radiation. He then combined this theory with a detailed balance argument to obtain Planck's equilibrium distribution for thermal radiation.[6] But why do these two completely different derivations, which have in common only Planck's quantum hypothesis that the energy of the source of radiation is discrete, and otherwise are based on different physical and mathematical assumptions, lead to the same result? Surprisingly, it appears that this question has not been addressed, and it is generally ignored in textbooks on statistical mechanics.[7]

In this paper we propose to answer this question by considering a stochastic treatment of Einstein's model that illustrates the foundations of statistical mechanics. It will be shown that the equilibrium probability distribution obtained in this way is the same as the result obtained by applying Boltzmann's postulate of equal a priori probabilities for the microstates of a system composed of atoms and photons with fixed total energy. Although the counting of these configurations depends on particle statistics, which can be Boltzmann, Bose-Einstein, or Fermi-Dirac, the associated probability distribution is determined in our treatment by the *dynamics*, which is embodied in Einstein's transition probabilities for the emission and absorption of radiation. We obtain also a time dependent master equation[10] that describes the irreversible approach of radiation and matter to thermal equilibrium. In the Fokker-Planck approximation we obtain an analytic solution in excellent agreement with numerical results, some of which are presented here.

In Sec. 2 a historical account of Einstein's model for the thermal equilibrium of radiation with matter is presented and the detailed balance argument that Einstein used to derive Planck's formula for black-body radiation is described. In Sec. 3 we extend this treatment by assuming that the variables in Einstein's model are stochastic variables, and we derive a probability function that describes the stationary equilibrium of this model. We show that this probability function is proportional to the number of configurations of the atoms and photons at fixed total energy, in accordance with Boltzmann's fundamental postulate of statistical mechanics and the symmetries based on quantum statistics. Thus, the counting associated with Bose-Einstein statistics for indistinguishable particles, which gives the probability distribution for photons in statistical mechanics,[11, 12] is obtained here from the quantum dynamics embodied in Einstein's transition probabilities for the absorption and emission of photons by atoms. Likewise, we obtain the corresponding results associated with Boltzmann's statistics for atoms that are treated as distinguishable particles, or with Fermi-Dirac statistics for atoms that satisfy Pauli's exclusion principle. In Sec. 4 we obtain the most probable configuration by evaluating the maximum of the equilibrium probability function. This maximum corresponds to the maximum value of Boltzmann's entropy function, which is the justification in statistical mechanics for the second law of thermodynamics. In Sec. 5 we consider a master equation[10] for the probability distribution that describes the evolution of Einstein's model when it is initially in an arbitrary non-equilibrium state, and we show that it always approaches a unique function which is the equilibrium probability obtained in Sec. 3. We define an entropy function that increases monotonically in time (a proof is given in Appendix A), and show that its maximum value determines the stationary or equilibrium probability. The time evolution and the approach to equilibrium of the probability function is illustrated by numerical solutions of this master equation. In Sec. 6 we approximate the master equation by a Fokker-Planck equation, and we obtain an analytic solution in the form of a Gaussian function with a time-dependent mean value and a width parameter that is found to be in excellent agreement with our numerical solutions. Finally we consider a limiting case where the photons act as a thermal bath for the atoms, which corresponds to an extension of a statistical model for the approach to thermal equilibrium by Paul and Tatiana Ehrenfest as extended recently by Ambegaokar and Clerk.[13] A summary and some conclusions are presented in Sec. 7.

2 Historical background: Einstein's quantum theory of radiation

In 1916 Einstein introduced a theory for the emission and absorption of electromagnetic radiation by atoms which anticipated aspects of the modern theory of quantum electrodynamics, and applied it to a derivation of Planck's black-body distribution for thermal radiation.[5] His model for matter in thermal equilibrium with radiation consists of atoms or molecules with discrete energy levels that exchange energy with the electromagnetic radiation inside a cavity with reflecting walls. For simplicity, we assume that these atoms have only two levels with an energy difference ϵ, and that the radiation has frequencies in the range ν to $\nu + \Delta\nu$. Instead of applying Maxwell's classical electromagnetic theory, Einstein assumed that the interaction of radiation with matter gives rise to quantum transitions between the energy levels of these atoms which are associated with the absorption and emission of radiation. The transition probabilities per unit time for the stimulated absorption and emission of radiation by an atom are assumed to be proportional to the electromagnetic energy density ρ_ν in the cavity, in analogy with the exchange of energy between an electromagnetic oscillator and radiation in classical theory. In addition, Einstein introduced a probability for the *spontaneous* emission of radiation from an excited state of the atom, independent of the radiation in the cavity, to take into account the classical radiation of a charged oscillator. Einstein's absorption probability p_a and emission probability p_e have the form

$$p_a = B_a \rho_\nu \tag{1}$$

$$p_e = A + B_e \rho_\nu, \tag{2}$$

where B_a and B_e are undetermined coefficients for absorption and stimulated emission respectively, and A is the coefficient for spontaneous emission.[6]

Einstein's derivation of Planck's black-body formula proceeds as follows: In thermal equilibrium the average number n_g of atoms in the ground state times the probability for absorbing radiation per unit time must be equal to the average number n_e of atoms in the excited state times the probability for emitting radiation per unit time. This reasoning leads to the *detailed balance* equation

$$p_a n_g = p_e n_e. \tag{3}$$

Equation 3 implies that

$$\frac{n_g}{n_e} = \frac{A}{B_a \rho_\nu} + \frac{B_e}{B_a}. \tag{4}$$

Next, Einstein assumed that the atoms are in thermal equilibrium at a temperature T, and determined the ratio n_g/n_e by invoking the canonical distribution in statistical mechanics,

$$\frac{n_e}{n_g} = e^{-\epsilon/kT}. \tag{5}$$

If we substitute Eq. (5) into Eq. (4) we obtain a relation for the equilibrium thermal radiation (black-body) energy density ρ_ν as a function of the temperature T in the cavity:

$$\rho_\nu = \frac{A}{(B_a e^{\epsilon/kT} - B_e)}. \tag{6}$$

By mid-1900 it had been discovered experimentally that for high temperatures and long wavelengths (small frequencies), the black-body radiation energy spectrum depends linearly on the temperature. At about the same time Rayleigh[14] had found that the equipartition theorem implied that

$$\rho_\nu = \gamma \nu^2 kT, \tag{7}$$

where γ is a constant.[15] For $T >> \epsilon/k$, this limit is obtained from Eq. (6) provided that $B_a = B_e = B$, which yields the relation

$$\rho_\nu = \frac{A/B}{(e^{\epsilon/kT} - 1)}. \tag{8}$$

At this point Einstein appealed to Wien's remarkable theoretical result that ρ_ν has a scaling dependence on the variables ν and T (Wien's displacement law) of the form

$$\rho_\nu = \nu^3 f(\nu/T), \tag{9}$$

where f was an undetermined function. By comparing Wien's result with Eq. (8), Einstein deduced the frequency dependence of the two undetermined parameters, ϵ and the ratio A/B,

$$\epsilon = h\nu, \tag{10}$$

$$\frac{A}{B} = \alpha\nu^3, \tag{11}$$

where h and $\alpha = h\gamma$ are universal constants. In this way, Einstein obtained Planck's black-body formula, but by a path quite different from the one taken earlier by Planck.

In this brilliant *tour de force* in which the probabilistic foundation of quantum theory was fist enunciated, Einstein not only derived Planck's formula, but by an independent route, he also obtained the fundamental quantum relation, Eq. (10), between the frequency ν of the emitted and absorbed radiation and the energy difference ϵ between two atomic levels – a relation that had been introduced by Planck and thirteen years later by Bohr. The constant $\alpha = 8\pi h/c^3$ also had been obtained by Planck. This constant also can be obtained from the constant γ in the Rayleigh-Jeans limit, Eq. (7), which implies that $\alpha = \gamma h$. This result was well known to Einstein, who had obtained this limit from a relation of Planck which he described in his famous 1905 paper on a heuristic' view of light.[16] But in his 1916 paper he commented only that to calculate the numerical value of the constant α, one would have to have an exact theory of electrodynamics and mechanical processes.[6]

In his original model Einstein assumed that the atoms could move freely, and he also demonstrated that the momentum transfer by the absorbed and emitted radiation was given by $h\nu/c$ along a direction "determined by 'chance' according to the present state of the theory." In this manner Einstein abstracted the fundamental concept of photons of different frequencies as the quantum states of electromagnetic radiation "entirely from statistical mechanics considerations."[17] It also follows from these considerations that the number density n_ν of photons in a radiation field of frequency ν and energy density ρ_ν is given by $n_\nu = \rho_\nu/h\nu$, although this relation was not stated explicitly in his paper. Einstein's remarkable "quantum hypothesis on the radiation exchange of energy"[6] was confirmed when the quantum theory of electromagnetic radiation was developed, giving an explicit expression for the coefficients A and B, and showing that the ratio $(A/B)(1/h\nu) = 8\pi\nu^2/c^3$ corresponds to the number of momentum states of the photons per unit frequency interval, as had been conjectured by Bose.[11]

Because the quantum theory is invariant under time reversal, it may seem surprising that Einstein transition probabilities for the absorption and emission of radiation, Eqs. (1) and (2), are different, due to the extra contribution for spontaneous emission. But these probabilities are averages over the direction of momentum of the transition probabilities for microstates with photons of fixed momentum. In the quantum dipole approximation, the probability of emission of a photon with momentum $\vec{p}$ is proportional to $n(\vec{p})+1$, where $n(\vec{p})$ is the initial number of photons, while the probability for absorption with the same initial number of photons is proportional to $n(\vec{p})$. When integrated over momenta, these probabilites yields Einstein's transition probabilities. For transitions between microstates, however, the proper comparison should be made by considering the absorption probability for $n(\vec{p}) + 1$ photons in the initial state, in which case these transition probabilities are the same. It should be stressed that the transition matrix elements between photon states are symmetric under the exchange of any pair of such states, and therefore photons must be treated as indistinguishable particles.

3 Extension of Einstein's detailed balance argument to stochastic variables

Even in thermal equilibrium, transitions associated with the absorption and emission of photons are occurring continuously, and therefore the number of atoms in the ground state n_g and in the excited state, n_e, as well as the number of photons n_p in the radiation field, must be considered to be stochastic variables which fluctuate in time. Hence the variables in Einstein's detailed balance equation, Eq. (3), correspond to some average value of these quantities. In order to describe Einstein's model in further detail, we introduce a probability function $P_{\rm eq}$ for the values of these stochastic variables. In accordance with the constraints of a fixed number of atoms $n = n_g + n_e$ and a fixed total energy $E = n_p h\nu + n_e \epsilon$, we can express $P_{\rm eq}$ as a function of a single integer k, where $n_g = k$, $n_e = n - k$, $n_p = n_q - n + k$, and $n_q = E/h\nu$. For $n \leq n_q$, the range of k is $0 \leq k \leq n$, while for $0 \leq n_q < n$, the corresponding range of k is $n - n_q \leq k \leq n$. The probability that there are k atoms in the ground state, and that one of them absorbs a photon during the interval of time δt is given by

$$Q_a(k) = k p_a(k) P_{\rm eq}(k) \delta t. \tag{12}$$

The corresponding probability that one of the $n - k$ atoms in the excited state emits a photon is given by

$$Q_e(k) = (n - k) p_e(k) P_{\rm eq}(k) \delta t. \tag{13}$$

The number of photons n_p in the cavity is obtained by dividing the energy in the cavity by $h\nu$, and consequently $n_p = \rho_\nu V \Delta\nu / h\nu$, where V is the volume of the cavity and $\Delta\nu$ is the width of the excited state of the atom. Then the basic transition probabilities for emission and absorption of photons, Eqs. (1) and (2), can also be expressed in terms of the number of photons n_p in the cavity,

$$p_a(k) = B'_a n_p \tag{14}$$

$$p_e(k) = B'_e (g + n_p), \tag{15}$$

where $B'_a = B_a h\nu / V\Delta\nu$, $B'_e = B_e h\nu / V\Delta\nu$, and $g = (8\pi/c^3) V \nu^2 \Delta\nu$ is the number of photon momentum states of frequency ν in an interval $\Delta\nu$.

The condition for thermal equilibrium requires that a configuration of the system with $n_e = n - k$ atoms in the excited state have the same probability $Q_e(k)$ to emit a photon during a time interval δt as the probability $Q_a(k+1)$ that a configuration with $n_g = k + 1$ atoms in the ground state absorb a photon during this time interval. This requirement implies the extended detailed balance relation

$$Q_a(k + 1) = Q_e(k). \tag{16}$$

If we neglect the correlations between the number of atoms and the number of photons in a given state, Einstein's detailed balance relation, Eq. (3), can be recovered by summing both sides of Eq. (16) over k, where the quantities n_g, n_e, and n_g now refer to averages over the distribution $P_{\rm eq}(k)$.

We now proceed to solve this extended detailed balance equation for $P_{\rm eq}(k)$ by substituting Eqs. (14) and (15) for p_a and p_e respectively in Eqs. (12) and (13), which leads to the recurrence relation,

$$P_{\rm eq}(k+1) = \frac{(n-k)p_e(k)}{(k+1)p_a(k+1)}P_{\rm eq}(k) = \frac{B'_e(n-k)(g+n_p)}{B'_a(k+1)(n_p+1)}P_{\rm eq}(k). \tag{17}$$

This relation can be solved for the equilibrium distribution $P_{\rm eq}(k)$, and we obtain

$$P_{\rm eq}(k) = \Big(\frac{B'_e}{B'_a}\Big)^k \Omega_a(k)\Omega_p(k)\chi, \tag{18}$$

where

$$\Omega_a(k) = \frac{n!}{n_g!\, n_e!}, \tag{19}$$

and

$$\Omega_p(k) = \frac{(g+n_p-1)!}{(g-1)!\, n_p!}, \tag{20}$$

with $n_g = k$, $n_e = n-k$, and $n_p = n_0 + k$, with $n_0 = n_q - n$. We see that $\Omega_a(k)$ is the well-known expression for the number of configurations of the atoms according to Boltzmann's statistics (distinguishable particles), while Ω_p is the corresponding expression for the number of configurations of photons according to Bose-Einstein statistics (indistinguishable particles). The constant χ is a normalization factor given by the condition $\sum P(k) = 1$, which yields

$$\chi^{-1} = \sum_k \big(\frac{B'_e}{B'_a}\big)^k \Omega_a(k)\Omega_p(k). \tag{21}$$

To recover Boltzmann's postulate, however, it also is necessary that $B'_a = B'_e$. As we have seen, Einstein required this condition in order to obtain the classical equipartition theorem at high temperatures, but subsequently it was shown to follow directly from quantum electrodynamics.

If the atoms in this model behave like fermions, we must include the effect of the Pauli exclusion principle in the probability expressions, Eqs. (12) and (13). We introduce the variables g_g and g_e for the number of degenerate ground states and excited states of the atom. Then $g_g - k$ is the number of unoccupied ground states and $g_e - n + k$ is the number of unoccupied excited states, and we have

$$Q_a^F(k) = k(g_e - n + k)p_a(k)P_{\rm eq}^F(k)\delta t, \quad (22)$$
$$Q_e^F(k) = (n-k)(g_g - k)p_e(k)P_{\rm eq}^F(k)\delta t. \quad (23)$$

If we equate $Q_a^F(k+1) = Q_e^F(k)$, we obtain the recurrence relation

$$P_{\rm eq}^F(k+1) = \frac{B_e'(g_g-k)(n-k)(g+n_p)}{B_a'(g_e-n+k+1)(k+1)(n_p+1)}P_{\rm eq}^F(k). \quad (24)$$

This relation implies that

$$P_{\rm eq}^F = (\frac{B_e'}{B_a'})^k \Omega_a^F(k)\Omega_e(k)\chi, \quad (25)$$

where

$$\Omega_a^F(k) = \frac{g_g!}{(g_g-k)!k!}\frac{g_e!}{(g_e-n+k)!(n-k)!}, \quad (26)$$

which is the expression for the number of configurations that have k atoms in the ground state and $n-k$ atoms in the excited state for Fermi-Dirac statistics.[2]

4 The most probable configuration and thermal equilibrium

In our stochastic treatment of Einstein's model for atoms in equilibrium with radiation, the most probable configuration occurs at the maximum value of $P_{\rm eq}(k)$, Eq. (17). According to statistical mechanics, this maximum corresponds also to the condition for thermal equilibrium. For large values of n, n_e, n_p, and g, the Stirling approximation for the factorial in Eqs. (19) and (20) gives the relations

$$\ln(\Omega_a(k)) \approx -n[\frac{n_g}{n}\ln(\frac{n_g}{n}) + \frac{n_e}{n}\ln(\frac{n_e}{n})] \quad (27)$$
$$\ln(\Omega_p(k)) \approx n_p \quad [(1+\frac{g}{n_p})\ln(1+\frac{g}{n_p}) - \frac{g}{n_p}\ln(\frac{g}{n_p})]. \quad (28)$$

If we assume that $B'_a = B'_e$, we have $\ln(P_{\rm eq}(k)) = \ln(\Omega_a(k)) + \ln(\Omega_p(k)) + \ln(\chi)$, and the maximum value for $P_{\rm eq}(k)$ is obtained in this approximation by the condition $d\ln(P_{\rm eq}(k))/dk = 0$, which implies

$$\frac{d\ln(\Omega_a(k))}{dk} + \frac{d\ln(\Omega_p(k))}{dk} = 0, \tag{29}$$

where

$$\frac{d\ln(\Omega_a(k))}{dk} = -\ln(\frac{n_g}{n_e}) \tag{30}$$

and

$$\frac{d\ln(\Omega_p(k))}{dk} = \ln(\frac{g}{n_p} + 1). \tag{31}$$

This condition leads to the relation

$$\frac{\bar{n}_g}{\bar{n}_e} = \frac{g}{\bar{n}_p} + 1, \tag{32}$$

where $\bar{n}_g = k_m$, $\bar{n}_e = n - k_m$, and $\bar{n}_p = n_0 + k_m$. This relation corresponds to Eq. (4) obtained from Einstein's detailed balance equation, Eq. (3), with $B_a = B_e = B$, $\rho_\nu = \bar{n}_p h\nu/V\Delta\nu$, and $g = (A/B)Vh\nu\Delta\nu$. But at this point, Einstein did not apply the energy conservation relation,[8] which we have written in the form $\bar{n}_p = n_0 + \bar{n}_g$, but instead he invoked the Gibbs canonical distribution for $\bar{n}_g/\bar{n}_e$, Eq. (5), and in this way he obtained Planck's black-body formula for ρ_ν, Eq. (8). We obtain from Eq. (32) a quadratic equation for the most probable value k_m of k:

$$k_m = \frac{1}{4}[(n - 2n_0 - g \pm \sqrt{(n - 2n_0 - g)^2 + 8n(g + n_0)}]. \tag{33}$$

The appropriate sign for the square root in Eq. (33) is determined by the condition that the most probable number $n_g = k_m$ of atoms in the ground state, and the most probable number of photons, $n_p = n_0 + k_m$, must both be positive. Because the right-hand side of Eq. (32) is greater than one, it is convenient to parameterize this solution by setting $\bar{n}_g/\bar{n}_e = g/\bar{n}_p + 1 = e^\Delta$, where Δ is a positive number. Moreover, at this point we can make contact with statistical mechanics, by recognizing that $\Delta = \epsilon/k_B T$, where T is identified with the equilibrium temperature of the cavity, and k_B is Boltzmann's constant.[9] In our stochastic treatment of Einstein's detailed balance condition, T is a positive parameter which depends on the value of the constants n, n_0, and g, and we recover Einstein's result, Eq. (8), without having to invoke the Gibbs canonical distribution, Eq. (5), as Einstein did in his original work.[8] The reason is that atoms and radiation can reach thermal equilibrium when treated as an isolated system, as has been shown here, without the aid of an external heat reservoir.

It is tempting to identify the ratios $k_m/n = 1/Z_a$ and $(n-k_m)/n = e^{-\epsilon/k_BT}/Z_a$, where $Z_a = 1 + e^{-\epsilon/k_BT}$, with the canonical probabilities introduced by Gibbs[18] for atoms to be in the ground state and excited states, respectively, where Z_a is the partition function for the atoms. But this identification would not be quite correct, because in our extension of Einstein's model, the number of photons and the number of atoms in a given configuration are strictly correlated, while such a correlation is absent if we treat the atoms in equilibrium with an external heat bath, as was originally done by Einstein.[6] According to Gibbs, the probability of a configuration that has k atoms in the ground state and $n-k$ atoms in an excited stated in thermal equilibrium with a heat bath at temperature T is given by

$$P_G(k) = \Omega_a(k)(p_g)^k(p_u)^{n-k}. \tag{34}$$

Then the mean value of k is given by

$$<k>_G = \sum kP_G(k) = \frac{n}{(1+e^{-\epsilon/k_BT})}, \tag{35}$$

which is equal to k_m; the magnitude of the fluctuations of k is given by

$$<\Delta k^2>_G = \sum[k^2 - <k>_G^2]P_G(k) = n\frac{e^{-\epsilon/k_BT}}{(1+e^{-\epsilon/k_BT})^2}. \tag{36}$$

But this result differs from the fluctuations of k obtained by approximating $P_{\text{eq}}(k)$ by a Gaussian distribution about the mean value k_m. In this case, we find that

$$\frac{1}{<\Delta k^2>} = -\frac{d^2\ln(\Omega_a\Omega_p)}{d^2k} = \frac{n}{n_g n_e} + \frac{g}{n_p(g+n_p)}, \tag{37}$$

evaluated at $k_m = n/(1+e^{-\epsilon/k_BT})$, which gives

$$\frac{n_g n_e}{n} = n\frac{e^{-\epsilon/k_BT}}{(1+e^{-\epsilon/k_BT})^2} \tag{38}$$

and

$$\frac{n_p(g+n_p)}{g} = \frac{g e^{h\nu/k_B T}}{(e^{h\nu/k_B T}-1)^2}. \qquad (39)$$

The first term in Eq. (37) gives the same contribution to the mean square deviation, $<\Delta k^2>_G$, Eq. (36), that is obtained from the Gibb's probability distribution, Eq. (34), while the second term is the corresponding fluctuation $<(\Delta n_p)^2>_G$ that is associated with a gas of photons in thermal equilibrium. Hence

$$\frac{1}{<(\Delta k)^2>} = \frac{1}{<(\Delta n_g)^2>_G} + \frac{1}{<(\Delta n_p)^2>_G}. \qquad (40)$$

In Einstein's extended model, the fluctuations in the number of photons can be neglected provided that the condition

$$\frac{<(\Delta n_g)^2>_G}{<(\Delta n_p)^2>_G} = \frac{(e^{\epsilon/k_B T}-1)^2}{(e^{\epsilon/k_B T}+1)^2}\frac{n}{g} \ll 1, \qquad (41)$$

is satisfied. For this inequality to be satisfied at all temperatures, it is necessary and sufficient that $n << g$, in which case the photons act as a thermal bath for the atoms. But for the temperature T to be determined only by the state of the photon gas, it also is necessary that in addition $n << n_0$.

To show that the equilibrium configuration obtained at the maximum value of the probability function $P_{\rm eq}(k)$ corresponds to thermal equilibrium, Boltzmann associated the maximum value of the logarithm of the number of configurations Ω with the thermodynamic entropy. We set

$$S_a = k_B \ln(\Omega_a), \qquad (42)$$

and

$$S_p = k_B \ln(\Omega_p) \qquad (43)$$

for the statistical entropies of the atoms and the photons, respectively. The condition for the most probable state of the system, Eq. (29), corresponds to the second law of thermodynamics, which states that at equilibrium the total entropy $S = S_a + S_b$ of an isolated system is a maximum.

In this simple model, the entropies S_a and S_p can be expressed as functions of the energies $E_a = n_e\epsilon$ and $E_p = n_p h\nu$, respectively, and the temperatures T_a and T_p for the atoms and photons in Einstein's model are given by the relations

$$\frac{dS_a}{dE_a} = \frac{1}{T_a} = \frac{k_B}{\epsilon}\ln(\frac{n_g}{n_e}), \qquad (44)$$

$$\frac{dS_p}{dE_p} = \frac{1}{T_p} = \frac{k_B}{h\nu}\ln(\frac{g}{n_p} + 1). \tag{45}$$

Thus the maximum condition for the total statistical entropy leads to the thermodynamic condition for thermal equilibrium:

$$T_a = T_p = T. \tag{46}$$

We remark that, according to this definition of temperature, the value T_a for the atoms is not restricted to positive values, because the entropy of the atoms is not a monotonically increasing function of the energy E_a. For example, T_a becomes negative when $n_g \leq n_e$, but, as we have shown above, such a condition is not possible for atoms in thermal equilibrium with electromagnetic radiation. Thus, under appropriate conditions the photons can act as a thermal bath for the atoms, but the atoms cannot act as a thermal bath for the photons.

From the dynamical point of view developed here, the statistical entropies S_a and S_p and the energies E_a and E_p are stochastic variables which vary as a function of time, as is also the case for the total entropy $S = S_a + S_b$. This behavior is illustrated in Figs. 1 and 2 which show the variation and fluctuations in the energy and entropy as calculated using the absorption and emission transition probabilities, Eqs. (14) and (15), for the case $n = g = n_q = 100$. In these calculations we fixed the unit of time by setting $B = 1$, and we determined whether transitions occur during time intervals $\delta t = 0.001$ by using a random number generator. Notice that in addition to rapid fluctuations in the energy and entropy of the atoms and photons, there also is a slower and correlated variation associated with the exchange of energy and entropy between the atoms and photons which vary irregularly about the most probable value. As expected, the fluctuations in energy and entropy about the mean are related approximately by the thermodynamic relations

$$\delta E_a = T\delta S_a, \tag{47}$$

and

$$\delta E_p = T\delta S_p. \tag{48}$$

But these conditions are satisfied here only approximately because the total energy $E = E_a + E_p$ is fixed, while the total entropy $S = S_a + S_p$ is a stochastic variable. Indeed, as shown in Fig. 2, the total entropy exhibits fluctuations which are smaller than the separate fluctuations of the entropies of the atoms and the photons, and it is bounded from above by the maximum of the total entropy.

5 master equation for the evolution of Einstein's model

We now consider the evolution of Einstein's model when it is initially in an arbitrary non-equilibrium state. For example, at $t = 0$ all the atoms can be in the ground state with a number of photons in the cavity, or alternatively, a number of atoms can be in the excited state without any photons initially present in the cavity. For a time dependent probability function $P(k,t)$, Einstein's transition probabilities for emission and absorption of radiation per unit time, Eqs. (14) and (15), determine uniquely the probability $P(k, t+\delta t)$ at a slightly later time $t + \delta t$. We follow here the treatment of stochastic variables described in van Kampen's book.[10] After the time interval δt, the configuration of atoms and photons represented by the integer k can occur at $t + \delta t$ under three different conditions:

1. At time t there are $n_g = k + 1$ atoms in the ground state, and during the time interval δt one of these atoms absorbs a photon to make a transition to the excited state.

2. At time t there are $n_e = n - k + 1$ atoms in the excited state, and during the time interval δt one of the atoms in the excited state emits a photon and makes a transition to the ground state.

3. At time t there are $n_g = k$ atoms in the ground state and $n_e = n - k$ atoms in the excited state, and during the time interval δt none of these atoms absorbs or emits a photon.

We add the probabilities for these three mutually exclusive events and obtain

$$\begin{aligned} P(k, t+\delta) &= W(k, k+1)\delta t P(k+1, t) + W(k, k-1)\delta t P(k-1, t) \\ &+[1 - ((W(k+1, k) + W(k-1, k))\delta t] P(k, t), \end{aligned} \quad (49)$$

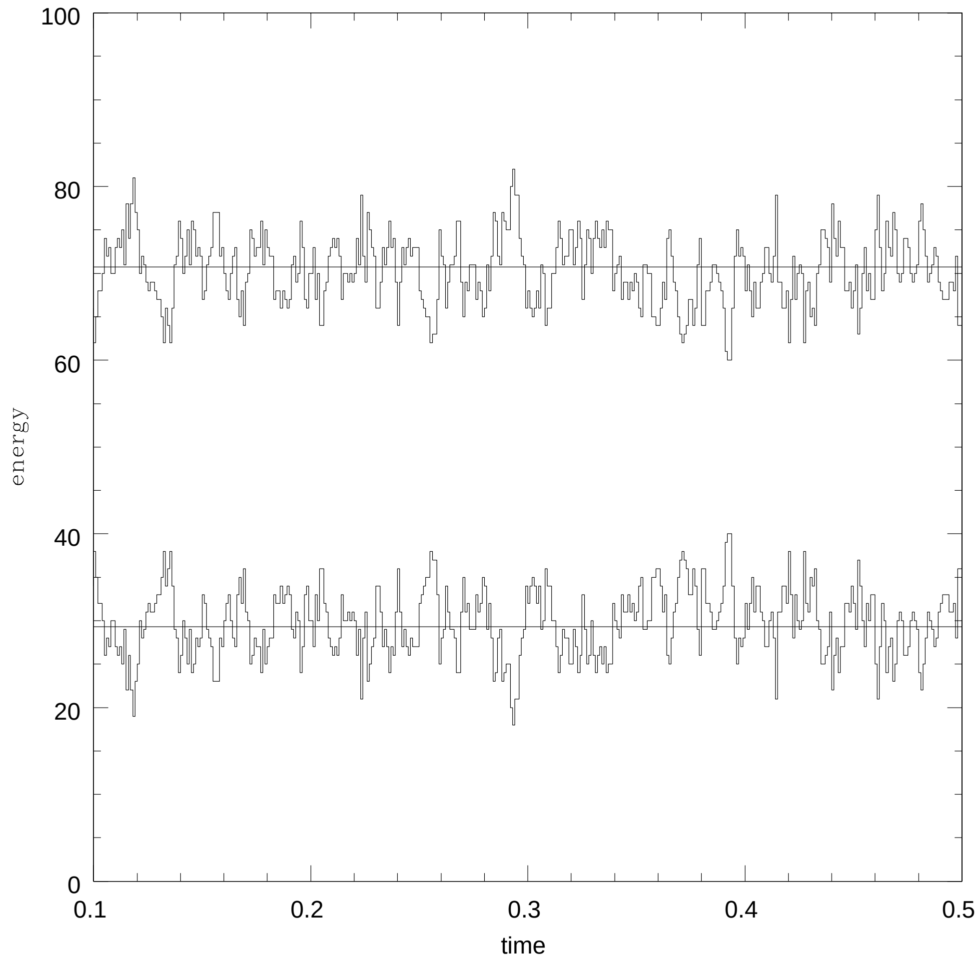

Figure 1: Fluctuations of the energy for atoms (lower curve) and photons (upper curve) in thermal equilibrium

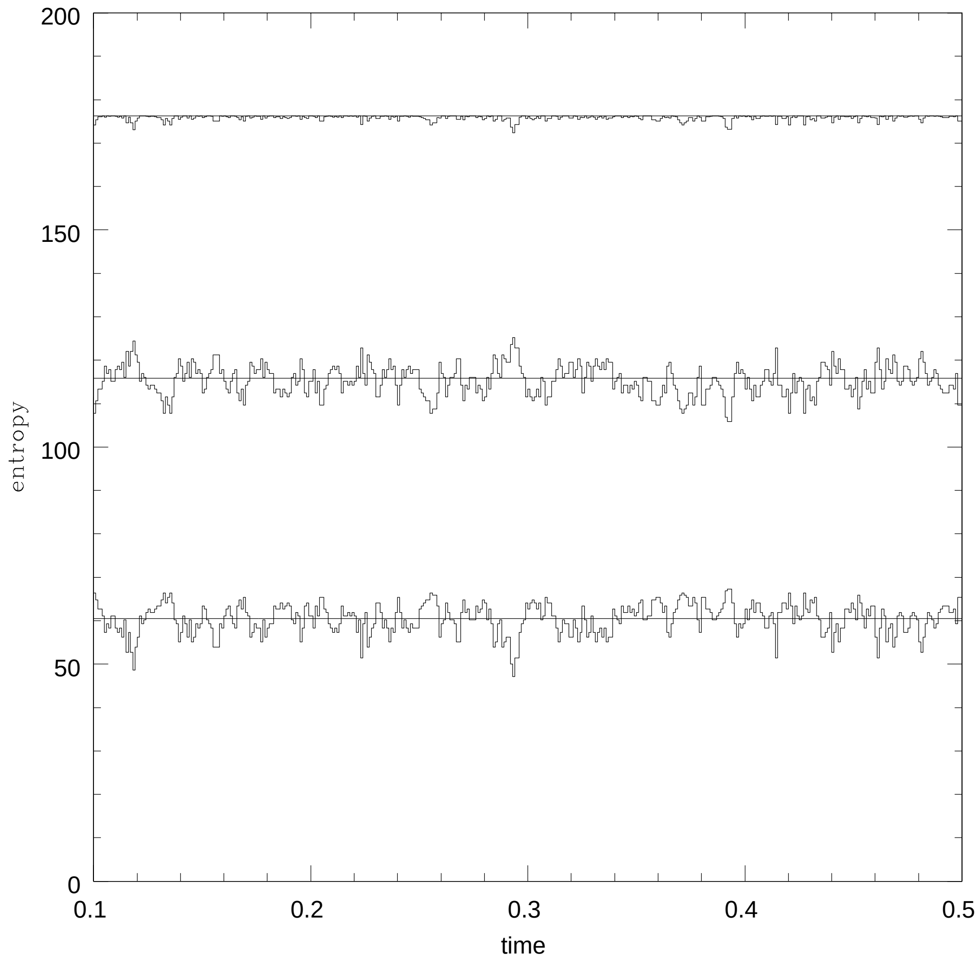

Figure 2: Fluctuations of the entropy for atoms (lower curve) and photons (middle curve) and for the total entropy (upper curve) in thermal equilibrium

where

$$W(k-1,k) = kp_a(k), \tag{50}$$

and

$$W(k+1,k) = (n-k)p_e(k). \tag{51}$$

The transition probabilities $W(k',k)$, where $k' = k \pm 1$, satisfy the boundary conditions $W(-1,0) = W(0,-1) = W(n+1,n) = W(n,n+1) = 0$. In the limit $\delta t \to 0$, we obtain a first order linear differential equation for $P(k,t)$, which can be written in matrix form as

$$\frac{dP(k,t)}{dt} = \sum_{k'} W(k,k')P(k',t), \tag{52}$$

where

$$W(k,k) = -kp_a(k) - (n-k)p_e(k). \tag{53}$$

Note that the matrix elements $W(k',k)$ satisfy the condition $\sum_{k'} W(k',k) = 0$, leading to the conservation of probability relation $\sum_k dP(k,t)/dt = 0$.

The condition $dP_s(k)/dt = 0$ for a stationary solution $P_s(k)$ of Eq. (52) is that

$$\sum_{k'} W(k,k')P_s(k) = 0, \tag{54}$$

which can be expressed in the form

$$\begin{aligned} &W(k,k+1)P_s(k+1) - W(k+1,k)P_s(k) \\ &= W(k-1,k)P_s(k) - W(k,k-1)P_s(k-1) = C \end{aligned} \tag{55}$$

for $0 \leq k \leq n$, where C is a constant independent of k. For $k = 0$ and $k = n$, we find that $C = 0$, and consequently we recover the extended detailed balance equation for the equilibrium distribution $P_{\rm eq}(k)$, Eq. (17), with $P_s(k) = P_{\rm eq}(k)$.

More generally, the solution of the master equation, Eq. (52), can be expanded in the form[10]

$$P(k,t) = P_s(k) + \sum_j c_j(k)e^{-\lambda_j t}, \tag{56}$$

where the coefficients $c_j(k)$ are eigenvectors of the matrix $W(k,k')$ with eigenvalues $-\lambda_j$,

$$\sum_{k'} W(k,k')c_j(k') = -\lambda_j c_j(k). \tag{57}$$

The stationary or equilibrium solution $P_s(k)$ is a unique eigenstate of $W(k, k')$ with the eigenvalue $\lambda_0 = 0$, see Eq. (54).

It can be shown that the other eigenvalues λ_j are positive definite,[10] and therefore all the solutions of Eq. (52) converge to the equilibrium solution. Another proof of this convergence is given in Appendix A by constructing an entropy function that increases monotonically with time. The lengths of the eigenvectors c_j are determined by the initial conditions $P(k, 0)$.

We illustrate the evolution of the probability function $P(k, t)$ to the equilibrium probability $P_{\rm eq}(k)$, by numerically evaluating the solution of the master equation, Eq. (52), for two different initial conditions. In Fig. 3 we consider the case when initially there are $n = 200$ atoms in the excited state and no photons, so that $n_q = 200$ with $g = 200$, and show the probability function $P(k, t)$ at the end of each of 10 consecutive time intervals $\delta t = 0.02$. At time $t = .2$ the solution has nearly approached the equilibrium solution, which according to Eq. (33) has its maximum at $k_m = 100\sqrt{2}$. This numerical solution suggests that a very good approximation to $P(k, t)$ is a Gaussian function with time dependent parameters for the mean value of k and the mean square width $(\Delta k)^2$. This is indeed the case, as will be shown in Sec. 6. In Fig. 4 we show the corresponding evolution starting at $t = 0$ for a uniform distribution $P(k, 0) = 1/n$, with the same total energy $n_q = 200$, as in Fig. 3. In this case the initial evolution is not represented by a Gaussian function, but this form is again approached near equilibrium. Both cases evolve to the same final form because we have chosen the same total energy.

6 The Fokker-Planck equation

Numerical solutions of the master equation, Eq. (52) (see for example Fig. 3), suggest that for large values of the parameters n, n_0, and g, the probability $P(k, t)$ is a continuous function which is well approximated by a Gaussian function with time dependent parameters for the mean value of k and the mean width Δk. We obtain such an approximate solution by assuming that $P(k, t)$ is a differentiable function of a continuous variable k, and expanding $P(k \pm \delta k, t)$ to second-order in δk with $\delta k = 1$. We set

$$P(k \pm 1, t) \approx P(k, t) \pm \frac{dP(k, t)}{dk} + \frac{1}{2}\frac{d^2P(k, t)}{dk^2}, \tag{58}$$

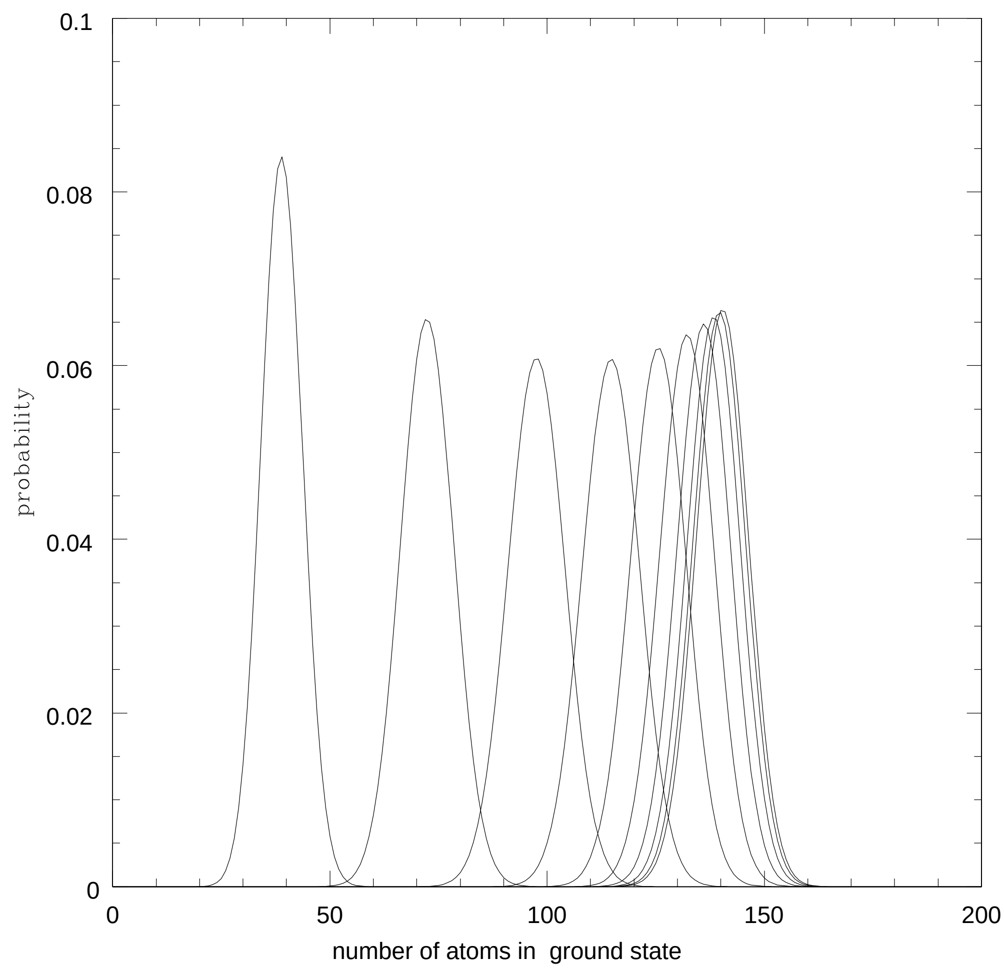

Figure 3: Time evolution of the probability function $P(k,t)$ at the end of each of 10 consecutive time intervals $\delta t = .02$, for $g = 200$, when initially there are $n = 200$ atoms in the excite state and no photons.

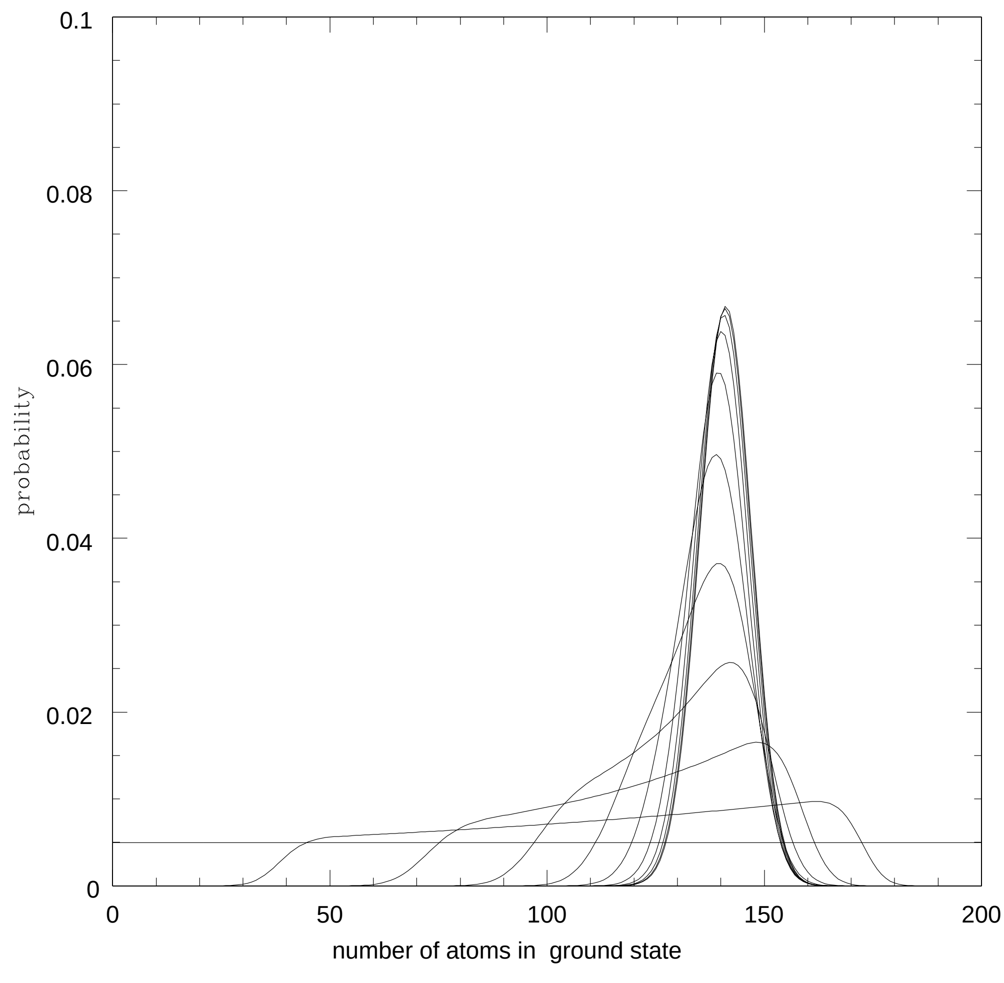

Figure 4: Time evolution for the probability function $P(k,t)$ at the end of each of 10 consecutive time intervals $\delta t = .02$, for g and $n = 200$, when initially $P(k,0) = 1/(n+1)$ and $n_q = 200$.

and approximate the master equation, Eq. (52), by the Fokker-Planck equation

$$\frac{\partial P(k,t)}{\partial t} = \frac{\partial}{\partial k}[a(k)P(k,t] + \frac{\partial^2}{\partial k^2}[b(k)P(k,t)], \tag{59}$$

where

$$a(k) \;=\; k(k+n_0) - (n-k)(g+n_0+k), \tag{60}$$

and

$$b(k) \;=\; \frac{1}{2}[k(k+n_0) + (n-k)(g+n_0+k)] \tag{61}$$

(with $B' = 1$). For large values of n and k, Eq. (59) can be solved approximately by assuming that $P(k,t)$ is a Gaussian function,

$$P(k,t) = \sqrt{\frac{1}{2\pi\delta(t)}}e^{-(k-k_m(t))^2/2\delta(t)}, \tag{62}$$

where $k_m(t)$ and $\delta(t)$ are time dependent parameters. We have

$$\frac{\partial P(k,t)}{\partial t} = [-\frac{1}{2\delta}\frac{d\delta}{dt} + \frac{(k-k_m)}{\delta}\frac{dk_m}{dt} + \frac{(k-k_m)^2}{2\delta^2}\frac{d\delta}{dt}]P(k,t), \tag{63}$$

$$\frac{\partial P(k,t)}{\partial k} \;=\; -\frac{(k-k_m)}{\delta}P(k,t), \tag{64}$$

$$\frac{\partial^2 P(k,t)}{\partial k^2} \;=\; [-\frac{1}{\delta} + \frac{(k-k_m)^2}{\delta^2}]P(k,t). \tag{65}$$

If we substitute Eqs. (63)–(65) in the Fokker-Planck equation, Eq. (59), and equate the coefficients of $(k-k_m)^j$ for $j = 0, 1$ and 2, we obtain first-order nonlinear differential equations for $k_m(t)$ and $\delta(t)$. We neglect a term $db(k)/dk$ that is of order $1/n$ and obtain for the $j = 1$ terms,

$$\frac{dk_m(t)}{dt} = -a(k_m(t)). \tag{66}$$

For the $j = 0$ and $j = 2$ terms, we obtain the *same* equation (a consistency requirement for the validity of our Gaussian ansatz),

$$\frac{d\delta(t)}{dt} + 2a'(k_m(t))\delta(t) = 2b(k_m(t)), \tag{67}$$

where

$$a'(k) = \frac{da(k)}{dk} = 4k + 2n_0 - g - n. \tag{68}$$

Equations (67) and (68) also can be obtained from the master equation, Eq. (52), by evaluating the time derivatives of the averages $k_m(t) = <k>$ and $\delta(t) = <(\Delta k)^2>$, assuming that the probability function $P(k,t)$ is sharply peaked at $k = k_m(t)$.

If we assume that initially $k = k_m(0)$, where $0 \leq k_m(0) \leq n$, the solution of Eq. (66) is given by

$$k_m(t) = \frac{(k_+ - k_- \phi e^{-\lambda t})}{(1 - \phi e^{-\lambda t})}, \tag{69}$$

where

$$\phi = \frac{(k_m(0) - k_+)}{(k_m(0) - k_-)}, \tag{70}$$

$$\lambda = \sqrt{(n - 2n_0 - g)^2 + 8n(n_0 + g)}, \tag{71}$$

and

$$k_\pm = \frac{1}{4}(n - 2n_0 - g \pm \lambda). \tag{72}$$

Here time is measured in units of $1/B'$, and in the limit $\lambda t >> 1$, we see that $k_m(t)$ approaches k_+, which is equal to the most probable value of k at equilibrium obtained previously, Eq. (33.

The solution for $\delta(t)$, Eq. (67), where initially $\delta(0) = \delta_0$, is given by

$$\delta(t) = \frac{1}{n} e^{-\xi(t)} \int_0^t dt' e^{\xi(t')} b(k_m(t')) + \delta_0 e^{-\xi(t)}, \tag{73}$$

where

$$\xi(t) = \frac{2}{n} \int_0^t dt' a'(k_m(t')). \tag{74}$$

For $\lambda t >> 1$, we have $\xi(t) \approx 2\lambda t$, and $\delta(t)$ approaches the equilibrium value

$$\delta = \frac{b(k_+)}{a'(k_+)} = \frac{k_+(n - g) + n(g + n_0)}{2(4k_+ + 2n_0 + g - n)}, \tag{75}$$

which can be shown to correspond to the value for $<(\Delta k)^2>$ at equilibrium, Eq. (37) obtained previously.

In the limit that both n_0 and g are much larger than n, the changes in the numbers of photons in the cavity can be neglected in the expression for the probabilities for the absorption and emission of photons, Eqs. (14) and (15), and we have

$$p_a \approx B' n_0, \tag{76}$$

and

$$p_e \approx B'(g + n_0). \tag{77}$$

In this case the photons act as a heat bath for the atoms at a temperature determined by g and n_0, where $T = (1/h\nu)\ln(g/n_0 + 1)$. In this limit, the time dependent solution, Eqs. (69) and (73), simplifies to the form

$$k_m(t) = np + (k_m(0) - np)e^{-\lambda t}, \tag{78}$$

and

$$\delta(t) = \frac{n_0}{\lambda}[p(1 - e^{-2\lambda t}) + (1 - e^{\Delta})(\frac{k_m(0)}{n} - p)e^{-\lambda t}(1 - e^{-\lambda t})], \tag{79}$$

where $\lambda = n_0(e^{h\nu/k_B T} + 1)$ and $p = 1/(1 + e^{-h\nu/k_B T})$ is the canonical probability of finding an atom in the ground state at temperature T.

For systems in contact with a thermal bath, our model explains the puzzle that a ratio of transition probabilities like p_e/p_a,which is determined by the underlying dynamics of the system, can also be expressed in terms of the canonical Gibbs probability function, which depends on the temperature of the heat bath.[19] Indeed, as we have shown here, the temperature of the heat bath is determined by the magnitude of this ratio. In this limit we find that Einstein's model, in the version discussed here, corresponds mathematically to the Ehrenfests's"dog-flea" model,[20] which was recently extended to finite temperatures by Ambegaokar and Clerk.[13] Hence Eqs. (78) and (79) provide also an approximate analytic solution for this model, which previously had been solved by Kac[21] only for the special case that $p = 1/2$ corresponding to infinite temperature.

7 Summary

We have shown that a stochastic treatment of a simplified version of Einstein's 1916 model for atoms in interaction with photons, illustrates various aspects of the foundations of statistical mechanics. From the underlying quantum dynamics of this model, which is consistent with modern quantum electrodynamics, we obtained directly the equilibrium probability distribution P_{eq} in accordance with the familiar results obtained in statistical mechanics. For atoms treated as distinguishable entities, we found that this equilibrium probability is proportional to the number of configurations associated with Boltzmann's statistics, while for atoms that obey the Pauli exclusion principle, the corresponding statistics is Fermi-Dirac, and for photons it is Bose-Einstein. Conventionally, these probability distributions are derived in statistical mechanics by using a postulate introduced by Boltzmann[1] in 1877, which states that in equilibrium all the microstates of a system at a fixed energy are equally probable.

For the evolution of the Einstein model we discussed a master equation which describes the approach of the probability distribution to an unique stationary solution that corresponds to the equilibrium distribution, starting from any arbitrary initial state. In the Fokker-Planck approximation we obtained an analytic solution of this equation which is in excellent agreement with numerical solutions, some of which were presented here. Associated with this probability function we described an entropy function that increases monotonically in time reaching a maximum value at the thermal equilibrium distribution.

We must add, however, an important caveat. In quantum mechanics a pure state of an isolated system can be described by a wavefunction, and at any time t when there are atoms in both the ground state and the excited state, as well as photon states, this wave function is a linear combination of wave functions describing these states. Therefore transition probabilities, which are obtained from bilinear terms of this wavefunction, contain interference terms that have been ignored here. In the literature this approximation is known as the random phase approximation or decoherence, but there does not seem to be a general consensus for how to justify this approximation from first principles, and a deeper understanding is lacking. Moreover, there is the famous problem with the measurement process associated with the Copenhagen interpretation of quantum mechanics. Such a process, which is implied here by the application of transition probabilities repeated *ad infinitum* during short intervals of time δt, is obviously not taking place in a macroscopic system that is evolving to thermodynamic equilibrium, unless one believes that a Maxwell-like demon is continuously carrying out such measurements. In our view, however, the success of the stochastic detailed balance approach described here justifies the application of the Copenhagen interpretation to transition probabilities per unit time in the absence of any identifiable measurement process, and/or the existence of an observer.

From a historical perspective, it is interesting to speculate that Einstein, who was a master of fluctuation theory, could have carried out stochastic calculations similar to the ones we have done here. Then, from the time-asymmetric master equation resulting from his microscopic quantum theory of radiation in interaction with matter, he would apparently have provided a justification for the statistical approach to thermal equilibrium, which previously Boltzmann had claimed for classical systems that satisfied time-symmetric dynamics. As far as we know, however, Einstein never did such a calculation, and his contemporaries (and textbook writers up to the present) did not notice the fundamental flaw that as a microscopic theory his quantum theory of radiation is not time-reversal invariant.

Recently, Ambegaokar and Clerk[13] discussed the 1906 "dog-flea" model of the Ehrenfests,[20] which provided an early model to illustrate Boltzmann's ideas. In a special limit, we have shown that the extension of this model to finite temperatures[13] is mathematically equivalent to Einstein's model for atoms interacting with radiation, when the atoms have only two levels. An analytic solution for the original Ehrenfests' model was not obtained until 1947 by Kac,[21] and we have now also obtained an analytic solution for the finite temperature extension of this model,[22] applying the Fokker-Planck approximation, Eqs. (78) and (79).

A Entropy

We discuss the definition of entropy and its evolution when Einstein's model is not initially in equilibrium. It would appear that a natural extension for entropy is the quantity $\sum_k P(k,t)\ln\Omega(k)$, but this expression does not have the desired property that the entropy increase monotonically with time. Instead, this property is satisfied by a related expression,[10, 23]

$$S(t) = -\sum_k P(k,t)\ln\frac{P(k,t)}{\Omega(k)}. \tag{80}$$

In the case that $P(k,t)$ is sharply peaked at some value $k(t)$, as we have found when $P(k,t)$ approaches the equilibrium distribution $P_{\mathrm{eq}}(k)$, the term,

$$-\sum_k P(k,t)\ln P(k,t), \tag{81}$$

is small compared to

$$\sum_k P(k,t)\ln\Omega(k). \tag{82}$$

In turn, this term can then be approximated by $\ln\Omega(k(t))$, and we have for the entropy $S(t)$,

$$S(t)\approx\ln\Omega(k(t)). \tag{83}$$

If we apply the master equation, Eq. (52), to the definition for entropy, Eq. (80), we obtain

$$\frac{dS(t)}{dt}=-\sum_{k,k'}W(k,k')P(k',t)\ln\frac{P(k,t)}{\Omega(k)}. \tag{84}$$

By substituting the relation

$$W(k,k)=-(W(k+1,k)-W(k-1,k), \tag{85}$$

and setting

$$Z(k,t)=\frac{P(k+1,t)}{\Omega(k+1)}-\frac{P(k,t)}{\Omega(k)}, \tag{86}$$

we obtain

$$\frac{dS(t)}{dt}=\sum_k[W(k+1,k)P(k,t)-W(k,k+1)P(k+1,t)]\ln Z(k,t). \tag{87}$$

If we substitute the relation

$$W(k,K+1)\Omega(k+1)=W(k+1,k)\Omega(k), \tag{88}$$

we obtain

$$\frac{dS(t)}{dt}=\sum_k W(k+1,k)\Omega(k)Z(k,t)\ln Z(k,t), \tag{89}$$

which proves that[10]

$$\frac{dS(t)}{dt}\geq 0. \tag{90}$$

Thus, the entropy defined in Eq. (80) increases monotonically toward a maximum value corresponding to thermal equilibrium. Recently proposed generalizations of this form of the entropy[24] are incompatible with this fundamental requirement.

B Acknowledgements

I would like to thank Vinay Ambegaokar for his insightful comments and for calling my attention to the discussion of the Ehrenfests' model by M. Kac,[21] and Theo Nieuwenhuizen for several helpful suggestions to clarify some of the ideas presented in this paper.

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[1] L. Boltzmann, “”Uber die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmtheorie und der Wahrscheinlichkeitsrechnungen respektive den Sätzen über das Wärmegleichgewichht,” Wien. Ber. **76**, 373–435 (1877). These articles are reprinted in *Wissenschaftliche Abhandlungen von Ludwig Boltzmann*, edited by F. Hasenöhrl (Chelsea Publishing, New York, 1968), Vol. 2, p. 164.

[2] R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, 1962).

[3] M. Planck, “Zur Theorie des Gestzes der Energieverteilung in Normalspectrum,” Verhandl. der Deutschen Physikal. Gesellsch. **2**, 237-245 (1900). Reprinted in Max Planck, *Physikalisch Abhandlungen und Vorträge* (Friedr. Vieweg & Sohn, Braunschweig, 1958), Vol. 1, 698-706

[4] In order to count the number of microstates (called “complexions” by Boltzmann) in a model consisting of a one-dimensional molecular gas, Boltzmann introduced the idea of distributing the total energy in discrete elements of magnitude ϵ, but afterward he took the limit $\epsilon = 0$ as required by classical physics. For his model consisting of Hertzian oscillators with frequency ν, Planck essentially took this discretation idea directly from Boltzmann, including his formula for the total number of

configurations, but then he ignored the classical limit, and instead set the value as $\epsilon = h\nu$, where h is a constant.

[5] In November 1916 Einstein wrote to his friend Michele Besso, "A splendid idea has dawned on me about the absorption and emission of radiation ...," which led him to a new and distinct derivation of Planck's radiation formula. See A. Pais, *Subtle is the Lord: The Life and Science of Albert Einstein* (Oxford University Press, 1982), p. 405.

[6] A. Einstein, "Zur Quantentheorie der Strahlung," Phyzikalisches Zeitschrift **18**, 121–128 (1917). An earlier version appeared under the title "Strahlungs Emission und Absorption nach der Quantum theory" in Deutsches Physikalisches Gesellschaft Verhandlungen **18**, 318–323 (1916). Reprinted with annotations in *The Collected Works of Albert Einstein*, edited by A. J. Kox, M. J. Klein, and R. Schulman (Princeton Univ. Press, 1966), Vol. 6. An English translation can be found in Van der Waarden, *Sources of Quantum Mechanics* (North-Holland, Amsterdam, 1967), p. 63.

[7] In some textbooks, for example, C. Kittel, *Elementary Statistical Physics* (Wiley, 1958), p. 171, it is shown that detailed balance implies equal probability of the microstates, provided that the transition probability between any pair of these states is the same in both directions. But due to the occurence of an additional probability for spontaneous emission, this condition is not satisfied by Einstein's theory. The reason is that Einstein's probabilities, Eqs. (1) and (2), refer to transitions between "coarse grained" configurations which are averages over the direction of momentum of the photons.

[8] Einstein assumed that the atoms constituted a gas in thermal equilibrium at temperature T, and obtained the energy distribution of radiation ρ_ν by the requirement that the quantum absorption and emission of radiation "does not disturb" the distribution of atomic states given by statistical mechanics.

[9] In statistical mechanics constraints such as energy conservation are introduced by the method of Lagrange multipliers. In this case, the variation of the number of atoms in the excited state n_e and the number of

photons n_p can be treated as independent variables, while the constraint of fixed total energy of atoms and radiation, $E = n_e\epsilon + n_p h\nu$, is taken into account by the well known Lagrange multiplier $\beta = 1/k_B T$.

[10] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).

[11] S.N. Bose, "Plancks Gesetz und Lichquanthypothese," Zeitschrift für Physik **26**, 178-181 (1924).

[12] A. Einstein, " Quantum theorie des einatomigen idealen Gases", Sitzungsberichte, Preussiche Akademie der Wissenschaften, 1924, 261-267

[13] V. Ambegaokar and A. A. Clerk, "Entropy and time," Am. J. Phys. **67**, 1068-1073 (1999). In a note added in proof, B. Widom is quoted as remarking "that there are 'purists' who think that the Ehrenfest model is not a first principle explanation of irreversibility because there is a 'stochastic element' in the model which makes it 'not deterministic, as real dynamics is..." But the laws of physics are based on quantum mechanics which is probabilistic. Indeed, a stochastic treatment is essential in Einstein's theory of matter interacting radiation, and as we have shown here, in a certain limit his model corresponds to the Ehrenfests' model. It is remarkable that the Ehrenfests introduced a probabilistic model to describe the origin of irreversibility in physical systems 20 years before the development of modern quantum mechanics. It is plausible that Paul Ehrenfest, who was a close friend of Einstein and frequently discussed physical problems with him, might have influenced Einstein's thoughts on his quantum theory of radiation.

[14] J. S. W. Rayleigh, "Remarks upon the Law of Complete Radiation," Phil. Mag. **49**, 539-540 (1900).

[15] J. H. Jeans, "On the Partition of Energy between Matter and Radiation" Phil. Mag. **10**, 91-98 (1905). In a postscript, Jeans showed that $\gamma = 8\pi/c^3$ had been given incorrectly by Rayleigh, who acknowledged his error of a factor 8 in Nature **72** 243-244 (1905). See also A. Pais in *Subtle is the Lord: The Life and Science of Albert Einstein* (Oxford University Press, 1982) p. 134

[16] A. Einstein, “”Uber einen die Erseugung und Verwandlungen des Lichten betreffenden heuristischen Gesichtpunkt,” Annalen der Physik **17**, 132–148 (1905).

[17] A. Pais, *Subtle is the Lord: The Life and Science of Albert Einstein* (Oxford University Press, 1982), p. 410.

[18] J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (Ox Bow Press, Woodbridge, 1981).

[19] In Ref. [10] van Kampen regards $P_{\rm eq}$ as “known from equilibrium statistical mechanics,” and states that a recurrence relation like Eq. (17) for $P_{\rm eq}$ provides a connection between the transition probabilities p_a and p_e “which must hold if the system is closed and isolated.” Here we take the view that these transitions probabilities are known from quantum mechanics, and therefore determine $P_{\rm eq}$, as shown in Eq. (18), providing a dynamical justification for Boltzmann’s fundamental postulate of equal *apriori* probabilities.

[20] P. and T. Ehrenfest, “Über eine Aufgabe aus der Warscheinlichkeitsrechnung die mit der kinetischen Deutung der Entropievermehrung zusammenhängt,” Math. Naturw. Blätter **3** 128–xx (1906), and “Über zwei bekannte Einwände gegen das Boltzmannsche H-Theorem,” Physikalische Zeitschrift **8**, 311–xx (1907). Reprinted in *Paul Ehrenfest, Collected Scientific Papers*, edited by Martin Klein (North-Holland, Amsterdam, 1959), p. 128. The term “dog-flea” to describe this model was not used by the Ehrenfests in print.

[21] M. Kac, “Random walk and the theory of Brownian motion.” Amer. Math. Monthly **54**, 369-391 (1947). Reprinted in *Mark Kac: Probability, Number Theory and Statistical Physics, Selected Papers*, edited by K. Baclawski and D. Donsker (MIT Press, Cambridge, MA, 1979)p.240

[22] To demonstrate the monotonic increase of total entropy in the finite temperature extension of the Ehrenfests’ model one must appeal to thermodynamics for the relation between entropy and heat exchange for systems in thermal equilibrium.[13] But this is unnecessary in our treatment of the Einstein model where the heat bath is an intrinsic part of the dynamical system.

[23] J. von Neumann, *Mathematical Foundations of Quantum Mechanics* (Princeton Univ. Press, 1955). Translated from the German by R. T. Beyer (Springer, Berlin 1932). For a modern discussion of this quantum mechanical expression for the entropy, and the arrow of time which is determined by the direction of entropy increase, see, J. L. Lebowitz "Microscopic origins of irreversible macroscopic behavior," Physica A **263**, 516–527 (1999).

[24] M. Nauenberg, "Critique of q-entropy for thermal statistics," Phys. Rev. E **67**, 036114-1 036114-6 (2003).