Differential Equation of Thermal Equilibrium, Quantum Conditions, and Relation between Boltzmann, Fermi-Dirac, and Bose-Einstein Distributions

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Abstract

The Boltzmann distribution is commonly interpreted as a classical approximation of the quantum-mechanical Fermi-Dirac and Bose-Einstein distributions. We arrive at a different conclusion by directly investigating the three equilibrium distributions without considering statistical variations. A general differential equation of thermal equilibrium is obtained that applies to any particles. Simple integration yields the Boltzmann distribution. Furthermore, quantum conditions are established, ruling the occupation numbers of (i) fermions by utilizing Pauli's exclusion principle and (ii) bosons by utilizing Einstein's rate-equation approach to Planck's law of blackbody radiation. By exploiting the respective quantum condition, integration of the same differential equation of thermal equilibrium yields either the Fermi-Dirac or the Bose-Einstein distribution. It suggests that the Boltzmann distribution is a general distribution of thermal equilibrium, whereas the Fermi-Dirac and Bose-Einstein distributions are special cases of the Boltzmann distribution, ruled by specific conditions. This suggestion is further underlined by the fact that inserting the respective quantum condition directly into the Boltzmann distribution delivers either the Fermi-Dirac or the Bose-Einstein distribution. This finding implies that fermions and bosons simultaneously obey both their own specific and the general Boltzmann distribution.

1. Introduction

In statistical mechanics, the Boltzmann distribution [1],

$$\frac{n_i}{n_0} = \frac{1}{\mathrm{e}^{(E_i - E_0)/k_\mathrm{B}T}}, \tag{1}$$

the Bose-Einstein distribution [2,3],

$$n_{i,BE} = \frac{1}{\mathrm{e}^{(E_i - E_0)/k_\mathrm{B}T} - 1}, \tag{2}$$

and the Fermi-Dirac distribution [4,5,6],

$$n_{i,FD} = \frac{1}{e^{(E_i - E_0)/k_\mathrm{B}T} + 1}, \tag{3}$$

quantify the occupation number n_i of an energy level with energy E_i at a given temperature T. The indices i and 0 denote the energy level of interest and a reference energy level, respectively. The indices BE and FD denote Bose-Einstein and Fermi-Dirac statistics, respectively. k_B is Boltzmann's constant, hence $k_\mathrm{B}T$ is the thermal energy.

All three distributions can be obtained from the canonical ensemble [7,8,9] or the grand canonical ensemble [7,8,9]. Their difference can be derived based on the assumption that classical particles are distinguishable, whereas fermions and bosons are not, and fermions obey Pauli's exclusion principle [10], whereas bosons do not.

In this paper, we carefully examine the principally known relation between absolute, relative, and fractional occupation numbers. We derive quantum conditions that apply to Fermi-Dirac statistics, namely Pauli's exclusion principle, or Bose-Einstein statistics, namely that (in our chosen example) only real photons trigger absorption, whereas real and vacuum photons trigger emission. We establish the differential equation of thermal equilibrium and integrate it with boundary conditions that either remain general, thereby deriving the Boltzmann distribution, or additionally make use of either quantum condition, thereby deriving the Fermi-Dirac or Bose-Einstein

distribution. We also derive the equations for the ground-state occupation numbers in Fermi-Dirac and Bose-Einstein distributions. The obtained results suggest that the Fermi-Dirac and Bose-Einstein distributions are special cases of the Boltzmann distribution.

2. Absolute, relative, and fractional occupation numbers

In the present work, we assume a total number n_t of identical systems. Depending on the physical situation under consideration, the number of systems may be constant, e.g. systems including fermions (such as electrons), or variable, e.g. systems including bosons (such as photons) that can be created or annihilated. Each system comprises two discrete, non-degenerate energy levels, namely an excited state, i, with level energy E_i, and the ground state, $j = 0$, with level energy E_0.

Among these n_t two-level systems, n_0 systems are in the ground state, whereas n_i systems are in the excited state. Consequently,

$$n_t = n_i + n_0 . \tag{4}$$

The numbers n_i and n_0 are the absolute occupation numbers of the two energy levels.

We can then determine the relative occupation number a_i of an energy level i with respect to the occupation number of the ground state,

$$a_i = \frac{n_i}{n_0} . \tag{5}$$

For $i = 0$, we obtain

$$a_0 = \frac{n_0}{n_0} = 1, \tag{6}$$

because we compare the absolute occupation number of the ground state to itself. We can also determine the fractions of systems that are in their excited state,

$$b_i = \frac{n_i}{n_t} = \frac{n_i}{n_i + n_0} = 1 - b_0 , \tag{7}$$

or in their ground state,

$$b_0 = \frac{n_0}{n_t} = \frac{n_0}{n_i + n_0} = 1 - b_i . \tag{8}$$

The numbers b_i and b_0 are the fractional occupation numbers of the two energy levels; their sum is calibrated to unity. As Eqs. (7) and (8) underline, the fractional occupation numbers b_i and b_0 are equal to the absolute occupation numbers per system, n_i/n_t and n_0/n_t, respectively. It follows that

$$a_i = \frac{n_i}{n_0} = \frac{b_i}{b_0} = \frac{b_i}{1 - b_i} \quad \Leftrightarrow \quad b_i = \frac{a_i}{1 + a_i} , \tag{9}$$

i.e., Eq. (5) contains the same information as Eqs. (7) and (8).

Obviously, knowledge of the absolute occupation numbers allows one to determine the relative occupation number of the excited state via Eq. (5) and the fractional occupation numbers via Eqs. (7) and (8). In contrast, knowledge of the relative and fractional occupation numbers does not allow one to determine the absolute occupation numbers. For example, fractional occupation numbers of $b_0 = 80\%$ in the ground state and $b_i = 20\%$ in the excited state, equivalent to a relative occupation number of $a_i = 25\%$ in the excited state, can mean that out of $n_t = 5$ available systems $n_0 = 4$ systems are in the ground state and $n_i = 1$ system is in the excited state or out of $n_t = 3.5\times10^{12}$ participating systems $n_0 = 2.8\times10^{12}$ systems are in the ground state and $n_i = 0.7\times10^{12}$ systems are in the excited state. In both examples, we obtain $b_0 = 80\%$, $b_i = 20\%$, and $a_i = 25\%$.

When interpreting the fractional occupation numbers b_0 and b_i as probabilities, it means that each single system has a probability of b_0 to be in its ground state and a probability of b_i to be in its excited state i, but the total number n_t of participating systems is possibly unknown. For example, if we fabricate a crystal that contains an unknown concentration of rare-earth ions, we can nevertheless calculate the Boltzmann factors in the crystal-field levels of the electronic ground-state manifold of the rare-earth ions by use of Eq. (1), provided that we know their level energies and the crystal temperature [11]. The rare-earth concentration is not relevant. In this statistical

interpretation, it can even be a single participating system with a single occupation, in our example a single rare-earth ion, i.e., $n_t = 1$, that can be found 80% of time in its ground state and 20% of time in its excited state.

In the following investigation, it is important to keep the differences between absolute, relative, and fractional occupation numbers, as defined above, in mind.

3. Differential equation of thermal equilibrium

Derivation of the Boltzmann, Fermi-Dirac, and Bose-Einstein distributions is a profound task in statistical physics. The reason is that initially all possible states are considered and then the state of thermal equilibrium is obtained, e.g., by maximizing the entropy. Here we present an approach that does not determine the statistical variation around a thermal equilibrium but directly derives the equilibrium distribution. It applies to any number n_t of systems, avoids the complications encountered in other derivations, and sheds new light on the relation between the three different distributions.

The definition of an energetic equilibrium between two energy states 0 and i is that the total energy E_t in both energy states must be equal,

$$E_t(0) = E_t(i). \tag{10}$$

The definition of a thermal equilibrium is that, in addition to the requirement of Eq. (10), both energy states must be at the same temperature T,

$$T(0) = T(i). \tag{11}$$

These two requirements are not identical.

Let us first evaluate the second requirement. The total kinetic energy of a gas, a liquid, or a solid body typically comprises translational, vibrational, and rotational energies of its particles relative to its internal coordinate frame (internal kinetic energy), plus the kinetic energy of its center of mass relative to an external reference coordinate frame (external kinetic energy). Temperature is defined in physics as the mean kinetic energy of each of the particles of a gas, a liquid, or a solid body relative to its internal coordinate system [12], whereas the external kinetic energy of the entire body relative to an external reference coordinate system is irrelevant. A cold body (say: a meteorite) may move fast, whereas a hot body (say: a hot plate on a stove) may be at rest, relative to an external reference coordinate system (say: the house in which we live). According to the definition of the temperature scale in Kelvin, the mean kinetic (translational, vibrational, and rotational) energy of a single particle with respect to the internal coordinate system of the body at temperature T equals the thermal energy $k_B T$ [12]. When two bodies of the same substance, density, pressure, etc., one containing twice as many particles as the other, hence having twice the volume of the other, are at the same temperature, then one body contains twice as much total internal kinetic energy as the other. Hence, the kinetic energy of a number n of particles in a specific energy level i at temperature T amounts to n times the thermal energy,

$$E_k = nk_B T, \tag{12}$$

no matter what the energy E_i of this specific energy level is. This is the direct consequence of Eq. (11).

Now we consider the first requirement. The potential energy of a single particle that occupies a level i with energy E_i is necessarily E_i, because this is the physical meaning of the energy E_i. As a simple example, consider the energy levels E_n with main quantum number n of the hydrogen atom in Bohr's model [13], which are potential energies due to the attractive Coulomb force between the electron and the proton. Hence, the potential energy of these n particles in an arbitrary energy level with energy E is

$$E_p = nE. \tag{13}$$

Compared to these n particles occupying the level with energy E, the $n + dn$ particles that occupy a level with elevated energy $E + dE$ must have the same total energy E_t, for a thermal equilibrium to be established. Therefore,

$$E_t = E_k(E) + E_p(E) = E_k(E + dE) + E_p(E + dE). \tag{14}$$

This is the direct consequence of Eq. (10).

Substituting Eqs. (12) and (13) into Eq. (14) yields

$$nk_B T + nE = (n + dn)k_B T + (n + dn)(E + dE). \tag{15}$$

By arbitrarily setting the potential energy E to zero (we will reintroduce a potential-energy value during the subsequent integration), resolving the brackets, and neglecting the second-order infinitesimal term $dndE$, we obtain the differential equation

$$\frac{dn}{n} = -\frac{dE}{k_\mathrm{B}T}\,. \tag{16}$$

This is the differential equation of thermal equilibrium. It relates the relative change dn/n in absolute occupation number n to the change dE in potential energy at constant temperature T, i.e., constant mean kinetic energy $k_\mathrm{B}T$ of each particle. From its derivation we understand the underlying physics. In a higher-energy level, each particle has a higher potential energy, whereas its kinetic energy remains constant, because the temperature remains constant; therefore, its total energy increases when elevated from a lower-energy to a higher-energy level. The only possible way of readjusting the total energy E_t of Eq. (14) of all particles in the higher energy level is then by decreasing the number $n + dn$ of particles that occupy the higher-energy level (or, equivalently, each particle's probability of occupying the higher-energy level). Therefore, dn must be negative, as is the case in Eq. (16).

Since the only assumptions in its derivation are (i) the equivalence of total energy of both energy states and (ii) the same temperature of all particles occupying these two energy states to establish a thermal equilibrium, the differential equation of thermal equilibrium, Eq. (16), is universally valid and independent of the particles involved. Consequently, by simple integration we will derive from it the Boltzmann distribution, the Fermi-Dirac distribution, and the Bose-Einstein distribution.

4. Boltzmann distribution

In this Section, we will derive the Boltzmann distribution from the differential equation of thermal equilibrium and provide an example that illustrates the considerations made in the previous Section.

4.1. Derivation of Boltzmann distribution

Integration of the differential equation of thermal equilibrium, Eq. (16), over the absolute occupation numbers n_0 of the ground state with energy E_0 and n_i of an excited state i with energy E_i,

$$\int_{n_0}^{n_i} \frac{dn}{n} = -\frac{1}{k_\mathrm{B}T}\int_{E_0}^{E_i} dE\,, \tag{17}$$

provides that the mean absolute occupation numbers n_i and n_0 of the two levels in thermal equilibrium at temperature T are related to each other by

$$a_i = \frac{n_i}{n_0} = \frac{1}{\mathrm{e}^{(E_i - E_0)/k_\mathrm{B}T}}\,. \tag{18}$$

By simple integration of the differential equation of thermal equilibrium, we have obtained the Boltzmann distribution of Eq. (1). In Eq. (18), we can also set $i = 0$, thereby deriving that

$$a_0 = \frac{1}{\mathrm{e}^{(E_0 - E_0)/k_\mathrm{B}T}} = 1\,, \tag{19}$$

as expected from Eq. (6).

Since we have not imposed a specific condition on the absolute occupation numbers n_0 and n_i, Eq. (17) is the most general way of integrating the differential equation of thermal equilibrium, Eq. (16). Therefore, the Boltzmann distribution of Eq. (18) or (1) is the most general distribution function that describes a thermal equilibrium. Any other distribution function must be a special case of the Boltzmann distribution of Eq. (18) or (1), and we will show in the following Sections that this statement specifically accounts for the Fermi-Dirac and Bose-Einstein distributions.

According to Eqs. (7) and (8), the Boltzmann factors b_i and b_0 of the two energy levels are

$$\begin{aligned} b_i &= \frac{n_i}{n_\mathrm{t}} = \frac{n_i}{n_i + n_0} = \frac{n_0\,\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}}{n_0 + n_0\,\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}} \\ &= \frac{\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}}{1+\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}} \\ &= \frac{1}{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}+1} \end{aligned} \tag{20}$$

and

$$\begin{aligned} b_0 &= \frac{n_0}{n_\mathrm{t}} = \frac{n_0}{n_i + n_0} = \frac{n_0}{n_0 + n_0\,\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}} \\ &= \frac{1}{\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}+1} \end{aligned} . \tag{21}$$

The Boltzmann distribution of Eq. (18) or (1) quantifies the relative occupation number a_i of an excited state with respect to the ground state in thermal equilibrium. Via Eqs. (20) and (21) one can then calculate the Boltzmann factors, i.e., the fractional occupation numbers b_i and b_0 of the systems or probabilities b_i and b_0 of a single system being found in its excited or ground state, respectively. For example, a single two-level atom with known level energies has the probabilities b_i and b_0 of being found in its excited or ground state, respectively, at a given temperature T. Many atoms have the same probabilities. Therefore, the Boltzmann distribution applies to any number of systems. It is not restricted to a large or even infinite number of systems, as is the assumption in the canonical ensemble [7,8,9] or the grand canonical ensemble [7,8,9]. (Alternatively, one can interpret n_i and n_0 as the absolute occupation numbers and b_i and b_0 as the fractional occupation numbers of the two energy levels of a single system that allows for multiple occupations of its energy levels.)

However, the total number n_t of systems and the absolute occupation numbers n_i and n_0 of the energy levels E_i and E_0, respectively, are not specified by the Boltzmann distribution. It is the direct consequence of integrating Eq. (17) without imposing any condition on the absolute occupation numbers n_0 and n_i. Hence, there is a degree of freedom in the Boltzmann distribution that must be defined separately to resemble the specific physical situation under consideration. This point is important when comparing the Boltzmann distribution to the Fermi-Dirac and Bose-Einstein distributions.

Often the chemical potential μ is utilized to specify the total number n_t of systems. Alternatively, examples of $n_\mathrm{t} = 5$ or $n_\mathrm{t} = 3.5\times10^{12}$ were discussed in the previous Section. The choice depends on the physical situation under consideration; if we know that $n_\mathrm{t} = 3.5\times10^{12}$, we do not need the chemical potential μ.

4.2. Example: isothermal barometric formula of air pressure in the atmosphere

A special version of the differential equation of thermal equilibrium, Eq. (16), is the differential equation that leads to the isothermal barometric formula of atmospheric pressure.

From the ideal gas law,

$$P = \rho\frac{R_\mathrm{G}}{M}T = \frac{m}{V}\frac{N_\mathrm{A}k_\mathrm{B}}{M}T = \frac{1}{V}nk_\mathrm{B}T\,, \tag{22}$$

where P is the atmospheric pressure, R_G is the ideal gas constant, M is the molar mass, N_A is the Avogadro constant, and n, m, and ρ are the number, mass, and density, respectively, of particles in the volume V of the air element under consideration, we obtain the kinetic energy E_k as

$$E_\mathrm{k} = PV = nk_\mathrm{B}T \quad\Rightarrow\quad dE_\mathrm{k} = dPV = dnk_\mathrm{B}T \quad\Rightarrow\quad \frac{dE_\mathrm{k}}{E_\mathrm{k}} = \frac{dP}{P} = \frac{dn}{n}\,. \tag{23}$$

At a given temperature T in a given volume V, a relative change in kinetic energy equals a relative change in pressure, which equals a relative change in the number of particles.

The potential energy E of a single particle results from the gravitational force,

$$E = F_E h = mg_E h = \frac{k_\mathrm{B}M}{R_\mathrm{G}}g_E h \quad\Rightarrow\quad dE = \frac{k_\mathrm{B}M}{R_\mathrm{G}}g_E dh\,, \tag{24}$$

where F_E and g_E are the gravitational force and acceleration at the earth's surface, respectively, and h is the altitude above sea level or any other reference level. The roles of kinetic energy E_k and potential energy E_p become very clear in this example.

Inserting Eqs. (23) and (24) into the general differential equation of thermal equilibrium, Eq. (16), yields the specific differential equation of atmospheric pressure [14],

$$\frac{dP}{P} = -\frac{M}{R_G T} g_E dh\,, \tag{25}$$

and integration yields the isothermal barometric formula of atmospheric pressure [15],

$$\int_{P(h_0)}^{P(h_i)} \frac{dP}{P} = -\frac{M}{R_G T} g_E \int_{h_0}^{h_i} dh \quad \Rightarrow \quad \frac{P(h_i)}{P(h_0)} = e^{-\frac{M}{R_G T} g_E (h_i - h_0)}\,. \tag{26}$$

Over a reasonably small altitude range, over which the temperature is reasonably constant, the atmospheric pressure follows the Boltzmann distribution. Since the temperature and, thus, the kinetic energy of each air particle is approximately the same at the different altitudes, the only way in which the increasing altitude and, thus, increasing potential energy of each air particle can be compensated is by a reduction dn of air particles with increasing altitude, hence a reduction dP of pressure, see Eq. (25). The essential physics expressed by the differential equation of thermal equilibrium, Eq. (16), is beautifully illustrated in this example. The ideal gas law of Eq. (22), applied at all altitudes, fulfils the condition of Eq. (11). Had we derived the differential equation (25) from fundamental mechanical principles rather than utilizing Eq. (16), we could have further verified that the condition of Eq. (10) occurs in the derivation.

By the way, the isothermal barometric formula works equally well for good and bad weather, i.e., high and low atmospheric pressure, because only the relative atmospheric pressure $P(h_i)/P(h_0)$ at different altitudes is calculated by the Boltzmann distribution of Eq. (26). An absolute atmospheric pressure $P(h_i)$ or $P(h_0)$ is not specified in Eq. (26) and must be chosen according to the specific physical situation under consideration, good or bad weather. It is the same situation as for the Boltzmann distribution of Eq. (1), where the total occupation number n_t or the absolute occupation numbers n_0 and n_i are not specified and must be chosen according to the specific physical situation under consideration. If we want to know the absolute atmospheric pressure at an altitude of h_i = 100 m above the ground, we must measure the absolute atmospheric pressure on the ground, $P(h_0 = 0\text{ m})$, which can be high in good or low in bad weather, and then calculate $P(h_i = 100\text{ m})$ from Eq. (26) in the same weather condition. Even in this example, the chemical potential μ could, in principle, be introduced but would not be particularly helpful.

5. Fermi-Dirac distribution

In this Section, we will obtain a quantum condition for fermions and exploit it to derive the Fermi-Dirac distribution from the differential equation of thermal equilibrium.

5.1. Quantum condition for fermions: Pauli's exclusion principle

Fermions are half-spin particles that obey Pauli's exclusion principle [10]. Therefore, each system may have maximum one occupation, equivalent to being in its excited state with energy E_i, or it may be empty, equivalent to being in its ground state with energy E_0. The absolute occupation numbers are then equivalent to the probabilities of finding the system in its excited or ground state. Therefore,

$$n_{t,FD} = n_{i,FD} + n_{0,FD} = 1\,. \tag{27}$$

Fundamentally, Eq. (27) represents Pauli's exclusion principle, as the number $n_{i,FD}$ of occupations in an energy level i can never exceed one.

5.2. Fermi-Dirac distribution

We will now integrate the same differential equation of thermal equilibrium, Eq. (16), as we did in the previous Section when obtaining the Boltzmann distribution. However, this time we exploit the additional quantum condition of Eq. (27), relating the absolute occupation numbers n_i and n_0 to each other, thereby creating a result that is more specific than the general Boltzmann distribution. The mean absolute occupation number of an occupied ("excited") state i in Fermi-Dirac statistics is then given by

$$\int_{n_0=1-n_i}^{n_i} \frac{dn}{n} = -\frac{1}{k_B T}\int_{E_0}^{E_i} dE \quad \Rightarrow$$
$$\frac{n_i}{1-n_i} = e^{-(E_i-E_0)/k_B T} \quad \Rightarrow$$
$$n_i = \frac{e^{-(E_i-E_0)/k_B T}}{1+e^{-(E_i-E_0)/k_B T}} \quad \Rightarrow \quad . \tag{28}$$
$$n_i = \frac{e^{-(E_i-E_0)/k_B T}}{1+e^{-(E_i-E_0)/k_B T}} \frac{e^{(E_i-E_0)/k_B T}}{e^{(E_i-E_0)/k_B T}} \quad \Rightarrow$$
$$n_i = \frac{1}{e^{(E_i-E_0)/k_B T}+1} = n_{i,\mathrm{FD}}$$

By simple integration of the differential equation of thermal equilibrium, we have obtained the Fermi-Dirac distribution of Eq. (3). By again exploiting the additional quantum condition of Eq. (27), the mean absolute occupation number of an unoccupied ("ground") state 0 in Fermi-Dirac statistics is obtained as

$$\int_{n_0}^{n_i=1-n_0} \frac{dn}{n} = -\frac{1}{k_B T}\int_{E_0}^{E_i} dE \quad \Rightarrow$$
$$\frac{1-n_0}{n_0} = e^{-(E_i-E_0)/k_B T} \quad \Rightarrow \quad . \tag{29}$$
$$n_0 = \frac{1}{e^{-(E_i-E_0)/k_B T}+1} = n_{0,\mathrm{FD}}$$

Just for confirmation, with the quantum condition of Eq. (27), the mean absolute occupation number of an unoccupied ("ground") state of Eq. (29) can also directly be derived from the Fermi-Dirac distribution of Eq. (3) or (28),

$$n_{0,FD} = 1-n_{i,\mathrm{FD}} = 1-\frac{1}{e^{(E_i-E_0)/k_B T}+1} = \frac{e^{(E_i-E_0)/k_B T}}{e^{(E_i-E_0)/k_B T}+1} = \frac{1}{e^{-(E_i-E_0)/k_B T}+1}. \tag{30}$$

Equation (30) implies that $n_{\mathrm{i,FD}} + n_{0,\mathrm{FD}} = 1$, i.e., the two populations $n_{\mathrm{i,FD}}$ and $n_{0,\mathrm{FD}}$ obey the quantum condition of Eq. (27). The relative occupation numbers with respect to the unoccupied or ground state are then given by

$$a_{i,\mathrm{FD}} = \frac{n_i}{n_0} = \frac{n_{i,\mathrm{FD}}}{n_{0,\mathrm{FD}}} = \frac{e^{-(E_i-E_0)/k_B T}+1}{e^{(E_i-E_0)/k_B T}+1} = \frac{\dfrac{1+e^{(E_i-E_0)/k_B T}}{e^{(E_i-E_0)/k_B T}}}{e^{(E_i-E_0)/k_B T}+1} = \frac{1}{e^{(E_i-E_0)/k_B T}}, \tag{31}$$

which is the Boltzmann distribution of Eq. (1), and

$$a_{0,\mathrm{FD}} = e^{-(E_0-E_0)/k_B T} = 1, \tag{32}$$

as expected from Eq. (6). The fractional occupation numbers derive as

$$b_{i,\mathrm{FD}} = \frac{n_i}{n_t} = \frac{n_i}{n_i+n_0} = n_i = \frac{1}{e^{(E_i-E_0)/k_B T}+1} = b_i \tag{33}$$

and

$$b_{0,\mathrm{FD}} = \frac{n_0}{n_t} = \frac{n_0}{n_i+n_0} = n_0 = \frac{1}{e^{-(E_i-E_0)/k_B T}+1} = b_0 . \tag{34}$$

These results are the Boltzmann factors of Eqs. (20) and (21).

6. Bose-Einstein distribution

In this Section, we will obtain a quantum condition for bosons and exploit it to derive the Bose-Einstein distribution from the differential equation of thermal equilibrium.

6.1. Quantum condition for bosons

Deriving the condition that bosons must fulfil is significantly more involved than that for fermions, at least at our current level of understanding. Possibly, a simpler derivation can be found when the knowledge about the relations excavated in this paper has deepened.

We exploit Einstein's rate-equation approach [16] to Planck's law of blackbody radiation [17] in a modern interpretation, i.e., by use of knowledge that was partly unavailable to Einstein in 1917. Einstein assumed that two-level atomic systems with level energies E_2 and E_1 are present in the walls of the blackbody radiator and that photons at frequency ν are in resonance with the atomic transition,

$$h\nu = E_2 - E_1 . \tag{35}$$

h is Planck's constant, hence $h\nu$ is the photon energy. Photons are bosons, hence the mean number φ of photons per optical mode follows the Bose-Einstein distribution of Eq. (2),

$$\varphi = n_{i,BE} = \frac{1}{\mathrm{e}^{h\nu/k_\mathrm{B}T} - 1} . \tag{36}$$

The total photon energy per optical mode is

$$h\nu\varphi . \tag{37}$$

For a given spectral mode density $\tilde{M}(\nu)$ per unit frequency interval at frequency ν, the spectral energy density $\tilde{u}(\nu)$ per unit frequency interval at frequency ν generated by the mean number φ of photons per optical mode then amounts to

$$\tilde{u}(\nu) = \tilde{M}(\nu) h\nu\varphi . \tag{38}$$

When making the specific assumption that the optical system has the geometry of a simple three-dimensional box (or three-dimensional free space), which has a spectral mode density of $\tilde{M}(\nu) = 8\pi\nu^2/c^3$, then inserting Eq. (36) into Eq. (38) delivers Planck's law of blackbody radiation [17],

$$\tilde{u}(\nu, T) = \frac{8\pi h\nu^3}{c^3} \frac{1}{\mathrm{e}^{h\nu/k_\mathrm{B}T} - 1} . \tag{39}$$

In the present derivation, we do not make any assumption about the geometry of the optical system, i.e., it may as well be a one-dimensional Fabry-Perot resonator or a photonic-crystal fiber or a three- or two-dimensional photonic-crystal device. This approach leaves the mode structure and spectral mode density $\tilde{M}(\nu)$ of the optical system undefined, thereby allowing us to obtain a general result that holds true for any optical system.

The existence of a zero-point or vacuum energy, in optics manifested by vacuum photons, was proposed by Planck [18], further detailed by Einstein and Stern [19], and confirmed by Heisenberg [20]. Weisskopf suggested that spontaneous emission is triggered by this zero-point or vacuum energy [21–23]. Following this proposal, equivalently to Eq. (38), we interpret the vacuum spectral energy density $\tilde{u}_\mathrm{vac}(\nu)$ in terms of a mean number φ_vac of vacuum photons per optical mode,

$$\tilde{u}_\mathrm{vac}(\nu) = \tilde{M}(\nu) h\nu\varphi_\mathrm{vac} . \tag{40}$$

Naturally, the interaction probabilities of the spectral and the vacuum spectral energy density with the atoms are equal, because both represent electromagnetic radiation. Consequently, the Einstein coefficients A_{21} and B_{21} of spontaneous and stimulated emission, respectively, are related by

$$A_{21} = B_{21}\tilde{u}_\mathrm{vac}(\nu) . \tag{41}$$

Einstein's photon-rate equation balances the spontaneous-emission rate R_sp and the stimulated-emission rate R_st with the absorption rate R_abs, in spectral resonance and thermodynamic equilibrium with a two-energy-level atomic system with population densities N_2 and N_1 of upper and lower level, respectively,

$$\begin{aligned} &R_\mathrm{sp} + R_\mathrm{st} = R_\mathrm{abs} \quad \Leftrightarrow \\ &A_{21}N_2 + B_{21}\tilde{u}(\nu)N_2 = B_{12}\tilde{u}(\nu)N_1 \end{aligned}, \tag{42}$$

where B_{12} is the Einstein coefficient of absorption. Inserting Eqs. (38)–(41) into Eq. (42) yields

$$B_{21}\varphi_{\mathrm{vac}}N_2 + B_{21}\varphi N_2 = B_{12}\varphi N_1 . \tag{43}$$

This is the photon-rate equation for a single optical mode, which is independent of the spectral mode density $\tilde{M}(\nu)$ of the physical system under consideration. Therefore, it applies to any given geometry of the optical system and any mode structure introduced by this geometry.

Einstein considered [16] that the atomic system is in thermal equilibrium, hence the population densities N_2 and N_1 are related by the Boltzmann distribution of Eq. (1),

$$\frac{N_2}{N_1} = \frac{n_i}{n_0} = \frac{1}{\mathrm{e}^{h\nu/k_{\mathrm{B}}T}} . \tag{44}$$

Inserting Eqs. (44) and (36) into Eq. (43) yields

$$\varphi_{\mathrm{vac}}\left[1-\mathrm{e}^{-h\nu/k_{\mathrm{B}}T}\right] = \frac{B_{12}}{B_{21}} - \mathrm{e}^{-h\nu/k_{\mathrm{B}}T} . \tag{45}$$

This equation holds true for all frequencies ν and all temperatures T if

$$B_{12} = B_{21} . \tag{46}$$

As is well known, the Einstein coefficients of absorption and stimulated emission are equal. Inserting Eq. (46) into Eq. (45) results in

$$\varphi_{\mathrm{vac}} = 1 . \tag{47}$$

It means that the Einstein coefficient or rate constant A_{21} of spontaneous emission in Eq. (41) is induced by a vacuum spectral energy density that comprises one vacuum photon per optical mode in Eq. (40), as was already pointed out by Einstein and Stern [18] in 1913. Inserting the results of Eqs. (46) and (47) into Eq. (43) yields

$$N_2\left(\varphi+\varphi_{\mathrm{vac}}\right) = N_2\left(\varphi+1\right) = N_1\varphi . \tag{48}$$

Equation (48) expresses the same essence as Eq. (43), namely that the rates of absorption, on the one hand, and spontaneous and stimulated emission, on the other hand, are equal in thermodynamic equilibrium. We find from Eq. (48) that the ratio of population densities N_2 and N_1 of the two-level atomic system is in balance with the photon numbers φ and φ_{vac} in a single mode as

$$\frac{N_2}{N_1} = \frac{\varphi}{\varphi+\varphi_{\mathrm{vac}}} = \frac{\varphi}{\varphi+1} . \tag{49}$$

Since the ratio of population densities N_2 and N_1 is given by the Boltzmann distribution, we can exploit Eq. (44) to relate the photon numbers in a single mode to the absolute occupation numbers n_i and n_0 of an excited state and the ground state, respectively, in the Boltzmann distribution as

$$\frac{n_{i,BE}}{n_{0,BE}} = \frac{\varphi}{\varphi+\varphi_{\mathrm{vac}}} = \frac{\varphi}{\varphi+1} . \tag{50}$$

By doing so, we make the conceptual step of introducing a photonic excited and ground state, where the occupation number of the excited state is given by the Bose-Einstein distribution of Eq. (2) or (36). It leads to the relations

$$\begin{aligned} n_{i,BE} &= k\varphi \\ n_{0,BE} &= k\left(\varphi+\varphi_{\mathrm{vac}}\right) = k\left(\varphi+1\right) \end{aligned} . \tag{51}$$

Generally, deriving Eq. (51) from Eq. (50) allows one to introduce an arbitrary proportionality constant k. However, since we know from Eq. (46) that $\varphi_{\mathrm{vac}} = 1$, we can reason that exactly one vacuum photon per optical mode must appear, hence $k = 1$. The vacuum photon appears in the photonic ground state. Consequently,

$$\begin{aligned} n_{i,\mathrm{BE}} &= \varphi \\ n_{0,\mathrm{BE}} &= \varphi+\varphi_{\mathrm{vac}} = \varphi+1 \\ n_{0,\mathrm{BE}} &= n_{i,\mathrm{BE}}+\varphi_{\mathrm{vac}} = n_{i,\mathrm{BE}}+1 \end{aligned} \quad \Rightarrow . \tag{52}$$

This is the quantum condition for bosons. It is equivalent to the quantum condition for fermions of Eq. (27).

At first glance, the implication of Eq. (52) may look strange. How can the φ photons in an optical mode simultaneously occupy an excited state with absolute occupation number n_i and the ground state with occupation number n_0? At this point we should recall that photons are virtual particles representing fields that convey interactions between real particles, and it is the interactions that matter here, not the virtual particles. Those fields or photons that trigger absorption form the excited state of the photonic system, whereas those fields or photons that trigger emission form the ground state of the photonic system. The vacuum field or photon triggers only emission, hence it appears only in the ground state, whereas real fields or photons trigger both absorption and emission, hence they appear in both states. The difference in energy residing in the photonic excited and ground state is, thus, equal to the vacuum energy. Consequently, the total number $n_{\mathrm{t,BE}}$ of occupations amounts to

$$n_{\mathrm{t,BE}} = n_{0,\mathrm{BE}} + n_{i,\mathrm{BE}} = 2n_{i,\mathrm{BE}} + 1 . \tag{53}$$

The total number $n_{\mathrm{t,BE}}$ of occupations is variable in Bose-Einstein statistics, because photons can be created or annihilated.

Although it is not clear at the present state of investigation how the derived quantum condition of Eq. (52) must be interpreted when being applied to other bosons, such as ^{4}He atoms, we will provide evidence in the following Sub-section that it is applicable not only to photons but to bosons in general.

6.2. Bose-Einstein distribution

Again, we will integrate the same differential equation of thermal equilibrium, Eq. (16), as we did in the previous Sections when obtaining the Boltzmann and Fermi-Dirac distributions. However, this time we exploit the additional quantum condition of Eq. (52), relating the absolute occupation numbers n_i and n_0 to each other, thereby making the result more specific than the general Boltzmann distribution and different from the Fermi-Dirac distribution. The mean absolute occupation number of an occupied ("excited") state i in Bose-Einstein statistics is then given by

$$\begin{aligned}
&\int_{n_0=n_i+1}^{n_i} \frac{dn}{n} = -\frac{1}{k_\mathrm{B}T}\int_{E_0}^{E_i} dE \quad \Rightarrow \\
&\frac{n_i}{n_i+1} = e^{-(E_i-E_0)/k_\mathrm{B}T} \quad \Rightarrow \\
&n_i = \frac{e^{-(E_i-E_0)/k_\mathrm{B}T}}{1-e^{-(E_i-E_0)/k_\mathrm{B}T}} \quad \Rightarrow \quad . \\
&n_i = \frac{e^{-(E_i-E_0)/k_\mathrm{B}T}}{1-e^{-(E_i-E_0)/k_\mathrm{B}T}} \frac{e^{(E_i-E_0)/k_\mathrm{B}T}}{e^{(E_i-E_0)/k_\mathrm{B}T}} \quad \Rightarrow \\
&n_i = \frac{1}{e^{(E_i-E_0)/k_\mathrm{B}T}-1} = n_{i,\mathrm{BE}}
\end{aligned} \tag{54}$$

By simple integration of the differential equation of thermal equilibrium, we have obtained the Bose-Einstein distribution of Eq. (2). By again exploiting the additional quantum condition of Eq. (52), the mean absolute occupation number in the ground state is obtained as

$$\begin{aligned}
&\int_{n_0}^{n_i=n_0-1} \frac{dn}{n} = -\frac{1}{k_\mathrm{B}T}\int_{E_0}^{E_i} dE \quad \Rightarrow \\
&\frac{n_0-1}{n_0} = e^{-(E_i-E_0)/k_\mathrm{B}T} \quad \Rightarrow \quad . \\
&n_0 = \frac{1}{1-\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}} = n_{0,\mathrm{BE}}
\end{aligned} \tag{55}$$

Just for confirmation, with the quantum condition of Eq. (52), the mean absolute occupation number of an unoccupied ("ground") state of Eq. (55) can also directly be derived from the Bose-Einstein distribution of Eq. (2) or (54),

$$\begin{aligned} n_{0,\mathrm{BE}} &= n_{i,\mathrm{BE}} + 1 = \frac{1}{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}-1} + 1 \\ &= \frac{1+\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}-1}{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}-1} = \frac{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}}{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}-1}\frac{\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}}{\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}} \\ &= \frac{1}{\left(\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}-1\right)\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}} \\ &= \frac{1}{1-\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}} \end{aligned} . \tag{56}$$

Equation (56) implies that $n_{0,\mathrm{BE}} = n_{i,\mathrm{BE}} + 1$, i.e., the two populations $n_{0,\mathrm{BE}}$ and $n_{i,\mathrm{BE}}$ obey the quantum condition of Eq. (52). The relative occupation numbers with respect to the unoccupied state are then given by

$$\begin{aligned} a_{i,\mathrm{BE}} &= \frac{n_i}{n_0} = \frac{n_{i,\mathrm{BE}}}{n_{0,\mathrm{BE}}} = \frac{1-\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}}{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}-1} \\ &= \frac{\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}\,\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T} - \mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}}{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}-1} \\ &= \mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}\,\frac{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}-1}{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}-1} \\ &= \frac{1}{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}} \end{aligned} , \tag{57}$$

which is the Boltzmann distribution of Eq. (1), and

$$a_{0,\mathrm{BE}} = \mathrm{e}^{-(E_0-E_0)/k_\mathrm{B}T} = 1, \tag{58}$$

as expected from Eq. (6). The fractional occupation numbers derive as

$$\begin{aligned} b_{i,\mathrm{BE}} &= \frac{n_{i,\mathrm{BE}}}{n_{\mathrm{t,BE}}} = \frac{n_{i,\mathrm{BE}}}{n_{i,\mathrm{BE}}+n_{0,\mathrm{BE}}} = \frac{1}{\frac{n_{0,\mathrm{BE}}}{n_{i,\mathrm{BE}}}+1} \\ &= \frac{1}{\frac{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}-1}{1-\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}}+1} \\ &= \frac{1}{\frac{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}-\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}\,\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}}{1-\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}}+1} \\ &= \frac{1}{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}\,\frac{1-\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}}{1-\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}}+1} \\ &= \frac{1}{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}+1} = b_i \end{aligned} \tag{59}$$

and

$$
\begin{aligned}
b_{0,\mathrm{BE}} &= \frac{n_{0,\mathrm{BE}}}{n_{\mathrm{t,BE}}} = \frac{n_{0,\mathrm{BE}}}{n_{i,\mathrm{BE}} + n_{0,\mathrm{BE}}} = \frac{1}{\frac{n_{i,\mathrm{BE}}}{n_{0,\mathrm{BE}}} + 1} \\
&= \frac{1}{\frac{1 - \mathrm{e}^{-(E_i - E_0)/k_\mathrm{B}T}}{\mathrm{e}^{(E_i - E_0)/k_\mathrm{B}T} - 1} + 1} \\
&= \frac{1}{\frac{\mathrm{e}^{-(E_i - E_0)/k_\mathrm{B}T}\,\mathrm{e}^{(E_i - E_0)/k_\mathrm{B}T} - \mathrm{e}^{-(E_i - E_0)/k_\mathrm{B}T}}{\mathrm{e}^{(E_i - E_0)/k_\mathrm{B}T} - 1} + 1} \\
&= \frac{1}{\mathrm{e}^{-(E_i - E_0)/k_\mathrm{B}T}\,\frac{\mathrm{e}^{(E_i - E_0)/k_\mathrm{B}T} - 1}{\mathrm{e}^{(E_i - E_0)/k_\mathrm{B}T} - 1} + 1} \\
&= \frac{1}{\mathrm{e}^{-(E_i - E_0)/k_\mathrm{B}T} + 1} = b_0
\end{aligned}
\qquad (60)
$$

These results are the Boltzmann factors of Eqs. (20) and (21).

7. Relation between Boltzmann, Fermi-Dirac, and Bose-Einstein distribution

Figure 1 displays all occupation numbers in thermal equilibrium derived above in Boltzmann statistics (left-hand column), Fermi-Dirac statistics (middle column), and Bose-Einstein statistics (right-hand column). Displayed are the absolute occupation numbers n_i and n_0 (upper row), the relative occupation numbers a_i and a_0 (middle row), and the fractional occupation numbers b_i and b_0 (lower row). Negative values on the abscissa represent energy levels with $E_i < E_0$. In laser physics, population inversion, $n_i > n_0$, is sometimes interpreted as a negative temperature T in Boltzmann statistics. However, Eq. (14) does not hold true in this case, i.e., this situation is not in thermal equilibrium; hence, the Boltzmann distribution does not apply to this situation [24].

These results lead us to two fundamentally important conclusions concerning the distributions in thermal equilibrium. Firstly, the absolute occupation numbers n_i and n_0 (upper row) of Eqs. (28) and (29) in Fermi-Dirac statistics are different from those of Eqs. (54) and (55) in Bose-Einstein statistics. The reason is that the quantum-mechanical conditions of Eq. (27) in Fermi-Dirac statistics and Eq. (52) in Bose-Einstein statistics differ from each other. However, a comparison with absolute occupation numbers in Boltzmann statistics is impossible at this point, because the absolute occupation numbers are not specified in Boltzmann statistics (it can be bad or good weather; it can be $n_\mathrm{t} = 5$ or $n_\mathrm{t} = 3.5\times10^{12}$ atoms in our above-mentioned examples) and must be chosen according to the specific physical situation under consideration.

Secondly—this is the more important news—, the relative occupation numbers a_i and a_0 (middle row) of Eqs. (31) and (32) in Fermi-Dirac statistics and of Eqs. (57) and (58) in Bose-Einstein statistics are both identical to the Boltzmann distribution of Eqs. (18) and (19), respectively. Equivalently, the fractional occupation numbers b_i and b_0 (lower row) of Eqs. (33) and (34) in Fermi-Dirac statistics and of Eqs. (59) and (60) in Bose-Einstein statistics are both identical to the Boltzmann factors of Eqs. (20) and (21), respectively.

In Fermi-Dirac and Bose-Einstein statistics, the relative and fractional occupation numbers in thermal equilibrium are given by the Boltzmann distribution and the Boltzmann factors, respectively. What does this identity mean physically? Apparently, the Fermi-Dirac and Bose-Einstein distributions can both be considered special cases of the Boltzmann distribution. This result is already expected from the fact that, when integrating the differential equation of thermal equilibrium, Eq. (16), we have not specified the relation between n_i and n_0 in Boltzmann statistics, see Eq. (17), thereby deriving the general distribution function in thermal equilibrium, whereas we have specified their relation by the quantum condition of Eq. (27) or (52), see Eqs. (28) and (29) or (54) and (55), respectively, thereby deriving a more specific distribution function in thermal equilibrium. Each specific distribution function is a special case of the general distribution function.

To further justify this statement, we exploit the degree of freedom that is inherent to the Boltzmann distribution, namely that the total number n_t of systems is not specified and must be correctly chosen to describe the specific physical situation under consideration. Instead of introducing the quantum condition already when integrating the differential equation of thermal equilibrium, as we have done above, here we impose it on its general result, the Boltzmann distribution.

In the first situation, we choose the undefined number n_t in the Boltzmann distribution according to the condition of Eq. (27). Inserting Eq. (27) into the Boltzmann distribution of Eq. (18) yields

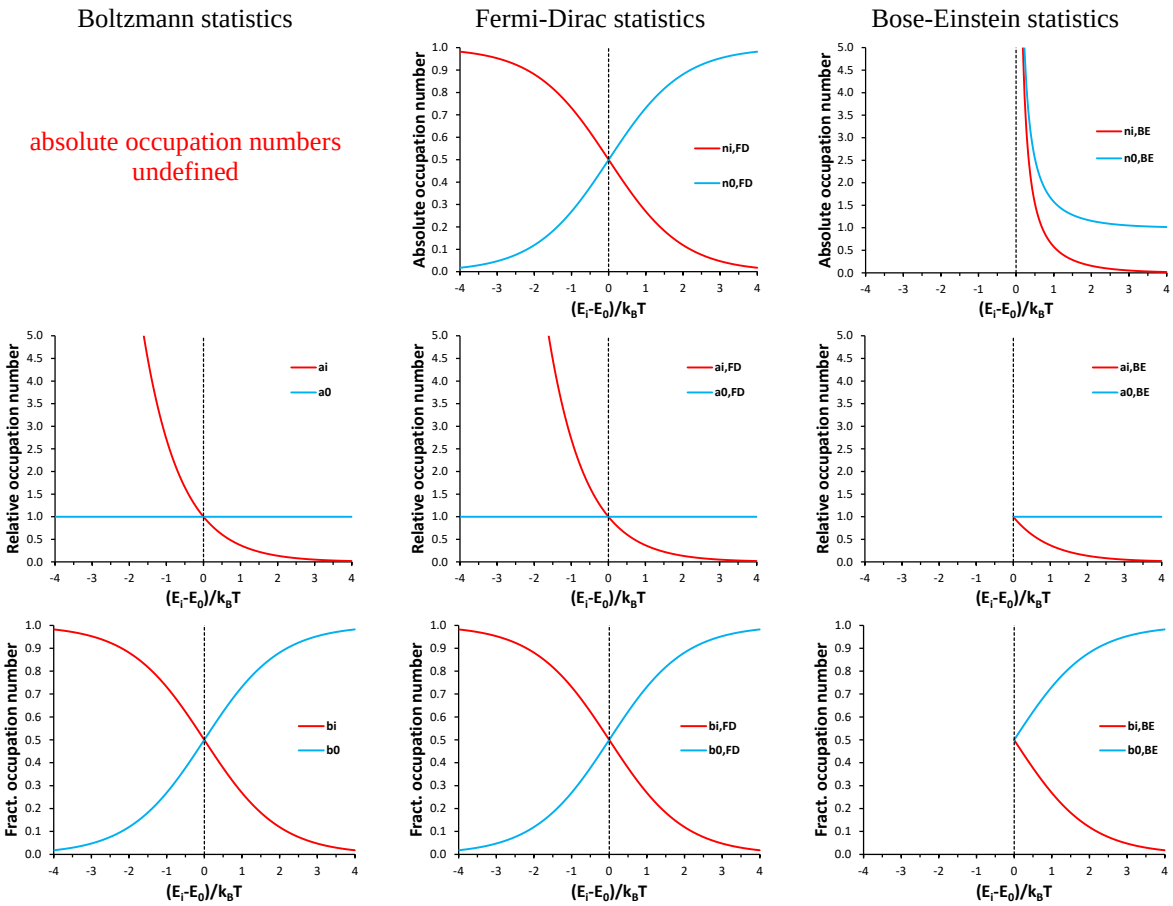

Fig. 1. Occupation numbers in thermal equilibrium in Boltzmann statistics (*left-hand column*), Fermi-Dirac statistics (*middle column*), and Bose-Einstein statistics (*right-hand column*). *Upper row*: Absolute occupation number n_i of the excited state from Eqs. (28) and (54) and n_0 of the ground state from Eqs. (29) and (55) in Fermi-Dirac and Bose-Einstein statistics, respectively. In Fermi-Dirac statistics, the red curve of n_i is the Fermi-Dirac distribution. In Bose-Einstein statistics, the red curve of n_i is the Bose-Einstein distribution. In the literature, usually only n_i is shown. Absolute occupation numbers are not specified by the Boltzmann distribution, because the Boltzmann distribution applies to any absolute occupation numbers. *Middle row*: Relative occupation number $a_i = n_i/n_0$ of the excited state of Eqs. (18), (31), and (57) and $a_0 = n_0/n_0 = 1$ of the ground state of Eqs. (19), (32), and (58) in Boltzmann, Fermi-Dirac, and Bose-Einstein statistics, respectively. In all three cases, this is the Boltzmann distribution. *Lower row*: Fractional occupation numbers $b_i = n_i / (n_0 + n_i)$ of the excited state of Eqs. (20), (33), and (59) and $b_0 = n_0 / (n_0 + n_i)$ of the ground state of Eqs. (21), (34), and (60) in Boltzmann, Fermi-Dirac, and Bose-Einstein statistics, respectively. In all three cases, these are the Boltzmann factors.

$$\frac{n_i}{n_0} = \frac{n_i}{1-n_i} = \mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T} \quad \Rightarrow \quad n_i = \frac{1}{\mathrm{e}^{(E_i-E_0)/k_\mathrm{B}T}+1} = n_{i,\mathrm{FD}} \,. \tag{61}$$

By defining the total number of systems as $n_t = n_0 + n_i = 1$, we have turned the Boltzmann distribution of Eq. (1) into the Fermi-Dirac distribution of Eq. (3). Equivalently,

$$\frac{n_i}{n_0} = \frac{1-n_0}{n_0} = \mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T} \quad \Rightarrow \quad n_0 = \frac{1}{\mathrm{e}^{-(E_i-E_0)/k_\mathrm{B}T}+1} = n_{0,\mathrm{FD}} \,. \tag{62}$$

The calculations are the same as in Eqs. (28) and (29), i.e., it makes no difference whether we impose the quantum condition directly on the integral boundaries or subsequently on the Boltzmann distribution. Now not only the relative and fractional occupation numbers but also the absolute occupation numbers in the Boltzmann and Fermi-Dirac distributions are identical, i.e., the two distributions have become entirely identical. By choosing the appropriate condition for the absolute occupation numbers of systems, namely Pauli's exclusion principle, we have turned the Boltzmann distribution into the Fermi-Dirac distribution. In other words, fermionic systems simultaneously fulfil the general Boltzmann distribution and the specific Fermi-Dirac distribution.

In the second situation, we choose the undefined number n_t in Boltzmann statistics according to the condition of Eq. (52). Inserting Eq. (52) into the Boltzmann distribution of Eq. (18) yields

$$\begin{aligned} &\frac{n_i}{n_0} = \frac{n_i}{n_i + 1} = \mathrm{e}^{-(E_i - E_0)/k_\mathrm{B}T} \quad \Rightarrow \\ &n_i = \frac{1}{\mathrm{e}^{(E_i - E_0)/k_\mathrm{B}T} - 1} = n_{i,\mathrm{BE}} \end{aligned} \quad . \tag{63}$$

By defining the total number of systems as $n_t = n_0 + n_i = 2n_i + 1$, we have turned the Boltzmann distribution of Eq. (1) into the Bose-Einstein distribution of Eq. (2). Equivalently,

$$\begin{aligned} &\frac{n_i}{n_0} = \frac{n_0 - 1}{n_0} = \mathrm{e}^{-(E_i - E_0)/k_\mathrm{B}T} \quad \Rightarrow \\ &n_0 = \frac{1}{1 - \mathrm{e}^{-(E_i - E_0)/k_\mathrm{B}T}} = n_{0,\mathrm{BE}} \end{aligned} \quad . \tag{64}$$

The calculations are the same as in Eqs. (54) and (55), i.e., it makes no difference whether we impose the quantum condition directly on the integral boundaries or subsequently on the Boltzmann distribution. Now not only the relative and fractional occupation numbers but also the absolute occupation numbers in the Boltzmann and Bose-Einstein distributions are identical, i.e., the two distributions have become entirely identical. By choosing the appropriate condition for the absolute occupation numbers of systems, namely the number of bosons (here: photons) that feed the (here: atomic) excited and ground state (here: in a blackbody radiator), we have turned the Boltzmann distribution into the Bose-Einstein distribution. In other words, bosonic systems simultaneously fulfil the general Boltzmann distribution and the specific Bose-Einstein distribution.

In both situations, we started from the Boltzmann distribution and appropriately specified the total number n_t of systems by Eq. (27) or (52), which turned the Boltzmann distribution into either the Fermi-Dirac distribution of half-integer-spin quantum systems or the Bose-Einstein distribution of integer-spin quantum systems. Equations (27) and (52) do not represent quantum-mechanical corrections to Boltzmann statistics but define the physical situation to which we apply the general Boltzmann distribution.

8. Discussion

Firstly, a clarification concerning the graphs in Fig. 1 deems appropriate. The identical two-level systems we introduced in Section 2 can have only one excited-state energy E_i. In real physical situations we often encounter systems with several or many different excited-state energies E_i, such that several or many points in these graphs are realized simultaneously. (i) An example which we usually describe by the Boltzmann distribution, without specifying the involved number of systems, is an atom—in fact, often many atoms—with a partially filled shell, in which we investigate a single excitation. However, the atom usually has several or many excited states, and the Boltzmann distribution is simultaneously applied to all these excited states. (ii) An example of a situation involving fermions is a semiconductor, in which electrons occupy many different energy states, but only one electron can occupy each energy state. (iii) An example of a situation involving bosons is a Fabry-Perot resonator with an infinite number of resonance frequencies and corresponding longitudinal modes [25], which are all occupied by photons with respective photon energies in thermal equilibrium, i.e., in the absence of an external light source. All these situations can be described by assuming one or more systems for each occurring excited-state energy E_i. As is well known, the fractional occupation numbers are derived by normalization of the sum of all probabilities to unity,

$$b_i = \frac{\exp\left[-\left(E_i - E_0\right)/\left(k_B T\right)\right]}{\sum_j \exp\left[-\left(E_j - E_0\right)/\left(k_B T\right)\right]} \, . \tag{65}$$

These are the Boltzmann factors of multi-level systems. These factors apply to the state of thermal equilibrium in Boltzmann, Fermi-Dirac, and Bose-Einstein statistics.

Since the days when Fermi-Dirac and Bose-Einstein statistics were established, Boltzmann statistics has been interpreted as a "classical limit" to these two quantum-mechanical statistics. The right-hand sides of Eqs. (1), (2) , and (3) are often compared to each other in the way displayed in Fig. 2. We find this and similar comparisons in journal papers (see among others [26,27]), textbooks (see among others [28,29]), and numerous lecture slides and readers of university courses worldwide.—For good reason, Kittel and Kroemer did not include the Boltzmann distribution in their figure [30] but merely pointed out a classical limit where the Fermi-Dirac and the Bose-Einstein distribution converge.—In the comparison of Fig. 2, the quantum-mechanical Bose-Einstein and Fermi-Dirac distributions seemingly diverge from the "classical" limit of the Boltzmann distribution when the energy gap of $E_i - E_0$ in the two-level systems becomes increasingly smaller than the thermal energy $k_B T$. This comparison is invalid, because the Fermi-Dirac distribution of Eq. (3) and the Bose-Einstein distribution of Eq. (2) quantify absolute occupation numbers n_i (the red curves in the upper row in Fig. 1), whereas the Boltzmann distribution of Eq. (1) quantifies relative occupation numbers n_i / n_0 (the red curve in the middle row in Fig. 1). This comparison is equally invalid as comparing in Fig. 1 the upper and medium rows to each other in either Fermi-Dirac statistics (middle column) or Bose-Einstein statistics (right-hand column), only to find out that absolute and relative occupation numbers have different meanings. Only additional information about $n_t = n_0 + n_i$ allows one to determine the absolute occupation numbers in the Boltzmann distribution and compare them correctly with the absolute occupation numbers in the Fermi-Dirac and Bose-Einstein distributions. This is exactly what we did in Eqs. (61) and (63), and we found that the absolute occupation numbers in the Boltzmann distribution become identical to those in either the Fermi-Dirac or the Bose-Einstein distribution when we choose the appropriate additional information.

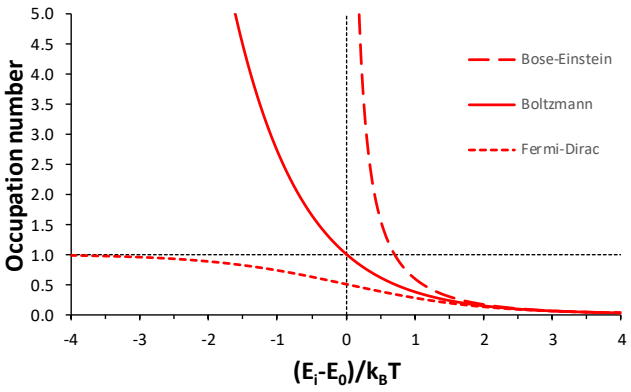

Fig. 2. Frequently performed but physically invalid comparison between the relative occupation number n_i/n_0 of Eq. (1) in the Boltzmann distribution (red curve in Fig. 1, left-hand column, middle row) with the absolute occupation numbers n_i of Eqs. (3) and (2) in the Fermi-Dirac distribution (red curve in Fig. 1, middle column, upper row) and the Bose-Einstein distribution (red curve in Fig. 1, right-hand column, upper row), respectively. One cannot specify the ordinate axis caption "Occupation number" in more detail, because relative and absolute occupation numbers are displayed in the same figure.

Key to this derivation is the realization that the systems that follow Fermi-Dirac and Bose-Einstein statistics do not only have an excited state but also a ground state. The absolute occupation number of this ground state, hence also the relative and fractional occupation numbers have been quantified in this paper. When the appropriate, independently derived condition that quantifies the absolute occupation numbers is applied to the Boltzmann distribution, it becomes identical to either the Fermi-Dirac or the Bose-Einstein distribution, hence the latter two appear to be special cases of the former and our two-level systems can simultaneously fulfil the general Boltzmann distribution and either the Fermi-Dirac or the Bose-Einstein distribution.

It was proposed already by Bose that classical particles are distinguishable and obey Boltzmann statistics, whereas quantum particles are indistinguishable; they obey either Fermi-Dirac or Bose-Einstein statistics. This difference has even been utilized as an ingredient to derive (examples of) these statistics. Combination of this proposal with the findings of this paper leads to the probably absurd situation where fermions and bosons would simultaneously be classical and quantum particles that are simultaneously distinguishable and indistinguishable. Attempts have been made to derive all three (and other) distributions from a single differential equation [31] or to describe fermions and bosons as classical particles and establish a generalized distribution function that includes

all three distributions [32]. Vice versa, the argument that classical particles must be distinguishable has been questioned [33].

The results presented in this paper do not provide the final answers to all our questions and ideas revolving around classical and quantum-mechanical statistics and will, thus, not settle the discussion. Indeed, these findings raise new questions. For example, can a simpler derivation of the specific condition contained in Eqs. (52) and (53) be established? How must we interpret this quantum condition, when it is not applied to fields or virtual bosons, such as photons, but to "real" bosons, such as ^{4}He atoms? Does the above-demonstrated relation between the distribution functions in thermal equilibrium also hold true for all those situations which are not in thermal equilibrium? What kind of statistics are we dealing with when Boltzmann statistics does not follow the specific condition of either Eq. (27) or Eqs. (52) and (53), but another condition, e.g. $n_t = 5$ or $n_t = 3.5\times10^{12}$? Can any of these potential statistics be called "classical", or does "classical" statistics possibly exist only in the limit of the energy gap in the two-level system becoming significantly larger than the thermal energy and/or in the limit of an infinite number of systems? Are "classical" particles distinguishable, whereas "quantum" particles are not? Does the distinction between "classical" and "quantum" particles make sense at all? Is this intriguing property potentially a place holder for another physical parameter? Besides Fermi-Dirac and Bose-Einstein statistics, is there possibly a third way or even more ways, with their respective specific conditions, in which quantum statistics can behave? Probably, there will be more questions arising from these findings, hence these findings will likely serve only as a starting point for a renewed discussion.

9. Conclusion

We have derived the Boltzmann, Fermi-Dirac, and Bose-Einstein distributions by establishing the differential equation of thermal equilibrium and integrating it with either general or specific boundary conditions. The results suggest that the Fermi-Dirac and Bose-Einstein distributions are special cases of the Boltzmann distribution. The general Boltzmann distribution turns into the specific Fermi-Dirac or Bose-Einstein distribution when the total number of participating systems is chosen to obey either Pauli's exclusion principle or, in the presented bosonic example, the numbers of photons that feed the atomic excited and ground states in a blackbody radiator, respectively. These quantum conditions, which have been physically justified in an independent manner, provide complete identity between two different distributions. It appears that the Boltzmann distribution does not represent a "classical limit" to the Fermi-Dirac and Bose-Einstein distributions, but the required quantum-mechanical information is contained in these specific conditions and becomes inherent to the Boltzmann distribution by entering the specific condition either *a priori* during integration of the differential equation of thermal equilibrium or subsequently into the Boltzmann distribution. This finding implies that Boltzmann statistics covers quantum-statistical phenomena.

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Declaration of Conflict of Interest

The author declares no conflict of interest.

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