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New Quantum Statistics and the Theory of Bose–Einstein Condensation

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Abstract A new form of Quantum Statistics is deduced from a general model of interactions between particles based on Probability Theory and by the minimization of energy of quantum states. As a result of the theory a new definition of entropy is obtained, together with a generalization of the Pauli's exclusion principle valid for fermions and bosons. The new statistics obtained for these two kinds of matter, is expressed as function of the number of occupied quantum states $\omega(\varepsilon)$ at energy level ε, and it is an alternative and complementary form of the classical statistics of Bose–Einstein and Fermi–Dirac. New informations are deduced about the "condensation" of matter into single states of quantum coherence and a unified description of BEC phenomena is drawn for bosons and fermions.

Keywords Probability · Entropy · Quantum systems · Bose–Einstein condensation

1 Introduction

The form at present adopted for Quantum Statistics relative to energy distribution function of material particles and radiation fields, treated as gas in thermal equilibrium, was first proposed by Bose and Einstein in the years 1924–1925 [6, 10], and by Fermi and Dirac in 1926 [11, 12]. Bose–Einstein (BE) and Fermi–Dirac (FD) statistics describe the behavior of two kinds of matter which are quite different, so as to define two great families of particles: bosons which comply to BE distribution, and fermions which instead comply to FD distribution. Which of the two statistics we have to use in a particular case depends on experience: for example energy distribution of photons and gas particles He-4 follows BE statistics, the one of electrons and gas particles He-3 follows FD statistics. In general particles with magnetic moment's value zero or integer (0, 1, 2, ...), in unit $\hbar = h/(2\pi)$, are bosons; those with magnetic moment's value half-integer (1/2, 3/2, ...) are fermions.

Quantum Statistics describe the collective behavior of collections of particles such as electrons, atoms and photons, and is part of Quantum Mechanics, the theory of physical

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laws of matter and radiation at this elementary level. A basic assumption of quantum theory is that energy, at microscopic level, assumes only discrete values which are integer multiples of a certain fundamental quantity or quantum. We call these discrete values as allowed energy levels for particles. To each level there correspond one or more quantum states, with the same energy, and every state may be empty or occupied by only a particle or more. This is the way energy is distributed among particles of a collection in Quantum Mechanics. If ε is the energy of a level, the total number of quantum states of the level is denoted by $g(\varepsilon)$. The function $g(\varepsilon)$ is called degeneracy of energy level ε. In general, given a system of particles, the entire energy levels and quantum states, form what is called the microscopic configuration of the system. As far as the way particles occupy quantum states of an energy level, we know that two or more bosons may occupy the same quantum state; on the contrary fermions comply with Pauli's exclusion principle which forbid two fermions to stay in the same quantum state. FD statistics explains fermions' behavior since it includes in its structure the Pauli's principle.

The methods used to deduce Quantum Statistics BE and FD base themselves on maximizing the probability of microscopic configuration and they are an extension of the one Boltzmann proposed in his fundamental work published in 1877 [4], where he deduced the classical Maxwell's law of distribution of velocity for gases only by statistical reasoning and founded the Second Law of Thermodynamics on probability theory. These methods are still presented nowadays in elementary and basic physics textbooks.

In the following we shall present a different deduction of Quantum Statistics, which is based on finding the minimum energy microscopic configuration. This new method is deduced from a total general probability model, the author first presented in 1996 as an application to the study of software systems' complexity [2].

By this original approach we deduce two new statistics for bosons and fermions, we shall denote respectively as BEω and FDω. While distributions BE and FD are functions of level degeneracy $g(\varepsilon)$, therefore of all possible quantum states for energy ε, new distributions BEω and FDω are functions of $\omega(\varepsilon)$, the number of quantum states effectively occupied by particles at ε energy level. This form of statistics makes it possible to deduce new information about the collective behavior of particles, such as to define exactly the finite energy interval occupied by quantum states and the existence of singularities in states distribution, responsible for (bosonic and fermionic) matter's "condensation" into an unique state of quantum coherence. The existence of such a phenomenon is known as Bose–Einstein Condensation or BEC and it has been established experimentally since 1926 for liquid He-4, more recently for liquid He-3 isotope [17]. In the 1990s BEC was reached also with dilute gases of bosonic alkali-atoms by many research groups [1, 9]. The statistical theory we propose in this work, defines physical conditions for coherent quantum state to exist in bosonic and fermionic gases, whether in case of degeneracy (like liquid He-4 and He-3), or in case of dilute gases. A generalized formulation of exclusion principle valid for fermions and the equivalent one for bosons, is deduced from the probability model we use to draw the new form of Quantum Statistics; hence conditions for transition to BEC are drawn for a fermionic gas from the "collapse" of Pauli's principle. By the classical work of Bardeen, Cooper and Shhrieffer on superconductivity [3] known as BCS theory, we know this transition happens through the formation of so-called Cooper pairs, that is the pairing of two half-integer spin fermions into one integer spin boson. The work we propose here gives a look at the same phenomena using an approach based on completion of statistical theory started by the "giant" Boltzmann.

2 Boltzmann's Method and the Deduction of Quantum Statistics BE and FD

In the long scientific debate that lasted all the second half of the XIX century, relative to research to deduce the Second Principle of Thermodynamics from the laws of Mechanics, a fundamental result is represented by the 1877 Boltzmann's memoir which we have already mentioned. In it the Austrian physicist introduces what the Ehrenfests called "the Boltzmann's statistical method" [7], aimed at drawing the second principle not from a dynamical model of gas atoms, such as in his previous work, but only from pure mathematical reasoning through what we can now define as a probability model. Since this work is closely connected with the way Quantum Statistics were first deduced from this method, in this chapter we shall give a brief summary of the subject, with some details about statistical reasoning and formulas which will be referred to in the following chapter. We can express in modern language the goal of this effort as the deduction of the energy distribution function among particles of an entire system. Referring to the fundamental hypotheses of the Quantum Theory we mentioned in the introduction, the distribution function can be defined as follows. If ε_i, $i = 1, 2, 3, \ldots$ is the discrete set of energy values the particles of a system are allowed to occupy, the distribution function is given by $n_i = n(\varepsilon_i)$, $i = 1, 2, 3, \ldots,$ where n_i is the number of particles of the system with energy ε_i. Let N be the number of material particles in the system and consider this is in thermal equilibrium with whole energy value equal to a constant value E. Then we have two more conditions to consider in determining the distribution function:

$$\sum_i n_i = N \quad \text{and} \quad \sum_i n_i \varepsilon_i = E$$

relative to total number of particles conservation and total energy conservation respectively.

In the continuous case, which is a valid approximation for the discrete case when energy levels $\varepsilon_i, \varepsilon_{i+1}$ are very close and the numbers n_i are very large, the energy distribution function is expressed as $dn(\varepsilon) = f(\varepsilon)d\varepsilon$, where $dn(\varepsilon)$ is the number of particles with energy between ε and $\varepsilon + d\varepsilon$ and $f(\varepsilon)$ is a function of energy.

The constraints about particles number and energy conservation are then expressed as

$$\int_\varepsilon f(\varepsilon)d\varepsilon = N \quad \text{and} \quad \int_\varepsilon \varepsilon f(\varepsilon)d\varepsilon = E$$

where the integration takes place over the interval of possible energy values.

In the following we shall use indifferently the discrete and the continuous notation.

Given a set of energy values, there will be in general more than one way to realize a certain distribution function. All these different ways will be obtained by varying the microscopic configuration of the system, that is the distribution of particles among energy levels and among quantum states of every energy level.

Let us consider a distribution function $(n_1, n_2, n_3, \ldots)$ and indicate with $W = W(n_1, n_2, n_3, \ldots)$ the whole number of microscopic configuration for the distribution given. Of course somehow or other the quantity W is a measure of probability of the distribution $(n_1, n_2, n_3, \ldots)$: the higher the value of W, the higher the probability of the distribution. Like Boltzmann, two fundamental hypotheses are to be introduced at this point:

(a) independently of the initial state, the isolated system in thermal equilibrium evolves to the state with most probable distribution or with maximum number of microscopic configurations W;

(b) equal *a priori* probability of all the possible microscopic configurations (or microstates) of the system with the same total energy (this one assumed only tacitly by Boltzmann).

Without entering too subtle considerations here about the meaning of these hypotheses, we want to point out they are pure mathematical hypotheses; this is true particularly for the second one which is related to axiomatic reasoning about probability theory. From a physical point of view both of them are a posteriori justifiable only, after comparing the results obtained from theory with those of experience.

Therefore assuming the preceding hypotheses we shall get the stationary state of the system by maximizing W, under the constraints on total particles number and total energy, hence by solving the problem

$$\max_{n1,n2\ldots} \quad W(n_1, n_2, n_3, \ldots), \tag{1a}$$

$$\sum_i n_i = N, \tag{1b}$$

$$\sum_i n_i \varepsilon_i = E. \tag{1c}$$

Function W and system's entropy S are linked by the famous equation $S = k \log W$, where k is the Boltzmann's constant.

By opportune definitions of function W, Quantum Statistics can be deduced by problem (1a–1c). To do this we have to take into account the degeneracy of quantum states expressed by $g(\varepsilon)$ (also referred to as the weight of the state with energy ε), and the *indistinguishability* of particles. That particles are to be considered as indistinguishable it is only an alternative (and historical) way to say how microstates are to be counted in function W. On the contrary with respect to classical Maxwell–Boltzmann statistics, two microstates which differ only due to the exchange of two particles represent the same state, and in the enumeration of states must be counted as only a single state. This way to count microstates, first proposed by Bose in deducing Planck's black body radiation formula through statistics, together with function $g(\varepsilon)$, results in two different expressions for W from which we get BE and FD statistics. As we have said above we shall give here only a brief summary of essential formulas; a complete classical treatment of the subject is given in [5]. Let us consider therefore a system in thermal equilibrium made up of N identical particles with mass m.

In BE statistics any of n_i particles in the same energy level ε_i, can occupy any of the $g_i = g(\varepsilon_i)$ possible quantum states for that level. Given this rule, all distinguishable arrangements with n_i particles distributed among g_i microstates, can be calculated by combinatorial analysis as

$$C'(g_i, n_i) = \frac{(g_i + n_i - 1)!}{n_i!(g_i - 1)!}.$$

Hence the function W for the whole system is given by the product

$$W(n_1, n_2, \ldots) = \prod_i \frac{(g_i + n_i - 1)!}{n_i!(g_i - 1)!}. \tag{2}$$

The solution of problem (1a–1c) where W is given by (2) is the well known BE distribution

$$n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} - 1} \tag{3}$$

with α and β constants whose value is determined through constraint conditions.

In this work we adopt the original notation used in [5] and define $A = e^{-\alpha}$; hence (3) can be written as

$$n_i = \frac{A g_i}{e^{\beta \varepsilon_i} - A}. \tag{4}$$

A varies in the interval

$$0 < A \leq 1 \tag{5}$$

and when $A = 1$ we say that the gas is *degenerate* since this value maximizes the ratio between particles and quantum states for every energy levels. In fact let us consider the ratio

$$\rho_i = \frac{n_i}{g_i} = \frac{A}{e^{\beta \varepsilon_i} - A}$$

and the derivative

$$\frac{d\rho_i}{dA} = \frac{e^{\beta \varepsilon_i}}{(e^{\beta \varepsilon_i} - A)^2} > 0.$$

Since this is positive, ρ_i is a monotone increasing function of A which attains its maximum value for $A = 1$.

FD statistics can be deduced from Boltzmann's method too. In this case we have to assume that only one of n_i particles in the same energy level ε_i, can occupy one of the $g_i = g(\varepsilon_i)$ possible quantum states for that level. Given this rule, which is the same as exclusion principle, all distinguishable arrangements with n_i particles distributed among g_i microstates, can be calculated by combinatorial analysis as

$$C(g_i, n_i) = \frac{g_i!}{n_i!(g_i - n_i)!}.$$

Hence the function W for the whole system is given by the product

$$W(n_1, n_2, \ldots) = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}. \tag{6}$$

FD distribution is the solution of problem (1a–1c) where W is given by (6), and it is given by the following expression

$$n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} + 1} \tag{7}$$

with α and β constants whose value is determined again through constraint conditions.

Let us adopt in this case too the old original notation and define $A = e^{-\alpha}$, hence (7) can be written as

$$n_i = \frac{A g_i}{e^{\beta \varepsilon_i} + A}. \tag{8}$$

In this case A values are between 0 and infinite

$$0 < A \leq \infty. \tag{9}$$

For the case of FD statistics, gas degeneration is achieved when $A = \infty$. As before it is easy to see that the ratio

$$\rho_i = \frac{n_i}{g_i} = \frac{A}{e^{\beta\varepsilon_i} + A}$$

is a monotone increasing function of A and that $\rho_i \to 1$ as $A \to \infty$. A complete treatment of this limit condition, which is deeply involved with what we have called the "collapse" of Pauli's exclusion principle, will be given in the following after the introduction of FDω statistics.

As far as function $g(\varepsilon)$ is concerned, in the case of a particle with mass m in a three-dimensional infinitely deep potential well of volume V (that is constrained to move in a space of volume V and no force acting on it), the most general expression is given by the equation (see [14])

$$g(\varepsilon) = V\frac{4\pi}{h^3}M(2m^3\varepsilon)^{1/2} \tag{10}$$

or

$$g(\varepsilon) = Vb\varepsilon^{1/2} \tag{11}$$

where

$$b = \frac{4\pi}{h^3}M(2m^3)^{1/2}, \tag{12}$$

h is Planck's constant and the factor M is equal to the total number of possible projections of particle angular momentum. Therefore if a particle has only intrinsic angular momentum (spin) of value $\underline{S}$, we get $M = 2S + 1$. For example this is the case of electrons where $S = 1/2$ and $M = 1$. Since the last chapter of this work will be concerned with the study of atomic gases, we have to consider M in this general case. In a neutral atom the nuclear spin $\underline{I}$ and the total electron angular momentum $\underline{J}$ get coupled, giving rise to the total angular momentum $\underline{F} = \underline{J} + \underline{I}$; therefore we assume that M is given by the Lande interval rule for hyperfine splitting of energy levels [16]:

$$M = (J + I) - |J - I| + 1. \tag{13}$$

Finally constants A and β are determined through constraint conditions on the total number of particles and on the total energy of the system in thermal equilibrium. The formulas we write for A, A_0 below, are slightly different from those in [5] since they include the general expression (10) for $g(\varepsilon)$.

For β we get

$$\beta = \frac{1}{kT} \tag{14}$$

where k is Boltzmann's constant we already mentioned and T is the absolute temperature of the system.

The constant A in BE distribution (4) is found to be equal to

$$A = A_0\left(1 - \frac{1}{2\sqrt{2}}A_0 + \frac{(3\sqrt{3}-4)}{12\sqrt{3}}A_0^2 - \cdots\right) \tag{15}$$

where

$$A_0 = \frac{n_\delta}{M}\frac{h^3}{(2\pi mkT)^{3/2}} \tag{16}$$

with n_δ number of particles for unit volume (density). Obviously $A \approx A_0$ is a good approximation for A if $A \ll 1$.

In the case of FD distribution (8), when $A \ll 1$ we still get $A \approx A_0$ as a good approximation. If on the contrary it is $A \gg 1$, we have to use the following formula

$$\ln A \approx \frac{h^2}{2mkT}\left(\frac{3n_\delta}{4\pi M}\right)^{2/3}. \tag{17}$$

As we said, the above equation for A can be obtained from those in [5] through simple manipulation, taking into account the factor M in (10). We have also used here the density of particles n_δ instead of the total number N. In the following we shall refer to density or total number indifferently, for function $g(\varepsilon)$ too. The meaning will be specified in the context.

3 A General Probability Model. Structure and Entropy of a System

We have seen in the preceding chapter how Quantum Statistics BE an FD, can be drawn by maximizing the probability of microscopic configuration of the system. It's an aim of this work to present an alternative form of the same distribution functions for bosons and fermions, obtained by minimizing the system's energy. To get this result it is necessary to step into abstraction and to define first a very general model based on probability theory. We shall see then in the following chapter, how this model can be used to study quantum systems made of many identical particles.

The more general way to represent a system independently from its features, is to take into account only the *events* concerning its parts, hence, mathematically speaking, to take into account the probability space of these events. Let (Ω, F, P) be the probability space of the system, where $\Omega = (\omega_i, i = 1, 2, 3, \ldots)$ is the space of elementary events (or elementary outcomes) ω_i, finite or countable, F a σ-algebra of Ω, P a probability measure defined on Ω.[1] Given any two events of F, say E_i and $E_j, i = 1, 2, 3, \ldots, j = 1, 2, 3, \ldots$, we define E_{ij} as the event which consists in the occurrence of both events E_i and E_j, or

$$E_{ij} = E_i \cap E_j.$$

From properties of σ-algebra it follows that $E_{ij} \in F$ too.

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[1] A collection F of subsets of Ω is called σ-algebra if it is an algebra, hence it has the properties: (a) $\Omega \in F$; (b) $c \in F \Rightarrow \overline{c} \in F$; (c) $c_1, c_2, c_3, \ldots, c_k \in F \Rightarrow \bigcup_{i=1}^{k} c_i \in F$ and the property (c) holds when $k = \infty$ too. P is a function defined on F, which satisfies the following conditions: (a) $P(c) \geq 0$ for any $c \in F$; (b) $P(\Omega) = 1$; (c) if $c_i \in F, i = 1, 2, \ldots$ and $c_i \cap c_j = \phi$ then

$$P\left(\bigcup_{i=1}^{\infty} c_i\right) = \sum_{i=1}^{\infty} P(c_i).$$

See Sinai [18] for a complete treatment.

Let us indicate with p_i, p_j and q_{ij} the probabilities of E_i, E_j and E_{ij} respectively

$$p_i = P(E_i),$$
$$p_j = P(E_j),$$
$$q_{ij} = P(E_{ij})$$

and write them as

$$p_i = \sigma_{ij} + \pi_{i(j)}, \tag{18a}$$
$$p_j = \sigma_{ij} + \pi_{j(i)}, \tag{18b}$$
$$q_{ij} = \sigma_{ij} + \pi_{i(j)} \cdot \pi_{j(i)}. \tag{18c}$$

We note immediately that if $\sigma_{ij} = 0$ then E_i and E_j are independent events, therefore we can say that σ_{ij} is a probability measure of mutual dependence between E_i and E_j; $\pi_{i(j)}, \pi_{j(i)}$ a probability measure of mutual independence of E_i from E_j an of E_j from E_i respectively. A deduction of probability decomposition (18a–18c) can be given through algebraic decomposition of events in F [2], but this is unnecessary since the model is completely justified by the condition of existence we find below. Given the probabilities (p_i, p_j, q_{ij}), we find necessary conditions a triplet $(\sigma_{ij}, \pi_{i(j)}, \pi_{j(i)})$ to exist simply by putting

$$\pi_{i(j)} = p_i - \sigma_{ij},$$
$$\pi_{j(i)} = p_j - \sigma_{ij}$$

and substituting in (18c). Doing so we get the quadratic equation

$$\sigma_{ij}^2 + (1 - p_i - p_j)\sigma_{ij} - q_{ij} + p_i p_j = 0 \tag{19}$$

which has real solutions for

$$\Delta_{ij}^2 = (1 - p_i - p_j)^2 - 4(p_i p_j - q_{ij}) \geq 0$$

hence for

$$q_{ij} \geq p_i p_j - \frac{1}{4}(1 - p_i - p_j)^2. \tag{20}$$

Expression (20) is the existence condition of probability model (18a–18c). Note this is obviously true if

$$q_{ij} \geq p_i p_j. \tag{21}$$

The solution of (18a–18c) is given by

$$\sigma_{ij} = \frac{1}{2}(p_i + p_j - 1 + \Delta_{ij}), \tag{22a}$$
$$\pi_{i(j)} = \frac{1}{2}(p_i - p_j + 1 - \Delta_{ij}), \tag{22b}$$
$$\pi_{j(i)} = \frac{1}{2}(p_j - p_i + 1 - \Delta_{ij}). \tag{22c}$$

The model (18a–18c) and the resulting equations (22a–22c) are a way to represent the relations among the elements of the system in the abstract, through a probability space associated with the set of events concerning these elements. We need to develop further the model to look for a concise expression representing the system as a whole.

We assume in the following that the events of the σ-algebra we are interested with, are a finite number Λ, hence $i = 1, 2, 3, \dots, \Lambda$, $j = 1, 2, 3, \dots, \Lambda$. Therefore we exactly define the system we are concerned with as the set of events $(E_1, E_2, \dots, E_\Lambda)$ of the σ-algebra F of the probability space (Ω, F, P).[2]

We can write p_i as

$$p_i = \sigma_i + \pi_i, \tag{23}$$

with σ_i and π_i defined as

$$\sigma_i = \frac{1}{\Lambda - 1} \sum_{j \neq i} \sigma_{ij}, \tag{24}$$

$$\pi_i = \frac{1}{\Lambda - 1} \sum_{j \neq i} \pi_{i(j)}. \tag{25}$$

From (18c) probability σ_{ij} can be written

$$\sigma_{ij} = \pi_{j(i)} \left(\frac{q_{ij}}{\pi_{j(i)}} - \pi_{i(j)} \right)$$

and by substituting in (24), after some algebraic manipulation, we get

$$\sigma_i = \sum_{j \neq i} \pi_j \frac{\pi_{j(i)}}{\sum_{i \neq j} \pi_{j(i)}} \left(\frac{q_{ij}}{\pi_{j(i)}} - \pi_{i(j)} \right).$$

We put by definition

$$r_{ij} = \frac{\pi_{i(j)}}{\sum_{j \neq i} \pi_{i(j)}} \left(\frac{q_{ij}}{\pi_{i(j)}} - \pi_{j(i)} \right) \tag{26}$$

hence

$$\sigma_i = \sum_{j \neq i} \pi_j r_{ji}$$

and from (23) it follows

$$p_i = \pi_i + \sum_{j \neq i} \pi_j r_{ji}. \tag{27}$$

The correlation parameters (26) between events E_i and E_j can be written for every pair (i, j), with $i \neq j$. Note that if two events are independent, the corresponding r_{ij} is zero. Therefore they are an expression of mutual dependence of events, whose probabilities are

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[2] Since the set of events we consider is finite, the notion of algebra suffices to develop the probability theory we need. Since going into the subject in depth is outside the aim of this work, and it does not matter the physical implications of the theory, we continue to use standard definitions of probability.

given by (27) as functions of independent probabilities (of the occurrence of the event itself π_i) and conditional probabilities (of the occurrence of the event depending on the "independent" occurrences of the other ones $\sum_{j\neq i}\pi_j r_{ji}$). Whatever the meaning of (26) and (27) may be, the correlation parameters r_{ij} are closely involved with the entropy of the system, as we shall see soon.

Let us call Relational Structure of the system of events $(E_1, E_2, \ldots, E_\Lambda)$, as we defined it above, the product[3]

$$R = \prod_i \prod_{j\neq i} |r_{ij}|. \tag{28}$$

On the analogy of Boltzmann we define the entropy of the system as

$$S = -k \ln R \tag{29}$$

or

$$S = -k \sum_i \sum_{j\neq i} \ln |r_{ij}|. \tag{30}$$

The minus sign is necessary since R is a measure of the order of the system, or of the cohesion of its events, S is a measure of the disorder of the system: if all events are independent $r_{ij} = 0$, $R = 0$ and $S \to \infty$; on the contrary $S = 0$ if $r_{ij} = 1$ for all pairs of events. Note also that probabilities p_i and q_{ij} define the state of the system independently of the "path" or the evolution occurred, hence entropy as defined in (29) is a function of state coordinates only. It has the property of additivity too, as we can see below. Equation (30) can be written as

$$S = \sum_i S_i = \sum_i \sum_{j\neq i} S_{ij}$$

where

$$S_{ij} = -k \ln |r_{ij}| \tag{31}$$

is the entropy of the relation between events E_i and E_j;

$$S_i = -k \sum_{j\neq i} \ln |r_{ij}|$$

is the entropy of the event E_i (better of its relations with other events). Hence the entropy of the whole system equals the sum of the entropies of its events. The minimum entropy is that of a relation between two events (31), which we write again with no subscripts so as to highlight how it depends on correlation r

$$S = -k \ln |r|.$$

By differentiating we get

$$dS = -k \frac{dr}{|r|}$$

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[3] Quantity R exactly defines, from a mathematical point of view, what Cybernetics calls the *Structure* of a system [15, 19], that is the whole of relations among its elements. This *Structure* is neither matter nor energy, it is information only. That is why we adopt this name for R. Matter and energy, hence physical evolution, enter the system through entropy.

and remembering the Second Principle of Thermodynamics in its differential form $dS = \frac{dQ}{T}$, where dQ is the amount of heat the system exchanges through a reversible process (infinitesimal) occurring at temperature T, we finally obtain the differential equation

$$\frac{dr}{|r|} = -\frac{dQ}{kT}. \tag{32}$$

Equation (32) connects the Relational Structure of a system with physical quantities such as energy and temperature and it is responsible for the evolution of the system to occur.

4 Application to Quantum Systems. Generalized Pauli's principle

This chapter is concerned with the application of the theory developed in the preceding chapter to a quantum system, consisting of many identical particles distributed on a finite number of energy levels $\varepsilon_l, l = 1, 2, \ldots$.

Because of *degeneracy* of energy level ε, we know every level has as many quantum states as those given by function $g(\varepsilon)$. They are all accessible quantum states and may be occupied or not by some particles. Let us define a new function, say $\omega(\varepsilon)$,[4] whose value equals the number of quantum states of energy level ε which are occupied at least by one particle.

For every energy level $l, l = 1, 2, 3, \ldots$, let n_l be the number of particles and $N = \sum_l n_l$ the total number of particles, $g_l = g(\varepsilon_l)$ the number of accessible quantum states and $\omega_l = \omega(\varepsilon_l)$ the number of occupied quantum states. Of course the following condition holds for every l:

$$1 \le \omega_l \le n_l. \tag{33}$$

In the following we have to consider both energy levels and quantum states. Therefore in writing symbols of physical quantities we adopt the convention: from left to right the first subscript indicates the energy level, the second subscript, or group of subscripts between parentheses, indicates the quantum state in the level.

Let us consider then the events below with their probabilities:

$E_{l,i}$ = quantum state i of level l is occupied (by a particle) , $p_{l,i} = P(E_{l,i})$;

$E_{l,(i,j)}$ = quantum states i and j of level l are occupied (by two particles), $q_{l,(i,j)} = P(E_{l,(i,j)})$;

$l = 1, 2, 3, \ldots; i = 1, 2, 3, \ldots, \omega_l; j = 1, 2, 3, \ldots, \omega_l$.

Hence (18a–18c), (26) and (27) become

$$p_{l,i} = \sigma_{l,(i,j)} + \pi_{l,i(j)}, \tag{34a}$$

$$p_{l,j} = \sigma_{l,(i,j)} + \pi_{l,j(i)}, \tag{34b}$$

$$q_{l,(i,j)} = \sigma_{l,(i,j)} + \pi_{l,i(j)} \cdot \pi_{l,j(i)}, \tag{34c}$$

$$r_{l,(i,j)} = \frac{\pi_{l,i(j)}}{\sum_{j\neq i} \pi_{l,i(j)}} \left(\frac{q_{l,(i,j)}}{\pi_{l,i(j)}} - \pi_{l,j(i)} \right), \tag{35}$$

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[4] The symbol ω is the same one used generally in Probability Theory to mean elementary outcomes of space Ω: in fact the concepts of occupation of a quantum state and of elementary outcome are closely connected.

$$p_{l,i} = \pi_{l,i} + \sum_{j \neq i} \pi_{l,j} r_{l,(j,i)} \tag{36}$$

where the summation takes place over the ω_l occupied states only.

We assume that:

(1) quantum states of a certain level have the same probability values; hence we can omit the subscripts of these states and leave the level subscript only as follows

$$\begin{aligned} &p_{l,i} = p_l, \\ &q_{l,(i,j)} = q_l, \\ &\sigma_{l,(i,j)} = \sigma_l, \\ &\pi_{l,i(j)} = \pi_{l,j(i)} = \pi_l, \\ &r_{l,(i,j)} = r_{l,(j,i)} = r_l; \end{aligned}$$

(2) the occupied quantum states of a certain level have the same number of particles; hence if $n_{l,i}$ is the number of particles in state i of level l this is given by, for every i

$$n_{l,i} = \frac{n_l}{\omega_l}. \tag{37}$$

The existence condition (20) of the general probability model (18a–18c) becomes

$$p_l - q_l \leq \frac{1}{4} \tag{38}$$

and equations (22a–22c) and (26)

$$\begin{aligned} \sigma_l &= p_l - \frac{1}{2}(1 - \sqrt{1 - 4(p_l - q_l)}), \\ \pi_l &= \frac{1}{2}(1 - \sqrt{1 - 4(p_l - q_l)}), \\ r_l &= \frac{1}{(\omega_l - 1)}\left(\frac{q_l}{\pi_l} - \pi_l\right). \end{aligned} \tag{39}$$

By substituting in (39) the preceding expressions for σ_l and π_l we get

$$r_l = \frac{1}{(\omega_l - 1)} \frac{p_l - \frac{1}{2}(1 - \sqrt{1 - 4(p_l - q_l)})}{\frac{1}{2}(1 - \sqrt{1 - 4(p_l - q_l)})}. \tag{40}$$

We can now give an axiomatic definition of bosons and fermions founded on the correlation parameter r_l. We define as *bosons* those particles with $r_l > 0$, *fermions* those with $r_l < 0$. As we shall see this classification is completely coherent with the usual division of matter into these two kinds. Let us look at the conditions for r_l to be positive or negative. Because of the hypotheses we have assumed, (36) can be written as

$$p_l = \pi_l(1 + (\omega_l - 1)r_l) \tag{41}$$

from which follows

$$r_l = \frac{1}{(\omega_l - 1)}\left(\frac{p_l}{\pi_l} - 1\right).$$

Hence for quantum systems consisting of bosons the condition $p_l > \pi_l$ holds, the opposite $p_l < \pi_l$ for quantum systems consisting of fermions. These conditions are not easy to manipulate because of the presence of independent probability π_l. Simpler conditions which imply p_l and q_l probabilities only, can be deduced directly from (40). We get $r_l > 0$ if

$$p_l > \frac{1}{2}(1 - \sqrt{1 - 4(p_l - q_l)})$$

or

$$q_l > p_l^2. \tag{42}$$

On the contrary it is $r_l < 0$ if

$$q_l < p_l^2. \tag{43}$$

Condition $q_l > p_l^2$ holds for bosons and it says the probability of the same event occurring twice (two particles occupy one or two distinct quantum states of the same energy level) is higher than the square probability of a single event occurring. The opposite condition $q_l < p_l^2$ is true for fermions. Inequalities (42) and (43) are the most general statistical description of properties of bosons and fermions, and they include Pauli's exclusion principle as a particular case. To see this we rewrite inequality (43) with all subscripts as

$$q_{l,(i,j)} < p_{l,i}^2$$

and assume the probabilities are given by ratios of occupancy numbers to total number of particles.

Therefore we get

$$p_{l,i} = \frac{n_{l,i}}{N}$$

and from Bayes' formula[5]

$$q_{l,(i,j)} = P(E_{l,(i,j)}) = P(E_{l,j}/E_{l,i}, E_l) \cdot P(E_{l,i}/E_l) \cdot P(E_l)$$

where

$$P(E_l) = \frac{n_l}{N},$$

$$P(E_{l,i}/E_l) = \frac{n_{l,i}}{n_l},$$

$$P(E_{l,j}/E_{l,i}, E_l) = \frac{n_{l,j} - 1}{n_l - 2}$$

---

[5] Bayes' formula gives the probability of events A *and* B, $P(A, B)$, through conditional probability of A given B, $P(A/B)$, as $P(A, B) = P(A/B)P(B)$.

hence

$$q_{l,(i,j)} = \frac{n_{l,i}(n_{l,j}-1)}{N(n_l-2)}.$$

From (43), after some algebraic manipulations and remembering $n_{l,i} = n_{l,j}$ and (37), we get

$$\frac{n_l}{\omega_l} < \frac{N}{N-(n_l-2)}$$

and therefore we can write for the ratio n_l/ω_l

$$1 \le \frac{n_l}{\omega_l} < \frac{1}{1-\delta_l}$$

where

$$\delta_l = \frac{n_l-2}{N}.$$

If it is $\delta_l < \frac{1}{2}$ or

$$n_l < \frac{N}{2} + 2 \tag{44}$$

it is $\frac{1}{1-\delta_l} < 2$ too, hence in that case the number of particles in each quantum state i of energy level l is given by

$$n_{l,i} = \frac{n_l}{\omega_l} = 1 \tag{45}$$

since it is an integer number. Equation (45) is a way to represent Pauli's exclusion principle for fermions; therefore this principle is valid only in the case of (44), when the particles with the same energy level are less than half the total number of particles of the system. When

$$n_l \ge \frac{N}{2} + 2 \tag{46}$$

the exclusion principle "collapses" and its validity quits. We shall see in the following the importance of condition (46) in determining the transition to BEC for fermions.

By analogous reasoning from (42) we get for bosons

$$n_{l,i} = \frac{n_l}{\omega_l} > \frac{1}{1-\delta_l} > 1. \tag{47}$$

5 The New Quantum Statistics BEω and FDω

For the quantum system we defined in Sect. 4, let $e_{l,i}$, $i = 1, 2, \ldots, \omega_l$, be the energy of the quantum state i of the energy level l. Because of hypothesis (1) of Sect. 4 we can put $e_{l,i} = e_l$ too. Let us consider then the mean energy of a general quantum state i in each level, as a function of occupied quantum states

$$e(\omega_1, \omega_2, \ldots) = \sum_l p_{l,i} e_{l,i} = \sum_l p_l e_l.$$

Since p_l is given by (41), the mean quantum state energy e can be written as:

$$e(\omega_1, \omega_2, \ldots) = \sum_l \pi_l (1 + (\omega_l - 1) r_l) e_l. \tag{48}$$

It is to be expected that the state of thermal equilibrium of the system corresponds with a minimum of mean energy e, hence with the following stationary conditions:

$$\frac{\partial e(\omega_1, \omega_2, \ldots)}{\partial \omega_l} = 0, \quad l = 1, 2, \ldots$$

or

$$r_l e_l + [1 + (\omega_l - 1) r_l] \frac{\partial e_l}{\partial \omega_l} = 0. \tag{49}$$

We adopt two different definitions for energy e_l, one for each kind of matter. For the case of bosons we define energy e_l as

$$e_l(\omega_l) = \varepsilon_l \left(1 + \frac{n_l - 1}{\omega_l} \right) \tag{50}$$

that is the energy e_l is given by ε_l times the number of particles in the state, assuming that

- the quantum state is occupied at least by one particle;
- the remaining $(n_l - 1)$ particles in level l are equally distributed among $\omega_l$occupied quantum states.

We call function $e_l(\omega_l)$ above the *bosonic mode* of energy distribution (or *associative mode*, remember that $r_l > 0$ for bosons). Hence for the bosonic mode the derivative is

$$\frac{\partial e_l}{\partial \omega_l} = -\varepsilon_l \frac{n_l - 1}{\omega_l^2}$$

by substituting this in (49) and solving the equation, we finally get the total number of particles in energy level l:

$$n_l - 1 = \frac{\omega_l^2 r_l}{(1 - r_l)}. \tag{51}$$

Equation (51) is the Bose–Einstein distribution as function of occupied quantum states ω_l, which we also call BEω distribution.

Let us now write stationary conditions (49) for fermions. Since we know that condition $r_l < 0$ holds for these particles, in the following we shall write $-|r_l|$ instead of r_l. Equation (49) becomes

$$-|r_l| e_l + [1 - (\omega_l - 1)|r_l|] \frac{\partial e_l}{\partial \omega_l} = 0 \tag{52}$$

and we define energy e_l for the case of fermions as

$$e_l(\omega_l) = Q_l \left(1 - \frac{n_l - 1}{\omega_l} \right). \tag{53}$$

We get the energy e_l of a quantum state by subtracting the energy equally distributed among other states, from the total energy Q_l of the level l and assuming that

- the quantum state is occupied by at least one particle;
- the remaining $(n_l - 1)$ particles in level l are equally distributed among ω_l occupied quantum states.

We call function $e_l(\omega_l)$ above the *fermionic mode* of energy distribution (or *dissociative mode*). It is important to note that fermionic mode is the same as Pauli's exclusion principle. In fact we get from (53) $\frac{e_l}{Q_l} = 1 - \frac{n_l - 1}{\omega_l} > 0$ by definition, therefore $\omega_l > n_l - 1$. Since $1 \leq \omega_l \leq n_l$ obviously holds (see (33)), there must be $\omega_l = n_l$ too. It also follows that $n_l e_l = Q_l$, hence Q_l is really the total energy of level l.

For the fermionic mode the derivative is

$$\frac{\partial e_l}{\partial \omega_l} = Q_l \frac{n_l - 1}{\omega_l^2}$$

by substituting this in (52) and solving the equation, we finally get the total number of particles in energy level l:

$$n_l - 1 = \frac{\omega_l^2 |r_l|}{(1 + |r_l|)}. \tag{54}$$

Equation (54) is the Fermi–Dirac distribution as function of occupied quantum states ω_l, which we also call FDω distribution.

From the definition of entropy we have given in Sect. 2 and (32), we can get BEω and FDω distributions as function of the energy level ε_l. In that which follows we omit the indication of level subscript l, since the dependence on the energy level is meant by the dependence on the energy ε only. By integrating the differential equation (32), after assuming that $dQ = d\varepsilon$ (i.e. the energy the system exchanges through a reversible infinitesimal transformation), we get[6]

$$\int_1^{|r|} \frac{dx}{x} = -\frac{1}{kT} \int_0^{\varepsilon} dy$$

hence

$$|r| = e^{-\frac{\varepsilon}{kT}}. \tag{55}$$

By substituting the preceding expression for r in (51) and (54) we get BEω and FDω statistics as function of energy. Therefore

$$n(\varepsilon) - 1 = \frac{\omega^2(\varepsilon)}{e^{\frac{\varepsilon}{kT}} - 1} \tag{56}$$

is the BEω statistics which holds for bosons, and

$$n(\varepsilon) - 1 = \frac{\omega^2(\varepsilon)}{e^{\frac{\varepsilon}{kT}} + 1} \tag{57}$$

is the FDω statistics which holds for fermions.

From the general definition of entropy (30) and from (55) we get the entropy of a quantum system

$$S = \sum_l (\omega_l - 1)\omega_l \frac{\varepsilon_l}{T}. \tag{58}$$

---

[6] We assume that $|r| = 1$, hence $S = 0$, when $\varepsilon = 0$.

The energy levels whose particles occupy all the same quantum state ($\omega_l = 1$), or *condense* into a single quantum state, give zero contribution to the entropy of the system; that is the entropy of the system is zero if and only if all of its components occupy the same quantum state.

6 Equivalence of BE, BEω and FD, FDω Statistics. Existence Conditions of Occupied Quantum States

BE and BEω statistics are equal since both of them give the distribution of particles (bosons) of a system as function of energy. The same is true for FD and FDω statistics if particles are fermions. In the following we shall draw the conclusion of this equivalence as far as $\omega(\varepsilon)$ and $g(\varepsilon)$ functions are concerned. The most important result of this analysis, we shall widely use in the rest of this work, is concerned with the definition of a finite interval $(\varepsilon_m, \varepsilon_M)$ for energy of particles, instead of the infinite interval $(0, \infty)$ which classical statistics assume.

For the case of bosons, BEω statistics (56) can be written as

$$n(\varepsilon) = \frac{\omega^2(\varepsilon) + (e^{\beta\varepsilon} - 1)}{e^{\beta\varepsilon} - 1} \tag{59}$$

with $\beta = \frac{1}{kT}$. Assuming the distributions (4) and (59) are equal, we get

$$\omega^2(\varepsilon) = \frac{(e^{\beta\varepsilon} - 1)}{e^{\beta\varepsilon} - A} A \left[g(\varepsilon) - \frac{(e^{\beta\varepsilon} - A)}{A} \right]. \tag{60}$$

In order that occupied quantum states exist for energy ε, there must be $\omega^2(\varepsilon) > 0$ or

$$g(\varepsilon) > \frac{e^{\beta\varepsilon} - A}{A}. \tag{61}$$

We know from (11) that function $g(\varepsilon)$ (for unit volume) has the form

$$g(\varepsilon) = b\sqrt{\varepsilon} \tag{62}$$

with b given by the general formula (12). If we define the function

$$f(\varepsilon, T, A) = \frac{e^{\beta\varepsilon} - A}{A} \tag{63}$$

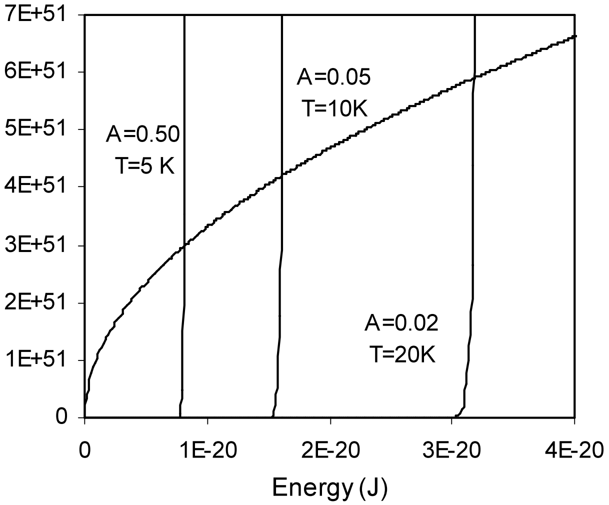
then the existence condition (61) determines the range of admissible values for energy, $\varepsilon_m < \varepsilon < \varepsilon_M$, where $g(\varepsilon) > f(\varepsilon, T, A)$. A graph of functions $g(\varepsilon)$ and $f(\varepsilon, T, A)$ in the case of He-4 and different values of T and A is reproduced in Fig. 1. It is important to note that at zero value of energy $\varepsilon = 0$, we get

$$f(0, T, A) = \frac{1 - A}{A}. \tag{64}$$

Let us consider now the derivative of $f(\varepsilon, T, A)$ with respect to temperature T

$$\frac{df}{dT} = \frac{\partial f}{\partial T} + \frac{\partial f}{\partial A}\frac{dA}{dT}$$

Fig. 1 Function g and f for He-4 at high energy



where

$$\begin{aligned}\frac{\partial f}{\partial T} &= -\frac{\varepsilon}{AkT^2}e^{\frac{\varepsilon}{kT}} < 0,\\ \frac{\partial f}{\partial A} &= -\frac{1}{A^2}e^{\frac{\varepsilon}{kT}} < 0\end{aligned} \tag{65}$$

and we also know [14] that $\frac{dA}{dT} < 0$. Therefore when T decreases:

- A increases up to the maximum value $A = 1$ (see (5)) and the value (64) of function f for $\varepsilon = 0$ tends to 0;
- at constant A (65) says that $f(\varepsilon, T, A)$ increases.

Fig. 2 shows the overall *movement* of function f when T is varying, still in the case of He-4.

When T decreases, the *space* between curves g and f decreases, hence the number of occupied quantum states $\omega(\varepsilon)$ decreases too; since the quantity of matter of the system (the total number of particles N) is constant, the ratio $\frac{n(\varepsilon)}{\omega(\varepsilon)}$ must increase for every occupied energy level ε.

The triplet (ε, T, A) which satisfies the conditions

$$g(\varepsilon) = f(\varepsilon, T, A), \tag{66a}$$

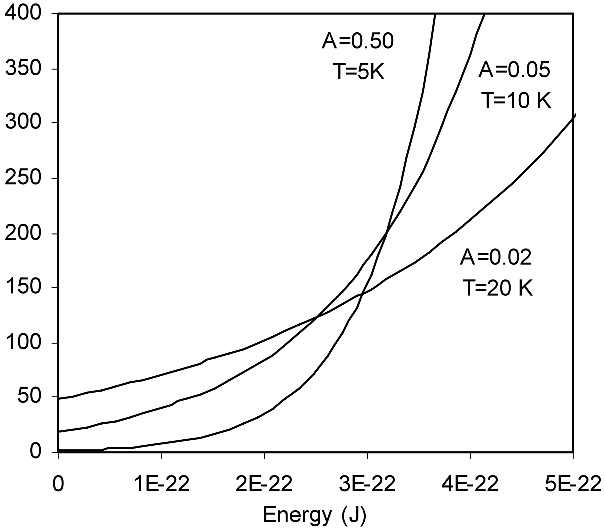
$$\frac{\partial g(\varepsilon)}{\partial \varepsilon} = \frac{\partial f(\varepsilon, T, A)}{\partial \varepsilon} \tag{66b}$$

corresponding with geometrical tangency of curves $g(\varepsilon)$ and $f(\varepsilon, T, A)$, defines a single state of quantum coherence, where all particles of the system *condense* into the same quantum state. The state of matter defined by (66a–66b) is known as Bose–Einstein Condensate or BEC.

The theory can be simply extended to fermions. Let us write FD statistics (57) as

$$n(\varepsilon) = \frac{\omega^2(\varepsilon) + (e^{\beta\varepsilon} + 1)}{e^{\beta\varepsilon} + 1} \tag{67}$$

Fig. 2 Function f for He-4 at low energy



with $\beta = \frac{1}{kT}$ as usual. Assuming the distributions FD and FDω (8) and (67) are equal, we get $\omega^2(\varepsilon)$ in the case of fermions

$$\omega^2(\varepsilon) = \frac{(e^{\beta\varepsilon}+1)}{e^{\beta\varepsilon}+A} A\left[g(\varepsilon) - \frac{(e^{\beta\varepsilon}+A)}{A}\right] \tag{68}$$

with $g(\varepsilon)$ still given by (62). The existence condition $\omega^2(\varepsilon) > 0$ is true if

$$g(\varepsilon) > \frac{e^{\beta\varepsilon}+A}{A}. \tag{69}$$

If we define the function

$$\varphi(\varepsilon, T, A) = \frac{e^{\beta\varepsilon}+A}{A} \tag{70}$$

we can draw the same conclusion as before by substituting the function $f(\varepsilon, T, A)$ with $\varphi(\varepsilon, T, A)$ and the value (64) of f at $\varepsilon = 0$ with

$$\varphi(0, T, A) = \frac{1+A}{A}. \tag{71}$$

Therefore the existence condition (69) still determines the range of admissible values for energy, $\varepsilon_m < \varepsilon < \varepsilon_M$, where $g(\varepsilon) > \varphi(\varepsilon, T, A)$; besides the way φ varies with T is the same we have seen before in the case of f since the derivatives are equal, $\frac{\partial\varphi}{\partial T} = \frac{\partial f}{\partial T}$ and $\frac{\partial\varphi}{\partial A} = \frac{\partial f}{\partial A}$.

As far as parameter A is concerned, it varies in the interval $(0, \infty)$ (see (19)) and its value is increasing while temperature T is decreasing. At the same time the value of φ at $\varepsilon = 0$, given by (71), tends to 1 for $A \to \infty$. Another important difference is due to Pauli's principle in the case of fermions. Until this principle remains valid, the ratio $\frac{n(\varepsilon)}{\omega(\varepsilon)}$ is constrained to be equal 1, therefore

$$\int_\varepsilon \omega(\varepsilon) d\varepsilon = N \tag{72}$$

or, in other words, the *space* between curves $g(\varepsilon)$ and $\varphi(\varepsilon, T, A)$ will contain at least as many occupied quantum states as particles.

When T decreases and $\varphi(0, T, A) = \frac{1+A}{A} \approx 1$, the space within curves g and φ decreases too until $\omega(\varepsilon) = g(\varepsilon)$[7] and the value of (72) is less than N. Once this condition is reached (or more exactly the condition (46) as we know from Sect. 3), a violation of Pauli's exclusion principle will occur in order that two or more particles may occupy the same quantum state and the process of creation of Cooper pairs starts. This simple mechanism is responsible for BEC phenomenon in the case of fermions.

We have already seen how the energy of particles can vary only in a finite interval $(\varepsilon_m, \varepsilon_M)$. It is simple to prove that bosons can assume minimum energy $\varepsilon_m = 0$, while fermions always have energy higher than zero $\varepsilon_m > 0$. Let us consider now systems of bosons or fermions in conditions of *degeneracy*. In the case of bosons we know this condition corresponds with the values $A = 1$ and $f(\varepsilon = 0, T, A = 1) = 0$ (see (64)). The function $g(\varepsilon)$ too is zero for $\varepsilon = 0$, therefore the minimum admissible energy is $\varepsilon_m = 0$.

On the contrary this minimum energy is not admissible in the case of fermions. In fact in this case *degeneracy* is given by $A = \infty$ and $\varphi(\varepsilon = 0, T, A = \infty) = 1$ (see (71)), therefore $\varepsilon_m > 0$. The value of ε_m can be calculated from the equation $\varphi = g$ assuming $\varphi \approx 1$, which gives $\varepsilon_m = \frac{1}{b^2}$ or, from (12)

$$\varepsilon_m = \frac{h^6}{32\pi^2 M^2 m^3}.$$

7 Physical Conditions for BEC in Bosons and Fermions

Let us apply the theory of quantum statistics BEω and FDω to the study of BEC transition in quantum systems. We shall consider first the case of bosons. The single states of quantum coherence are defined by (66a–66b) which become:

$$\frac{1}{A} e^{\beta\varepsilon} - 1 = b\sqrt{\varepsilon}, \tag{73a}$$

$$\frac{\beta}{A} e^{\beta\varepsilon} = \frac{1}{2} \frac{b}{\sqrt{\varepsilon}}. \tag{73b}$$

If we consider T (or β) as an independent variable, (73a–73b) define a pair of values (ε_0, A_0) as function of T, which correspond with singularity conditions. We easily get for ε_0 (only positive solutions)

$$\sqrt{\varepsilon_0} = \frac{1}{2b}(\sqrt{1 + 2kTb^2} - 1) \tag{74}$$

and from (73b)

$$A_0 = \frac{2\sqrt{\varepsilon_0}}{kTb} e^{\frac{\varepsilon_0}{kT}}. \tag{75}$$

As to the way ε_0 and A_0 vary with T we also get

$$\varepsilon_0(T = 0) = 0,$$

$$\lim_{T\to\infty} \varepsilon_0(T) = \infty.$$

---

[7] When $\omega(\varepsilon) = g(\varepsilon)$ we say the gas is a *Fermi sea* in which exactly one atom occupies each low-energy state.

By the identity, valid for $x \to 0$

$$\sqrt{1+x} = 1 + \frac{1}{2}x + o(x)$$

(74) for $T \to 0$ can be written as

$$\sqrt{\varepsilon_0} = \frac{1}{2b}(kTb^2 + o(T))$$

hence it follows $\varepsilon_0 = o(T)$ too. By substituting this in (75) we easily get

$$\lim_{T\to 0} A_0(T) = 1.$$

The following condition obviously holds

$$\lim_{T\to\infty} A_0(T) = 0.$$

Therefore in the case of bosons, singularities in the quantum state distribution are characterized by the triplet (T, ε_0, A_0) which varies continuously from

$$(T = 0, \varepsilon_0 = 0, A_0 = 1) \tag{76}$$

to

$$(T = \infty, \varepsilon_0 = \infty, A_0 = 0). \tag{77}$$

Therefore BEC may occur either when the system (gas) is in *degeneracy* conditions ($A_0 = 1$), or while it is dilute ($0 < A_0 < 1$). Let us now find general physical conditions for BEC transition into any single state (T, ε_0, A_0) within the bounds (76) and (77).

If $(\varepsilon_m, \varepsilon_M)$ is the range of possible energy values, as given by the existence condition (61), n_δ is the density of particles, we get from BE statistics

$$\int_{\varepsilon_m}^{\varepsilon_M} \frac{Ab\sqrt{\varepsilon}}{e^{\beta\varepsilon} - A} d\varepsilon = n_\delta$$

which by the change of variable $\beta\varepsilon = x$ can be written as

$$A\int_{\frac{\varepsilon_m}{kT}}^{\frac{\varepsilon_M}{kT}} \frac{\sqrt{x}}{e^x - A} dx = \frac{n_\delta}{b(kT)^{\frac{3}{2}}}. \tag{78}$$

Given two real numbers u and v, $0 \le u < v$, let us define the function of A, $0 < A \le 1$

$$B_{(u,v)}(A) = A\int_u^v \frac{\sqrt{x}}{e^x - A} dx. \tag{79}$$

We can write

$$B_{(0,\infty)}(A) = B_{(0,\frac{\varepsilon_m}{kT})}(A) + B_{(\frac{\varepsilon_m}{kT},\frac{\varepsilon_M}{kT})}(A) + B_{(\frac{\varepsilon_M}{kT},\infty)}(A)$$

from which by substituting $B_{(\frac{\varepsilon_m}{kT},\frac{\varepsilon_M}{kT})}(A)$ with the value (78) we get

$$B_{(0,\frac{\varepsilon_m}{kT})}(A) + B_{(\frac{\varepsilon_M}{kT},\infty)}(A) = B_{(0,\infty)}(A) - \frac{n_\delta}{b(kT)^{\frac{3}{2}}}.$$

Since the first member of the preceding equation is positive, the following condition obviously holds

$$\frac{n_\delta}{b(kT)^{\frac{3}{2}}} < B_{(0,\infty)}(A).$$

Until this condition is true, BE and BEω statistics are valid. Therefore as to the values of density and temperature, we get the space where single states of quantum coherence can exist (what we call BEC region too), simply by inverting the above formula, or

$$\frac{n_\delta}{b(kT)^{\frac{3}{2}}} \geq B_{(0,\infty)}(A) \tag{80}$$

where the equal sign defines the condition so that BEC transition occurs.

As for temperature T within BEC region we get from (80):

$$T \leq T_c = \frac{1}{k}\left(\frac{n_\delta}{bB_{(0,\infty)}(A)}\right)^{\frac{2}{3}} \tag{81}$$

where T_c is the critical temperature at the transition. By substituting b with the value (12) we get for the BEC region of the (n_δ, T) plane

$$\frac{n_\delta}{M(mT)^{\frac{3}{2}}} \geq \frac{4\sqrt{2}\pi}{h^3}k^{\frac{3}{2}}B_{(0,\infty)}(A). \tag{82}$$

The state of bosonic gases in *degeneracy* conditions is characterized by the value $A = 1$ and [14]

$$B_{(0,\infty)}(1) = \frac{\sqrt{\pi}}{2}\sum_{k=1}^{\infty}\frac{1}{k^{3/2}} \approx 2.314.$$

Assuming these values for superfluid He-4 and density $n_\delta = 1.877 \times 10^{28}$ atoms m^{-3}, mass $m = 6.644 \times 10^{-27}$ kg, $M = 1$, since $J = 0$ and $I = 0$ in the fundamental state (see (13)), we get from (81) the critical temperature[8] is $T_c = 2.8$ K. In this case the formula (81) and the T_c value obtained are the same as those given by classical BE theory, but the proceeding we have got as a consequence of BEω statistics is quite general and can be used for dilute gas too. BEC phenomena in dilute bosonic gases have been observed since 1995. A survey of experimental work and observations is given in [13] and in [8]. Table 1 contains a collection of data about observations of BEC in alkali-atom gases. Density and temperature are assumed equal to typical values observed in such experiments: $n_\delta = 10^{20}$–10^{21} atoms m^{-3}, $T = 0.5$–2 μK. The numeric value of parameter A is calculated through the formulas (15) and (16), *ratio* is the quantity defined in (80).

A graph of the values obtained for *ratio* is given in Fig. 3 together with the function $B_{(0,\infty)}(A)$: we see from this figure that BEC phenomena in dilute bosonic gases occur on the border of BEC region. As far as superfluid He-4 is concerned, we know that BEC is reached at density value of liquid helium and $T = 2.18$ K, which is less than the temperature T_c calculated before. The *ratio* (80) obtained for this value of T is reproduced in Table 1 and Fig. 3 too.

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[8] Calculations are performed using the International System of Units (SI), with $h = 6.626 \times 10^{-34}$ J s, $k = 1.381 \times 10^{-27}$ J K^{-1}.

Table 1 BEC data for bosonic alkali atoms and He-4

Atom	I	J	M	b	T (K)	n_δ (m^{-3})	A	$B(A)$	Ratio
Cs-133	7/2	1/2	8	5.062E+64	2.00E−06	1.00E+21	0.145	0.136	0.136
Rb-85	5/2	1/2	6	1.939E+64	5.00E−07	1.00E+20	0.286	0.284	0.284
Rb-87	3/2	1/2	4	1.361E+64	2.00E−06	1.00E+21	0.466	0.508	0.506
He-4	0	0	1	3.307E+61	2.18	1.88E+28	1.00	2.315	3.436

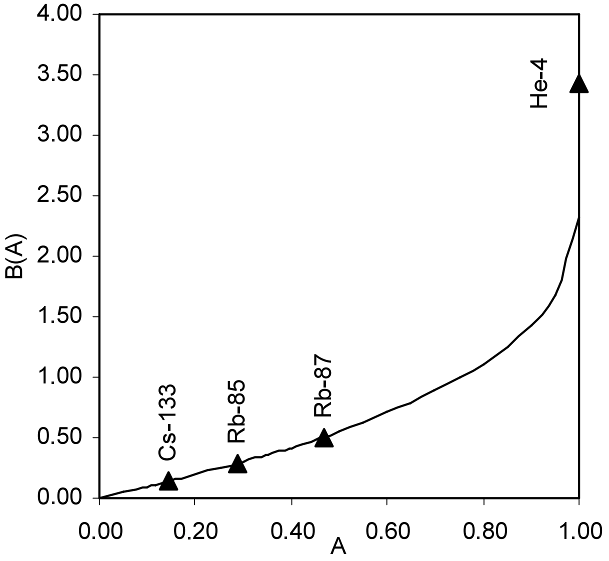

Fig. 3 BEC region for bosons

Equation (81) gives the upper limit of temperature in the BEC region for bosons. As for the lower limit, another equation can be simply obtained from the singularity conditions (66a–66b): assuming A is fixed, there will exist a minimum value of T, corresponding with tangency of curves $g(\varepsilon)$ and $f(\varepsilon, T, A)$, so that when T is less than this value no contact point can exist between g and f. Let us suppose $A \ll 1$o r $2kTb^2 \gg 1$, then we easily get from (73a–73b) the relation between energy and temperature which is valid when the system is in a single state of quantum coherence:

$$\varepsilon = \frac{1}{2}kT. \tag{83}$$

By substituting this in (73a) we get the minimum value of T as a function of A:

$$T_{\min} = \frac{2(\sqrt{e} - A)^2}{kA^2b^2}. \tag{84}$$

Therefore in order that BEC can occur for dilute bosonic gases, the temperature T must be within the range

$$\frac{2(\sqrt{e} - A)^2}{kA^2b^2} \le T \le \frac{1}{k}\left(\frac{n_\delta}{bB_{(0,\infty)}(A)}\right)^{\frac{2}{3}}. \tag{85}$$

The (85) expresses the complex relation between density and temperature, through parameter A, in BEC phenomena as far as bosonic matter is concerned.

The simple mathematical reasoning that leads to (80) in the case of bosons, can be extended to fermions.

We have seen in Sect. 5 that FDω statistic results in the existence condition (69) which is necessary in order that occupied quantum states may exist, hence in the finite range of energy values $(\varepsilon_m, \varepsilon_M)$. Therefore by integrating FD distribution over the interval of possible energy values, we get

$$\int_{\varepsilon_m}^{\varepsilon_M} \frac{Ab\sqrt{\varepsilon}}{e^{\beta\varepsilon} + A} d\varepsilon = n_\delta.$$

Given any two real numbers u and $v, 0 \leq u < v$, let us first define the function of $A, 0 \leq A < \infty$

$$F_{(u,v)}(A) = A \int_u^v \frac{\sqrt{x}}{e^x + A} dx \tag{86}$$

then by the same change of variable $\beta\varepsilon = x$ and following the same procedure as before, we arrive at the formula which represents the BEC region for fermions, as far as density and temperature are concerned:

$$\frac{n_\delta}{b(kT)^{\frac{3}{2}}} \geq F_{(0,\infty)}(A). \tag{87}$$

Obviously the formulas (81) and (82) holds in the case of fermions too, by substituting the function $B_{(0,\infty)}(A)$ with the function $F_{(0,\infty)}(A)$.

An investigation about temperatures of fermionic gases at BEC, can be done simply by using (87). Table 2 reports the results of this research together with the values of the ratio (87) in the case of K-40 and Li-6 atoms. We have assumed the values of density are in the range $n_\delta = 10^{18}$–10^{20} atoms m^{-3}, then we have obtained the corresponding values of T, assuming the equal sign in (87) and looking for the best numerical approximation. The numerical value of the parameter A is calculated through the formula (16) in the case $A < 1$, the formula (17) in the case $A > 1$.

It is to be noted also that the ratio between density and temperature in (87), means that if density increases (decreases) 10 ^{3} times, temperature must increase (decrease) 10^2 times, in order that the ratio doesn't vary. The same is true for (16) and (17). Therefore in the case of density $n_\delta = 10^{21}$ atoms m^{-3}, we get a temperature 100 times higher than in the case of density $n_\delta = 10^{18}$ atoms m^{-3} and the other quantities remain unchanged.

Table 2 BEC data for fermionic alkali atoms and He-3

Atom	I	J	M	b	T (K)	n_δ (m^{-3})	Log$_{10}(A)$	$F(A)$	Ratio
K-40(a)	4	1/2	9	9.399E+63	6.00E−08	1.00E+18	−0.798	0.134	0.141
K-40(b)	4	1/2	9	9.399E+63	2.00E−07	1.00E+19	−0.582	0.213	0.232
K-40(c)	4	1/2	9	9.399E+63	7.00E−07	1.00E+20	−0.398	0.313	0.354
Li-6(d)	1	1/2	3	1.828E+62	2.00E−07	1.00E+18	0.308	1.147	1.192
Li-6(e)	1	1/2	3	1.828E+62	9.00E−07	1.00E+19	0.317	1.165	1.249
Li-6(f)	1	1/2	3	1.828E+62	4.00E−06	1.00E+20	0.331	1.192	1.332
He-3	1/2	0	2	4.326E+61	0.0026	1.178E+28	320.162		40022

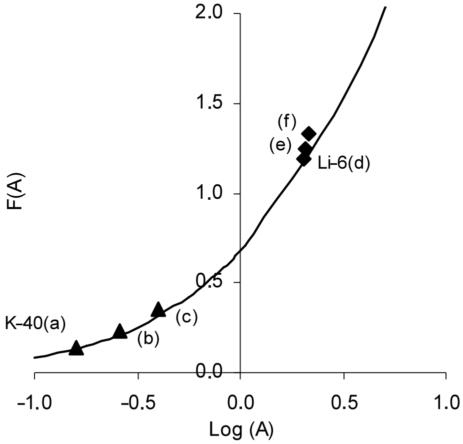

Fig. 4 BEC region for highly dilute fermionic gases. (See also Table 2 for the calculated values of K-40 and Li-6)

The same values together with the function $F_{(0,\infty)}(A)$ are reproduced in Fig. 4, which represents the BEC region for fermions, in the case of highly dilute gases.

Data concerning superfluid He-3 are also reported in Table 2, together with calculated value of *ratio* (87) in this case.

Obviously in the case of fermions too we can write the singularity conditions corresponding with geometrical tangency of curves $g(\varepsilon)$ and $\varphi(\varepsilon, T, A)$ (see (70)). In this case (73a–73b) become

$$\frac{1}{A}e^{\beta\varepsilon} + 1 = b\sqrt{\varepsilon}, \tag{88a}$$

$$\frac{\beta}{A}e^{\beta\varepsilon} = \frac{1}{2}\frac{b}{\sqrt{\varepsilon}} \tag{88b}$$

and assuming again $A \ll 1$ or $2kTb^2 \gg 1$, hence that (83) holds, we finally get the relations which are equivalent to (84), (85) in the case of fermions:

$$T_{\min} = \frac{2(\sqrt{e} + A)^2}{kA^2b^2}, \tag{89}$$

$$\frac{2(\sqrt{e} + A)^2}{kA^2b^2} \le T \le \frac{1}{k}\left(\frac{n_\delta}{bF_{(0,\infty)}(A)}\right)^{\frac{2}{3}}. \tag{90}$$

8 BEC Transition in Fermions

The formula (87) gives only an approximate description of BEC transition for fermions, since it does not take into account the exclusion principle which is deeply involved with the physical process fermions follow to condensate into one single quantum state. That is immediately evident in the case of degenerate fermionic quantum systems: as $A \to \infty$, function $F_{(0,\infty)}(A) \to \infty$ and from the analogous of (81) for fermions we get the condensate temperature is $T = T_c = 0$ K. On the contrary we know that the observed experimental value for temperature in the case of superfluid He-3 is $T = 2.6$ mK. In order that we can get the exact conditions of BEC transition in fermionic gases, we need to consider FDω statistics together with the violation of Pauli's principle as given by condition (46).

Let $n(\varepsilon)$ and $\omega(\varepsilon)$ be the number of particles and of occupied quantum states for unit volume at energy level ε. Because of Pauli's principle the equation $n(\varepsilon) = \omega(\varepsilon)$ holds for every energy, hence the following equation holds too:

$$\int_{\varepsilon} \omega(\varepsilon) d\varepsilon = n_\delta \tag{91}$$

where the integration takes place over the finite interval $(\varepsilon_m, \varepsilon_M)$ of possible energy values. Condition (46) can be written as

$$V \cdot n(\varepsilon_M) \cdot \Delta\varepsilon_M \geq \frac{N}{2} + 2 \tag{92}$$

where V is the gas volume, N the total number of particles and $\Delta\varepsilon_M$ is given by the uncertainty principle of Heisenberg as the energy interval around ε_M so that only those levels (with energy close to ε_M) differ physically for which the energy differ not less than $\Delta\varepsilon_M$. By assuming $\frac{N}{2} \gg 2$ relation (91) become

$$n(\varepsilon_M) \cdot \Delta\varepsilon_M \geq \frac{1}{2} n_\delta$$

or, since $n(\varepsilon) = \omega(\varepsilon)$

$$\omega(\varepsilon_M) \cdot \Delta\varepsilon_M \geq \frac{1}{2} n_\delta. \tag{93}$$

Relations (91) and (92) establish conditions for BEC transition in fermionic quantum systems. They can be rewritten in explicit form using (68):

$$\int_{\varepsilon_m}^{\varepsilon_M} \left[\frac{(e^{\beta\varepsilon} + 1)}{(e^{\beta\varepsilon} + A)} A \left(g(\varepsilon) - \frac{(e^{\beta\varepsilon} + A)}{A} \right) \right]^{\frac{1}{2}} d\varepsilon = n_\delta, \tag{94}$$

$$\frac{(e^{\beta\varepsilon_M} + 1)}{e^{\beta\varepsilon_M} + A} A \left[g(\varepsilon_M) - \frac{(e^{\beta\varepsilon_M} + A)}{A} \right] (\Delta\varepsilon_M)^2 \geq \frac{1}{4} n_\delta^2. \tag{95}$$

Let us now use the preceding equations to find the conditions for BEC transition in the case of degeneracy of the quantum system. If we define

$$\omega_D(\varepsilon) = \lim_{A\to\infty} \omega(\varepsilon)$$

it is easy to get

$$\omega_D(\varepsilon) = [(g(\varepsilon) - 1) \cdot (e^{\beta\varepsilon} + 1)]^{\frac{1}{2}}. \tag{96}$$

By replacing $\omega(\varepsilon)$ with $\omega_D(\varepsilon)$, and $g(\varepsilon)$ with $b\sqrt{\varepsilon}$, (94) and (95) become

$$\int_{\varepsilon_m}^{\varepsilon_M} [(b\sqrt{\varepsilon} - 1)(e^{\beta\varepsilon} + 1)]^{\frac{1}{2}} d\varepsilon = n_\delta, \tag{97}$$

$$(b\sqrt{\varepsilon_M} - 1)(e^{\beta\varepsilon_M} + 1)(\Delta\varepsilon_M)^2 \geq \frac{1}{4} n_\delta^2. \tag{98}$$

The existence condition for occupied quantum states, $\omega_D(\varepsilon) > 0$, is given simply by $g(\varepsilon) > 1$ which results in a minimum value of energy

$$\varepsilon_m = \frac{1}{b^2}. \tag{99}$$

From (98) we get that temperature T must be $T \leq T_c$ with T_c given by

$$T_c = \frac{\varepsilon_M}{k \cdot \log\left[\frac{n_\delta^2/4}{(b\sqrt{\varepsilon_M}-1)(\Delta\varepsilon_M)^2} - 1\right]}. \tag{100}$$

In order to calculate $\Delta\varepsilon_M$ we have to consider a generic particle with mass m and momentum $\underline{p}$. As to the uncertainties Δx of x coordinate and Δp_x of momentum projection on x direction, the Heisenberg's principle says that $\Delta p_x \Delta x = h$, and analogous equations can be written for the other components y, z. Therefore by multiplying all three equations and assuming that $\Delta p_x = \Delta p_y = \Delta p_z$ we get

$$(\Delta p_x)^3 \Delta V = h^3 \tag{101}$$

with $\Delta V = \Delta x \Delta y \Delta z$, is the uncertainty of the volume occupied by the particle. The total uncertainty of momentum is:

$$\Delta p = (\Delta p_x^2 + \Delta p_y^2 + \Delta p_z^2)^{\frac{1}{2}} = \sqrt{3}\Delta p_x$$

and by substituting Δp_x obtained above in (101) we get the equation

$$\frac{(\Delta p)^3}{3\sqrt{3}} \Delta V = h^3. \tag{102}$$

Since $\varepsilon = \frac{p^2}{2m}$ it can be easily proved that $\Delta p = (\frac{m}{2\varepsilon})^{\frac{1}{2}} \Delta\varepsilon$, and by substituting this in (102) we obtain the equation

$$\Delta\varepsilon = \left(\frac{6\varepsilon}{m}\right)^{\frac{1}{2}} \frac{h}{\sqrt[3]{\Delta V}}.$$

As far as the uncertainty ΔV is concerned, we can assume it is equal to the mean admissible volume for each particle

$$\Delta V = \frac{1}{n_\delta}.$$

Therefore as to the uncertainty of energy we finally get

$$\Delta\varepsilon = \left(\frac{6\varepsilon}{m}\right)^{\frac{1}{2}} \sqrt[3]{n_\delta} h. \tag{103}$$

We can now find a numerical solution of (97) which is compatible with condition (98) for $T < T_c$ and T_c given by (100), in the case of superfluid He-3. We assume density $n_\delta = 1.178 \times 10^{28}$ atoms m^{-3}, as that of liquid helium 3, and mass $m = 5.006 \times 10^{-27}$ kg. By the change of variable $\varepsilon = 10^{-23}x$ and after some simple numerical manipulations[9] (97) and (100) become

$$\int_0^{10^{23}\varepsilon_M} (e^{\frac{0.724\cdot x}{T}} - 1)x^{\frac{1}{4}}dx = 1.007 \times 10^{26},$$

$$T \le T_c = \frac{\varepsilon_M}{k(33.315 - \frac{3}{2}\log \varepsilon_M)}.$$

The search for a numerical solution (ε_M, T) of the preceding equations, leads to the values $\varepsilon_M = 0.467 \times 10^{-23}$ J, $T \le T_c = 0.00297$ K, and the best approximation of the integral is obtained for $T = 0.0026$ K.

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[9] As to the lower limit of the integral we make the approximation $10^{23}\varepsilon_m \approx 0.534 \times 10^{-100} \approx 0$.