Origin and foundations of Bose-Einstein statistical mechanics

Author: Paula Mallol Travesset
Facultat de Física, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain.

Advisor: Luis Navarro Veguillas

Abstract: The objectives of this study are to analyze the origins of the statistical mechanics of Bose-Einstein (1924), which are based on a quantum treatment of indistinguishable particles, and to understand how its formulation was possible prior to the birth of the wave mechanics proposed by Schrödinger (1926).

I. INTRODUCTION

The aim of this study is to analyze the foundations of Bose-Einstein statistics. In other words, to discover the origins of this new quantum statistics that was proposed by the physicist Satyendra Nath Bose in 1924. Later, Albert Einstein used it to introduce important advances in this field of physics.

One of the main reasons of this study is the surprising fact that this statistics was formulated previously to the appearance of Schrödinger's wave mechanics, which did not emerge until the beginning of 1926. In addition, we will try to show how the thought of Bose, Einstein and other contemporary theoretical physicists, such as De Broglie, influenced on Schrödinger and on the first idea of the possible existence of a wave field associated with each molecule, that is, the birth of the new concept of particle-wave duality.

To properly substantiate these essay, the articles corresponding to the two authors of the new statistics, together with other documents of historical nature related to the central theme of our study, are analyzed to clarify the controversy mentioned initially. For a better understanding, the key ideas that lead to the new statistics are explained and the most important expressions, which are used in the development of the original articles, are rewritten using updated notation.

In order to perform a more detailed study, this paper is divided into four parts. The first part corresponds to Bose's original article (Section II), where a new treatment of particles and a new deduction of Planck's law are introduced. The second part presents Einstein's original articles (Section III), where the quantum theory for ideal gas molecules and the most relevant results of the introduction of this new treatment are explained. Finally, the implications and the first highlights of these new advances are described (Section IV).

II. PHOTON GAS (1924)

II.A Satyendra Nath Bose (S. N. Bose)

S. N. Bose was a theoretical physicist born in 1894 in Calcutta (India), where he studied. In 1924, he was professor at the University of Dhaka (Bangladesh) and he focused his research on statistical mechanics. The same year, he wrote the article ≪Planck's law and the light quantum hypothesis≫ [2], which is considered a fundamental contribution to the birth of quantum statistics. The main reason that motivated Bose to perform this study was his disagreement with the deductions of Planck's law that were described so far and, as it is shown later, to present a new way to obtain this law by using the radiation quantum hypothesis and disregarding Maxwell's electromagnetism.

Bose tried to publish his paper, but it was not accepted. Therefore, he asked Einstein if he considered it interesting and, if so, to publish it translated into German. Einstein considered the article as a great breakthrough, and he decided to recommend its publication in one of the most important scientific journals of that time: *Zeitschrift für Physik*. As mentioned later, Einstein applied the same treatment to formulate the quantum theory of the ideal monatomic gas one week later.

II.B ≪Planck's law and the light quantum hypothesis≫

In his article, Bose began by arguing that the deductions of the formula, which related the spectral density of energy of the radiation and the average energy $\bar{E}$ of an aggregate of monochromatic harmonic oscillators, were not coherent since the bases of the quantum theory were not consistent with the laws of classical electrodynamics:

$$\rho d\nu = (\frac{8\pi\nu^2 d\nu}{c^3})\bar{E} \qquad (1)$$

First of all, the factor in parentheses, which corresponds to the undulatory part, is related with the electromagnetism of Maxwell and involves a continuous spectrum of both frequencies and energies. On the other hand, the concept of discrete energy packages, which corresponds to a quantum picture, came into play for the calculation of the average energy. These facts led him to look for a new deduction of Planck's law in a totally quantum way, that is, incorporating the idea of the light quantum (later called photons), and, as before mentioned, disregarding Maxwell's electromagnetism.

Bose operated in the phase space of a photon, where each state is included in a cell of volume h^3 and characterizes each quantum with an energy $h\nu$ and a moment of magnitude $\frac{h\nu}{c}$, both corresponding to a zero mass particle. Once the three position coordinates, which correspond to volume V, and the three moment coordinates, which translated to spherical coordinates its differential corresponds to $d^3p = 4\pi p^2 dp$, are integrated for the volume of the phase space mentioned that corresponds to the frequency range (ν, ν+dν), the following expression is obtained:

$$\int ... \int dxdydzdp_x dp_y dp_z = (\frac{4\pi h^3 \nu^2}{c^3})V d\nu \tag{2}$$

Once the result is obtained, it is divided by the volume previously mentioned h^3, which is the volume assigned to each cell, and then the total number of cells can be determined. Bose indicated, without any additional explanation, that a factor 2 corresponding to the number of possible polarizations of each quantum has to be taken into account. In this way, the total number of cells for the mentioned frequency range is expressed as:

$$A(\nu) = (\frac{8\pi V \nu^2}{c^3})d\nu \tag{3}$$

Next, Bose calculated how many ways N quanta could be distributed in the different cells corresponding to the frequency ν following the ≪combinatorial method≫ of his admired Boltzmann. In other words, he tried to find the compatible distributions with the macroscopic state of the system, which is defined by the occupation numbers $p_0(\nu)$, $p_1(\nu)$, $p_2(\nu)$,... where $p_n(\nu)$ indicates the number of cells that contains n photons, obtaining:

$$\Omega(\nu) = \frac{A(\nu)!}{p_0(\nu)!p_1(\nu)!p_2(\nu)!...} \tag{4}$$

The total number of states, that is, the total number of possible distributions, is given by the expression below:

$$\Omega = \prod_{\nu} \Omega(\nu) \tag{5}$$

Therefore, following Stirling's approximation, the entropy is proportional to:

$$ln(\Omega) = \sum_{\nu} [A(\nu) ln A(\nu) - \sum_{n} p_n(\nu) ln p_n(\nu)] \tag{6}$$

In order to obtain the equilibrium state, Bose maximized expression (6) taking into account the constraints to keep constant both the energy and the number of photons. So, using the method of Lagrange multipliers, $p_n(\nu)$ are obtained. Then, an expression of the total energy of radiation is determined by replacing them in (7):

$$E = \sum_{\nu} N(\nu) h\nu = \sum_{\nu,n} n p_n(\nu) h\nu \tag{7}$$

Finally, passing to the frequency continuum, Bose obtained the following expression:

$$E = \int \frac{8\pi h \nu^3}{c^3} V \frac{1}{\exp \frac{h\nu}{\kappa T} - 1} d\nu \tag{8}$$

Once the density of spectral energy $\rho(\nu)$ per volume unit is defined as the ratio between the energy of the interval (ν, ν+dν) and the total volume, equation (8) is equivalent to the well-known Planck's formula:

$$\rho(\nu) d\nu = \frac{8\pi h \nu^3}{c^3} \frac{1}{\exp \frac{h\nu}{\kappa T} - 1} d\nu, \tag{9}$$

where $\frac{1}{\kappa T}$ represents Lagrange's multiplier for energy, and κ is Boltzmann constant.

II.C Indistinguishability and non-conservation of the number of quanta

It is important to highlight two points of Bose's treatment that deserve a special attention. It was not because he assigned them, but because it is deduced from the employed method. From the beginning, Bose defined two constraints: one corresponding to the conservation of total energy and the other one to the conservation of the number of quanta. However, looking at his resolution method, it can be observed that only the first one is employed. This is due to the fact that the number of quanta is not conserved because of the emission processes and the absorption of photons.

The authentically innovative point of the new deduction of the Planck's is the treatment of photons as if they were indistinguishable particles. Bose introduced a new idea through equation (4) without emphasizing it. The fact of distributing the quanta in the different cells without specifying which quantum goes to each cell and only focusing on how many quanta go to each cell makes possible to deduce the assigned indistinguishability.

Surprisingly, Bose did not realize what he was doing, as he recognized later, since he thought he was repeating the same that Boltzmann had done until that moment. Nevertheless, the difference between them is that what Boltzmann considered to be energy packages (indistinguishable) that were distributed in molecules (distinguishable), Bose considered to be indistinguishable photons distributed in distinguishable cells.

III. MOLECULES GAS (1924-1925)

III.A Albert Einstein

Albert Einstein was a German theoretical physicist who was born in 1879 in Ulm (Germany). In 1905, he published the Theory of Special Relativity, together with other works that were crucial for the development of statistical physics and quantum physics. Lately, he published the Theory of General Relativity in 1915, and he was awarded with the Nobel Prize in Physics in 1921 for his discovery of the equation of the photoelectric effect.

As mentioned in the previous section about Bose, Einstein received his article about photons gas in 1924, with the corresponding innovations he pretended to introduce. Einstein realized that the same type of new statistics could be applied to an ideal monatomic gas, given the existing analogy between the molecules gas and the quanta gas, which he had exploited in several occasions before. One week later, Einstein presented the new method proposed by Bose to the Prussian Academy of Science in order to establish a quantum theory for ideal gas that did not exist until then [3].

III.B ≪Quantum theory of the monatomic ideal gas≫

Einstein operated in the phase space of a monatomic molecule, that is, particles with mass m; unlike Bose, who dealed with photons, which have zero mass. In the same way, the volume of the phase space region of a molecule with energy within the interval (ε, ε+dε) can be determined. To calculate it, the position coordinates corresponding to the total volume V are integrated, together with the contribution of the momenta differential in spherical coordinates $d^3p = 4\pi p^2 dp$. Considering that $p{=}\sqrt{2m\varepsilon}$, the analogous expression to (2) is the following one:

$$\int ... \int dxdydzdp_xdp_ydp_z = 8\pi V(\frac{m^3\varepsilon}{2})^{\frac{1}{2}}d\varepsilon \tag{10}$$

If the phase space of the molecule is divided into cells of extension h^3 in the same way as in Bose's method, and, then, the result is divided by the volume of each cell, the total number of cells associated with the energy range (ε, ε+dε) is:

$$A(\varepsilon) = 8\pi\frac{V}{h^3}(\frac{m^3\varepsilon}{2})^{\frac{1}{2}}d\varepsilon \tag{11}$$

Considering N as the total number of molecules, the number of possible distributions of N molecules in the mentioned energy range is determined by calculating the product for all energies. Consequently, the total number of distributions that are compatible with the macroscopic state are also obtained (12).

$$\Omega = \prod_{\varepsilon}\frac{A(\varepsilon)!}{p_0(\varepsilon)!p_1(\varepsilon)!p_2(\varepsilon)!...}, \tag{12}$$

where $p_n(\varepsilon)$ represents the number of cells in the interval (ε, ε+dε) that are occupied by n molecules. This expression is comparable to (5), for the photon gas. Taking into account the constraints of the total energy and the number of molecules, Einstein maximized ln(Ω) using Stirling's approximation and the method of Lagrange multipliers.

The fact of not looking exclusively for a deduction of Planck's law as in the case of Bose, made it possible that Einstein obtained unpredictable results when he formulated the quantum theory for ideal gases.

III.C Some remarkable results

Classical statistics as limit of the new statistics

Einstein introduced the "degeneration parameter", which allows rewriting the results obtained as developments in series of powers of this parameter. If only the first term of each series is considered, it can be verified that the results obtained correspond to the classical theory. Thus, the successive powers of λ provide additional corrections to the classic results. The mentioned parameter is expressed as follows:

$$\lambda = h^3\frac{N}{V}(2\pi m\kappa T)^{\frac{-3}{2}} \tag{13}$$

As more valid is the condition $\lambda{\ll}1$, which means "low" densities of particles and a "high" absolute temperature, the results obtained are closer to the classics ones. This fact allowed Einstein to conceive the classic theory of ideal gases as a limit case of the new quantum theory.

Performing the development that corresponds to the average energy $\bar{E}$ per particle, Einstein obtained the following equation:

$$\frac{\bar{E}}{N} = \frac{3}{2}\kappa T(\frac{\sum_{\tau=1}^{\infty}\tau^{\frac{-5}{2}}\lambda^{\tau}}{\sum_{\tau=1}^{\infty}\tau^{\frac{-3}{2}}\lambda^{\tau}}) \tag{14}$$

For the case $\lambda^2{\ll}\lambda$, it can be approximated to:

$$\frac{\bar{E}}{N} = \frac{3}{2}\kappa T[1 - 0,1768h^3\frac{N}{V}(2\pi m\kappa T)^{\frac{-3}{2}}], \tag{15}$$

where it can be observed that the classical result for the mean energy per particle is always higher than the one obtained by the previous expression.

Energy distribution

On the other hand, the following expression is obtained for the energy distribution:

$$n(\varepsilon) = cte.exp^{\frac{-\varepsilon}{\kappa T}}(1 + \lambda exp^{\frac{-\varepsilon}{\kappa T}} + ...) \tag{16}$$

where $n(\varepsilon)$ represents the average number of molecules with energy within the interval (ε, ε+dε). The term in parentheses is related to the quantum correction, which can cause that the new result differs from the classical one. It can be noticed that the lower the energy ε, the greater the quantum correction is.

Equipartition theorem

In the thermal equilibrium, the classical equipartition theorem states that the mean energy of a system is equally divided between the different degrees of freedom. However, the theorem is not valid when quantum effects become important, as it can be tested with the aid of (14). To obtain precise results from the classical theorem, it is necessary that the thermal energy κT be much larger than the spacing between the quantum energy levels of the system. Otherwise, certain degrees of movement might be "frozen", and then the energy is not distributed in an equitable way.

Entropy

Einstein obtained a formula for the entropy that, firstly, it turned out to be extensive, that is, there is no need to introduce a factor $\frac{1}{N!}$, known as Gibbs's factor. Previously, this factor was needed to avoid a non-extensive expression of the entropy.

Secondly, Einstein affirmed that, at zero absolute temperature, all molecules are in a single cell, that is, in the cell with the lowest possible energy. This fact implies that only a possible distribution exists. Therefore, when the logarithm of the number of microstates that are compatible with the macroscopic state of the system is equal to 1, a null value for the entropy is obtained according to the third law of thermodynamics (Nernst principle).

Bose-Einstein condensation

In a later article [4], Einstein detected the existence of the phenomenon of ≪condensation≫, which takes place below a certain temperature for a given N and V. It consists in the accumulation of particles in the same cell, that is, in the cell of lower energy (the fundamental state, with current terminology). Nowadays, it can be understood as a great reduction in the velocity of the gas molecules, fact that makes not possible to determine their location due to the uncertainty principle. Therefore, there is a loss of the individuality of molecules that are treated as a unique condensate identity. The condensed phase, the only one existing at zero absolute temperature, implies an annulment of entropy.

Einstein suggested the helium and the electron gas as possible candidates for the detection of this phenomenon, but everything remained as a simple academic topic until 1938. This year, F. London used this idea as a possible explanation for the transition phase of He I to He II. Finally, in 1995, Scientists from JILA (Joint Institute for Laboratory Astrophysics, University of Colorado) observed for the first time, a condensate of atoms of Rubidium 87 thanks to the laser cooling of atoms.

IV. FIRST IMPACT OF BOSE-EINSTEIN STATISTICS

IV.A Loss of statistical independence

Einstein found the opposition of Ehrenfest, who did not conceive the idea of using a non-independent statistical treatment for particles that, in fact, had been employed in the new method without being indicated in either of the two published articles of 1924. Einstein justified it by arguing that using a treatment in which particles were considered as statistically independent identities, different results would be obtained: on the one hand, Wien's law for radiation, and, on the other hand, the classical equation of state for the monatomic ideal gas.

In order to differentiate both treatments (non-statistical independence versus statistical independence), Einstein began by distributing for both cases n particles in the energy range (ε, ε+dε) of a total of N particles in k cells. In this way, considering the number of microstates that are compatible with the constraints of the system, the entropy and the occupation numbers of the system can be obtained by using the usual process.

Firstly, taking into account that there is no statistical independence, the identical particles N are distributed in k cells. Einstein attributed this form of evaluation to Bose and obtained expressions that did not appear in the mentioned article, but that could be found in a later paper. The starting expression is:

$$\Omega = \prod_{\varepsilon} \frac{(k(\varepsilon) + n(\varepsilon) - 1)!}{(k(\varepsilon) - 1)!n(\varepsilon)!} \tag{17}$$

Secondly, if there were statistical independence, it is necessary to assign a cell to each molecule and, then, multiply it by the factor in parenthesis below, which represents all the possible ways to distribute the N molecules, in order to obtain exactly n molecules in each energy interval (ε, ε+dε). The number of microstates is then:

$$\Omega = \prod_{\varepsilon} k(\varepsilon)^{n(\varepsilon)} (\frac{N!}{\sum_{\varepsilon} n(\varepsilon)!}) \tag{18}$$

Einstein verified the validity of its treatment based on equation (17) by obtaining an extensive entropy and a null value for entropy at the zero absolute temperature, according to Nernst principle. Otherwise, performing the independent statistical treatment based on equation (18), both requirements are not satisfied at the same time. In this way, Einstein considered to have demonstrated the need for the new treatment and the approximation character of the classic treatment.

IV.B Influence on Schrödinger

In the article published by Einstein in 1925, he considered an ideal experiment in which a gas of volume V is communicated with another one of infinite volume through a wall that allows going through only molecules with energy corresponding to the interval (ε, ε+dε). Einstein computed the main relative quadratic fluctuation of the main number of molecules with the considered energy:

$$\overline{(\frac{\Delta(\varepsilon)}{n(\varepsilon)})^2} = \frac{1}{n(\varepsilon)} + \frac{1}{k(\varepsilon)}, \tag{19}$$

where $\overline{n(\varepsilon)}$ is the mean value of the number of particles and k(ε) is the number of cells that have the mentioned energy range.

Thanks to previous ideas of De Broglie based on the association of a scalar wave field to each material particle, Einstein affirmed the association of the second term $\frac{1}{k(\varepsilon)}$, which only depends on the energy range considered and on the volume of the gas, with the value of the mean quadratic fluctuation of this field. However, he did not demonstrate it.

Finally, it should be noted that these ideas of De Broglie and Einstein served as a basis for the formulation of wave mechanics by Schrödinger at the beginning of 1926.

V. CONCLUSIONS

Thanks to Bose's disagreement with the existing deductions of Planck's law that combined the laws of classical electrodynamics and quantum concepts such as quanta, he managed to deduce the new indistinguishable treatment of photons. He achieved it by distributing the photons in the different cells and considering how many there were in each cell, without specifying which of them were in each particular cell.

This new quantum treatment prompted Einstein to formulate a quantum theory for the ideal monatomic gas. This theory allowed obtaining remarkable results such as the possibility of conceiving classical statistics as a limit case of the new statistics through the introduction of the degeneration parameter, the loss of general validity of equipartition theorem when quantum effects become relevant, a new law for the energy distribution of the molecules of an ideal gas in thermal equilibrium, and the annulment of entropy at zero absolute temperature.

The previous results were obtained regardless of the usual statistical independence of the molecules of an ideal gas, as criticized by Ehrenfest. The study of certain statistical fluctuations in Einstein's ideal experiment led him to intuit the existence of a scalar wave field associated to each material molecule under the new quantum treatment.

After this brief study based on what could be considered to be the birth of quantum statistics, it is noted that one of the most relevant aspects is the fact that all these contributions are prior to quantum mechanics since it is not until the beginning of 1926 when Schrödinger formulated wave mechanics. As seen so far, this fact could be surprising and perhaps contradictory. However, to establish the basis of quantum statistics, only the introduction of an indistinguishable treatment of particles and the constant h are required.

Not only occurs this chronological distortion contrary to what a priori one might think, but also it goes beyond that. In other words, the fact is that the birth of quantum mechanics did not influence the formulation of the new quantum statistic, but it was just the opposite. This fact is confirmed when Schrödinger himself admitted the influence that the ideas of De Broglie and of Einstein had on the evolution of his own thoughts towards the formulation of wave mechanics in 1926. [5]

Acknowledgments

I would like to express a special gratitude to my supervisor, Luis Navarro Veguillas, whose contribution in stimulating suggestions and encouragement helped me to coordinate the work. I also extend sincere thanks to my family and friends for their unconditional support, specially to my cousin Elisenda.

[1] CPAE, The collected papers of Albert Einstein, Princeton: Princeton University Press, 1987-2018. Free access to the originals and to their English translation in http://einsteinpapers.press.princeton.edu.

[2] S. N. Bose, ≪Wärmegleichgewicht im Strahlungsfeld bei Anwesenheit von Materie≫, *Zeitschrift für Physik*, vol. 27, pp. 384-393, 1924. English translation in O. Theimer and B. Ram, ≪The beginning of quantum statistics≫, *American Journal of Physics*, vol. 44, pp. 1056-1057, 1976.

[3] A. Einstein, ≪Quantentheorie des einatomigen idealen Gases≫. *Sitzungsberichte der Preussischen Akademie der Wissenschaften* (Berlin), *Physikalisch-mathematische Klasse*, vol. 22, pp. 261-267, 1924. Original and English translation in [CPAE], vol. 14, document 283, 2015.

[4] A. Einstein, ≪Quantentheorie des einatomigen idealen Gases. Zweite Abhandlung≫. *Sitzungsberichte der Preussischen Akademie der Wissenschaften* (Berlin), *Physikalisch-mathematische Klasse*, vol. 23, pp. 3-14, 1925. Original and English translation in [CPAE], vol. 14, document 385, 2015.

[5] E. Schrödinger, ≪Quantisierung als Eigenwertproblem. Erste Mitteilung≫. *Annalen der Physik*, vol. 79, pp. 361-376. English translation in E. Schrödinger, Collected papers on wave mechanics, New York: Chelsea, 1982. Schrödinger's recognition is on p. 9 of the translation.