Exact solution of particle's occupation number in the Lambert Boltzmann Distribution using Lambert W function

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Abstract

By applying the exact Stirling formula and the exact function $\ln(n!)$, the occupation number of particles was calculated based on the statistics of Boltzmann distribution for a finite number of particles n. The exact analytical expression of occupation number of particles (n_i) is found in terms of the Lambert W function and is more general than that usually calculated by the standard Boltzmann distribution based on the Stirling approximation $\ln(n!) = n\ln(n) - n$. The new expression in the exact and algebraic closed form eliminates the need for the complex iterative computation. Its high accuracy is proved by a comparison of calculating occupation number of particles (n_i) with respective numerical solution.

Keyword: Occupation number of particles ,Lambert Boltzmann distribution, Finite number of particles, Lambert W function.

1. Introduction

The Stirling approximation to $\ln(n!)$ is typically introduced to physical chemistry students as a step in the derivation of the exponential Boltzmann distribution. However, naïve application of this approximation leads to incorrect conclusions. For example student of physical chemistry are often introduced to the statistical treatment of the occupation number n_i as given by Boltzmann's distribution equation:

$$n_i = \exp[-\alpha - \beta \varepsilon_i] \tag{1}$$

Using Stirling's approximation [1, 2]

$$\ln(n!) = n\ln(n) - n \tag{2}$$

The applicability range of Eq. (2) is limited to very large values of *n*, the exponential Boltzmann distribution is limited strictly to $n \succ\succ\succ 1$ and applies only for ε not too large. However, the distribution is used in the literature even for $\varepsilon \to \infty$ and $n \to 0$, where Eq. (1) does not be appropriate. It is interesting that Stirling’s approximation, Eq.(1), fails and the more precise Stirling formula, Eq.(3) [2] is required to determine the occupation number n_i.

$$\ln(n!) = \left(n + \frac{1}{2}\right)\ln(n) - n + \frac{1}{2}\ln(2\pi) \tag{3}$$

For a finite number of particles, the occupation number of particle has been determined by Kakorin [3], but no details, analysis or more explanation and discussion were made for how determining it.

In this paper, basing on the work of Kakorin [3], we present more details, analysis and discussion to calculated the expression of the occupation number n_i of particles based on Boltzmann statistics for a finite number of particles. We compare the obtained result with this obtained by usual exponential Boltzamnn statistics using the stirling approximation $\ln(n!) = n\ln(n) - n$.

2. Methodology

By applying the exact Stirling formula and the exact function $\ln(n!)$ based on the statistics of Boltzmann distribution for a finite number of particles n, we calculate the occupation number of particles. Analytical expression of n_i was expressed in terms of the primary branch of the Lambert function W_0.

Using numerical method as Newton–Raphson's method, the occupation number of particles was also calculated and compared with this obtained by applying exact Striling formula.

3. Results and discussion

Based on the Boltzmann statistics with a finite number of particles n, the expression of occupation number n_i is [3]

$$\frac{1}{2n_i^*} = -\ln(n_i^*) - A \quad (4)$$

where A, represent some constant in the Boltzmann statistics.

Eq. (4) can be solved numerically by an iterative method. This is not necessary; the exact solution of this equation is given by the so-called Lambert W-function [4]. This function was postulated to solve the equation:

$$W(z)\exp W(z) = z \quad (5)$$

The Lambert W-function allows the explicit solution of entire classes of differential equations, which actually only could be solved numerically and is experiencing today a renaissance in various fields of sciences and engineering [5-12].

The expression of the occupation number of particles is given by:

$$\frac{1}{2\,n_i} = -\ln(n_i) - \alpha - \beta\,\varepsilon_i \tag{6}$$

Where ε_i is the energy of state (i), $\beta = 1/kT$ (k is the Boltzmann constant and T is the temperature and α is the Lagrange multiplier.

Eq. (6) is a transcendental equation that can be solved exactly with the results written in closed form in terms of the Lambert W function using the approach proposed by Hadj Belgacem [13-17].

For further calculation, we introduce the abbreviations:

$$A = \alpha + \beta\,\varepsilon_i \tag{7}$$

and $z = -\frac{Exp(A)}{2}$ (8)

We obtain the implicit equation

$$\frac{1}{2\,n_i} = -\ln(n_i) - A \tag{9}$$

For solving Eq. (9) we suppose that

$$n_i = Exp(-A)\frac{z}{W(z)} \tag{10}$$

Inserting Eq. (10) into Eq. (9) yields

$$\frac{1}{2\,Exp(-A)\frac{z}{W(z)}} = -\ln\left(Exp(-A)(\frac{z}{W(z)})\right) - A$$

$$\frac{W(z)}{2\;Exp(-A)(-\frac{Exp(A)}{2})} = -\ln\big(Exp(-A)\big) - \ln\left(\frac{z}{W(z)}\right) - A$$

$$W(z) + \ln\left(\frac{W(z)}{z}\right) = 0 \tag{11}$$

Rearranging Eq. (11) and employing an exponential in Eq. (13)

$$W(z)+\ln(W(z))-\ln(z)=0 \quad (12)$$

$$Exp(W(z)+\ln(W(z))-\ln(z))=1 \quad (13)$$

$$W(z)\,Exp W(z)=z \quad (14)$$

We find that Eq. (14) represents the definition of the Lambert W-function, as already established in Eq. (5).

Consequently, our supposition in Eq. (10) is justified.

The exact solution for the occupation number n_i is after resubstitution for z and replacing A is

$$n_i=-\frac{1}{2W\left(-\frac{1}{2}Exp(\alpha+\beta\,\varepsilon_i)\right)} \quad (15)$$

The Lambert W-function is a complex and multi-valued function with an infinite number of branches, only two of them having real values. If x is real, then for $-\frac{1}{e}\le x\le 0$, there are two possible real values of $\mathrm{W}(\mathrm{x})$, as displayed in reference [4]. The branch satisfying $-1\le W(x)$ is denoted $\mathrm{W}_0(\mathrm{x})$; the branch satisfying $\mathrm{W}(\mathrm{x})\le -1$ is denoted $\mathrm{W}_{-1}(\mathrm{x})$. Where are $\mathrm{W}(-\frac{1}{\mathrm{e}})=-1$ and $W(0)=0$. Both real branches $W_0(x)$ and $W_{-1}(x)$, for x real are presented in figure1.

For practical application, to find the branch of $W(x)$ that correctly describes the evolution of the occupation number $\mathrm{n_i}$ additional reasonable considerations are required. At the limit when the occupation number n_i tend to infinity ($\mathrm{n_i}\to\infty$), the expression of the general occupation number calculated in this work using the exact striling formula must be equal to the usual one calculating by using the striling approximation.

Inserting appropriate parameters $n_0 = 1000$, $\alpha = -\ln(n_0) - \frac{1}{2n_0}$ in Eq.(14); $n_0 = 1000$, $\alpha = -\ln(n_0)$ in Eq.(1). The occupation number can be represented in figure 2 as a function of $\beta \varepsilon_i$, where ε_i is the energy of the state and $\beta = \frac{1}{kT}$.

To illustrate what kinds of the Lambert W function branch's that computes the real value of n_i. We compare in the figure 2 the evolution of the general occupation number n_i calculate with the primary branch W_0 (figure 2.a) and with the second branch W_{-1} (figure 2.b) using Eq.14 with usual one calculating by using the striling approximation using Eq.(1) (figure 2.c…)

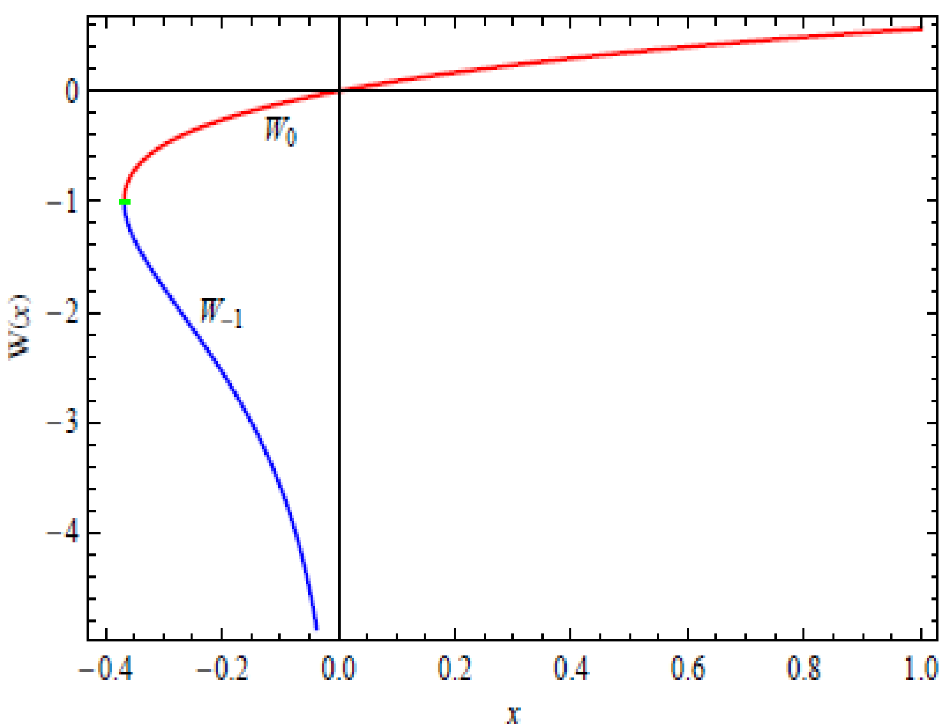

Figure 1: The two branches of the Lambert W function $W_{-1}(x)$ in blue color and $W_0(x)$ in red.

The comparison of the general occupation number evolution showed in the figures (2.a) and (2.b) with the usual occupation number figure (2.c) demonstrate that W_0 (x) is the branch that appropriately describes the evolution of the general occupation number as a function of $\beta \varepsilon_i$.

To validate the obtained general analytical solution of the occupation number, we compare it in figure 3 with the numerical solution of Eq. (3) obtained using the Newton–Raphson's method. It is easily seen that an excellent agreement is achieved for all values of the $\beta \varepsilon_i$.

4. Conclusion

In summary, the Lambert W-function was successfully used to determine an exact analytical solution for calculating the occupation number n_i of particles in the case of Boltzmann statistics for a finite number of particles. The exact solution for the occupation number n_i was expressed in terms of the primary branch of the Lambert function W_0. Comparing with numerical result shows that the proposed solution is in a good agreement.

Practically, this occupation number n_i is simple to compute since the Lambert W-function is readily available in standard computational packages and can be easily implemented in other mathematical formulas, for example to calculate the partition function Z and the constant volume heat capacity C_v in Boltzmann statistics.

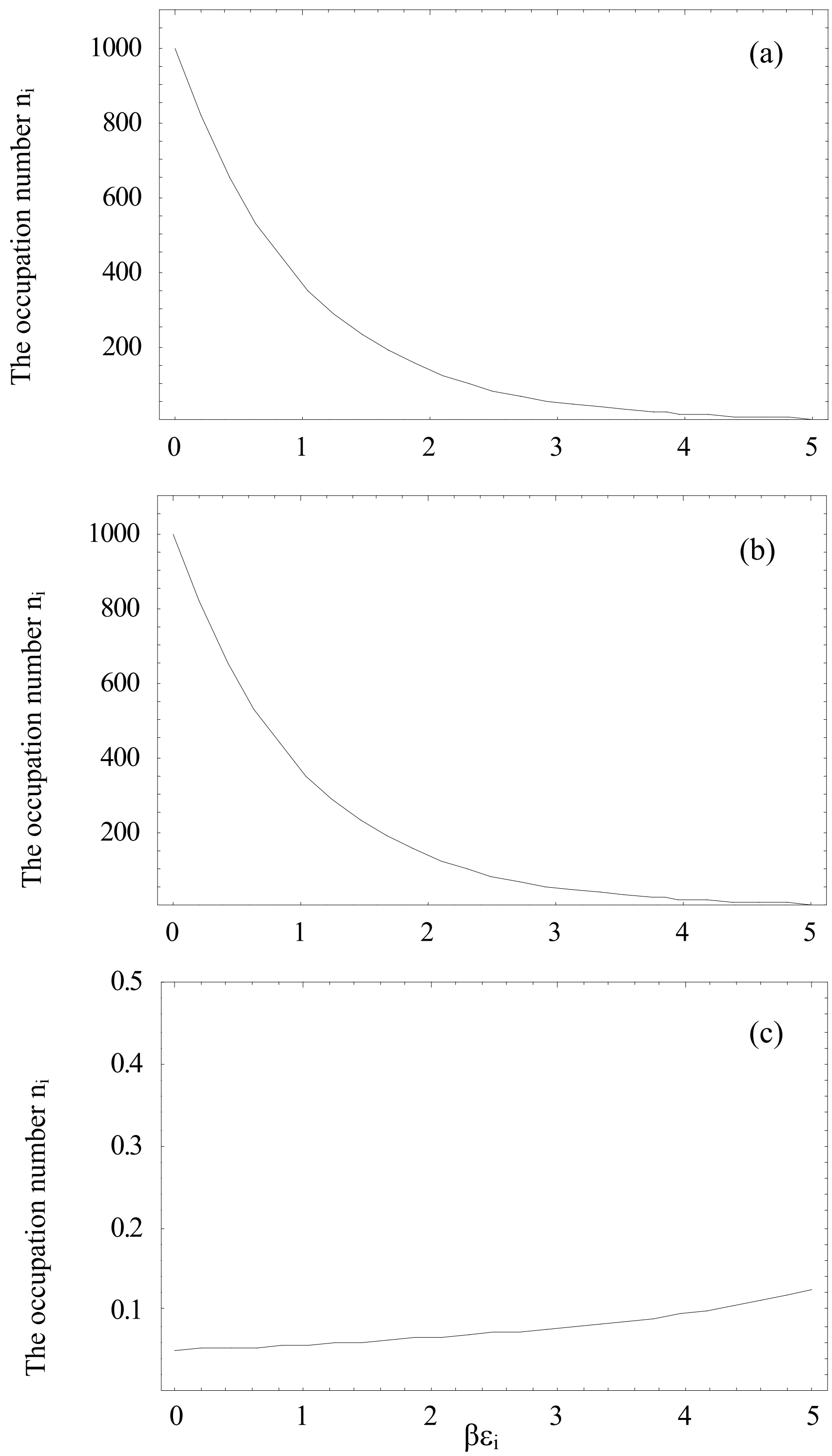

Figure 2: (a) Exponential Boltzmann distribution n_i from Eq1versus $\beta\varepsilon_i$, where ε_i is the energy of the state and $\beta = \frac{1}{kT}$; **(b)** Lambert –Boltzmann distribution n_i Eq.14 versus $\beta\varepsilon$ with the primary branch of the Lambert W function W_0 and **(c)** Lambert–Boltzmann distribution n_i Eq.14 versus $\beta\varepsilon_i$ calculated with the secondary branch of the Lambert W function W_{-1} .

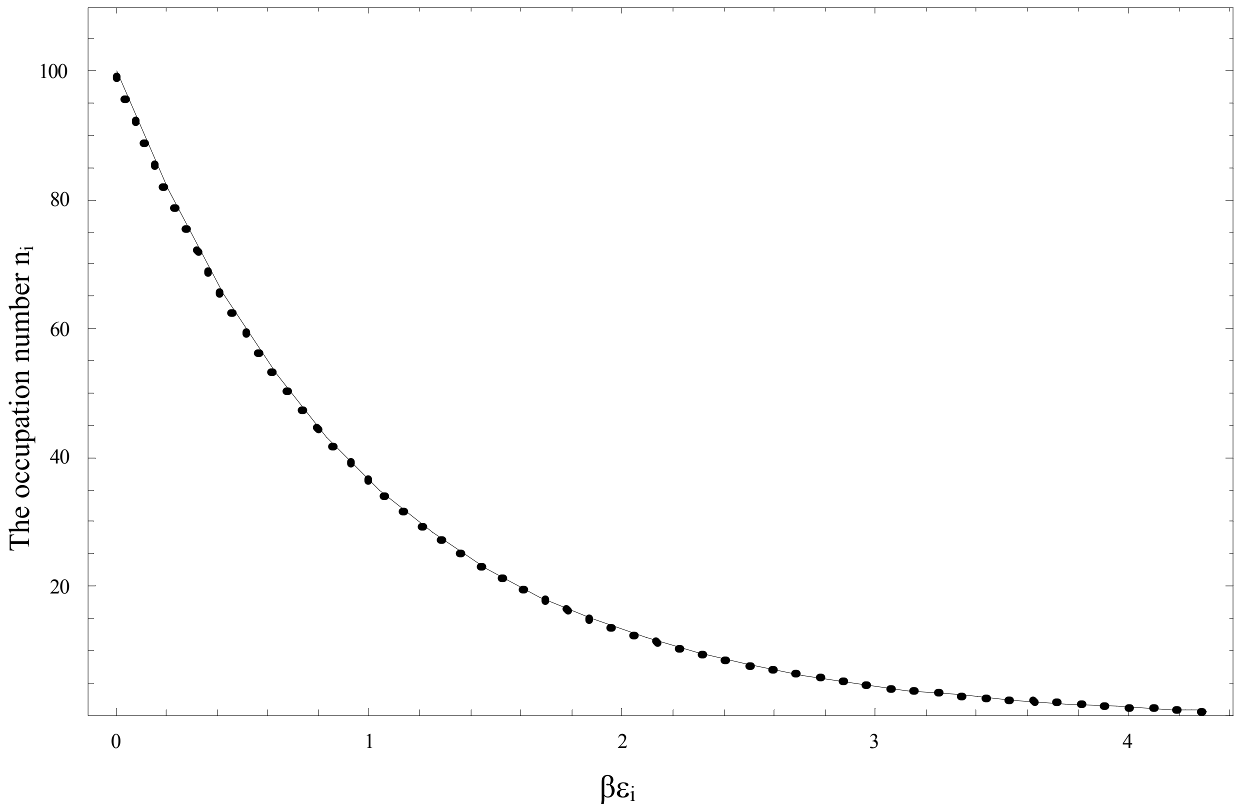

Figure 3: the occupation number n_i as a function of $\beta\varepsilon_i$. The dashed curve gives the occupation number as calculated from numerical solution. The solid curve gives the present result.

References

[1] D. K. Russel, J. Chem. Educ. 73, 299 (1996)

[2] A. S. Wallner, K. A. Brandt, J. Chem. Educ. 76, 1395 (1999)

[3] S. Kakorin, Am. J. Phys. 77, 1 (2009)

[4] R. M. Corless, G. H Gonnet, D. E. G. Hare, D. J. Jeffrey, D. E. Kunth. Adv. Comp. Math 5, 329 (1996)

[5] B.W. Williams, Phys. Lett. A 334, 117 (2005)

[6] R. Chen, X. Zheng, W. Deng, Z. Wu, Solid State Electron. 51, 975 (2007)

[7] W. Bian, J. He, L. Zhang, J. Zhang, M. Chan, Micro. electron. Reliab. 49, 897 (2009)

[8] D. A. Morales, Can. J. Phys. 83, 67 (2005)

[9] A. Vial, Eur. J. Phys. 28, 657 (2007)

[10] R. D. H. Warburton, J. Wang, Am. J. Phys. 72, 1404 (2004)

[11] G.W. Parker, Am. J. Phys. 45, 606 (1977)

[12] C. Hadj Belgacem, Silicon 8, 1469 (2018)

[13] C. Hadj Belgacem M. Fnaiech, J. Elec. Mater. 39, 2248 (2010)

[14] C. Hadj Belgacem M. Fnaiech, J. Mat. Sci. 46, 1913 (2011)

[15] C. Hadj Belgacem Eur. J. Phys. 35, 055025 (2014)

[16] C. Hadj Belgacem, Silicon 8, 397 (2016)

[17] C. Hadj Belgacem, Journal of Taibah University for Science, 11, 328 (2017)