Gibb's paradox for distinguishable

K. M. Udayanandan[1], R. K. Sathish[1], A. Augustine[2]
[1]*Department of Physics, Nehru Arts and Science College, Kerala-671 314, India.*
[2]*Department of Physics, University of Kannur, Kerala 673 635, India.*

E-mail: udayanandan_km@rediffmail.com

(Received 22 March 2014, accepted 17 November 2014)

Abstract

Boltzmann Correction Factor (BCF) N! is used in micro canonical ensemble and canonical ensemble as a dividing term to avoid Gibbs paradox while finding the number of states and partition function for ideal gas. For harmonic oscillators this factor does not come since they are considered to be distinguishable. We here show that BCF comes twice for harmonic oscillators in grand canonical ensemble for entropy to be extensive in classical statistics. Then we extent this observation for all distinguishable systems.

Keywords: Gibbs paradox, harmonic oscillator, distinguishable particles.

Resumen

El factor de corrección de Boltzmann (BCF) N! se utiliza en ensamble microcanónico y ensamble canónico como un término divisor para evitar la paradoja de Gibbs, mientras se busca el número de estados y la función de partición para un gas ideal. Para osciladores armónicos este factor no viene sin que éstos sean considerados para ser distinguibles. Mostramos aquí que BCF llega dos veces para osciladores armónicos en ensamble gran canónico para que la entropía sea ampliamente usada en la estadística clásica. Luego extendemos esta observación para todos los sistemas distinguibles.

Palabras clave: paradoja de Gibbs, oscilador armónico, partículas distinguibles.

PACS: 03.65.Ge, 05.20-y **ISSN 1870-9095**

I. INTRODUCTION

Statistical mechanics is a mathematical formalism by which one can determine the macroscopic properties of a system from the information about its microscopic states.

According to various system conditions, in statistical mechanics we have three ensembles micro canonical ensemble (MCE), canonical ensemble (CE) and grand canonical ensemble (GCE) to find the thermodynamics.

Properties of a given system should be the same in all ensembles. This equivalence of ensembles is a fundamental principle in statistical mechanics. Another fundamental concept is the extensivity of entropy. In an earlier communication [1] R. K. Sathish *et al.* had shown that for harmonic oscillator in MCE and CE the extensivity of entropy can be established without dividing the number of micro states and partition function by BCF but in GCE the partition function has to be multiplied by BCF. In [1] they considered harmonic oscillator as a quantum system in GCE.

In this article we do the GCE considering harmonic oscillator as a classical system. We found that the BCF comes twice to make the entropy extensive. This interesting observation is found to be common for all systems which consist of distinguishable particles.

II. CANONICAL ENSEMBLE

The energy of a harmonic oscillator is:

$$\varepsilon = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 q^2 , \tag{1}$$

where *'p'* is the momentum, *'q'* is the position and *'m'* is the mass of particle. For a single oscillator, partition function is given by:

$$Q_1 = \sum_r \exp\left(-\beta\left[\frac{p_r^2}{2m} + \frac{1}{2} m\omega^2 q_r^2\right]\right), \tag{2}$$

where *'r'* represents all the possible states of the oscillator. Solving this, we get [2]:

$$Q_1 = \left(\frac{kT}{\hbar\omega}\right)^3 . \tag{3}$$

The partition function of the N oscillator system would then be:

$$Q_N = \left(\frac{kT}{\hbar\omega}\right)^{3N}. \quad (4)$$

The Helmholtz free energy is given by:

$$A = -kT \ln Q_N, \quad (5)$$

$$A = 3NkT \ln\left(\frac{\hbar\omega}{kT}\right). \quad (6)$$

The entropy is given by: [2]

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,\,N}. \quad (7)$$

Solving we get:

$$S = 3Nk\left[\ln\left(\frac{kT}{\hbar\omega}\right)+1\right]. \quad (8)$$

III. GRAND CANONICAL ENSEMBLE

The grand partition function is given by [2]:

$$Z = \sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}. \quad (9)$$

Substituting the value of Q_{N} we get:

$$Z = \frac{1}{1 - z\left(\frac{kT}{\hbar\omega}\right)^3}, \quad (10)$$

$$\ln Z = -\ln\left[1 - z\left(\frac{kT}{\hbar\omega}\right)^3\right]. \quad (11)$$

Number of particles:

$$N = z\frac{\partial(\ln Z)}{\partial z}, \quad (12)$$

$$N = \frac{z\left(\frac{kT}{\hbar\omega}\right)^3}{1 - z\left(\frac{kT}{\hbar\omega}\right)^3}. \quad (13)$$

Rearranging:

$$z = \frac{N}{N+1}\left(\frac{kT}{\hbar\omega}\right)^3. \quad (14)$$

The Landau free energy and entropy are given by [3]:

$$\phi = -kT \ln Z, \quad (15)$$

$$S = -\left(\frac{\partial \phi}{\partial T}\right)_{T,\,\mu}. \quad (16)$$

Then we get:

$$S = 3Nk\left[1+\ln\left(\frac{kT}{\hbar\omega}\right)\right] - Nk\ln N + Nk\ln(N+1). \quad (17)$$

This entropy is not extensive and is not identical to the value obtained in the case of CE but will be the same for large N.

IV. MODIFICATION

We have the GCE partition function as:

$$Z = \sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}. \quad (18)$$

If this partition function is modified by multiplying externally by BCF and dividing the CE partition function by BCF we get the modified partition function as:

$$Z' = N!\sum_{N_r=o}^{\infty} z^{N_r}\frac{Q_{N_r}}{N_r!}, \quad (19)$$

$$= N!\sum_{N_r=0}^{\infty} z^{N_r}\frac{\left(\frac{kT}{\hbar\omega}\right)^{3N}}{N_r!}, \quad (20)$$

$$Z' = N!\exp\left[z\left(\frac{kT}{\hbar\omega}\right)^3\right], \quad (21)$$

$$Z' = N\ln N - N + z\left(\frac{kT}{\hbar\omega}\right)^3. \quad (22)$$

Number of particles:

$$N = z\frac{\partial}{\partial z}\ln Z', \quad (23)$$

$$N = z\left(\frac{kT}{\hbar\omega}\right)^3 . \quad (24)$$

Rearranging:

$$z = N\left(\frac{\hbar\omega}{kT}\right)^3 . \quad (25)$$

Using the expression for entropy we get:

$$S = 3Nk\left[1+\ln\left(\frac{kT}{\hbar\omega}\right)\right]. \quad (26)$$

This is extensive and equal to the equation obtained for CE.

V. ENTROPY OF THE SYSTEM OF DISTINGUISHABLE PARTICLES. GENERAL TECHNIQUE

For all distinguishable particles there is no need to divide the canonical partition function by $N!$ as per the definition of Gibb's paradox. But we observe that this create some discomfort in the derivation. We show that if we divide the canonical partition function by $N!$ inside the summation and then multiply by $N!$ outside the summation this discomfort can be avoided. So let us consider a general system with single partition function Q_1. Then the general grand partition function will be:

$$Z = N!\sum_{N_r=0}^{\infty}\left(\frac{(zQ_1)^{N_r}}{N_r!}\right), \quad (27)$$

Then:

$$Z = N!e^{zQ_1}, \quad (28)$$

$$\ln Z = \ln N! + zQ_1, \quad (29)$$

$$N = zQ_1, \quad (30)$$

$$\phi = -kT(\ln N! + kTzQ_1) . \quad (31)$$

Substituting and using:

$$\mu = kT\ln z, \quad (32)$$

we get:

$$S = Nk\ln Q_1 + \frac{NkT}{Q_1}\frac{\partial Q_1}{\partial T}. \quad (33)$$

For harmonic oscillators:

$$Q_1 = \left(\frac{kT}{\hbar\omega}\right)^3, \quad (34)$$

and then we get:

$$S = 3Nk\left[1+\ln\left(\frac{kT}{\hbar\omega}\right)\right]. \quad (35)$$

The Equation 33 is common for any system and we can obtain the entropy very easily. Similarly general formula for any thermodynamic quantity can be obtained for all distinguishable systems.

VI. CONCLUSIONS

In this short article we showed that, in the case of classical harmonic oscillator and for all distinguishable particles the partition function has to be multiplied and divided by BCF in GCE to make the entropy extensive. But this multiplication is not visible in MCE and CE since they cancel of. In the case of GCE it is not cancelled because of the summation in the partition function. Thus to find the thermodynamics we suggest that the grand partition function for all distinguishable particles must be modified as:

$$Z' = N!\sum_{N_r=0}^{\infty} Z^{N_r}\frac{Q_{N_r}}{N_r!}. \quad (36)$$

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