Gibbs Paradox in Grand Canonical Ensemble

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Abstract
Boltzmann Correction Factor (BCF) $N!$ is used in Micro Canonical Ensemble (MCE) and Canonical Ensemble (CE) as a dividing term to reduce the over counting of the states while finding the number of states and partition function. For Grand Canonical Ensemble the indistinguishability was taken into account while deriving the Partition Function (PF) and hence generally the BCF doesn't appear for GCE. We show here that BCF comes as a multiplying factor for harmonic oscillators in GCE for entropy to be extensive.

Keywords: Ensembles, Boltzmann correction factor.

Resumen
El Factor de Corrección de Boltzmann (FBC) $N!$ se utiliza en Ensamble Micro Canónico (MCE) y Ensamble Canónico (CE) como un término divisorio para reducir el exceso de conteo de los estados, mientras encontramos el número de estados y la función de partición. Se ha tomado en cuenta la indistinguibilidad para el Gran Ensamble Canónico mientras se derivaba la Función de Partición (PF) y por lo tanto generalmente el BCF no aparece para la GCE. Mostramos aquí que ese BCF se presenta como un factor de multiplicación de osciladores armónicos en GCE para entropía extensiva.

Palabras clave: Ensambles, corrección del factor de Boltzmann.

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I. INTRODUCTION

Gibbs paradox is an unphysical situation developed when two ideal gases were mixed. When two samples of ideal gases of same temperature and particle density were mixed, it was found that the entropy of the mixed system is different from the sum of the entropies of individual system, which was unsubstantial because of the extensive property of entropy. This problem was resolved by Gibbs in an ad-hoc fashion by dividing the number of microstates of an ideal gas by $N!$.

In this paper, we revisit the Gibbs paradox in the context of harmonic oscillators. Equivalence of ensembles is a fundamental requirement in statistical mechanics. At all temperatures CE and MCE are same while at high temperature and low density GCE must be equivalent to MCE and CE. Another fundamental concept is the extensiveness of entropy. In this short communication we show that for classical harmonic oscillators in MCE and CE formalism the extensiveness of entropy can be established without dividing the number of micro states and partition function by BCF. But in GCE we multiply the partition function by a factor to make the entropy extensive. Then we can get the same thermodynamics for the three ensembles without considering the concept of indistinguishability. It is the extensive nature of the entropy that makes the three ensembles equivalent**.**

In section II the Jacobian transformation technique is used to obtain the number of microstates Ω. Then using the Boltzmann relation, $S=k\ln\Omega$ the entropy was calculated. In section III, we obtained the partition function and from this partition function Helmholtz free energy was calculated. From Helmholtz free energy, entropy is obtained using the standard relation. In section IV, the grand partition function is obtained for both Fermi and Bose system and the value of the $\ln Z$ for both systems at high temperature is obtained. This makes the three ensembles equivalent. Then when the entropy was evaluated, using standard relation, it was found to be not extensive in nature. To make it extensive we used the Boltzmann corrective factor $N!$. The grand partition function is multiplied with BCF to make entropy extensive.

II. MICRO CANONICAL ENSEMBLE

The Jacobian transformation technique can be applied in the case of transformation in phase space. Phase space is a space spanned by generalized co-ordinates and generalized momenta. Hence the equation of transformation between two phase space spanned by q_i's and p_i's and Q_i's and P_i's is

$$dq_i dp_i = J dQ_i dP_i. \tag{1}$$

Consider N independent Harmonic oscillators. Each Harmonic Oscillator will have three degrees of freedom. Then energy

$$E = \sum_{i=1}^{3N}\left[\frac{p_i^2}{2m} + \frac{1}{2}m\omega^2 q_i^2\right]. \tag{2}$$

Rearranging

$$\sum_{i=1}^{3N}\left[\frac{p_i^2}{2mE} + \frac{1}{2}\frac{m\omega^2}{E}q_i^2\right] = 1. \tag{3}$$

Putting

$$q_i = \sqrt{\frac{2E}{m\omega^2}}Q_i, \tag{4}$$

$$p_i = \sqrt{2mE}P_i, \tag{5}$$

$$\sum_{i=1}^{3N}\left(P_i^2 + Q_i^2\right) = 1. \tag{6}$$

This is a transformation in phase space. Using the transformation equations we transform to a phase space spanned by Q_i's and P_i's. Thus the volume between the two phase space is related by an equation

$$\int d^{3N}q_i d^{3N}p_i = J^{3N}\int d^{3N}Q_i d^{3N}P_i. \tag{7}$$

If we denote $X_i = Q_i \quad for \quad i = 1\cdots\cdots 3N$
$X_{i+3N} = P_i \quad for \quad i = 1\cdots\cdots 3N$ the Eq. (6) can be represented as

$$\sum_{i=1}^{6N} X_i^2 = 1. \tag{8}$$

Thus we get

$$\int d^{3N}q_i d^{3N}p_i = J^{3N}\int d^{6N}X_i \tag{9}$$

$$\int d^{3N}q\, d^{3N}p = J^{3N}V_{6N}. \tag{10}$$

Where V_{6N} is the volume of the sphere with unit radius in $6N$ dimensional space. J can be obtained from the transformation equation.

$$J = \begin{vmatrix} \left(\sqrt{\frac{2E}{m\omega^2}}\right)^{3N} & 0 \\ 0 & \left(\sqrt{2mE}\right)^{3N} \end{vmatrix} \tag{11}$$

$$J = \left(\frac{2E}{\omega}\right)^{3N}. \tag{12}$$

Using the relation

$$V_n = \frac{\pi^{\frac{n}{2}}R^n}{(\frac{n}{2})!}, \tag{13}$$

n-dimensional volume $V_{6N} = \frac{\pi^{3N}}{(3N)!}$. Thus phase space volume

$$\int d^{3N}q_i d^{3N}p_i = \frac{1}{(3N)!}\left(\frac{2\pi E}{\omega}\right)^{3N}. \tag{14}$$

Hence the number of micro states Ω becomes

$$\Omega = \frac{Phase\,space\,volume}{h^{3N}}. \tag{15}$$

$$\Omega = \frac{1}{(3N)!}\left(\frac{E}{\hbar\omega}\right)^{3N}, \tag{16}$$

where $\hbar = \frac{h}{2\pi}$; h=Planck constant. Using the expression for Ω, the entropy of the system is

$$S = k ln\left[\frac{1}{(3N)!}\left(\frac{E}{\hbar\omega}\right)^{3N}\right], \tag{17}$$

where k= Boltzmann constant.

Using Stirling formula

$$S = 3Nk\left[\ln\left(\frac{E}{3N\hbar\omega}\right) + 1\right]. \tag{18}$$

Using the expression

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}. \tag{19}$$

we get

$$E = 3NkT. \tag{20}$$

Hence

$$S = 3Nk\left[\ln\left(\frac{kT}{\hbar\omega}\right)+1\right]. \tag{21}$$

III. CANONICAL ENSEMBLE

The thermodynamics for CE is obtained from the partition function

$$Q_N = \sum_r e^{-\beta\epsilon_r}. \tag{22}$$

Using the usual techniques of SM we get

$$Q_N = \left[\frac{1}{\hbar\omega\beta}\right]^N. \tag{23}$$

Helmholtz free energy

$$A = -kT\ln Q_N = -3NkT\ln\left(\frac{KT}{\hbar\omega}\right). \tag{24}$$

Entropy

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N}, \tag{25}$$

which gives S as

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

IV. GRAND CANONICAL ENSEMBLE

There are large numbers of systems with classical energy exhibiting quantum properties. Hence we take the quantum statistics for finding the partition function in GCE which is,

$$Z = \prod_i \ln(1+ze^{-\beta\epsilon_i}), \tag{27}$$

for Fermi Dirac case and

$$Z = \prod_i \frac{1}{\ln(1-ze^{-\beta\epsilon_i})}, \tag{28}$$

for Bose Einstein case.

Evaluating $\ln Z$ we get

$$\ln Z = \left(\frac{1}{\hbar\beta\omega}\right)^3 g_4(z), \tag{29}$$

for Bose systems

$$\ln Z = \left(\frac{1}{\hbar\beta\omega}\right)^3 f_4(z), \tag{30}$$

for Fermi systems where $g_4(z)$ and $f_4(z)$ are Bose-Einstein and Fermi-Dirac functions. For high temperature $g_4(z)$ and $f_4(z)$ becomes z. Hence

$$\ln Z = \left(\frac{1}{\hbar\beta\omega}\right)^3 z, \tag{31}$$

for both systems. Using the basic expression for obtaining N

$$N = z\frac{\partial \ln Z}{\partial z}, \tag{32}$$

we get

$$z = N(\hbar\beta\omega)^3, \tag{33}$$

Helmholtz free energy

$$A = -kT\ln Z + NkT\ln z, \tag{34}$$

which gives

$$A = -kTN + NkT\ln N\left(\frac{\hbar\omega}{kT}\right)^3. \tag{35}$$

Using the expression for entropy we get

$$S = 4Nk + Nk\ln\left[\frac{1}{N}\left(\frac{kT}{\hbar\omega}\right)^3\right]. \tag{36}$$

This equation is not equivalent to equations for S in MCE and CE and the most notable factor is that it is not **extensive.** To make it extensive we have to add $\ln N!$ to the obtained entropy. Then

$$S = 3Nk\left[\ln\left(\frac{E}{N\hbar\omega}\right)+1\right]. \qquad (37)$$

which is extensive and equal to the earlier equations obtained.

V. CONCLUSIONS

In this short communication we want to show that BCF comes in GCE contrary to the belief that they are necessary in MCE and CE only. The expression for the grand partition function must be modified for harmonic oscillators as

$$Z = N!\prod_i \ln(1+ze^{-\beta\epsilon_i}), \qquad (38)$$

for Fermi Dirac case and

$$Z = N!\prod_i \frac{1}{\ln(1-ze^{-\beta\epsilon_i})}, \qquad (39)$$

for Bose Einstein case. It is interesting to see that it is only necessary for harmonic oscillators and not for any other systems.

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