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SHORT COMMUNICATION

Energy, entropy and work function in a molecule with degeneracy

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ABSTRACT

In this paper, we have deduced some thermodynamic properties for a molecular system with degeneracy based in the postulates of the statistical mechanics. We obtain analytical expressions for internal energy U, heat capacity C_v , entropy *S* and work function o Helmholtz free energy A. It is predicted in this research the thermodynamic behavior of U, C_v, *S* and *A* in the limit of high and low temperature.

Keywords**:** Statistical mechanics, degeneracy, internal energy, heat capacity, entropy, work function, limit of high and low temperature

1. INTRODUCTION

In the statistical and microscopic description of any system, the partition function plays determinant role and is defined as the total sum of states of the system [1]:

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$$Z = \sum g(E_n) e^{-\frac{E_n}{K_B T}} \tag{1}$$

where: n labels the total energy E_n , K_B is the Boltzman´s constant and $g(E_n)$ it is the number of degenerate states with the same energy E_n. The use of the equation (1) [1,2] allows to obtain a statistical and microscopic description of the energy and the thermal capacity.

The concepts of the statistical mechanics must be considered if we want to do a microscopic description of a physical system. Recently Mäkelä [3,4] constructed a microscopic model of "Stretched Horizon" of a Schwarzschild and Reissner-Nordström black holes and obtained an analytical expression for the partition function from the point of view of an observer on its stretched horizon. Malaver [5-7] studied the behavior of the thermal capacity C_V for Schwarzschild and Reissner-Nordström black holes when $T>>T_C$ and $T<<T_C$ where T_C is the characteristic temperature and found that the value for C_V if $T>>T_C$ is the same that would be obtained in an ideal diatomic gas if are considered the rotational and translational degrees of freedom, respectively. Viaggiu [8] present a statistical analysis in gravitons and derived equations for the partition function and the mean energy. Malaver [9] obtained an analytical expression for the thermal capacity for gravitons and we studied the, behavior of C_V in the limit of high and low temperature (Arteaga, [10], Armas [11]).

The aim of this paper is studies the thermodynamic behavior of a molecular system with degeneracy used the methods of the statistical mechanics. This paper is outlined in the following manner: the section II we present the equations for statistical mechanics in the limit of high temperatures. In section III we present an analysis of the fluctuations of the energy with extremely high temperatures. In section IV it is shown the thermodynamic behavior of U, C_V, S and A for low temperatures. Finally in section V, we conclude.

2. STATISTICAL MECHANICS IN THE LIMIT OF HIGH TEMPERATURE

According Reif [1] and Nash [2], the canonical partition function for a N identical particles with internal degrees of freedom can be written as

$$Z_T = z^N \tag{2}$$

where: z is the partition function for any one of an assembly of identical unit. We have defined z as

$$z = \sum g(\varepsilon_n) e^{-\frac{\varepsilon_n}{K_B T}} \tag{3}$$

The ε_n terms represent the energies associated with every possible quantum state of the single unit and $g(\varepsilon_n)$ the degenerate energy states.

In this paper, we have taken the form of the energy term for a molecule as $\varepsilon_n = an^{\alpha}$, where a and α are positive real constants and n a positive integer. Every energetic level n have $bn^{\beta+\gamma}$ degenerate energy states where b, β and γ are positive constants.

The partition function (3) is given by for

$$z = \sum bn^{\beta+\gamma} e^{-\frac{an^{\alpha}}{K_B T}} \tag{4}$$

For molecules with extremely high temperatures the summation in (4) can be replaced by the corresponding integral

$$z = \sum_{0}^{\infty} bn^{\beta+\gamma} e^{-\frac{an^{\alpha}}{K_B T}} = \int_{0}^{\infty} bn^{\beta+\gamma} e^{-\frac{an^{\alpha}}{K_B T}} dn \tag{5}$$

Substituting the change of variable $y = c^{1/\alpha} n$ and $n^{\beta+\gamma} = \frac{y^{\beta+\gamma}}{c^{\frac{\beta+\gamma}{\alpha}}}$ in the integral (5) and replacing $c = a / K_B T$ we have

$$z = \frac{b}{c^{\frac{\beta+\gamma+1}{\alpha}}} \int_{0}^{\infty} y^{\beta+\gamma} e^{-y^{\alpha}} dy \tag{6}$$

With the definite integral (6) the following result is obtained

$$z = \frac{b}{c^{\frac{\beta+\gamma+1}{\alpha}}} \frac{\Gamma\left(\frac{\beta+\gamma+1}{\alpha}\right)}{\alpha} = b\left(\frac{K_B T}{a}\right)^{\frac{\beta+\gamma+1}{\alpha}} \frac{\Gamma\left(\frac{\beta+\gamma+1}{\alpha}\right)}{\alpha} \tag{7}$$

where: $\frac{\Gamma\left(\frac{\beta+\gamma+1}{\alpha}\right)}{\alpha}$ is the gamma function associated with the partition function *z*.

The canonical partition function Z_T can be written as

$$Z_T = \left[b\left(\frac{K_B T}{a}\right)^{\frac{\beta+\gamma+1}{\alpha}} \frac{\Gamma\left(\frac{\beta+\gamma+1}{\alpha}\right)}{\alpha} \right]^N \tag{8}$$

Defining the statistical internal energy with the following expression [1]

$$U = NK_B T^2 \left(\frac{\partial \ln z}{\partial T} \right)_V \tag{9}$$

The thermal energy of a gas that contains n of these molecules is

$$U = \left[\frac{(\beta + \gamma + 1)}{\alpha} \right] NK_B T \tag{10}$$

For the heat capacity to constant volume

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \left[\frac{(\beta + \gamma + 1)}{\alpha} \right] NK_B \tag{11}$$

In statistical mechanics, the work function o Helmholtz free energy A is defined as

$$A = -K_B T \ln Z \tag{12}$$

Substituting eq. (8) in (12) we have for the work function

$$A = -NK_B T \ln \left[\frac{b \left(\frac{K_B T}{a} \right)^{\frac{\beta+\gamma+1}{\alpha}} \Gamma\left(\frac{\beta + \gamma + 1}{\alpha} \right)}{\alpha} \right] \tag{13}$$

The relation between *A* and the thermodynamic entropy *S* is

$$A = U - TS \tag{14}$$

With (13) and the eq. (10) in eq. (14) we obtain

$$S = NK_B \left\{ \frac{\beta + \gamma + 1}{\alpha} + \ln \left[\frac{b \left(\frac{K_B T}{a} \right)^{\frac{\beta+\gamma+1}{\alpha}} \Gamma\left(\frac{\beta + \gamma + 1}{\alpha} \right)}{\alpha} \right] \right\} \tag{15}$$

In this paper, we have calculated the values of U, C_V, A and S with α = 2 and the particular cases $\beta = 1$, $\beta = 2$, $\gamma = 0$.

For the case α= 2, β=1, γ=0, using (6) , (7) and eq. (8) we obtain

$$Z = \left(\frac{bK_B T}{2a} \right)^N \tag{16}$$

Of the eq. (10) we have for the internal energy U

$$U = NK_B T \tag{17}$$

With (11), (13) and (15) the analytical expressions for C_V, A and S, can be written as

$$C_V = NK_B \tag{18}$$

$$A = -NK_B T \ln\left(\frac{bK_B T}{2a} \right) \tag{19}$$

$$S = NK_B \left[1 + \ln\left(\frac{bK_B T}{2a} \right) \right] \tag{20}$$

For the case α = 2, β = 2, γ = 0, we have for the partition function Z

$$Z = \left[\left(\frac{K_B T}{a} \right)^{3/2} \frac{\sqrt{\pi}}{4} \right]^N \tag{21}$$

and for U, C_V, A and S we found

$$U = \frac{3}{2} NK_B T \tag{22}$$

$$C_V = \frac{3}{2} NK_B \tag{23}$$

$$A = -NK_B T \left[\frac{3}{2} \ln\left(\frac{K_B T}{a} \right) - 0.814 \right] \tag{24}$$

$$S = NK_B\left[0.686 + \frac{3}{2}\ln\left(\frac{K_B T}{a}\right)\right] \tag{25}$$

3. FLUCTUATIONS OF ENERGY WHEN T→∞

In agreement with (1), the dispersion of the energy can be written in the form [1] :

$$\overline{(\Delta E)^2} = \overline{(\Delta U)^2} = \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial E}{\partial \beta} \tag{26}$$

what is equivalent to

$$\overline{(\Delta U)^2} = \overline{U^2} - \overline{U}^2 = K_B T^2 \left(\frac{\partial E}{\partial T}\right)_V = K_B T^2 C_V \tag{27}$$

and the relative energy fluctuation is given by

$$\frac{\Delta U}{U} = \frac{T\sqrt{K_B C_V}}{U} \tag{28}$$

substituting (10) and (11) in eq. (26) we obtain

$$\frac{\Delta U}{U} = \frac{1}{\sqrt{\frac{(\beta+\gamma+1)}{\alpha}N}} \tag{29}$$

the fluctuation of energy can be written as

$$\frac{\Delta U}{U} = \frac{1}{\sqrt{\frac{(\beta+\gamma+1)}{\alpha}N}} \to 0 \quad \text{when} \quad N \to \infty \tag{30}$$

The value of the fluctuation depends on the parameters α, β, γ associated with the function gamma.

4. BEHAVIOR OF U, C_V, S AND A IN THE LIMIT OF LOW TEMPERATURE

For low temperatures the partition function summation (4) can be written as

$$z = be^{-\frac{a}{K_B T}} + b2^{\beta+\gamma} e^{-\frac{a2^{\alpha}}{K_B T}} + \ldots \tag{31}$$

where: $n = 1,2\ldots$

With the eq. (9) we obtain for the internal energy

$$U = aN\left[\frac{e^{-\frac{a}{K_B T}} + 2^{\alpha+\beta+\gamma} e^{-\frac{a2^{\alpha}}{K_B T}} + \ldots}{e^{-\frac{a}{K_B T}} + 2^{\beta+\gamma} e^{-\frac{a2^{\alpha}}{K_B T}} + \ldots}\right] \tag{32}$$

From (12), (14), (21) and (22), the expressions for C_V, A and S are given by for

$$C_V = \frac{Na^2}{K_B T^2}\left[\frac{\left(e^{-\frac{a}{K_B T}} + 2^{2\alpha+\beta+\gamma} e^{-\frac{a2^{\alpha}}{K_B T}} + \ldots\right)\left(e^{-\frac{a}{K_B T}} + 2^{\beta+\gamma} e^{-\frac{a2^{\alpha}}{K_B T}} + \ldots\right) - \left(e^{-\frac{a}{K_B T}} + 2^{\alpha+\beta+\gamma} e^{-\frac{a2^{\alpha}}{K_B T}} + \ldots\right)^2}{\left(e^{-\frac{a}{K_B T}} + 2^{\beta+\gamma} e^{-\frac{a2^{\alpha}}{K_B T}} + \ldots\right)^2}\right] \tag{33}$$

$$A = -NK_B T \ln\left[be^{-\frac{a}{K_B T}} + b2^{\beta+\gamma} e^{-\frac{a2^{\alpha}}{K_B T}} + \ldots\right] \tag{34}$$

$$S = \frac{aN}{T}\left[\frac{e^{-\frac{a}{K_B T}} + 2^{\alpha+\beta+\gamma} e^{-\frac{a2^{\alpha}}{K_B T}} + \ldots}{e^{-\frac{a}{K_B T}} + 2^{\beta+\gamma} e^{-\frac{a2^{\alpha}}{K_B T}} + \ldots}\right] + NK_B \ln\left[be^{-\frac{a}{K_B T}} + b2^{\beta+\gamma} e^{-\frac{a2^{\alpha}}{K_B T}} + \ldots\right] \tag{35}$$

4. CONCLUSIONS

In this paper, we have deduced expressions for Z, U, C_V, S and A in a molecular system with degeneracy in terms of the gamma function when $T\rightarrow\infty$ and have studied the thermodynamic behavior for $T\rightarrow 0$. For extremely high temperatures the values of the gamma function and the fluctuations of energy will depend on the parameters α, β, γ associated with the energy term and with the degeneracy factor.

The statistical mechanics can enrich the courses of thermodynamics, which contributes to a better compression of the thermal phenomena. The thermodynamic equations deduced from the postulates of the statistical mechanics are tractable mathematically and offer a wide explanation of many physical systems of interest.

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