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Relative Fluctuations of Energy in Molecules with Permanent Electric Dipole Moment in the Presence of an Electric Field

Manuel Malaver

Department of Basic Sciences, Maritime University of the Caribbean, Catia la Mar, Venezuela

Institute of Scholars, Muddhinapalya Bengaluru-560091, Karnataka, India

Department of Applied Physics, Engineering Faculty, Central University of Venezuela

ABSTRACT

In this work uses the Maxwell-Boltzmann in which the accessible quantum states of a set of particles are considered to explain the behavior of a system made up of N molecules with permanent electric dipole moment in the presence of an external electric field. The effect of temperature on the thermal capacity of the system is discussed, and relative energy fluctuations at the high and low temperature limits are studied. In this review paper it is found that the fluctuation will always be inversely proportional to the number of molecules in the system, which means that for N molecules the energy will always be completely determined.

***Corresponding author**

Manuel Malaver, Department of Basic Sciences, Maritime University of the Caribbean, Catia la Mar, Venezuela.

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Introduction

Molecules with permanent electric dipole moment, also called polar molecules are those that present a charge separation due to the different electronegativity of their atoms, resulting in one positive and one negative extreme [1]. In an electric dipole there is a separation of the positive and negative charges found in any electromagnetic system. A simple example of this system is a pair of electric charges of equal magnitude but opposite sign separated by a specific distance d [2]. For an electric dipole, the electric dipole moment vector of the load distribution points from the negative charge to the positive charge, and has a magnitude equal to the force of each charge multiplied by the distance between the charges. Many molecules have such dipole moments due to non-uniform distributions of positive and negative charges in the various atoms. This is the case of polar compounds such as hydrogen fluoride (HF), where electron density is unevenly shared between atoms [3].

In the statistical description of any system, the partition function plays a determining role and is defined as the total sum of the system states [4]:

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

where n is the total energy E_n, K_B is the Boltzmann constant and $g(E_n)$ is the number of degenerated states with the same energy En. This function is mainly involved in determining how the units are distributed over all possible quantum states of the system under study. Using equation (1) [4,5] provides a statistical and microscopic description of the thermodynamic variables describing the system.

The concepts of statistical mechanics must be considered if we are to make a microscopic description of a physical system. Mäkelä [6,7] built a microscopic model of "Stretched Horizon" of black holes by Schwarzschild and Reissner-Nordström and obtained an analytical expression for the partitioning function from the point of view of an observer on its extended horizon. Malaver [8,9] studied the behaviour of the thermal capacity C_V for both black holes when $T>>T_C$ and $T<<T_C$ where T_C is the characteristic temperature of the Schwarzschild black hole and found that the value for C_V if $T>>T_C$ is the same as would be obtained in an ideal diatomic gas if degrees of rotational and translational freedom, respectively. Viaggiu [10] presents a statistical analysis in gravitons and derived equations for partition function and mean energy. Malaver [11] finds that the vapour pressure of a paramagnetic solid depends on the magnetic susceptibility of the material and the applied external magnetic field. Mandl [12] used the concepts of statistical thermodynamics to understand the behaviour of paramagnetic solids and García-Colín Scherer [13] presents a thermodynamic analysis in magnetic systems. Malaver [14] also obtained an analytical expression for the thermal capacity of gravitons and studied the behavior of C_V at the high and low temperature boundary.

In this research, the relative fluctuations of energy at the high and low temperature limits have been determined for a system of N molecules with permanent electric dipole moment in an external electric field, for which the behaviour of thermal capacity with temperature has been analysed. It is found that the relative fluctuation is always inversely proportional to the number of molecules in the system which implies that the energy in any case will always be well defined.

Statistical Mechanics of Polar Molecules in an External Electric Field

Consider a molecule with permanent electric dipole moment p placed in an electric field , with p aligned parallel or antiparallel to the field [15] and taking into account that the energy of a dipole in an electric field will be given by and each state above the first level of energy is doubly degenerated with a separation of 2 p between each state , the partitioning function for this system will be given by:

$$Z = 1 + 2e^{-\frac{2\varepsilon p}{K_B T}} + 2e^{-\frac{4\varepsilon p}{K_B T}} + \ldots\ldots \quad (2)$$

Assuming that the other states are situated at energies high enough to make them really inaccessible [5], equation (2) can be written as:

$$Z = 1 + 2e^{-\frac{2\varepsilon p}{K_B T}} \quad (3)$$

According to the statistics of Maxwell-Boltzmann (MB) [4] the average energy of the system is expressed as follows:

$$\overline{E} = -\frac{\partial \ln Z}{\partial \beta} \quad (4)$$

where $\beta = 1/K_B T$. Solving equation (4) with the expression for Z , is obtained for the average energy per molecule:

$$\overline{E} = \frac{4\varepsilon p}{2 + e^{\frac{2\varepsilon p}{K_B T}}} \quad (5)$$

and for N molecules

$$E = N\overline{E} = \frac{2N\varepsilon p}{1 + \frac{1}{2}e^{\frac{2\varepsilon p}{K_B T}}} \quad (6)$$

$$E \to 0 \text{ for } T \to 0$$

$$E \to 4Np\varepsilon/3 \text{ for } T \to \infty \quad (7)$$

For the determination of entropy S one can use the expression for the free energy of Helmholtz $A=E-TS$ where A is defined in statistics MB as:

$$A = -NK_B T \ln Z \quad (8)$$

With (3), (6) and (8) the entropy of the N-molecule system is written as follows:

$$S = \frac{2N\varepsilon p}{T\left(1 + \frac{1}{2}e^{\frac{2\varepsilon p}{K_B T}}\right)} + NK_B \ln\left(1 + 2e^{-\frac{2\varepsilon p}{K_B T}}\right) \quad (9)$$

At the limits of high and low temperature is obtained for entropy

$$S \to 0 \text{ for } T \to 0$$

$$S \to NK_B \ln 3 \text{ for } T \to \infty \quad (10)$$

The thermal capacity at constant volume for N molecules is given by:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \quad (11)$$

By derivation of equation (6) we obtain:

$$\left(\frac{\partial E}{\partial T}\right)_V = \frac{8N\varepsilon^2 p^2 e^{\frac{2\varepsilon p}{K_B T}}}{K_B T^2\left(2 + e^{\frac{2\varepsilon p}{K_B T}}\right)^2} \quad (12)$$

Rearranging (6), the thermal capacity C_V can be written as follows:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{NK_B}{2}\left(\frac{2\varepsilon p}{K_B T}\right)^2 \frac{e^{\frac{2\varepsilon p}{K_B T}}}{\left(1 + \frac{1}{2}e^{\frac{2\varepsilon p}{K_B T}}\right)^2} \quad (13)$$

Thermal Capacity Dependency with Temperature

The specific parameter must be defined in equation (13) $\beta_p = 2\varepsilon p/K_B$ whe β_p has the temperature dimensions. In terms of β_p the expression (13) can be written as:

$$C_V = \frac{NK_B}{2}\left(\frac{\beta_p}{T}\right)^2 \frac{e^{\frac{\beta_p}{T}}}{\left(1 + \frac{1}{2}e^{\frac{\beta_p}{T}}\right)^2} \quad (14)$$

Because the function ex is equivalent to the sum of the infinite series $1 + x + x^2/2! + x^3/3! + \ldots..$ the significance of (14) in the two temperature limiting values can be determined.

The first limiting case to be considered is the behaviour of C_V at low temperatures, that is when $T \to 0$ or its equivalent $\beta_p >> T$ so that equation (14) is written as follows:

$$C_V = \frac{NK_B}{2}\frac{1}{(T/\beta_P)^2}\frac{e^{\frac{\beta_p}{T}}}{\frac{1}{4}\left(e^{\frac{\beta_p}{T}}\right)^2} = \frac{2NK_B}{(T/\beta_P)^2}\frac{1}{e^{\frac{\beta_p}{T}}} \qquad (15)$$

Developing exponential terms of $e^{\frac{\beta_p}{T}}$ we have to for (15)

$$C_V = \frac{2NK_B}{(T/\beta_P)^2}\frac{1}{e^{\frac{\beta_p}{T}}} = \frac{2NK_B}{(T/\beta_P)^2 + T/\beta_P + 1/2! + (1/3!)(\beta_P/T) + (1/4!)(\beta_p/T)^2 \ldots} \qquad (16)$$

According to (16), the first two terms in the denominator are close to zero but the following ones tend towards infinity so that $C_V \to 0$ for $T \to 0$ behavior similar to that observed in thermal capacity for crystalline solids [5].

The second limiting case is the situation at high temperatures, i.e. $T \to \infty$, which is equivalent to $T >> \beta_p$. When developing the exponential terms in equation (14) it is found that:

$$C_V = \frac{NK_B}{2}\left(\frac{\beta_p}{T}\right)^2 \frac{1 + \beta_p/T + (1/2!)(\beta_p/T)^2 + (1/3!)(\beta_p/T)^3 + \ldots}{\left(1 + \frac{1}{2}\left(1 + \beta_p/T + (1/2!)(\beta_p/T)^2 + (1/3!)(\beta_p/T)^3 + \ldots\right)\right)^2} \qquad (17)$$

In the denominator only 3/2 is retained because and its superior powers are negligible because 3/2 >> $\beta p/T$ and for the same reason in the numerator you can cancel all terms except the one and it turns out

$$C_V = \frac{2NK_B}{9}\left(\frac{\beta_p}{T}\right)^2 \qquad (18)$$

According to (18) when $T \to \infty$ will have to be $C_V \to 0$ being the same result as in the previous limiting case. It is to be expected then that C_V reaches a maximum value between the extremes of high and low temperature, implying that at the maximum

$$\frac{dC_V}{dT} = 0 \qquad (19)$$

and differentiation of (14) can be expressed as:

$$\frac{dC_V}{dT} = \frac{NK_B}{2}\left[\frac{d}{dT}\left(\frac{\beta_p}{T}\right)^2 \frac{e^{\frac{\beta_p}{T}}}{\left(1 + \frac{1}{2}e^{\frac{\beta_p}{T}}\right)^2} + \left(\frac{\beta_p}{T}\right)^2 \frac{d}{dT}\left(\frac{e^{\frac{\beta_p}{T}}}{\left(1 + \frac{1}{2}e^{\frac{\beta_p}{T}}\right)}\right)\right] = 0 \qquad (20)$$

From equation (20) the maximum value of C_V will be reached when the condition is met

$$\frac{\beta_p}{2T} = \frac{1 + \frac{1}{2}e^{\frac{\beta_p}{T}}}{-1 + \frac{1}{2}e^{\frac{\beta_p}{T}}} \qquad (21)$$

Expressing (21) as a function of parameter $x = \beta_p/2T$ we have

$$x = \frac{1 + \frac{1}{2}e^{2x}}{-1 + \frac{1}{2}e^{2x}} \qquad (22)$$

Equation (22) can be solved by successive iterations using the fixed-point iteration method [16] (see appendix) and choosing the electric field Ɛ, the appropriate permanent dipolar moment p and the Boltzmann constant, calculate the respective temperatures for which thermal capacities reach their highest values. Table I shows p values for different polar molecules, together with the maximum temperatures and C_V reached for a specific electric field, where it has been considered that N=6.02x10^{23} molecules, K_B = 1.38X10^{-23} J/K and Ɛ = 1x10^6 V/m.

Table No 1: Permanent dipole moments of some molecules with the respective maximum temperatures and thermal capacities reached. In all the cases Ɛ=1x10^6 V/m

Molecule	p(x10^{-30} C.m)*	$(C_V)_{máx}$ (J/K)	Temperature (K)
CO	0.501	6.36	0.0274
HCl	3.740	6.33	0.204
HF	6.035	6.33	0.330

*Source: [17] Chupp et al. (2019)

Figure 1 shows the variation of thermal capacity with temperature for molecules with different dipole moments. In all the cases studied $(C_V)_{máx}$ is the same for all three substances and not depend on p value or electric field Ɛ. The approximate solution for (22) is x ~ 1.3273 por lo que . $\beta_p/T = 2\varepsilon p/K_B T \approx 2.6546$ Replacing β_p/T in expression (14) for C_V and with assigned values for N y K_B is obtained for the thermal capacity C_V = 6.33 J/K , which is consistent with the highest C_V value for the three studied cases, independent of the permanent dipole moments of the molecules while the temperatures at which C_V is maximized are increased by the dipole moments of the molecules.

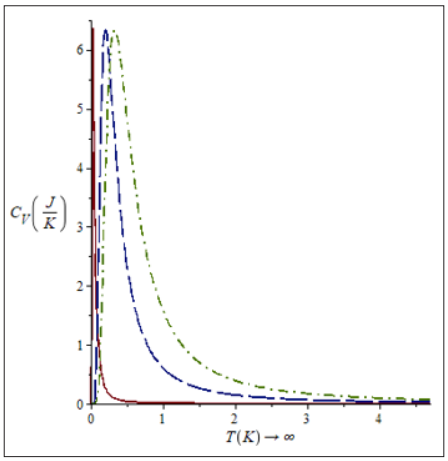


Figure N°1: Thermal Capacity C_V against temperature for the chosen molecules. The solid line corresponds to CO, the long-dash line to HCl, dash-dot line to HF.

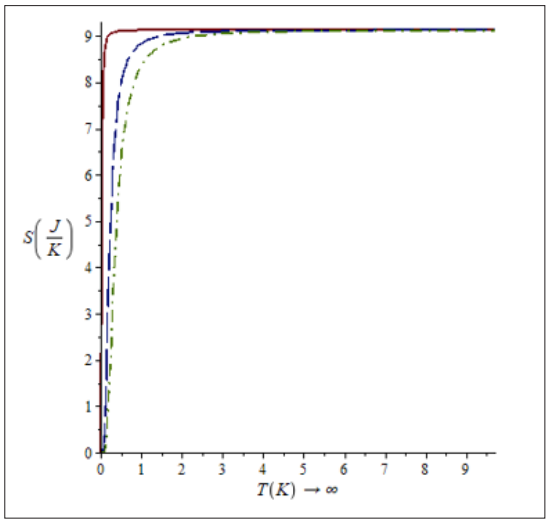


Figure N°2: Variation of entropy vs temperature for the molecules considered. The solid line corresponds to CO, the long-dash line to HCl, dash-dot line to HF.

Figure 2 shows how entropy changes with temperature for all cases studied. As is to be expected, when $T \to \infty$ we have $S \to NK_B \ln 3$ which is equivalent to 9.13 J/K, for each of the individual molecules.

Relative fluctuations of energy

It is already known that the average energy and total energy of the system for N molecules is given by (5) and (6) respectively. The standard deviation is defined as [4]:

$$(\Delta E)^2 = \overline{E^2} - \overline{E}^2 \qquad (23)$$

Then, deriving *lnZ* twice with respect to β is that

$$\frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 + \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} \qquad (24)$$

but $\overline{E^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$ and from (24) it follows that

$$(\Delta E)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial \overline{E}}{\partial \beta} = K_B T^2 \left(\frac{\partial \overline{E}}{\partial T}\right)_V = K_B T^2 C_V \qquad (25)$$

From equation (25) is obtained for the relative fluctuation [4,12]

$$\frac{\Delta E}{E} = \frac{\left(K_B T^2 C_V\right)^{1/2}}{E} \qquad (26)$$

The fluctuation can then be determined for the high-temperature limiting situation, i.e. β_p / T << 1 . Replacing (7) and (13) in (26) and considering $e^{\frac{\beta_p}{T}} \approx 1 + \frac{\beta_p}{T}$ can be written for the quotient $\Delta E/E$:

$$\frac{\Delta E}{E} = \frac{\left(K_B T^2 \frac{NK_B}{2}\left(\frac{\beta_p}{T}\right)^2 \frac{\left(1+\frac{\beta_p}{T}\right)}{\left(\frac{3}{2}+\frac{\beta_p}{2T}\right)^2}\right)^{1/2}}{\frac{4}{3}N\varepsilon p} \approx \frac{1}{\sqrt{2N}} \qquad (27)$$

so when $T \to \infty$ the relative fluctuation of energy is inversely proportional to the square root of the number of molecules and the fluctuations are very small, i.e. $\Delta E/E \to 0$. This means that for the macroscopic system where N ~ 10^{23} the energy of the system shall be fully determined [12].

For the temperature at which the peak of C_V is reached, the relative fluctuation can also be calculated. In this case it has to solve equation (22) from which one obtains $x = \beta_p / 2T = \varepsilon p / K_B T \approx 1.3273$ and replacing in (6), (14) and (26) we have:

$$\frac{\Delta E}{E} = \frac{\left(1+\frac{1}{2}e^{\frac{2\varepsilon p}{K_B T}}\right)\left(K_B T^2 C_V\right)^{1/2}}{2N\varepsilon p} \approx \frac{2.6}{\sqrt{N}} \qquad (28)$$

Again, the fluctuations are very small, indicating that at the maximum of Figure 3 energy has a well-defined value. The fact that $\Delta E/E$ is negligible means that the probability distribution $P(E)$ in statistics MB has an acute peak in mean energy $\overline{E}$, as shown in the following figure:

***P*(E)**

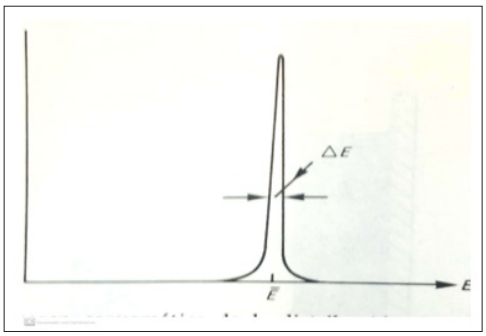


Figure N° 1. Probability distribution of energy $P(E)$ for a macroscopic system

Conclusions

In this paper we have studied the behaviour of molecules with permanent electric dipole moment subjected to an external electric field using the statistical mechanics of Boltzmann in which we consider that the physical variables describing a system are associated with the most probable quantum states that it may occupy. The variation of thermal capacity with temperature has been analysed and it is found that the maximum value of C_V for

molecules with different values of permanent electric dipole moment tends to 6.3 J/K and the temperatures at which thermal capacities reach their maximum values are increase by increasing the permanent dipole moments of the molecules. Relative fluctuations are also analysed when $T \to \infty$ and for temperatures where C_V reaches the maximum possible value.. In both cases $\Delta E/E \leq 10^{-12}$ so that for the cases studied the total energy of the collective of N molecules will always be completely determined.

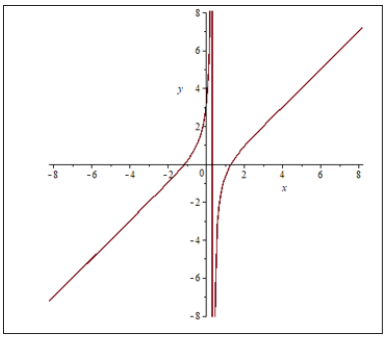
Appendix

Fixed Point Iteration Method

Following Burden and Faires [16] a fixed point of a function g is a number p for which $g(p)= p$. According to this definition if you want to find a root $f(p)=0$ you can choose a function g with a fixed point in p in several ways, for example as $g(x) = x- f(x)$. If this function g has a fixed point in p then the function defined as $f(x)= x – g(x)$ has a zero in p. On the basis of these considerations a root for equation (22) can be calculated if it is expressed as follows:

$$x = \frac{2 + e^{2x}}{-2 + e^{2x}} \quad \text{A.1}$$

Equation (29) will have a single real root in the interval [1,2] as illustrated in the following figure



With $p_o = 1.5$ the following table provides the results by the fixed point iteration method

n	A.1
0	1.5
1	1.221171205
2	1.422250902
3	1.264624374
4	1.160919214
5	1.489256280
6	1.226144574
7	1.416166114
8	1.267033648
9	1.377222522
10	1.291708503
11	1.355805891
12	1.306430780
13	1.343701044
14	1.236342291
15	1.405917143
16	1.273216327
17	1.371695471
18	1.295429927
19	1.352695176
20	1.308638277
21	1.341928095
22	1.316419529
23	1.335761609
24	1.320976252
25	1.332209602
26	1.323634883
27	1.325885939
28	1.328430412
29	1. 326491143
30	1.327967968
31	1.327411671
32	1.327266004
33	1.32737697
34	1.327292434

By rounding of significant numbers x ≈ 1.3273

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