Thermodynamic properties of diatomic molecules systems under anharmonic Eckart potential

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Abstract

Due to one of the most representative contributions to the energy in diatomic molecules being the vibrational, we consider the generalized Morse potential (GMP) as one of the typical potential of interaction for one–dimensional microscopic systems, which describes local anharmonic effects. From Eckart potential (EP) model, it is possible to find a connection with the GMP model, as well as obtain the analytical expression for the energy spectrum because it is based on \(SO(2,1)\) algebras. In this work we find the macroscopic properties such as vibrational mean energy \(U\), specific heat \(C\), Helmholtz free energy \(F\) and entropy \(S\) for a heteronuclear diatomic system, along with the exact partition function and its approximation for the high temperature region. Finally, we make a comparison between the graphs of some thermodynamic functions obtained with the GMP and the Morse potential (MP) for \(H Cl\) molecules.

Keywords: generalized Morse potential, thermodynamic functions.

1 Introduction

In the study of systems made up of many particles and phenomena of matter, statistical physics has been able to interpret and predict several macroscopic properties from them through the average of dynamic amounts over a specific number of particles. To obtain the macroscopic variables it is necessary to take into account that for real macroscopic systems the transitions between their quantum states occur randomly and quickly; for this reason, these macroscopic observables depend on the average of the expected dynamic values \([1, 2]\). From the point of view of quantum statistical mechanics it is particularly interesting that to resolve the thermodynamics of these systems, we must count with their dynamic equation (Eq. Schrödinger) which contains as close as possible the real information on the evolution of all above systems. A detailed study for any molecule should consider all the contributions to the energy, because in most cases one establishes that intrinsic movements (vibrations, rotations, etc.) of them that shape a particular gas (system) are independent of each other, then we proceed to study them separately \([3, 4]\).

The experiments based on spectroscopy show that there are anharmonicities in real molecular vibrations systems \([4, 5]\), therefore it is essential to know the algebraic model for the potential and the technique used to solve the Schrödinger equation. For example, anharmonicities are usually introduced in some models as a perturbation to the harmonic oscillator \([6, 7]\). There are several potential that can be considered to emulate the molecular vibrational spectrum of a gas composed of diatomic molecules (section 2) and can be compared through the experimental data \([8]\). The purpose of this work is to compare the thermodynamic properties of two anharmonic quantum models for one-dimensional systems (1D) \([9]\), which consist of exact solutions.

The fundamental characteristic of these anharmonic potentials consist of a finite energy spectrum and anharmonicites are introduced by means of dynamic groups obeying a particular algebra. Using the connection between the dynamic parameters of the potential GMP and EP, it is possible to take a more manageable expression to obtain the eigenvalues \([10]\), such that systems under study consist of heteronuclear molecules formed by a hydrogen ion and one of the four most electronegative ions of the VII A group in the periodic table (\(H F\), \(H Cl\), \(H Br\) and
we take into account also that the molecules are formed in the ground electronic state. In Section 3, we
derive the partition function without an approximation i.e. the “Zustandssumme” and with the approximation of
high vibrational temperatures to obtain the basic thermodynamic functions, such as the mean vibrational energy,
specific heat, free energy, etc. since they are only in terms of the model parameters. In Section 4 a comparative
analysis of some thermodynamic functions is obtained by the GMP and the MP, that has been studied in recent
works and are applied to HCl system [11]. Eventually, the concluding remarks are given in Section 5.

2 Generalized Morse Hamilton model

We considered initially the Schrödinger equation (1D) whose interaction is mediated through a potential intro-
duced by Deng and Fan [9]. This potential describes the energy spectrum of diatomic molecules as well as their
electromagnetic transitions, and is refered to literature as the generalized Morse potential (GMP) [10, 12].

\[
\left[ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + D \left( \frac{b}{\exp(ar) - 1} \right) \right] \psi(r) = E\psi(r); \quad b = \exp(ar) - 1.
\]  

(1)

Where \(0 \leq r < \infty\), \(D\) is the depth of the potential well, \(a\) is related with its width, \(r_e\) is the equilibrium position
with respect to a given origin and \(\mu\) is the reduced mass of the molecule. Sometimes the GMP is related to the
Manning–Rose potential also known as Eckart potential (EP). One can verify that this potential has the same
behavior as the internuclear potential of diatomic molecules [5, 12].

In order to obtain a dynamic equation with dimensionless variables, we make the change of variable
\(y = \exp x - 1\), the Schrödinger equation (1) is rewritten as:

\[
\left[ \frac{d^2}{dx^2} + \frac{2\mu D}{a^2\hbar^2} \left( 1 - \frac{b}{\exp(x - 1)} \right)^2 \right] \psi(x) = \frac{2\mu E}{a^2\hbar^2} \psi(x),
\]  

(2)

there are several ways to solve these kind of equations, one of them is the analytical form presented in [9], in which
by means of a new variable \(y\) and a function \(F(y)\), one can define

\[
y = (\exp x - 1)^{-1}
\]  

(3)

\[
\psi(x) = \Phi(y) = \frac{y^\eta}{(1 + y)^\beta} F(y),
\]  

(4)

where \(\alpha\) and \(\beta\) are chosen in a proper way, so there is a physical sense. When introducing (3) and (4) into (2), we
obtain the following equation:

\[
y (1 + y) \frac{d^2F}{dy^2} + \left[ 2(\eta - \nu + 1) y + (2\eta + 1) \right] \frac{dF}{dy} + \left[ (\eta - \nu)^2 + (\eta - \nu) - \frac{2\mu D}{a^2\hbar^2} b^2 \right] F(y) = 0.
\]  

(5)

One of the solutions already explored, corresponds to a confluent hypergeometric function and is given as follows:
\(F(y) =_2 F_1 (d; e; 2\eta + 1; -y)\) with

\[
d = \eta - \nu + l \\
e = \eta - \nu + 1 - l \\
l = \frac{1}{2} \left( 1 + \sqrt{1 + k^2} \right) = \frac{1}{2} \left( 1 + \sqrt{1 + \frac{2\mu D}{a^2\hbar^2} b^2} \right)
\]  

(6)

As it is desired that the \(\eta\) parameter is related to the system energy spectrum (solution of Eq. 5), then each
\(\epsilon_n\) can be expressed in terms of a \(\eta_n\), such that if \(\eta = \sqrt{k - \epsilon} \implies \epsilon_n = k - \eta_n^2\), with \(k\) a fixed parameter so
the energy spectrum becomes finite. It is concluded that the energy eigenvalues are given by:

\[
E_n = D - \frac{a^2\hbar^2}{8\mu} \left( n + l - \frac{bk(b + 2)}{n + l} \right)^2.
\]  

(7)

It is important to note that the quantum numbers \(n\) form a finite set of values, whose supreme \(n_{\text{max}}\) is assumed
integer (for the real case of molecular interactions this value has to be taken as its integer part),

\[
n = 0, 1, 2, \ldots, n_{\text{max}}; \quad n_{\text{max}} = \sqrt{kb(b + 2)} - l.
\]  

(8)
2.1 Connection between GMP and EP potentials

It has been found that in the eigenvalue problem there are symmetry algebras that offer an alternative solution to those already well-known. In particular a set of techniques based on the $SO(2, 1)$ algebra can be used, whose purpose is to build the hypergeometric Natanzon potentials [10, 13]. The aim of the above is to transform a Schrödinger equation in one of these potentials through $SO(2, 1)$ algebra, taking into account that their generator groups $\mathcal{J}_0$ and $\mathcal{J}_\pm = \mathcal{J}_1 \pm i \mathcal{J}_2$ form the Casimir operator $C$ that is written as $C = \mathcal{J}_0 (J_0 \pm 1) - \mathcal{J}_\mp \mathcal{J}_\pm$. The Schrödinger equation is rewritten in terms of the Casimir operator and takes the form $[H - E] \Psi(r, \phi) = G(r) [C - q] \Psi(r, \phi)$, where $q$ is the eigenvalue of $C$ whereas $E$ is the corresponding eigenvalue of the Hamiltonian $H$.

In general, GMP and EP are given by

$$V_{GMP} = K_1 \left( 1 - \frac{K_2}{\exp(\omega r) - 1} \right) + K_3, \quad (9)$$

$$V_E = A^2 + \frac{B^2}{A^2} - 2B \coth(\alpha r) + A(A - \alpha) \text{csch}(\alpha r)^2 \quad (10)$$

due to the set of constants $(K_1, K_2, K_3)$ and $(A, B, \alpha)$ can be related as follows:

$$A^2 + \frac{B^2}{A^2} = (1 + K_2 + \frac{1}{2}K_2^2) K_1 + K_4; \quad 2B = \frac{1}{2}K_1K_2(K_2 + 2); \quad A(A - \alpha) = \frac{1}{2}K_1K_2^2; \quad \alpha = \frac{\omega}{2}. \quad (11)$$

The $V_{GMP}$ and $V_E$ are the same function. The functional form of the hypergeometric Natanzon potentials are given by [10, 11]

$$V_N = \frac{1}{R} \left[ f z(r)^2 - (h_0 - h_1 + f) z(r) + h_0 + 1 \right] + \frac{z(r)^2(1 - z(r))^2}{R^2} \left[ a + \frac{a + (c_1 - c_0)(2Z(r) - 1)}{z(r)(z(r) - 1)} - 5\frac{\Delta}{4R} \right], \quad (12)$$

with $\Delta = \tau^2 - 4ac_0$, $\tau = c_1 - c_0 - a$ and $R = az(r)^2 + \tau z(r) + c_0$. The constants $(a, c_0, c_1, h_0, h_1, f)$ are called Natanzon parameters, besides the function $z(r)$ to satisfy

$$\frac{dz(r)}{dr} = \frac{2z(r)(1 - z(r))}{\sqrt{R}}. \quad (13)$$

One can check that the Natanzon parameters for Eckart potential are

$$a = c_0 = a^2 \quad c_1 = 0 \quad h_0 = \frac{(A^2 + B)^2}{A^2a^2} - 1$$
$$h_1 = \frac{4A(A - \alpha)}{a^2} \quad f = \frac{(A^2 - B)^2}{A^2a^2} - 1 \quad (14)$$

and $z(r)$ must be

$$z(r) = \exp(2ar). \quad (15)$$

With all the above, the energy spectrum of EP can be obtained according to Codriansky et al [10], where it is required that $E_n(n=0) = 0$ and this result leads to

$$E_n^{GMP} = A^2 + \frac{B^2}{A^2} - (A + \alpha n)^2 - \frac{B^2}{(A + \alpha n)^2}, \quad n = 0, \ldots, n_{max} \quad (16)$$

the value $n_{max}$ corresponds to an upper bound of $E_n$, which accomplishes $E(n) \leq V_E(r \to \infty) = (B - A^2)^2/A^2$ and therefore from Eq. [16] we obtain $n_{max} = \left\lceil (\sqrt{B} - A)/\alpha \right\rceil$, where $\lceil \rceil$ means the integer part of $(\sqrt{B} - A)/\alpha$, and also $B > A^2$ has to be accomplished.

If we compare the expression obtained for the GMP energy spectrum [7] and the other deduced for the EP [10], we note that this last expression is more useful for the following.
Table 1: Spectroscopic data of heteronuclear molecules formed by a hydrogen ion and ions of the VII A group

| Molecule | μ (Kg) | D (J)     | d (m)     | r_e (m)   |
|----------|--------|-----------|-----------|-----------|
| HF       | 1.5897 × 10^{-27} | 9.430 × 10^{-19} | 0.430 × 10^{-10} | 0.9171 × 10^{-10} |
| HCl      | 1.6276 × 10^{-27} | 8.520 × 10^{-19} | 0.570 × 10^{-10} | 1.2746 × 10^{-10} |
| HBr      | 1.6531 × 10^{-27} | 7.705 × 10^{-19} | 0.605 × 10^{-10} | 1.4130 × 10^{-10} |
| HI       | 1.6608 × 10^{-27} | 6.648 × 10^{-19} | 0.650 × 10^{-10} | 1.6040 × 10^{-10} |

3 Macroscopic response of diatomic molecular systems

One of the objectives of thermodynamics consists of estimating the free energy (what can be converted in work) which is obtained from the interchanged heat and mass by the system under study and the surroundings. This macroscopic behavior is the result of interactions that occur between the constituent elements of each system. In general they can be considered open or closed systems. In order to find an expression that describes the behavior of these systems that consider both the restrictions imposed and its evolution to the final equilibrium state, by means of the ensemble theory, we can build from the averages of microscopic quantities the fundamental equation of such systems [13].

Some of the systems whose microscopic components can factor their internal freedom degrees due to its well-defined symmetry are diatomic molecules. In particular we consider the set of gases made-up of heteronuclear systems [15].

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Some of the systems whose microscopic components can factor their internal freedom degrees due to its well-defined symmetry are diatomic molecules. In particular we consider the set of gases made-up of heteronuclear molecules: HF, HCl, HBr and HI, for this set the contribution to the total energy with more statistical weight corresponds to the vibrational energy [15, 13]. Naturally, it provides that each microstate of the system is characterized by extensive set of variables (N, V, T) with energy E_n.

3.1 Diatomic molecular system at the canonical ensemble for the GMP

Before studying the thermodynamic properties of the above set of molecules, it is necessary to obtain the anharmonic vibrational individual partition function of this kind of molecules:

\[ z_{GMP}^{\text{GMP}} = \sum_{n=0}^{\left[\sqrt{\frac{\pi}{\alpha}}\right]} e^{-\beta E_n}, \]  

(17)

where \( \beta = \frac{1}{k_B T} \), whereas the anharmonic energy spectrum \( E_n \) is given by [16]. The individual partition function is determined by the parameters \( (A, B, \alpha) \), which can be directly related to the mechanical energy of molecules. Introducing the parameter \( P = A^2 + B^2/\alpha^2 \), the exact partition function can be written as:

\[ z_{GMP}^{\text{GMP}} = e^{-\beta P} \sum_{n=0}^{\sqrt{\frac{\pi}{A}}} \exp \beta (A + \alpha n)^2 + \frac{B^2}{(A + \alpha n)^2}. \]  

(18)

When one considers the high temperature region \( T \gg 1 \) the energy states can be seen almost as a continuous spectrum, therefore we can replace with good approximation the sum by the integral in (Eq. 18):

\[ z_{GMP}^{\text{GMP}} = \frac{e^{-\beta P}}{\alpha} \int_{[\sqrt{\pi}]}^{[\sqrt{B}]} \exp \left[ \beta \left( m^2 + \frac{B^2}{m^2} \right) \right] dm, \]  

(19)

with \( m = A + \alpha n \). This integral can be evaluated exactly using the properties of the denote integral as well as the imaginary error function \( \text{erfi}(x) \),

\[ z_{GMP}^{\text{GMP}} = \frac{e^{-\beta P}}{\alpha} \left[ \frac{e^{-2\beta B} \sqrt{\beta}}{4\sqrt{\beta}} \left( e^{4\beta B} \text{erfi} \left( \frac{B}{A} - A \right) \sqrt{\beta} \right) + \text{erfi} \left[ 2\sqrt{\beta B} \right] - \text{erfi} \left( \left( \frac{B}{A} + A \right) \sqrt{\beta} \right) \right]. \]  

(20)

This equation represents the extended sum over all accessible microstates in the high temperatures region whose interaction is of the type GMP, and is only a function of parameters which are directly related to the energy that the system can exchange. For the set of diatomic molecules considered, it is necessary to list some useful values for their energetic study. In Table 1 we can find the reduced mass \( \mu \), the depths of of the GMP well (dissociation
energies) \(D\), the widths of GMP well \(d\) and the equilibrium points of the interaction potential \(r_e\). These values can be derived directly or indirectly from the spectroscopic data of the emission lines and we specially focus our attention in the \(X^1\Sigma^+\) state for each molecule [5].

By solving simultaneously (11), we find the values of \(A\) and \(B\) as follows:

\[
B = \frac{1}{4}Db(b + 2),
\]

\[
A^2 + \frac{B^2}{A^2} = K_1 \Rightarrow A^2 = \frac{K_1 - \sqrt{K_1 - 4B^2}}{2}, \quad K_1 = D\left(1 + b + \frac{1}{2}b^2\right).
\]

(21)

Figure 1: Graphs of anharmonic vibrational individual partition functions \(z^{GMP}\) (solid lines) and \(\tilde{z}^{GMP}\) (dashed lines) of \(HF\) (red), \(HCl\) (blue), \(HBr\) (green) and \(HI\) (black) as functions of \(\beta\). Solid lines represent the states that are counted in the region of high temperatures, while dashed lines denote all states that can be in all temperatures.

Substituting the values of \(J\) for each molecule, we can obtain numerically the individual partition function \(\tilde{z}^{GMP}\) as a function of \(\beta\). In Fig. 1 the approximate partition functions (solid curve) for values of \(\beta\) between 0 and 0.25 are presented, as well as the exact partition functions (dashed curve). As we can observe in the region \(0 < \beta < 0.25\), \(z^{GMP}\) is a good approximation of the exact "Zustandssumme" \(z^{GMP}\). In this interval one can verify that the integrals are slightly offset from value with respect to its accurate representation compared from their relative minimum. On the other hand, in the region corresponding to \(0.25 < \beta < 1\), we can verify the eight lines (approximate and exact) overlap. The statistical physics which follows from this model is a first approximation; for the realizations and transitions between quantum states of molecules, this approximation is valid for the temperature region lower than its dissociation energy. Nevertheless, a more realistic description requires states not tied to the potential.

Once we have found the individual partition function \(\tilde{z}^{GMP}\) in terms of GMP parameters, we can build the corresponding thermodynamic functions, which are presented in the following subsection.

### 3.1.1 Thermodynamic functions

Now we will study the thermodynamic properties of these systems derived from canonical ensemble.

The molar vibrational internal energy in the region of high temperature, is given by:

\[
u^{GMP} = -\frac{\partial}{\partial \beta} \ln z^{GMP} = -\frac{1}{\tilde{z}^{GMP}} \frac{\partial \tilde{z}^{GMP}}{\partial \beta}.
\]

(22)

If the analytical expression of \(z^{GMP}\) (Eq 20) is taken and then is replaced in (22), an analytical expression for \(u\) is obtained. It is clear that \(u\) depends on the parameters \((A, B, \alpha)\). Figure 2 shows the average vibrational energy of each molecule that has already been mentioned above. We can see in the region \((0 < \beta < 0.5)\), the curves exhibit...
the well-known characteristic monotone decreasing behavior. In \( \beta = 0 \), the value of \( u \) of the 4 systems correspond to different values. This is because of the GMP depth generated by each molecule is different and therefore the partition function counts different states, whereas in the range \((0.5 < \beta < 1)\) curves are overlapped.

Now we consider the vibrational contribution to the Helmholtz free energy per molecule in terms of the partition function \( \tilde{z} \) which is calculated for the region of high temperatures as

\[
f^{\text{GMP}} = -\frac{1}{\beta} \ln \tilde{z}^{\text{GMP}}
\]

We observe in Figure 3 that the curves of the molar Helmholtz free energy attain maximum values for different temperatures, which are \( \beta_{HF} = 0.3107 \), \( \beta_{HCl} = 0.5366 \), \( \beta_{HBr} = 0.4395 \) and \( \beta_{HI} = 0.8647 \). In addition, for systems \((HF, HCl, HBr and HI)\) their free energies decay asymptotically in the region of low temperatures. As we can see, there is a hierarchy for each system composed of one of four different molecules which are in contact with a thermal reservoir. So it can be interpreted as the available chemical work that sets out every gas. The graph 3 agrees with the experimental fact, in which a \( HF \)–gas has the corrosive properties severer than the others.

The vibrational specific heat at constant volume is obtained from the expression:

\[
c^{\text{GMP}}_v = \frac{\partial u^{\text{GMP}}}{\partial T} = -k_B \beta^2 \frac{\partial u^{\text{GMP}}}{\partial \beta}.
\]

By substituting the expression from (22) into (24), we verify that \( c^{\text{GMP}}_v / k_B \) (normalized by the Boltzmann constant) is also expressed in terms of the parameters of the potential. In Figure 4, we show the anomalous behavior of the specific heat when diatomic systems interact under the GMP. Anharmonicity effects are apparent to the values \( \beta_{HF} \leq 0.120 \), \( \beta_{HCl} \leq 0.168 \), \( \beta_{HBr} \leq 0.121 \) and \( \beta_{HI} \leq 0.221 \), each of these values correspond to the characteristic vibrational temperatures of the molecules \((\Theta_{HF} \approx 5954.11K, \Theta_{HCl} \approx 4300K, \Theta_{HBr} \approx 3787K and \Theta_{HI} \approx 3266K)\). Anharmonics contributions of the analytical model (24) depend mainly on the parameter \( \beta \). The specific heat for this model has a maximum for a value \( \beta = \beta_C \) corresponding to a temperature \( T = T_C \). This is due to the finite number of states of the algebraic model. It means for a system composed of diatomic molecules whose potential energy is of the type GMP, it has a critical temperature value in which the system become saturated and can no longer absorb more energy because all its exited states are occupied.

This model illustrates the behavior of the specific heat without regard to other degrees of freedom, so the relative value \( T_C \), for each molecule is \( T_C^{HF} = 13662.1K \), \( T_C^{HCl} = 8440.8K \), \( T_C^{HBr} = 13424.8K \) and \( T_C^{HI} = 4570.4K \). On the
Figure 3: Anharmonic vibrational contribution to the free energy per molecule $f_{GMP}$ of $HF$ (red line), $HCl$ (blue line) $HBr$ (green line) and $HI$ (black line) as function of $\beta$. It is observed that the maximum of the functions will reach larger values when the interaction potential hosts more states.

Figure 4: Specific heat $c_{v}^{GMP}/k_B$ for $HF$ (red line), $HCl$ (blue line), $HBr$ (green line) and $HI$ (black line) as function of $\beta$. 
Figure 5: Comparison between the curves of the GMP (solid line) and the Morse potential (dashed line). The parameters used have the following values $d^{-1} = a = 1.7543 \times 10^{10} m^{-1}$, $r_c$ or $x_e = 1.2746 \times 10^{-10} m$ and $D = 8.52 \times 10^{-19} J$, which are the spectroscopic values for the molecule $HCl$.

other hand, the region $T > T_C$ considers the continuum states, therefore the most important contribution is the translational.

Finally, we can express the entropy as a state function in terms of the partition function, the vibrational individual contribution to the entropy is obtained as

$$s^{GMP} = k_B \ln z^{GMP} + k_B \left( \frac{\partial \ln z^{GMP}}{\partial T} \right) = k_B \left[ \ln z^{GMP} - \beta \frac{\partial z^{GMP}}{\partial \beta} \right].$$

(25)

In this section we have obtained the most important thermodynamic functions, all in terms of the imaginary function error erfi$(x)$, because the energy spectrum is bounded for the GMP.

4 A comparison of some thermodynamic properties between GMP and Morse

There are many proposals to study the collective behavior of a system of diatomic molecules via the algebraic model of a potential interaction between the two ions [6, 11]. Morse potential has been a good proposal, since in recent articles has been resolved exactly and therefore the vibrational thermodynamic functions of the gas have been obtained. It is considered that the expression of one-dimensional Hamiltonian for the MP is,

$$H = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + D \left( 1 - \exp \left[ -\frac{(x - x_e)}{d} \right] \right)^2,$$

(26)

with $D$ the depth of potential, $d$ the width, $x_e$ the displacement from the equilibrium position and $\mu$ the reduced mass of the oscillating system. We note that MP is a particular case of the GMP when $b = 1$ and when $\exp (x/d) \gg 1$ (see Fig. 5). The individual vibrational spectrum of energy is written as

$$E_{n}^{MP} = \hbar \omega_0 \left( n + \frac{1}{2} - \frac{n^2}{N} \right), \quad n = 0, \ldots, \frac{N}{2}.$$

(27)

where $\omega_0$ is the harmonic oscillator frequency and $n$ is the number of quanta in the oscillator. M. Angelova et al [11] obtained analytical expressions of some thermodynamic vibrational functions. Some worth remarking with
regard to this potential model is the dependency of the \( N_0 \) parameter, which is the maximum number of bosons per oscillator. Thus, the individual partition function, molar internal energy and specific heat for the MP are as follow,

\[
\begin{align*}
    z_{MP} & = \frac{1}{\sqrt{2}} \sqrt{\frac{N_0 \pi}{\Theta k_B \beta}} e^{-\Theta k_B \beta/2(N_0+1)} \text{erfi}\left(\sqrt{\frac{\Theta k_B \beta}{2} N_0}\right) \\
    u_{MP} & = \frac{\Theta k_B}{2} \left( 1 + N_0 + \frac{1}{\Theta k_B} - \sqrt{2 \frac{N_0}{\Theta k_B \beta}} \frac{e^{N_0(\Theta k_B \beta/2)}}{\text{erfi}\left(\sqrt{\frac{\Theta k_B \beta}{2} N_0}\right)} \right) \\
    c_{MP} & = \frac{k_B}{2} + k_B \sqrt{\frac{\Theta k_B \beta N_0}{2\pi}} \left( \frac{\Theta k_B \beta N_0}{2} - \frac{1}{2} - \sqrt{\frac{\Theta k_B \beta N_0}{2\pi}} \frac{e^{N_0(\Theta k_B \beta/2)}}{\text{erfi}\left(\sqrt{\frac{\Theta k_B \beta}{2} N_0}\right)} \right).
\end{align*}
\]

As can be seen these functions also depend on the parameters of MP. By following the previous work \cite{11} we take the diatomic molecule \( HCl \) as an example for comparing the behavior of the thermodynamic properties between GMP–gas and MP–gas. It is important to note that in both gas models, GMP–gas (solid line) and MP–gas (dashed line), these thermodynamic properties depend explicitly on the \( \text{erfi}(x) \). Figure 6 shows the comparison between the individual partition functions in the interval \( \beta \in [0, 1] \). Both curves have the same behavior monotonous decreasing and reach zero asymptotically at the same value of \( \beta \). This is because both potentials contain almost the same quantum states. In Fig. 7 the internal energies of the two models also decay asymptotically for low temperature values, however for \( \beta \rightarrow 0 \), \( u_{MP}(0) \rightarrow 59.896 \times 10^{-20} \text{J} \) and \( u_{GMP}(0) \rightarrow 47.896 \times 10^{-20} \text{J} \). This indicates that in general a system with a Morse interaction is more energetic than a system with GMP interactions. Finally, we note in Fig. 8 that the specific heat for both models has the same intense effects of anharmonicities in the region \( \beta < 0.168 \). The maximum reached with the MP is shifted to the left with respect to GMP, such that \( T_{MP} \approx 9815 \text{K} \) and \( T_{GMP} \approx 8441 \text{K} \). This means that a Morse molecular interaction has the ability to energize many molecules and leave them in the quantum states more energetic than GMP–interaction, which agrees with the behavior of the internal energy afore mentioned.
Figure 7: This graph represents the vibrational internal energy $u_{\text{MN}}^M$ (dashed line) and vibrational internal energy $u_{\text{GMP}}^M$ (solid line) both in terms of the $\beta$ parameter.

Figure 8: Vibrational specific heat $c_{\text{MN}}^M/k_B$ (dashed line) compared to vibrational specific heat $c_{\text{GMP}}^M/k_B$ (solid line) as function of $\beta$. 
5 Concluding Remarks

In the present paper, we have reaffirmed once again that the potential derived from Deng and Fan models [9], as well as the Manning–Rosen type models [16] are good candidates to emulate the vibrational energy spectrum of the ground state of several diatomic molecules. In order to get a better description for heteronuclear diatomic molecules, in particular: \textit{H F}, \textit{H Cl}, \textit{H Br} and \textit{H I}, we considered the algebraic model of GMP which turns out to be a class of the Eckart potential due to its equivalences with algebraic group \textit{SO}(2, 1). Taking advantage that the exact energy spectrum model for the EP is easy to operate, we can obtain the individual partition function analytically and thus derived the vibrational contribution to the thermodynamic functions of these systems. Thermodynamic functions have already derived and have the particularity that they depend on the interaction of the model parameters (GMP) and hence the anharmonic effects are evident in the region of high–temperatures (between the dissociation energy and vibrational characteristic energy). Proof of this is the anomalous behavior in heat capacity [17]. However, at \( T \ll 1 \) we notice that the function \( e^{GMP}/k_B \) converges to the harmonic limit (\( \left[ (\sqrt{\beta - A})/\alpha \right] \rightarrow \infty \)), that is because the individual vibrational partition function takes into account a classical states density and therefore it continues to fulfill the principle of energy equipartition. It is very important to note, the algebraic model of \( V_{GMP} \) keeps up a pseudo–quantum behavior. In order to obtain a complete description we need to introduce a dynamic model which includes the collective aspects of the molecules that make up the gas [1, 2].

In order to verify the validity of the macroscopic system behavior formed by molecules \textit{H Cl}, we have compared some of the most important thermodynamic functions with the results obtained by other authors [18][19][20]. They used as potential interaction the Morse potential and the results with GMP. At the same time we realised that \( n_{\max} = \left[ (\sqrt{\beta - A})/\alpha \right] = 28 \) for GMP while \( n_{\max} = N_0 = 28 \) for MP. For that reason, the form of the thermodynamic functions analyzed here do not differ to a large degree. Although the exact solution to the energy spectrum can be considered and its characteristic functions could be obtained, the results show that the approach to high temperatures is good for considering a classic state density. On the other hand, this study may represent the first steps to characterize systems formed by lineal polyatomic molecules with different chemical nature.

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