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Approximating the Partition Function of Morse Oscillators

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Abstract A simple method is proposed leading to reasonable approximations of the partition function of Morse oscillators in terms of elementary functions.

Keywords Morse oscillators · Partition function

1 Introduction

The quantum systems with Morse potentials represent one of the few quantum mechanical problems which can be analytically solved. These potentials describe simple and realistic anharmonic oscillators which are very useful for solving various problems arising in physics and chemistry (e.g., vibrational motion of diatomic and polyatomic molecules, photo-dissociation, intra-and intermolecular energy transfer, etc.).

Vibrational contribution to various thermodynamic functions is expressed in terms of a partition function and its first two derivatives (internal energy and respectively, heat capacity) [1]. Therefore, an important problem is to calculate the partition function corresponding to the discrete spectrum of Morse oscillators. In general this is a sum of exponentials giving the internal energy in a form which is not suitable for rapid calculations. For this reason many authors try to express the partition function in terms of other analytical functions [2–4].

In this letter we should like to show that the partition function of the Morse systems can be satisfactory approximated using only *elementary* functions. We start in the second section with a short review of the theory of the Morse partition function following to propose in the next section two simple methods of approximating these functions separately in the domains of low and respectively high temperatures.

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2 The Partition Function of Morse Oscillators

The vibrations of the diatomic molecules in the case when rotations are neglected can be seen as a one-dimensional oscillation near the equilibrium distance x_0 [5–7]. These vibrations are well-described by one-dimensional Morse oscillators governed by the one-dimensional Schrödinger equation with Morse potentials [5],

$$V(x) = D\big[(1 - e^{-a(x-x_0)})^2 - 1\big], \tag{1}$$

which represents wells of depths $-D$ at $x = x_0$, in the energy scale in which $\lim_{r\to\infty} V(r) = 0$. Therefore, D is just the dissociation energy of the diatomic molecule. The parameter a is the constant of anharmonicity which can take only positive values.

In the energy scale we work the energy spectrum has a continuous part in the domain $[0, \infty)$ and a finite number of discrete levels

$$E_n = -\frac{\hbar^2\omega^2}{4D}(n - \mathcal{N})^2, \tag{2}$$

where m is the oscillator mass, and

$$\mathcal{N} = \frac{2D}{\hbar\omega} - \frac{1}{2}, \quad \omega = a\sqrt{\frac{2D}{m}}. \tag{3}$$

The principal quantum number takes the values $n = 0, 1, 2, \ldots, N$. The maximal number of vibrational bound state, N, of the quantum system described by the Morse oscillator is obtainable looking for the maximal condition in which the wave functions remain square integrable. In this way one finds that N is the integer part of $\mathcal{N}$. For this reason we introduce the new parameter ϵ defined as $\mathcal{N} = N + \epsilon$ understanding that this satisfies the conditions $0 \le \epsilon < 1$. With this parametrization the energy reads

$$E_n = -\hbar\omega\frac{(N + \epsilon - n)^2}{2N + 2\epsilon + 1}. \tag{4}$$

The statistics of an ideal gas of identical diatomic molecules, modeled by Morse oscillators, in thermodynamic equilibrium with a reservoir of temperature T is described by the quantum canonical distribution [8]. This gives the partition function of the discrete spectrum

$$Z = \sum_{n=0}^{n=N} e^{-\beta E_n}, \quad \beta = \frac{1}{k_B T}, \tag{5}$$

which can be put in the form

$$Z(x, N) = \sum_{n=0}^{n=N} x^{\frac{(N+\epsilon-n)^2}{2N+2\epsilon+1}}, \tag{6}$$

where $x = e^{\beta\hbar\omega} \in [1, \infty)$ concentrates the physical parameters. This variable is approaching to 1 for $T \to \infty$ and tends to infinity when $T \to 0$ K. The partition function allows one to obtain the principal thermodynamic functions among them we focus on the internal energy [1, 8]

$$U(x, N) = -\frac{1}{Z(x, N)}\frac{\partial Z(x, N)}{\partial\beta} = -\frac{\hbar\omega x}{Z(x, N)}\frac{\partial Z(x, N)}{\partial x}. \tag{7}$$

Observing that $\epsilon < 1$ we can write the Taylor expansion

$$Z(x,N) = \sum_{n=0}^{n=N} x^{\frac{(N-n)^2}{2N+1}} + \frac{\epsilon\beta\hbar\omega}{2} \sum_{n=0}^{n=N} \left(1 - \frac{(2n+1)^2}{(2N+1)^2}\right) x^{\frac{(N-n)^2}{2N+1}} + O(\epsilon^2), \tag{8}$$

whose second term is relatively small because of its factors which remain smaller than one. Therefore, if ϵ is small enough then we can take $\epsilon = 0$ remaining only with the first term of (8). In this case it is convenient to rewrite the partition function as

$$Z(x,N) = \sum_{n=0}^{n=N} x^{\frac{(N-n)^2}{2N+1}} = x^{\frac{N^2}{2N+1}} F(x,N), \tag{9}$$

where we introduced the new function

$$F(x,N) = \sum_{n=0}^{n=N} x^{-\frac{n(2N-n)}{2N+1}}, \tag{10}$$

defined on the domain $x \in [1, \infty)$ for any integer N. This function is maximal for $x = 1$ where $F(1, N) = N + 1$ and decreases rapidly to 1 for $x \to \infty$ such that $\lim_{x\to\infty}[x\, \partial_x F(x,N)] = 0$. In these circumstances the internal energy is given by the formula

$$U(x,N) = -\frac{\hbar\omega}{2}\frac{N^2}{N+1} - \frac{\hbar\omega x}{F(x,N)}\frac{\partial F(x,N)}{\partial x}, \tag{11}$$

whose first term is just the energy value at $T = 0$ K. Notice that in our approximation ($\epsilon = 0$) the internal energy at very high temperatures can be evaluated as

$$U(x,N) \simeq U(1,N) = -\hbar\omega\frac{N}{6}. \tag{12}$$

This result holds even for small values of $\epsilon \neq 0$ since the second term of (8) is proportional with β which vanishes when $T \to \infty$.

3 Approximating the Partition Function

The problem now is to find a satisfactory closed formula which should approximate the function $F(x,N)$ by elementary functions in the case of $\epsilon = 0$. There are many possibilities that may be selected according to the desired accuracy for the temperatures of physical interest. In what follows we propose two methods of satisfactory approximating the partition function on large domains of temperatures.

3.1 Approximations for Low Temperatures

The first solution we propose here is to consider functions of the form

$$\tilde{F}(x,N) = \exp\{\exp[\nu f(x)] - 1\} \tag{13}$$

where $\nu = \ln[\ln(N+1)+1]$ and $f : [1,\infty) \to [0,1]$ must be an elementary function satisfying the boundary conditions

$$f(1) = 1, \qquad \lim_{x\to\infty} f(x) = 0, \tag{14}$$

which guarantee that F and $\tilde{F}$ behave similarly when x goes to one or infinity. The partition function (6) may be approximated by the function

$$\tilde{Z}(x,N) = x^{\frac{N^2}{2N+1}} \tilde{F}(x,N) \tag{15}$$

which gives internal energies,

$$\tilde{U}(x,N) = -\frac{\hbar\omega}{2}\frac{N^2}{N+1} - \hbar\omega\nu x \frac{df(x)}{dx} e^{\nu f(x)}, \tag{16}$$

with simple algebraic structures, suitable for calculations.

The function f can be chosen in many ways but here we restrict ourselves to the case when f is a polynomial of the rank $k+1$ in $1/x$,

$$f(x) = \sum_{i=1}^{i=k} \frac{c_i}{x^i} + \left[1 - \sum_{i=1}^{i=k} c_i\right]\frac{1}{x^{k+1}}, \tag{17}$$

whose coefficients represent fit parameters. Obviously, these polynomials obey (14). The next step is to fix up the integer k and determine the linear independent coefficients, $c_1, c_2, \ldots, c_k$, using a convenient fit method. One of the most effective methods is that of the least-squares applied for approaching f to the function $\ln[\ln(F)+1]$ calculated according to Eq. (10). Technically speaking, we must chose a sequence $x_{min} = x_1, x_2, \ldots, x_m = x_{max}$ in a desired domain, $x \in [x_{min}, x_{max}]$, and calculate the quantity

$$\Theta(c_1, c_2, \ldots) = \sum_i \{f(x_i) - \ln[\ln F(x_i, N) + 1]\}^2 \tag{18}$$

whose minimization with respect to the coefficients c_i leads to a system of linear equations giving the values of these coefficients.

This method leads to satisfactory approximations even for small values of k and sequences with $m = 600$ points. The functions F and $\tilde{F}$ have apparently the same graphics such that we must evaluate the errors using the function of relative differences $\delta F = \tilde{F}/F - 1$. In Fig. 1 we present the results obtained for $N = 35$ on the domain $x \in [1, 10]$. The left curve is the graphic of the function δF in the case of $k = 2$ (when the constants calculated using the least-squares method are $c_1 = 0.7528164063$ and $c_2 = -0.3714400991$). In the right side of Fig. 1 the function δF is given in a more complicated conjecture when $k = 5$. We observe that the accuracy is increasing with k but there are errors arising in the domain of high temperatures, $x \in [1, 2]$.

The conclusion is that the above method is suitable for approximating the function F only in the domain of low temperatures, $x > 2$. In this domain $|\delta F|$ remains less than 10^{-2} for $k = 2$ or less than 1.5×10^{-3} if $k = 5$.

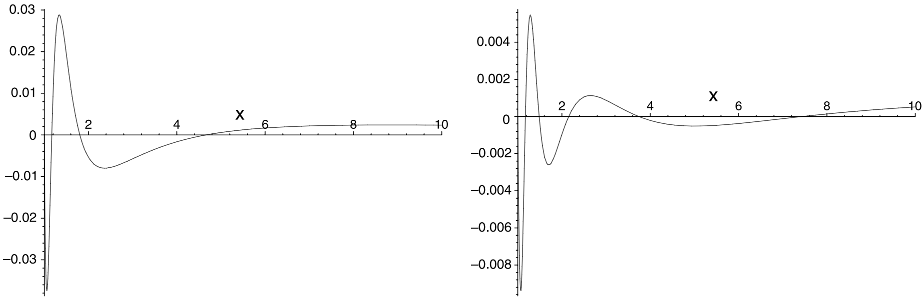

Fig. 1 The function $\delta F(x)$ on the domain [1, 10] for $k = 2$ (*left*) and $k = 5$ (*right*)

3.2 Approximations for High Temperatures

In the domain of high temperatures it is convenient to consider the variable

$$t = \frac{1}{\ln(x)} = \frac{k_B T}{\hbar\omega} \tag{19}$$

and the function $G(t, N) = F(e^{\frac{1}{t}}, N)$. This function can be approximated by the new function

$$\tilde{G}(t, N) = (N + 1)\frac{g(t)}{N + g(t)} \tag{20}$$

where $g(t)$ is a polynomial of the rank K of the form

$$g(t) = 1 + \sum_{i=1}^{i=K} C_i t^i, \tag{21}$$

depending on the fit constants $C_1, C_2, \ldots$. Then the approximative partition function

$$\tilde{Z}(t, N) = e^{\frac{1}{t}\frac{N^2}{2N+1}}\tilde{G}(t, N) \tag{22}$$

produces internal energies that read

$$\tilde{U}(t, N) = -\frac{\hbar\omega}{2}\frac{N^2}{N + 1} + \frac{\hbar\omega N t^2}{g(t)[N + g(t)]}\frac{dg(t)}{dt}. \tag{23}$$

As in the previous case, the coefficients C_i have to be determined using the method of least-squares for approaching the functions g and $NG/(N + 1 - G)$. This minces to chose a sequence $t_{min} = t_1, t_2, \ldots, t_m = t_{max}$ in the domain $[t_{min}, t_{max}]$ and calculate

$$\Theta'(C_1, C_2, \ldots) = \sum_i \left\{ g(t_i) - \frac{NG(t_i, N)}{N + 1 - G(t_i, N)} \right\}^2. \tag{24}$$

The minimization of this quantity will give us the coefficients C_i.

The concrete examples point out that this method of approximation leads to partition functions very close to the real ones. The errors can be showed off considering the function $\delta G = \tilde{G}/G - 1$ which has to measure the degree of accuracy. It is worth noting that for

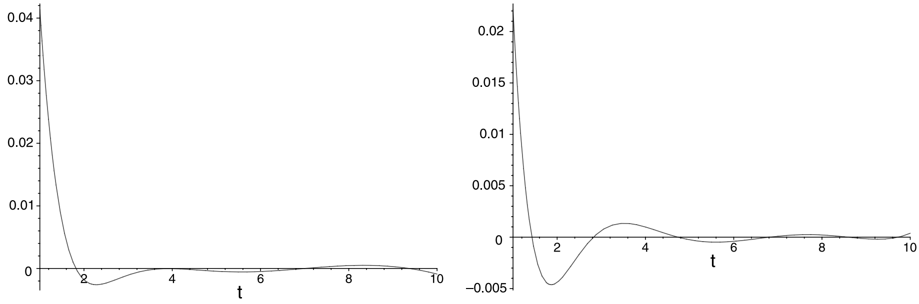

Fig. 2 The function $\delta G(t)$ on the domain $[1, 10]$ for $K = 3$ (*left*) and $K = 6$ (*right*)

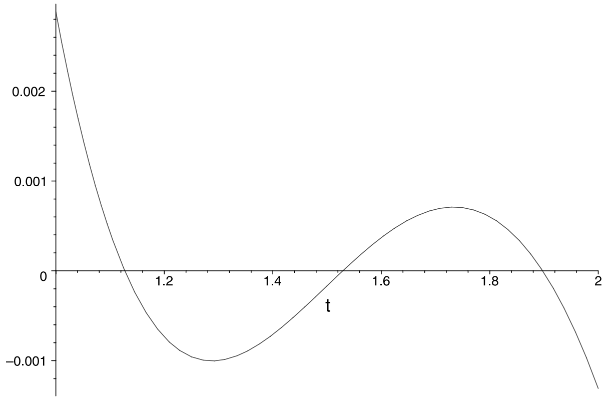

Fig. 3 The function $\delta G(t)$ for $K = 3$ in the domain $[1, 2]$

$N = 35$ and the large domain $t \in [1, 10]$ we obtain good results starting with $K = 3$ (Fig. 2 (left)). In addition, we observe that increasing the value of K the fit becomes better but not spectacularly improved, as one can see from Fig. 2 (right) where $K = 6$. On the other hand, it is obvious that significant errors arise in the domain of low temperatures, for $t < 2$.

Thus we can conclude that it is enough to consider the case of $K = 3$ for obtaining satisfactory approximations of the partition function at high temperatures, $t > 2$. It remains to investigate the sensitive domain $t \in [1, 2]$. Our tests indicate that in this domain one can use the same method based on the function $\tilde{G}$ since this can be determined with reasonable small errors (less than 2.5×10^{-3}) taking $K = 3$ (see Fig. 3). We note that the sequences used in the least-squares method contain a number of $m = 600$ points in all the cases discussed here.

4 Concluding Remarks

We presented two methods of approximating the partition function of the Morse oscillators which are complementary to each other, covering the whole domain of temperatures that may be of physical interest. The main point of our approach is the separation of the function (10) which plays a crucial role in developing approximation methods.

We hope that our results presented here will be useful for a rapid study of the thermodynamic functions of the ideal gas of Morse oscillators allowing one to point out how the principal thermodynamic quantities depend on temperature. Concrete examples will be considered elsewhere.

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