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RE-EXAMINING TRADITIONAL AND ROTATIONAL CANONICAL PARTITION FUNCTIONS FOR UNDERGRADUATE PHYSICAL CHEMISTRY: EXACT AND INSIGHTFUL VIEWS

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Abstract. This study explores the canonical partition function of both translational and rotational motion quantum mechanically and in the semi-classical limit (high temperature limit) at all conditions, including all temperatures. The treatment of physical chemistry textbooks of the translational and rotational partition functions is commented on. Exact quantum mechanical closed-form expressions, which are not available in any physical chemistry textbook, or the in literature for that matter, are reported for both types of partition functions at a wide range of temperatures and conditions are derived.

Keywords: particle-in-a-box, quantum translational partition function, undergraduate physical chemistry, de Broglie wavelength, theta function, rotational partition function

Introduction

Since concepts and ideas in quantum theory are often quite abstract, especially when students of physical chemistry are first exposed to the glorious world of wave-like particles, a simple example like a particle-in-a-box model is normally used to facilitate introducing the underlying quantum mechanical principles and the related calculations.

The particle-in-a-box model is central to students' quantum theory concepts grasping as many ideas, principles, and fundamentals are drawn on it when students learn about the quantum mechanics of the microscopic world. Having covered the underlying principles that emerge when teaching a particle-in-a-box model (translational motion), students are introduced to the concept of partition function which imparts information on the number of quantum states accessible to the system at hand. Understanding a key quantity such as the canonical translational partition function (TPF)) of a system in equilibrium is essential to the understanding of important thermodynamics state functions for undergraduate physical chemistry students. The system that is typically used to model translational motion is particle in a box.

All authors report the TPF in a closed form after having assumed that the translational energy levels are continuum, thereby justifying converting the sum over the translational states to an integral over these states. This approximation can be problematic as it is only valid if the de Broglie wavelength shorter than the container dimensions in which the particle is placed. Additionally, de Broglie wavelength must also be much smaller than the average separation of the constituent particles of the gas. It is intended in this study to fill in important physical rationales, along important mathematical steps, that are often left out by textbooks, add in important conditions, and supplement physical and mathematical corrections.

The purpose of this work is twofold: presenting the TPF at a moderately simpler level and easier terms that suit undergraduate students, thereby precluding the advance mathematics published elsewhere (Toutounji, 2011a; 2011b). Second, raising awareness among physical chemistry instructors and students that is the widely used TPF in all textbooks is only an approximation and can be wrong at times. Finally, the exact quantum mechanical expression of the rotational partition function (RTF) for a particle rotating in two dimensions that is valid at all temperatures is also derived.

Translational partition function, TPF (particle-in-a-box model)

Consider an atomic gas made of particles in a box of equal sides of length L. To make this report simple, it is assumed to be one-dimensional box (line) of length L. The energies of a particle-in-a-box with mass Min a one-dimensional box of length L are

$$E_n = \frac{1}{2M}\left(\frac{n\pi\hbar}{L}\right)^2, \quad n \geq 1 \tag{1}$$

with the eigenfunctions

$$\Psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right), \quad n \geq 1 \tag{2}$$

Note that the translational quantum number n cannot be *zero*, otherwise the energies and the wavefunctions will vanish. This is unphysical; that is, the particle has zero kinetic energy (zero momentum), and with $\Psi_0(x) = 0$ it means no particle. Additionally, setting $n = 0$ violates *Heisenberg uncertainty principle* which states that that position and momentum cannot simultaneously be determined exactly: the momentum and the position here are exactly known if n is set equal to zero. Thus n can never be *zero*.

The correct quantum translational partition function is given by

$$Z_q = \sum_{n=1}^{\infty} e^{-\beta E_n} = \sum_{n=1}^{\infty} e^{-\beta\frac{n^2h^2}{8ML^2}} \quad (3)$$
,

whereb is $1/kT$, with k being the Boltzmann constant. Most of the physical chemistry textbooks turn the sum in Eq.(3)into an integral

$$\int_{n=1}^{\infty} e^{-\beta\frac{n^2h^2}{8ML^2}} dn \quad (4)$$

assuming that the translational energy levels are closely-spaced. (*What if the energy levels were not closely spaced, as will be elucidated later on*?) The subscripts q and c are to denote quantum mechanical and classical Z, respectively. Moreover, in order to get a closed-form expression for the quantum translational partition function, textbooks would replace the integral lower limit 1 in Eq.(4) by 0 without a concrete justification

$$Z_c = \int_{n=1}^{\infty} e^{-\beta\frac{n^2h^2}{8ML^2}} dn \approx \int_{n=0}^{\infty} e^{-\beta\frac{n^2h^2}{8ML^2}} dn \quad (5)$$
.

Equating the lower limit of the integral to zero instead of unity is like setting $n = 0$, whereby students might be misled to believe so. Under the stated conditions therein, this is an acceptable mathematical approximation but inaccurate physical gesture as n cannot be set to zero, *vide supra*. The reason we could get away with it mathematically at high temperatures is because in

$$\begin{aligned} Z_c &= \int_{n=1}^{\infty} e^{-\beta\frac{n^2h^2}{8ML^2}} dn = \int_{0}^{\infty} e^{-\beta\frac{n^2h^2}{8ML^2}} dn - \int_{0}^{1} e^{-\beta\frac{n^2h^2}{8ML^2}} dn \\ &\approx \int_{0}^{\infty} e^{-\beta\frac{n^2h^2}{8ML^2}} dn = \frac{L}{h}\sqrt{2\pi MkT} \end{aligned} \quad (6)$$

the second term in Eq.(6) is negligibly small at high temperatures.[1)]

There are other important conditions which most textbooks fail to point them out whereby Eq.(5) and Eq. (6) are inapplicable even at high temperatures: not only is the sum in Eq.(5) wrong to turn into an integral, but the integral from 0 to 1 in Eq.(6) is not negligible, making the approximation in Eq.(6) very inaccurate even at high temperatures, *vide infra*.

Exact quantum mechanical treatment of TPF

First, I will look at the correct and exact evaluation of the sum in Eq.(3) which will hold true at all conditions. Second, in case it is allowed to turn the sum into an integral, I shall briefly comment on the exact analytic evaluation of the integral without neglecting the integral from 0 to 1 in Eq.(6).Starting with the expression in Eq.(3) and using the *Poisson-summation formula* (Schulman, 1996; Fernandez & Castro, 1996),[2)] one can obtain

$$Z_q = \frac{1}{2}\left(\vartheta_3(r) - 1\right), \tag{7}$$

where $r \equiv e^{-\beta\frac{h^2}{8ML^2}}$ and $\vartheta_3(r)$ is the special third theta function (Schulman, 1996).

Assuming that energy levels form a near continuum (semi-classical approximation), the TPF reads by Eq. (6). While the first integral in Eq.(6) gives

$$\int_0^\infty e^{-\beta\frac{n^2h^2}{8ML^2}} dn = \frac{L}{h}\sqrt{2\pi MkT} \tag{8}$$

and the second integral yields

$$\int_0^1 e^{-\beta\frac{n^2h^2}{8ML^2}} dn = \frac{L}{h}\sqrt{2\pi MkT}\ erf\left(\frac{h}{L}\sqrt{\frac{1}{8MkT}}\right) \tag{9}$$

Here erf (.) denotes the error function

$$erf(z) = \sqrt{\frac{2}{\pi}}\int_0^z \exp(-x^2)dx \tag{10}$$

Utilizing Eq.(9) and the definition of the complementary error function, erfc (.) -

$$erfc(z) = 1 - erf(z) \tag{11}$$

gives

$$Z_c = \frac{L}{h}\sqrt{2\pi MkT}\, erfc\left(\frac{h}{L}\sqrt{\frac{1}{8MkT}}\right) \tag{12}$$

Alternatively,

$$Q = \sum_{n=1}^{\infty} e^{-\beta\frac{n^2h^2}{8ML^2}} \tag{13}$$

$$Z_q = \sum_{n=1}^{\infty} e^{-\beta\frac{n^2h^2}{8ML^2}} = \sum_{m=0}^{\infty} e^{-\beta\frac{m^2h^2}{8ML^2}} - 1 \tag{14}$$

If the translational energy levels form a continuum spectrum (semiclassical approximation), then one may replace the sum with an integral in Eq.(14)

$$\begin{aligned} Z_q &= \sum_{m=0}^{\infty} e^{-\beta\frac{m^2h^2}{8ML^2}} - 1 = -1 + \int_0^{\infty} e^{-\beta\frac{m^2h^2}{8ML^2}} dm \\ &= -1 + \frac{L}{h}\sqrt{2\pi MkT} \end{aligned} \tag{15}$$

One notes that

$$\frac{L}{h}\sqrt{2\pi MkT}\; erf\left(\frac{h}{L}\sqrt{\frac{1}{8MkT}}\right) \to 1 \tag{16}$$

in a fully classical environment, and *not* in a quantum mechanical one. Since this *unity* term is much less than numerous translational states (comparable to Avogadro's number), it may thus be neglected, leading to Eq.(8).

Rotational partition functions, RPF (particle-on-a-ring model)

Consider a particle with moment of inertia I rotating in a circular path, the stationary energies of the particle read

$$E_m = \frac{(m\hbar)^2}{2I}, \quad |m| \le 1 \tag{17}$$

The two-dimensional quantum rotational partition function (RPF) is given by

$$Q_{rot} = \sum_{m=-\infty}^{\infty} g_m e^{-\beta E_m} = \sum_{m=-\infty}^{\infty} g_m e^{-\beta(m\hbar)^2/2I} \tag{18}$$

Where g_m stands for the degeneracy of each quantum mechanical state m. Assuming all the two-dimensional rotational states are *doubly* degenerate, except for the ground state $m = 0$, Q_{rot} reads

$$Q_{rot} = 2\sum_{m=-\infty}^{m=-1} e^{-\beta(m\hbar)^2/2I} + 2\sum_{m=1}^{\infty} e^{-\beta(m\hbar)^2/2I} + 1 \tag{19}$$

Equivalently, one may write

$$\begin{aligned} Q_{rot} &= 4\sum_{m=1}^{\infty} e^{-\beta(m\hbar)^2/2I} + 1 \\ &= 2\vartheta_3\left(e^{-\beta\hbar^2/2I}\right) - 1 \end{aligned} \tag{20}$$

The RPF is usually reported in almost all physical chemistry textbooks as semi-classical and not quantum mechanical, because the only quantum mechanical form for RPF is given in Eq.(20) which is not available for undergraduate students in any physical chemistry textbook except in this report. Typically done in textbooks for evaluating the two-dimensional RPF is as follows. Assuming closely spaced rotational levels at high temperatures, Q_{rot} may be written as

$$\begin{aligned} Q_{rot} &= \int_{-\infty}^{\infty} g_m e^{-e^{-\beta(m\hbar)^2/2I}} dm \\ &= -1 + 2\int_{-\infty}^{\infty} e^{-e^{-\beta(m\hbar)^2/2I}} dm \qquad (21) \\ &= \frac{2}{\hbar}\sqrt{2I\pi kT} - 1 \end{aligned}$$

Eq.(21) exhibits the RPF in the semi-classical limit. It is noteworthy that particle on-a-ring may be viewed as particle-in-a-box (line) bent into a circle by joining its ends. We are therefore looking at highly similar systems; that is, both are a free particle (zero potential energy) on a line and a free particle on a circle, which comes about by bending the line of length L and joining its ends. This "bending" is the reason for the presence of "2" out-front in Eq.(20) and Eq. (21) giving rise to a degeneracy of degree two. Upon looking more closely, therefore, one observes that the energies (kinetic energies) of both systems are essentially the same, except for the presence of the moment of inertia *I* for the rotational motion as opposed to the mass *M* for the linear translational motion. Furthermore, one can argue the particle-on-a-ring may be envisaged as a particle-on-a-line across a mirror, as such the RPF reads almost identical to that of TPF

$$Q_{rot} = 2.\frac{2\pi}{h}\sqrt{2I\pi kT} - 1, \qquad (22)$$

which is almost identical to that of TPF in Eq.(15), where 2p is the perimeter of the circle (like *L* in a particle-on-a-line) and the factor "2" at the very out front in Eq.(22) is to signify degeneracy, and the inertia moment *I* in Eq.(22) does the mass *M* for a particle-on-a-line as a linear motion; this correspondence between the rotational and translational motions stems from the fact that linear kinetic energy = $p^2/2M$, whereas rotational kinetic energy = $p^2/2I$.

Interestingly, both the particle-on-a-ring and particle-in-a-box models have the simplest eigenfunctions and relatively uneasy quantum partition functions. On the contrary, quantum harmonic oscillator have relatively more complicated eigenfunctions and straightforward partition function with a simple closed form that is valid at all temperatures.

NOTES

1. This case is reminiscent of the Morse oscillator in which case while the same mathematical assumption was illegitimate it was physically plausible (Toutounji, 2011a; 2011c).
2. For mathematical details *cf.* Toutounji (2011a; 2011c).

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