On the translational internal energy of a particle in a small box

V.S. Yorish

Thermocenter of the Russian Academy of Sciences, Institute for High Temperatures, Izhorskaya 13/19, Moscow 127 412, Russia

Abstract

Re-examination of the partition function and related thermodynamic functions of transla-
tion in a cubical box of very small volume fails to confirm the recent conclusion of Slanina
about unlimited growth of the internal energy. On the contrary the translational internal
energy for very small dimensions of the cube approaches zero in the limiting case. The source
of the discrepancy is the zero point energy which should be taken into account when the
partition function and some of related thermodynamic functions are calculated. The parti-
tion function calculation technique is also discussed. Simple and exact double formula
expressions are suggested instead of direct summation.

Keywords: Partition function; Thermodynamics

1. Introduction

In an article published in this journal, Slanina [1] paid attention to the possible
substantial deviation of the translational partition function and related internal
energy for a particle in a small cubic box from its conventional classic values. The
cause for such attention was the first information [2] about the presumed low
temperature nuclear fusion in palladium electrodes together with some other cases
where atomic and molecular species could find themselves in very small volumes.
There is no doubt that the conventional classical approach fails in such cases and
re-examination of the problem is required.

2. Results and discussion

It is convenient to consider the one dimensional case of a particle in an infinitely deep square well potential. The results can be extended easily to the three dimensional case.

The energy spectrum in this case is given [3] by

$$E(n) = \frac{h^2 n^2}{8ma^2} \tag{1}$$

where m is the mass of the particle, a is the width of the well, $n = 1, 2, \ldots$, is the quantum number and h stands for the Planck constant. It should be emphasized that the minimum energy is

$$E_0 = E(1) = \frac{h^2}{8ma^2} \tag{2}$$

not the bottom of the well.

Taking into account zero point energy we have the following expression for the quantum partition function

$$Q_q = \sum_{n=1}^{\infty} \exp\left(-\frac{E(n) - E(1)}{kT}\right) = \sum_{n=1}^{\infty} \exp(-\sigma(n^2 - 1)) \tag{3}$$

where $\sigma = h^2/8mkTa^2$.

For sufficiently small σ values it is possible to neglect the zero point energy and replace the summation (3) by the integration over all the quantum levels.

The conventional formula is then obtained [3]

$$Q_{cl} = 1/2\sqrt{(\pi/\sigma)} = 1/2\left(\frac{\pi}{\sigma}\right)^{1/2} \tag{4}$$

Using Eq. (3) and the usual thermodynamic relations [3] we obtain for the internal energy U

$$U/RT = \frac{\sum_{n=1}^{\infty} \sigma(n^2 - 1) \exp(-\sigma(n^2 - 1))}{\sum_{n=1}^{\infty} \exp(-\sigma(n^2 - 1))} = \frac{\sum_{n=1}^{\infty} \sigma n^2 \exp(-\sigma n^2)}{\sum_{n=1}^{\infty} \exp(-\sigma n^2)} - \sigma \tag{5}$$

The following expression is obtained for the molar internal energy of translational motion.

$$E/RT = 3\frac{\sum_{n=1}^{\infty} \sigma(n^2 - 1) \exp(-\sigma(n^2 - 1))}{\sum_{n=1}^{\infty} \exp(-\sigma(n^2 - 1))} = 3\frac{\sum_{n=1}^{\infty} \sigma n^2 \exp(-\sigma n^2)}{\sum_{n=1}^{\infty} \exp(-\sigma n^2)} - 3\sigma \tag{6}$$

It is readily seen that the only difference between our Eq. (6) and Eq. (5) of Ref. [1] is the second term. In the case where $\sigma \to \infty$ ($a \to 0$ and/or $T \to 0$ and/or $m \to 0$) the first term goes to 3σ and cancels the second one resulting in $E/RT \to 0$. Our conclusion is that in a small box, zero point energy ($E_0/RT = 3\sigma$) grows without limitation but internal energy decreases to zero. Detailed examination of the
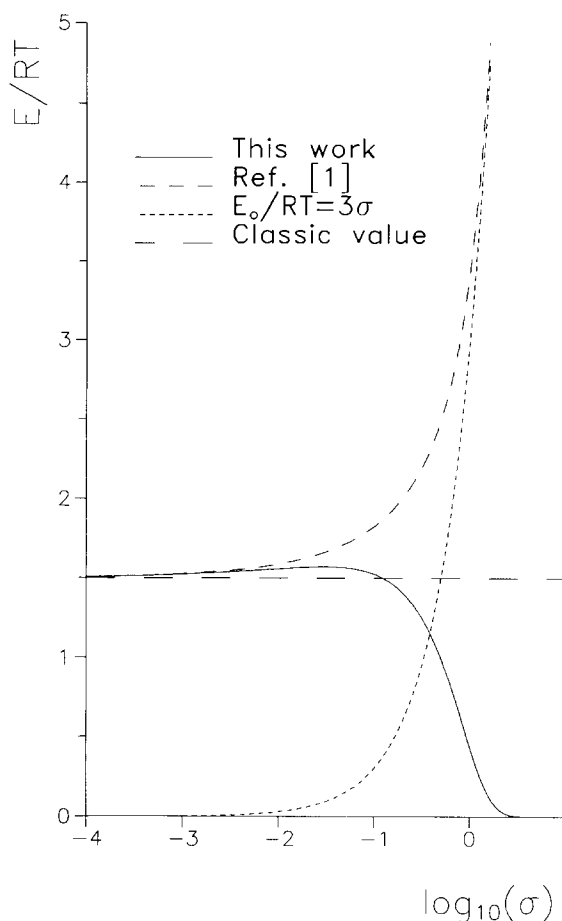
Fig. 1. Dependence of the reduced molar internal energy of translation in a cubical box E/RT on the reduced dimensionless quantity σ.

temperature dependence shows that the reduced internal energy has a very small and wide maximum and goes to the classic limit $E/RT = 3/2$ at $\sigma \to 0$.

The results obtained in this paper and in Ref. [1] are compared in Fig. 1. One can see that for large values of σ the reduced internal energy calculated in Ref. [1] nearly coincides with the reduced zero point energy. Table 1 demonstrates the application of our result to the case of hydrogen occlusion in the lattice of palladium. That is the example which was considered in Ref. [1]. The results presented indicate that accurate calculation of translational internal energy in a small area can lead to values both less and more than the value $E/RT = 1.5$ which is obtained using the conventional description of translational motion and is always much less compared to Slanina's values [1]. The physical meaning of the conclusion is very well understood because the translational motion in a small box is transformed into a type of vibration and in fact is frozen in the limiting case.

Table 1
Translational contribution to the reduced molar internal energy (E/RT) of species accommodated in palladium cells at room temperature $(T = 298.15 \text{ K})$

Species	$m \times 10^{-27}/\text{kg}$	$a \times 10^{-10}/\text{m}$	E/RT	
			This work	Ref. [1]
H	1.674	4.020	1.567	1.715
		3.884	1.565	1.723
		1.280	1.014	2.473
D	3.345	4.020	1.572	1.646
		3.884	1.572	1.651
		1.280	1.348	2.078
T	5.008	4.020	1.568	1.617
		3.884	1.569	1.622
		1.280	1.454	1.942
He	6.647	4.020	1.563	1.601
		3.884	1.564	1.604
		1.280	1.502	1.869

3. Double formula expression

The failure of the conventional partition function of translational motion in a small box is caused by replacement of rigorous summation by approximative integration. Slanina [1] considers the technique of direct summation as the single universal means for the purpose of accurate calculation neglecting other approaches. In this paper we study numerically one of the semiclassical approaches [4,5] and quantum expression (3) retaining the first few terms in both cases. A similar approach to the case of free internal rotation gave a surprisingly accurate result [6].

The semiclassical approximation (it is exact in this case) suggested in Refs. [4] and [5] is based on the Poisson transformation of Eq. (3) and is given by

$$Q_{sc} = \left(0.5\sqrt{(\pi/\sigma)} - 0.5 + \sqrt{(\pi/\sigma)} \sum_{n=1}^{\infty} \exp(-\pi^2 n^2/\sigma) \right) \exp(\sigma) \tag{7}$$

Let us consider Eqs. (3) and (7) retaining the first few terms in the respective sums

$$Q_q = \sum_{i=1}^{k} \exp(-(i^2-1)\sigma)$$

$$Q_{sc} = \left(0.5\sqrt{(\pi/\sigma)} - 0.5 + \sqrt{(\pi/\sigma)} \sum_{j=1}^{m} \exp(-\pi^2 j^2/\sigma) \right) \exp(\sigma) \tag{8}$$

and the following combined approximation

$$Q_{ca}(k,m,\sigma_0) = \begin{cases} Q_{sc}(m,\sigma) & \sigma \leq \sigma_0 \\ Q_q(k,\sigma) & \sigma > \sigma_0 \end{cases} \tag{9}$$
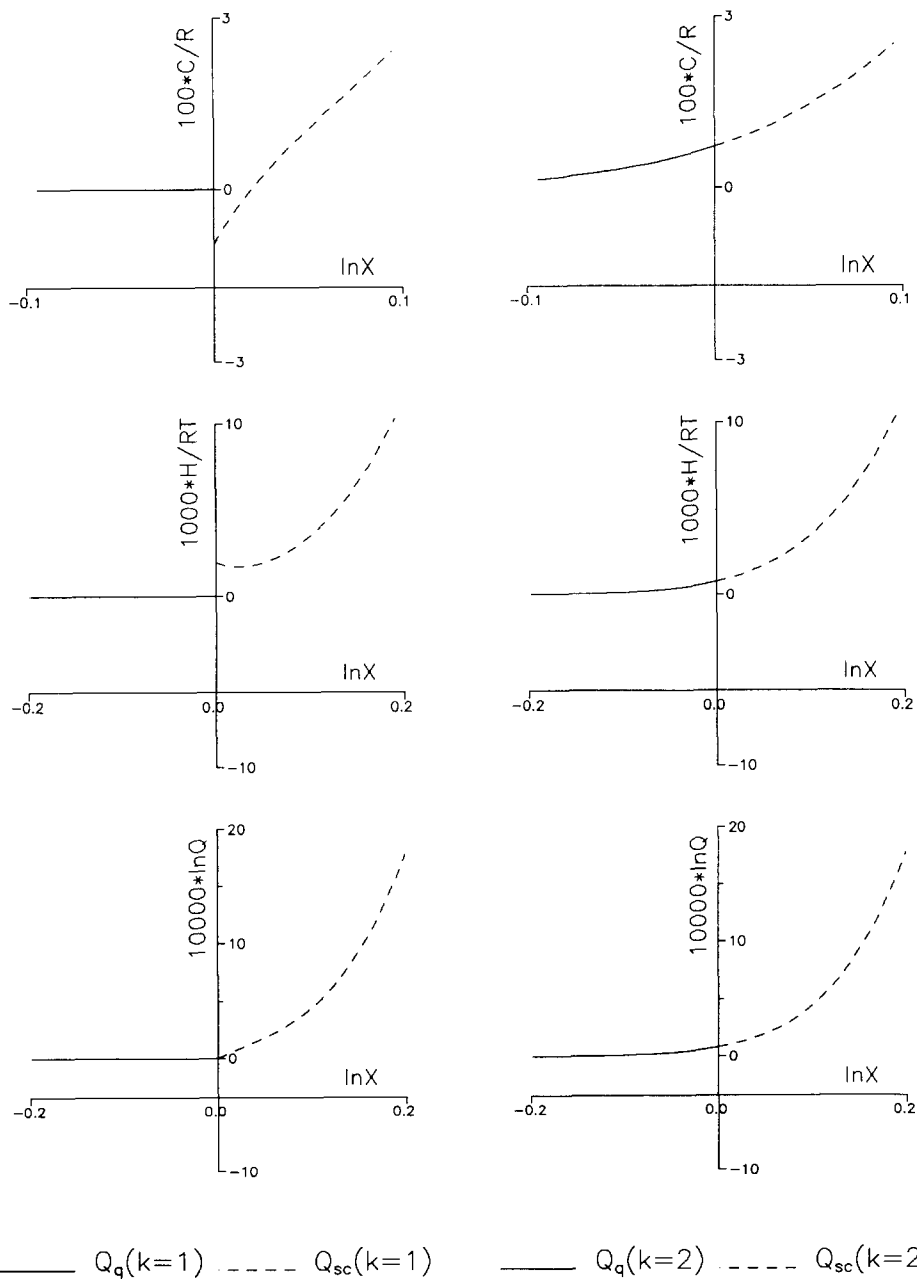
Fig. 2. One dimensional translational partition function and related thermodynamic functions near the point $\sigma = \pi$.

One can consider symmetric ($k = m$) and asymmetric ($k \neq m$) cases. In the symmetric case it is natural to find $\sigma_0 = \pi$, because

$$Q_q(k,\pi) = Q_{sc}(k,\pi) \tag{10}$$

for any k value.

In the asymmetric case the σ_0 value should be calculated numerically from the equation

$$Q_{sc}(m,\sigma_0) = Q_q(k,\sigma_0) \tag{11}$$

We examine only the symmetric case and the double formula expression (9) can be rewritten in the form

$$Q_{ca} = \begin{cases} Q_{sc}(k,\sigma) & \sigma \leq \pi \\ Q_q(k,\sigma) & \sigma > \pi \end{cases} \tag{12}$$

for practical use.

The function (12) is continuous and provides the correct behavior for both $\sigma \to 0$ and $\sigma \to \infty$ limits at any k value. However it has no continuity for temperature derivatives at $\sigma = \pi$, so related thermodynamic functions (internal energy, entropy and heat capacity) have a definite break at this point. As a criterion to choose an optimal k value we consider numerical closeness of heat capacity values related to both parts of Eq. (12).

Graphs are shown in Fig. 2 for $\ln(Q_{ca})$ and related thermodynamic functions versus $\ln X$ ($X = \sqrt{(\pi/\sigma)}$) at $k = 1$ and $k = 2$. The formulae used in these calculations are given in the Appendix. The graphs illustrate that visible discontinuity of both first and second temperature derivatives takes place only for $k = 1$. For $k = 2$ both energy and heat capacity values are continuous numerically. Numerical data on discontinuity and maximum deviation from exact values are summarized in Table 2.

Table 2
Numerical values at the point $\sigma = \pi$

Function	Equation for Q	Value	Deviation from exact value $\|100(F - F_{exact})/F_{exact}\|\%$
$10^4 \ln Q_{ca}$	A4a	0.806963	$< 2 \times 10^{-5}$
	A4b	0.806863	$< 2 \times 10^{-5}$
	Exact	0.806863	–
$10^2 E/RT$	A5a	0.7605138	$< 5 \times 10^{-5}$
	A5b	0.7605143	$< 5 \times 10^{-5}$
	Exact	0.7605140	–
$10^2 C/R$	A6a	0.7167095	$< 2 \times 10^{-4}$
	A6a	0.7167091	$< 2 \times 10^{-4}$
	Exact	0.7167102	–

As a result of the analysis the following expression can be recommended for practical use

$$Q_{ca} = \begin{cases} (0.5\sqrt{(\pi/\sigma)} - 0.5 + \sqrt{(\pi/\sigma)}(\exp(-\pi^2/\sigma) + \exp(-4\pi^2/\sigma)))e^{\sigma} & \sigma \leq \pi \quad (13a) \\ 1 + \exp(-3\sigma) & \sigma > \pi \quad (13b) \end{cases}$$

It should be noted that all values of internal energy given in Table 1 are reproduced using both $k = 1$ and $k = 2$ approximations in Eq. (12). So for many applications one can use the simplest expression

$$Q_{ca}(1) = \begin{cases} (0.5\sqrt{(\pi/\sigma)} - 0.5 + \sqrt{(\pi/\sigma)}\exp(-\pi^2/\sigma))\exp(\sigma) & \sigma \leq \pi \quad (14a) \\ 1 & \sigma > \pi \quad (14b) \end{cases}$$

bearing in mind the small inaccuracy of thermodynamic functions near the $\sigma = \pi$ point.

Appendix

Using the auxiliary variables

$$X = \sqrt{(\pi/\sigma)} \qquad Y = \exp(-\pi X^2) \qquad Z = \exp(-3\sigma)$$

$$P_1 = 0.5X - 0.5 + XY \qquad P_2 = P_1 + XY^4$$

$$D_1 = 0.5 + Y(1 - 2\pi X^2) \qquad D_2 = D_1 + Y^4(1 - 8\pi X^2)$$

$$S_1 = 2\pi XY(2\pi X^2 - 3) \qquad S_2 = S_1 + 8\pi XY^4(8\pi X^2 - 3)$$

the following expressions can be derived for thermodynamic functions of one dimensional translation.

For the case $k = 1$ in Eq. (12) (or Eq. (14))

$$F/RT = \ln Q = \begin{cases} \ln P_1 + \sigma & \sigma \leq \pi \quad (A1a) \\ 0 & \sigma > \pi \quad (A1b) \end{cases}$$

$$E/RT = \begin{cases} XD_1/(2P_1) - \sigma & \sigma \leq \pi \quad (A2a) \\ 0 & \sigma > \pi \quad (A2b) \end{cases}$$

$$C/R = \begin{cases} X^2(S_1/P_1 - (D_1/P_1)^2)/4 + 3XD_1/(4P_1) & \sigma \leq \pi \quad (A3a) \\ 0 & \sigma > \pi \quad (A3b) \end{cases}$$

For the case $k = 2$ in Eq. (12) (or Eq. (13))

$$F/RT = \ln Q = \begin{cases} \ln P_2 + \sigma & \sigma \leq \pi \quad (A4a) \\ \ln(1 + Z) & \sigma > \pi \quad (A4b) \end{cases}$$

$$E/RT = \begin{cases} XD_2/(2P_2) - \sigma & \sigma \leq \pi \quad (A5a) \\ 3\sigma Z/(1 + Z) & \sigma > \pi \quad (A5b) \end{cases}$$

$$C/R = \begin{cases} X^2(S_2/P_2 - (D_2/P_2)^2)/4 + 3XD_2/(4P_2) & \sigma \leq \pi \quad (A6a) \\ 9\sigma^2 Z(1 - Z/(1 + Z))/(1 + Z) & \sigma > \pi \quad (A6b) \end{cases}$$

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