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1990 J. Phys. A: Math. Gen. 23 4313

(http://iopscience.iop.org/0305-4470/23/19/016)

J. Phys. A: Math. Gen. 23 (1990) 4313–4320. Printed in the UK

On the shape dependence of the translational partition function

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Received 31 October 1989, in final form 30 April 1990

Abstract. The partition functions q of a particle moving in some two- and three-dimensional potentials with infinite barrier height were examined in order to investigate the influence of shape on the translational partition function. The partition functions of the square, rectangle, isosceles right triangle, equilateral triangle, circle and sphere were evaluated numerically or by suitable analytical methods. The results were fitted as empirical polynomials of square and cube roots of the classical limit κ of the partition function. The empirical relations were shown to hold over a wide range of κ. Their coefficients were compared with asymptotic expansions.

1. Introduction

The calculation of the partition function q of a particle in a box is usually based on the energy eigenvalues of a particle in a cube. The potential is given by zero inside the box and infinity on the boundary and on the rest of space. The summation over all states is approximated by an integration to give the well known formula [1 p 72]

$$q_{\text{trans}} \approx \kappa_3 = \left(\frac{2m\pi k_{\text{B}}T}{h^2}\right)^{3/2} V \tag{1}$$

where m, k_{B}, T, h and V have their usual meanings. In equation (1) the dependence of q_{trans} on terms proportional to the surface of the box and on higher terms is neglected. It can be also seen from (1) that κ_3 does not depend on the shape of the box.

In this paper the shape dependence of q for a particle moving in different boxes will be investigated. For some two- and three-dimensional potentials q will be evaluated either numerically or by appropriate summation techniques. The partition functions can be fitted to empirical formulae which are closely related to asymptotic expressions.

2. Computation of the partition functions

It is well known that the energy eigenvalues of a particle of mass m moving in some two- and three-dimensional boxes can be expressed as simple explicit formulae. For convenience the eigenvalues are listed in the appendix. In the simplest case the energies are of the form [2]:

$$E_n = \alpha n^2 \qquad n \in \mathbb{N} \qquad \alpha \in \mathbb{R}_+ \tag{2}$$

0305-4470/90/194313+08$03.50

and the partition function can be evaluated using the following expression

$$\sum_{s=1}^{\infty} \mathrm{e}^{-\alpha s^2} = \frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{1/2} - \frac{1}{2} + \epsilon \qquad \alpha \in \mathbb{R}_+ \tag{3}$$

which can be derived by the Euler Maclaurin sum formula [3 p 303], by θ transformation [4 p 54] or by the Poisson sum formula [5 p 86]. For $0 < \alpha < 0.2$ the deviation ϵ is less than 10^{-20}. By straightforward application of (3) q can be obtained for the one-dimensional box (q_{b}), the rectangle (q_{rect}) and the square (q_{squa}). The partition functions are listed in the appendix.

Comparing the partition function q_{iso} of a particle in an isosceles right triangle of small side a

$$q_{\mathrm{iso}} = \sum_{n_1=1}^{\infty} \sum_{n_2=n_1+1}^{\infty} \exp\left(-\frac{h^2}{8ma^2k_{\mathrm{B}}T}\left(n_1^2+n_2^2\right)\right) . \tag{4}$$

with q_{squa}, it can be easily seen that

$$q_{\mathrm{iso}} = \frac{q_{\mathrm{squa}} - q_{\mathrm{b}}}{2} \qquad q_{\mathrm{b}} = \sum_{n=1}^{\infty} \exp\left(-\frac{h^2}{4ma^2k_{\mathrm{B}}T}\,n^2\right) . \tag{5}$$

Both q_{b} and q_{squa} can be evaluated using (3). The partition functions for the equilateral triangle (q_{equi}), circle (q_{cir}) and sphere (q_{sphe}) were calculated numerically.

For a general right cylinder with an arbitrary base B and the height H the partition function q_{C} is given by

$$q_{\mathrm{C}} = q_H q_{\mathrm{B}} \tag{6}$$

where q_H and q_{B} are the partition functions of a particle in a one-dimensional box of length H and of the base B, respectively. By means of (6) q_{C} can be obtained for every right cylinder with known q_{B}.

3. Empirical formulae for the partition function

3.1. Derivation of the empirical formulae

The numerical summations are fairly cumbersome, thus a simple empirical formula for the partition function would be valuable. As an example we consider a particle confined to a rectangular two-dimensional box of sides a, b and of area A. We express the partition function q_{rect} (A1) in terms of its classical limit κ_2. The ratio between a and b is denoted by γ.

$$q_{\mathrm{rect}} = \kappa_2 - \frac{1}{2}\left(\sqrt{\gamma} + \frac{1}{\sqrt{\gamma}}\right)\sqrt{\kappa_2} + \frac{1}{4} \tag{7}$$

$$\kappa_2 = \frac{2m\pi k_{\mathrm{B}}T}{h^2} A. \tag{8}$$

Equation (7) has the functional form

$$q_2 = \kappa_2 + g_2\sqrt{\kappa_2} + h_2 \tag{9}$$

where q_2 is the partition function of a particle in a two-dimensional box. The coefficient g_2 depends on the shape of the rectangle. I conjecture that a functional form (9) also holds, at least by approximation, for other two-dimensional boxes with coefficients g_2 and h_2 depending only on the shape of the box. Equation (A2) is used to derive an expression such as (9) for q_{iso}. In order to check whether a similar formula also holds for q_{equi} and q_{cir}, g_2 and h_2 are determined by a least-squares fit [6] of the numerical results for q_{equi} and q_{cir}. A typical output for q_{cir} is shown in table 1. The coefficients and other details of the fits are given in table 2. With κ_2 lying between 13 and 13 000, a maximal deviation of less than 2×10^{-3} between the fitted value and the exact numerical result is observed in the case of q_{cir}. For q_{equi} no deviation can be observed within the accuracy of our computer. This means that all two-dimensional potentials analysed in this paper obey, at least to a very good approximation, an expression of the form (9). In the case of potentials, the partition function of which can be evaluated by (6), equation (9) holds in the range for which (6) can be used.

Table 1. Typical output for a least-squares fit of q_{cir}. M is the mass of the atom (u), A the area of the circle (10^{-20} m^2), T the temperature (K), κ_2 the value of the partition function for the asymptotic limit, q the exact partition function, q_{fit} the fitted value of the partition function, q_{asy}, asymptotic expansion for q from equation (22). $g_2 = -0.886\ 234(4)$ and $h_2 = 0.1672(2)$ are the empirical coefficients for (9) obtained from this fit. (The figures in parentheses give the standard deviation.)

M	A	T	κ_2	q	$q_{\mathrm{fit}} - q$	q_{asy}	$q_{\mathrm{asy}} - q$
4.003	10.0	100	13.13	10.0886	−0.001 50	10.0865	−0.002 05
4.003	10.0	200	26.26	21.8890	−0.000 88	21.8876	−0.001 41
4.003	10.0	300	39.39	33.9993	−0.000 62	33.9982	−0.001 15
4.003	20.0	400	105.05	96.1345	−0.000 20	96.1338	−0.000 69
4.003	20.0	600	157.58	146.6181	−0.000 09	146.6175	−0.000 56
4.003	20.0	1000	262.63	248.4312	0.000 02	248.4307	−0.000 43
4.003	30.0	1000	393.94	376.5163	0.000 07	376.5160	−0.000 35
4.003	70.0	900	827.27	801.9489	0.000 12	801.9487	−0.000 24
20.179	30.0	900	1787.43	1750.1286	0.000 10	1750.1284	−0.000 16
20.179	40.0	1000	2648.04	2602.6063	0.000 07	2602.6061	−0.000 13
20.179	70.0	1000	4634.08	4573.9146	−0.000 02	4573.9145	−0.000 10
20.179	90.0	1000	5958.10	5889.8589	−0.000 07	5889.8589	−0.000 09
39.948	40.0	100	524.23	504.1044	0.000 09	504.1040	−0.000 31
39.948	40.0	200	1048.46	1019.9279	0.000 12	1019.9277	−0.000 22
39.948	60.0	1000	7863.43	7785.0066	−0.000 15	7785.0065	−0.000 08
39.948	70.0	1000	9174.00	9089.2810	−0.000 19	9089.2810	−0.000 07
39.948	90.0	900	10615.63	10524.4831	−0.000 23	10524.4830	−0.000 06
39.948	100.0	1000	13105.71	13004.4227	−0.000 25	13004.4227	0.000 01

The partition function q_{rpep} of a particle in a rectangular parallelepipedon of sides a, b and c can be expressed as a function of its classical limit κ_3 (1) as follows:

$$q_{\mathrm{rpep}} = \kappa_3 + f_3\,\kappa_3^{2/3} + g_3\,\kappa_3^{1/3} + h_3 \tag{10}$$

$$f_3 = -\frac{1}{2}\,\frac{\gamma_1+\gamma_2+\gamma_1\gamma_2}{(\gamma_1\gamma_2)^{2/3}} \qquad g_3 = \frac{1}{4}\,\frac{1+\gamma_1+\gamma_2}{(\gamma_1\gamma_2)^{1/3}}$$

$$h_3 = -\tfrac{1}{8} \qquad b = \gamma_1 a \qquad c = \gamma_2 a.$$

Table 2. Coefficients in the empirical equations. The standard deviation is given in parentheses.

q	f	g	h	Equation
q_{equi}	—	−1.139 753 528 477†	0.333 333 333 33†	(9)
q_{cir}	—	−0.886 234 1(4)	0.167 23(2)	(9)
q_{sphe}	−1.208 994 027(8)	0.413 578(1)	−0.021 22(3)	(10)

† No standard deviation observed.

If an expression such as (9) holds for the base contribution q_B to the partition function of a right cylinder with height H and an area of the base A, a formula similar to (10) can be derived using equations (1) and (6).

$$q_c = \kappa_3 + f_3\,\kappa_3^{2/3} + g_3\,\kappa_3^{1/3} + h_3 \tag{11}$$

where

$$f_3 = \frac{g_2\gamma_c - \frac{1}{2}}{\gamma_c^{2/3}} \qquad g_3 = \frac{h_2 - g_2/2}{\gamma_c^{1/3}} \qquad h_3 = -\frac{1}{2}\,h_2 \qquad H = \gamma_c\sqrt{A}.$$

Coefficients f_3, g_3 and h_3 for a sphere were obtained by a least-squares fit of the numerical data of q_{sphe} . In the fit with κ_3 between 4 and 5400 000, a maximal deviation of 8×10^{-4} was observed. The results are listed in table 2.

The lower bound of the range of validity of (9) and (11) for q_{cir}, q_{equi} and q_{sphe} was tested numerically. For $\kappa_{2(3)} \geq 1$ the relative error in q was less than 1%, 0.005% and 2.5%, respectively.

3.2. Asymptotic expansions of the partition function

The coefficient g_2 in (9) is related in a simple manner with the area A and the perimeter p of the potential

$$g_2 \approx -\frac{p}{4\sqrt{A}}. \tag{12}$$

Relation (12) holds exactly for all two-dimensional potentials considered in this paper except for q_{cir}, for which it is fulfilled to a good approximation. We shall show that (12) is an asymptotic expansion of g_2.

The two-dimensional equation

$$\Delta u + \lambda u = 0 \qquad u = 0 \text{ on } \partial G \tag{13}$$

is defined in a simply connected domain of area A. The boundary ∂G of perimeter p has smooth arcs of length ζ_i and corners of angle α_i. For

$$W(t) = \sum_{n=1}^{\infty} \mathrm{e}^{-\lambda_n t} \qquad \lambda_n\text{: eigenvalues of (13)} \tag{14}$$

the following asymptotic expansion holds as $t \to +0$ [7 p 37, 8]:

$$W(t) \asymp \frac{A}{4\pi t} - \frac{p}{8\sqrt{\pi t}} + \sum_j c(\alpha_j) + \sum_i b(\zeta_i) \tag{15}$$

Table 3. Coefficients in the asymptotic expansions. The difference of the coefficients between the asymptotic and empirical equations is given in parentheses.

q	F	G	H
q_{equi}	—	−1.139 753 5284†	0.333 333 33†
q_{cir}	—	−0.886 227(7)	0.166 7(−5)
q_{sphe}	−1.208 993 96(6)	0.413 567(−9)	0.00(2)‡

† No deviation observed.
‡ H_3 for the sphere is exactly zero.

where

$$b(\zeta_i) = \frac{1}{12\pi} \int_{\zeta_i} k(l)\, \mathrm{d}l \qquad k(l)\text{: curvature} \tag{16}$$

and

$$c(\alpha_i) = \frac{1}{24} \left(\frac{\pi}{\alpha_i} - \frac{\alpha_i}{\pi} \right). \tag{17}$$

Comparing the Schrödinger equation of a particle in a box

$$-\frac{h^2}{8\pi^2 m} \Delta\psi = E\psi \qquad \psi = 0 \text{ on } \partial G \tag{18}$$

with (13) and the partition function q_2

$$q_2 = \sum_{n=1}^{\infty} \exp\left(-\frac{E_n}{k_{\mathrm{B}} T} \right) \tag{19}$$

with (14) we obtain

$$\lambda_n = \frac{8\pi^2 m E_n}{h^2} \tag{20}$$

and

$$t = \frac{h^2}{8\pi^2 m k_{\mathrm{B}} T}. \tag{21}$$

Substituting (20) and (21) into (15), we get the asymptotic expansion

$$q_2 \asymp \kappa_2 + G_2\sqrt{\kappa_2} + H_2 \qquad \kappa_2 \to \infty \tag{22}$$
$$G_2 = -\frac{p}{4\sqrt{A}}$$

which is in agreement with (12). The constant terms H_2

$$H_2 = \sum_j c(\alpha_j) + \sum_i b(\zeta_i) \tag{23}$$

were evaluated for the potentials considered here. They are compared with the results of the numerical fits in table 3.

The coefficient f_3 in the expansion (11) of the partition function of a right cylinder with surface S and volume V can be simplified using (12)

$$f_3 = -\frac{S}{4V^{2/3}}. \tag{24}$$

We now consider a three-dimensional equation (13) defined in a smooth convex domain. For $W(t)$ (14) the following asymptotic expansion holds as $t \to 0$ [9]:

$$W(t) \asymp \frac{V}{(4\pi t)^{3/2}} - \frac{S}{16\pi t} + \frac{1}{12\pi\sqrt{4\pi t}} \iint_S (k_1 + k_2)\,\mathrm{d}S + \frac{1}{512\pi} \iint_S (k_1 - k_2)^2\,\mathrm{d}S \qquad k_1, k_2\text{: principal curvatures.} \tag{25}$$

Using (20) and (21) the following asymptotic expression for q_3 can be obtained:

$$q_3 \asymp \kappa_3 + F_3(\kappa_3)^{2/3} + G_3(\kappa_3)^{1/3} + H_3 \tag{26}$$

where

$$F_3 = -\frac{S}{4V^{2/3}} \qquad G_3 = \frac{1}{12\pi V^{1/3}} \iint_S (k_1+k_2)\,\mathrm{d}S \qquad H_3 = \frac{1}{512\pi} \iint_S (k_1-k_2)^2\,\mathrm{d}S.$$

For a spherical domain (26) reads:

$$q_{\mathrm{sphe}} \asymp \kappa_3 - \left(\frac{9\pi}{16}\right)^{1/3} \kappa_3^{2/3} + \left(\frac{2}{9\pi}\right)^{1/3} \kappa_3^{1/3} \qquad \kappa_3 \to \infty. \tag{27}$$

The constant term vanishes in expansion (27). The coefficients determined from the numerical results are compared with (27) in table 3.

4. Conclusion

The partition function of a particle moving two-dimensionally in a square, in a rectangle, in an isosceles right triangle, in an equilateral triangle, in a circle and in the three-dimensional potential of the corresponding right cylinders and in a sphere were calculated either by numerical summation or by suitable analytical summation techniques. It was observed that for a particle moving in one of the two- or three-dimensional infinite hard wall cavities mentioned above, the partition function can be expressed to a very good approximation by a simple empirical formula. The empirical formulae were shown to have the same form as asymptotic expansions for the partition function in the limit of $T \to \infty$. The parameters in the empirical formulae and in the asymptotic expressions differ only slightly. The empirical formulae allow a simple calculation of the partition function of a particle like He or H_2 moving in a small box at low temperatures, e.g. for an atom in a cavity in a liquid.

The good agreement between the numerical results and the asymptotic expansions suggests the use of the expansions (15) and (25) for other two- and three-dimensional domains, if their eigenvalues cannot be calculated easily and if the boundaries are sufficiently regular. A detailed investigation on the relation between the shape of a box and the deviation between the asymptotic expansion and the exact partition function is under way.

Acknowledgments

The author wishes to thank W Witschel for suggesting the problem and for helpful discussions. The interest of R Baltin is gratefully acknowledged. This work was supported by the 'Eberhard Stiftung' and by the 'Fonds der Chemischen Industrie'.

Appendix

The energies E, degeneracies g, and the partition functions q (if an analytical expression exists) of a particle of mass m moving in boxes of various shapes are listed below.

Rectangle of sides a and b (square analogous) [2]:

$$E_{n_1,n_2} = \frac{h^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2}\right) \qquad n_1, n_2 \in \mathbb{N} \qquad g = 1$$
$$q_{\mathrm{rect}} = \frac{1}{4}\left[\left(\frac{8\pi m k_{\mathrm{B}} T a^2}{h^2}\right)^{1/2} - 1\right]\left[\left(\frac{8\pi m k_{\mathrm{B}} T b^2}{h^2}\right)^{1/2} - 1\right]. \tag{A1}$$

Isosceles right triangle with a small side of a [2]:

$$E_{n_1,n_2} = \frac{h^2}{8ma^2}\left(n_1^2 + n_2^2\right) \qquad n_2 > n_1 \qquad n_1, n_2 \in \mathbb{N} \qquad g = 1$$
$$q_{\mathrm{iso}} = \frac{m\pi a^2 k_{\mathrm{B}} T}{h^2} - \left(\frac{m\pi a^2 k_{\mathrm{B}} T}{2h^2}\right)^{1/2}\left(1 + \frac{1}{\sqrt{2}}\right) + \frac{3}{8}. \tag{A2}$$

Equilateral triangle of side a [8]:

$$E_{n_1,n_2} = \frac{2h^2}{9ma^2}\left(n_1^2 + n_2^2 - n_1 n_2\right) \qquad n_1 > n_2 \qquad n_1, n_2 \in \mathbb{N} \qquad g = 1. \tag{A3}$$

Circle of radius R_0 [7 p 37]:

$$E_{n,s} = \frac{h^2 j_{n,s}^2}{8\pi^2 m R_0^2} \qquad n \in \mathbb{N}_0. \tag{A4}$$

where $j_{n,s}$ is the sth positive zero of the Bessel function $J_n(x)$ of the first kind, $g_n = 2$ for $n \in \mathbb{N}$ and 1 for $n = 0$. For the calculation of q_{cir} all about 125 000 $j_{n,s}$ of 1000 or below were used.

Sphere of radius R_0 [10 p 96]:

$$E_{l,s} = \frac{h^2 \eta_{l,s}^2}{8\pi^2 m R_0^2} \qquad s \in \mathbb{N} \qquad l \in \mathbb{N}_0 \qquad g_l = 2l + 1 \tag{A5}$$

where $\eta_{l,s}$ is the sth positive zero of $J_{l+1/2}(x)$. For the calculation of $q_{\rm sphe}$ all about 500 000 $\eta_{l,s}$ of 2000 or less were used.

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