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A Formal Proof of Vessel-Shape Dependency of the Ideal-Gas One-Particle Partition Function of Translation

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An erroneous limiting behaviour of the conventional translational partition function q has been pointed out. Some general features of the exact translational partition function Q are given. A formal proof that Q (from a rigorous point of view) depends on the shape of vessel is presented. A possible relation of the result to experimental observations is briefly discussed.

Canonical ensemble partition function is expressed[1] for independent Boltzons and for independent corrected Boltzons as z^N and $z^N/N!$, respectively, where N is the number of particles and z denotes the one-particle partition function:

$$z = \sum_{i} e^{-\frac{\varepsilon_i - \varepsilon_0}{kT}}, \tag{1}$$

i. e. the sum over the quantum states i (ε_0 means the ground-state energy). The entropy calculation of both Boltzons and corrected Boltzons involves the essential term type:

$$\delta\, S\,(z) = \ln\, z + T \left(\frac{\partial \ln\, z}{\partial\, T}\right)_V . \tag{2}$$

It can be easily shown that for a non-degenerate ground state it is:

$$\lim_{T \to 0} \delta\, S\,(z) = 0. \tag{3}$$

Exact formulations for various kinds of motions are rarely encountered, the ones commonly used are simple approximations. The relation (3) can serve as a certain test of the approximation considered. The test, of course, concerns only mathematical correctness, the region of application itself, i. e. $T \to 0$, being physically unadvisable. It is self-evident that a proper calculation of entropy at very low temperatures will have to adopt appropriate quantum statistics.

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The partition function of a structureless particle is reduced to a one--particle translational partition function q, which is exclusively approximated by the usual formula:

$$q_o = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V. \tag{4}$$

where m means the mass of the particle, the other symbols having their usual meaning. Obviously, this approximation does not satisfy the requirement (3), because

$$\lim_{T\to 0} \delta S(q_o) = -\infty. \tag{5}$$

(It must be noted that many other approximative formulas, see e. g.[2], also fail in this test, the usual partition function of harmonic oscillator representing an exception among the simplest models. Of course, the limit behaviour can also be studied on other thermodynamic functions, e. g. on C_p.)

The cause of the above-mentioned failure of formula (4) must be sought in the way of its derivation. The one-particle partition function of translation is frequently derived from the energy spectrum of the particle closed in a rectangular prism (its sides are denoted as l_i). The procedure involves three approximations: the transition from summation to integration, the shift of the lower integration limit from 1 to 0, and, finally, also neglecting of the ground-state energy term (which is, however, insignificant in the entropy calculation). If the ground state energy term is ignored, then the exact partition function of translation of a particle in a rectangular prism reads as follows:

$$q(\sigma_1, \sigma_2, \sigma_3) = u(\sigma_1)\, u(\sigma_2)\, u(\sigma_3). \tag{6}$$

where

$$u(\sigma_k) = \sum_{i=1}^{\infty} e^{-\sigma_k i^2}. \quad \left(\sigma_k = \frac{h^2}{8\, mkTl_k^2} > 0\right) \tag{7}$$

Although we cannot express this exact partition function q in a closed shape, we can reveal some exactly valid functional dependences for the generating function u. For this purpose it is advantageous to make use of the cognation with the elliptic theta functions[3], namely with the ϑ_3 function of the zero argument $\vartheta_3(0, p)$:

$$u(\sigma) = \frac{\vartheta_3(0, \mathrm{p}) - 1}{2}, \tag{8}$$

where $p = e^{-\sigma}$. Utilization of transformation properties of the ϑ_3 function leads, e. g., to the following relation between the u function values at the σ and π^2/σ points:

$$u(\pi^2/\sigma) = -1/2 + 1/2\,(\sigma/\pi)^{1/2} + (\sigma/\pi)^{1/2}\, u(\sigma). \tag{9}$$

(This relation can also be obtained in a less straightforward way by the application of more usual means of mathematical analysis.)

This exact relation (9) will be used further, viz. in a discussion of the problem whether or not the exact translational partition function q can depend on the vessel shape. As it is known, q is not considered for vessel shapes other than the rectangular prism, since its uniformity for all vessels is intuitively presumed. For disproving of this presumption it would be quite sufficient to find two vessels of the same volume and of different shapes, for which q would be different at a given temperature, whereby the vessel-shape dependency of q would be proved. In particular, it would be sufficient to find two different rectangular prisms of the same volume for which their q would differ.

Let us consider a set of all rectangular prisms described by the triads $(\sigma, \pi^2/\sigma, \pi)$; at a chosen temperature their geometry dimensions can easily be deduced (see Eq. (7)). These rectangular prisms of constant volume also involve the cube (π, π, π). Let us now examine the possibility of identical q for all these rectangular prisms using the proof through contradictory. In terms of Eq. (6), this independency would also mean that it would have to be valid for all $\sigma > 0$:

$$\frac{q(\sigma, \pi^2/\sigma, \pi)}{q(\pi, \pi, \pi)} = \frac{u(\sigma)\, u(\pi^2/\sigma)\, u(\pi)}{u(\pi)\, u(\pi)\, u(\pi)} = 1, \tag{10}$$

which is reduced to the condition:

$$u(\sigma)\, u(\pi^2/\sigma) = u(\pi)^2. \tag{11}$$

Combination of Eqs. (9) and (11) allows one to eliminate the term $u(\pi^2/\sigma)$ and express $u(\sigma)$ as a function of σ and $u(\pi)$ parameters; the last term mentioned can be expressed[3] in a closed form by means of the Γ function:

$$u(\pi) = \frac{1}{2}\left(\frac{\Gamma(1/4)}{\sqrt{2}\,\pi^{3/2}} - 1\right). \tag{12}$$

Thus, from the presumption of validity of the condition (10), for the particular choice of, e. g., $\sigma = 1$ we get the value $0.394616\ldots$ for the u function at point 1, which contradicts the value determined by an independent, correct procedure:

$$u(1) = 0.386318\ldots. \tag{13}$$

Hence, the presumption (10) gives an incorrect result, and thus the initial presumption that q is identical for all rectangular prisms in the considered set is incorrect, too. Instead, it is true that in a given set of rectangular prisms of the same volume the one-particle partition function of translation depends on the ratio of the sides of the prisms at a given temperature. The requirement of continuity leads to the conclusion that this dependency must also be maintained on transition to rectangular prisms of volumes other than that for which the proof through contradictory was considered. The said requirement of continuity also makes the result transferable to any other arbitrary vessel shape. Thus, we arrived at the conclusion that the one-particle partition function of translation depends not only on temperature and volume but also on the shape of the vessel, even though we have not obtained any decisive result for the form and scope of this dependency. (Ref. 4 describes attempts to obtain some estimate of q for several simple bodies different from the rectangular prism, viz. sphere, hemisphere, and cylinder.)

Now it will be useful to elucidate two important questions: (i) Is not the proof given depreciated by the fact that the prisms considered were of unusually small dimensions, and (ii) Are such small dimensions thinkable for observation? On one side it is clear that the proof given considered the regions which would need a transition to the corresponding quantum statistics to give a proper physical description. In our context, however, the mathematical part of the problem was paid attention to, i. e. whether or not there is any vessel shape dependence at all. The proof given was thus of a kind of existence proof, and it did not represent any evaluation of the distinctness of this dependence. This existence proof of the dependence of q on the shape of vessel thus remains intact by consideration of unusually small dimensions. Nevertheless, on the other side, let us note that the field of inclusion phenomena[5] offers, e. g. in the case of zeolites or clathrates, cavities of molecular dimensions in which — under certain circumstances — the included particles can exhibit motions treatable as translation. The result obtained, however, does not say (as it is the case with every existence proof) anything about the construction of a proper solution of the problem. (Without any connection with the theme treated let us note that recently it has been recalled[6] that »an existence proof is the key for a jewel-box lying on the bottom of the ocean«.)

It need not be stressed that the possible vessel-shape dependency of q does not change anything in the so far found and proved excellent applicability of the approximation (4) to common situations. The proof of the vessel-shape dependency of q, of course, does not automatically implicate such dependency for thermodynamic properties of an ideal gas or even real gas. Elucidation of this problem will necessitate a transition to the ideal Bose-Einstein or Fermi-Dirac gas and, moreover, evaluation of the effect of interparticle interactions.

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SAŽETAK

Formalni dokaz da jednočestična particijska funkcija translacije idealnih plinova ovisi o obliku »posude«

Z. Slanina

Istaknuto je pogrešno granično ponašanje konvencionalne particijske funkcije translacije idealnog plina. Razmotrene su neke opće značajke egzaktne particijske funkcije Q za translaciju. Dan je formalan dokaz da Q ovisi o obliku »posude«.