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Asymptotic Lower Bound for the Relative Disparities of Truncated-Path-Integral Partition Functions

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Any truncated-path-integral partition function of a nonrelativistic quantum system in thermodynamic equilibrium—one obtained by means of the Feynman path-integral-procedure using a finite number of such integrals—is known to have a value not less than that of the exact one corresponding to it. A rigorous asymptotic lower bound obtained for the relative disparity in their values—the difference in their values divided by that of the exact partition function—confirms asymptotic positive-definiteness of the original upper bound. Values determined directly for a linear harmonic oscillator agree asymptotically with values of they bound.

KEY WORDS: Path integral; partition function; asymptotic; relative disparity; bound.

1. INTRODUCTION

The path-integral theory by which Feynman provided a novel space-time version of non-relativistic quantum mechanics[1] readily lent itself to statistical thermodynamic applications.[2] As a result, it furnished a procedure which has made it possible, in principle, to determine exactly all thermodynamic-equilibrium properties of non-relativistic quantum systems without requiring any eigen-values of their Hamiltonians to do so.

However, an important restriction on the procedure is that infinite numbers of path integrals must be evaluated for it to yield exact results.[3] This requirement cannot be met in practice and finite numbers of path integrals are invariably employed.[4, 5] A prudent suggestion has been made that the numbers which should be used for precision should be chosen

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empirically to be such that no effective changes in calculated thermodynamic properties would be produced when they are increased.[6] Nevertheless, the truncated path-integral partition functions which then do result are known to be upper bounds for the exact ones corresponding to them.[7–10] On the basis of how they have been derived, these bounds appear to be positive-semidefinite, serving only to rank the partition functions according to their values; their equality is not precluded. But intrinsic differences which actually do exist in their values turn out to be estimable from an asymptotic positive-definite lower bound that can be determined directly for their relative disparities. The display of this result and how it is obtained provides the motivation for the present paper.

For this purpose, the trace of an appropriately-ordered finite product of exponential functionals of the kinetic-energy and potential-energy operators of a non-relativistic quantum system—equivalent to a truncated-path-integral partition function—is given in Section 2, together with some of its properties. A rigorous asymptotic lower bound derived in Section 3 for the *relative disparity* of the truncated-path-integral partition function—the ratio of its excess value over that of its exact counterpart to the value of the latter—is expressible as an asymptotic series in the number of path integrals upon which it depends, the leading term of which proves to be positive-definite. Calculated values of the leading term for a one-dimensional harmonic oscillator are then compared in Section 4 with corresponding values which have been determined directly for them,[11] with the result that essential agreement between the two is attained asymptotically. Some brief discussion concerning possible limitations of the results which have been obtained is given there.

2. TRUNCATED-PATH-INTEGRAL PARTITION FUNCTIONS

Any system to be considered here is a member of a Gibbsian ensemble of non-interacting dynamically-identical non-relativistic quantum systems. It has the time-independent Hamiltonian (in atomic units throughout)

$$H = T + V \tag{1}$$

where the kinetic-energy operator of R particles comprising the system is

$$T \equiv -\sum_{k=1}^{R} \nabla_k^2/2m_k \tag{2}$$

m_k being the mass of the kth particle. The potential-energy operator of the system taken relative to its smallest value, restricted here to be finite (thus making it necessary to exclude systems with attractive Coulomb interactions), is

$$
\begin{aligned}
V \equiv V(\mathbf{r}_1, \ldots, \mathbf{r}_R) &\geqslant 0, \qquad && \text{all } \mathbf{r}_k \\
&\to +\infty, && \text{any } |\mathbf{r}_k| \to +\infty
\end{aligned} \tag{3}
$$

When in statistical-thermodynamic equilibrium, the system (ensemble) has the exact partition function (assuming that all traces exist)

$$
Z(\beta) \equiv \mathrm{Tr}\{\exp(-\beta H\}, \qquad \beta = 1/k_{\mathbf{B}} T \tag{4}
$$

where $k_{\mathbf{B}}$ is Boltzmann's constant and T is the absolute temperature. A representative truncated-path-integral partition function corresponding to it is

$$
Z(\beta; N) \equiv \mathrm{Tr}\left\{\left[\exp\left(-\frac{\beta V}{2N}\right)\exp\left(-\frac{\beta T}{N}\right)\exp\left(-\frac{\beta V}{2N}\right)\right]^N\right\} \tag{5}
$$

Pertinent restrictions of exchange-symmetry and/or exchange-antisymmetry are tacitly supposed to be fulfilled in both. (Because the trace is invariant to cyclic permutation of the factors and because each factor here is positive-definite, there are many other operators differing in form which will yield the same trace.) It has been established[7, 8] that

$$
Z(\beta; N) \geqslant Z(\beta; M) \geqslant Z(\beta), \qquad \text{for} \quad 2^n = N \leqslant M = 2^m, \qquad n, m = 0, 1, 2, \ldots \tag{6}
$$

and

$$
\lim_{N \to \infty} Z(\beta; N) \equiv Z(\beta) \tag{7}
$$

3. ASYMPTOTIC LOWER BOUND FOR PARTITION-FUNCTION DISPARITIES

To deal with the extent by which the value of a truncated-path-integral partition function exceeds that of its exact counterpart, we begin with the operator

$$
P(\beta; N) \equiv \exp\left(-\frac{\beta V}{2N}\right)\exp\left(-\frac{\beta T}{N}\right)\exp\left(-\frac{\beta V}{2N}\right) \tag{8}
$$

Because of the analyticity of its exponentials we can express it as

$$P(\beta; N) = \left(\sum_{n=0}^{\infty} \frac{(-\beta/N)^n (V/2)^n}{n!}\right)\left(\sum_{n=0}^{\infty} \frac{(-\beta/N)^n (T)^n}{n!}\right)\left(\sum_{n=0}^{\infty} \frac{(-\beta/N)^n (V/2)^n}{n!}\right)$$
$$= \sum_{n=0}^{\infty} \frac{(-\beta/N)^n}{n!} F_n(V \mid T \mid V) \tag{9}$$

where

$$F_n(V \mid T \mid V) \equiv \sum_{p,\, q,\, r \geqslant 0,\, (p+q+r=n)} \left(\frac{n!}{p!\, q!\, r!}\right)\left(\frac{V}{2}\right)^p (T)^q \left(\frac{V}{2}\right)^r \tag{10}$$

the latter series resulting from the straightforward term-by-term multiplication of the three foregoing series while retaining the indicated order of the operators and then collecting all resulting terms with the same total power of $(-\beta/N)$. For the first few terms, we get

$$F_0(V \mid T \mid V) = 1, \qquad F_1(V \mid T \mid V) = (T + V)$$
$$F_2(V \mid T \mid V) = (T + V)^2$$

and

$$F_3(V \mid T \mid V) = T^3 + \tfrac{3}{2} T^2 V + \tfrac{3}{2} V T^2 + \tfrac{3}{2} V T V + \tfrac{3}{4} T V^2 + \tfrac{3}{4} V^2 T + V^3 \tag{11}$$

As needed, other terms can be obtained from Eq. (10).

Since $P(\beta; N)$ is a positive-definite Hermitian operator, we may take its logarithm and get

$$[P(\beta; N)]^N = \exp(N \ln[P(\beta; N)])$$
$$= \exp\left(N \ln\left[\sum_{n=0}^{\infty} \frac{(-\beta/N)^n}{n!} F_n(V \mid T \mid V)\right]\right) \tag{12}$$

Expanding the logarithm in a power series of the excess of its argument over unity, we then obtain, as the result of some straightforward manipulation with the aid of Eq. (11),

$$[P(\beta; N)]^N = \exp\left(N \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{m} \left(\sum_{n=1}^{\infty} \frac{(-\beta/N)^n}{n!} F_n(V \mid T \mid V)\right)^m\right)$$
$$\approx \exp\left(-\beta H - \frac{\beta^3}{24 N^2} \{2[H, [T, V]] + [[T, V], V]\}\right) \tag{13}$$

as $N \to \infty$. Again because of the exponential's analyticity, we can express its dependence on $(\beta^3/24N^2)$ as a power series in that parameter and obtain for the truncated-path-integral partition function

$$Z(\beta; N) \approx \sum_{n=0}^{\infty} \frac{(-\beta^3/24N^2)^n}{n!} \times \left[\frac{\partial^n \operatorname{Tr}\{\exp(-\beta H - \lambda\{2[H,[T,V]] + [[T,V],V]\})\}}{\partial \lambda^n} \right]_{\lambda=0}$$

$$\approx \operatorname{Tr}\{\exp(-\beta H)\} - (\beta^3/24N^2) \operatorname{Tr}\{[[T,V],V] \exp(-\beta H)\} \quad (14)$$

so that the disparity from its exact counterpart is

$$Z(\beta; M) - Z(\beta) \approx -(\beta^3/24N^2) \operatorname{Tr}\{[[T,V],V] \exp(-\beta H)\} \quad (15)$$

Upon substituting the kinetic-energy operator of Eq. (2), followed by rearrangement, we finally obtain

$$\lim_{N \to \infty} \left(N^2 \frac{Z(\beta; N) - Z(\beta)}{Z(\beta)} \right) = \frac{\beta^3}{24} \sum_{k=1}^{R} \frac{\operatorname{Tr}\{\nabla_k V \cdot \nabla_k V \exp(-\beta H)\}}{m_k \operatorname{Tr}\{\exp(-\beta H)\}} \quad (16)$$

which expresses compactly the asymptotic positive-definiteness anticipated for the lower bound of the *relative disparity* of the partition-function. Its actual value will depend on the system to which it applies.

4. DISCUSSION

In order expose possible limitations of the foregoing theory, we consider a linear harmonic oscillator. This oscillator is a particle of mass m constrained to linear motion, with the potential-energy operator

$$V(x) = \tfrac{1}{2} m \omega^2 x^2, \qquad -\infty \leqslant x \leqslant +\infty \quad (17)$$

where x is the linear position of the particle and ω is its (circular) classical vibration frequency. For this case, it turns out that

$$\sum_{k=1}^{R} \frac{\operatorname{Tr}\{\nabla_k V \cdot \nabla_k V \exp(-\beta H)\}}{m_k \operatorname{Tr}\{\exp(-\beta H)\}} = \frac{\operatorname{Tr}\{|dV/dx|^2 \exp(-\beta H)\}}{m \operatorname{Tr}\{\exp(-\beta H)\}} = 2\omega^2 \frac{\operatorname{Tr}\{V \exp(-\beta H)\}}{\operatorname{Tr}\{\exp(-\beta H)\}} \quad (18)$$

the latter ratio being the equilibrium average of the potential energy of the particle. By the Virial Theorem, it is equal to half its total energy and thus has the value

$$\frac{\mathrm{Tr}\{V\exp(-\beta H)\}}{\mathrm{Tr}\{\exp(-\beta H)\}} = \frac{\omega}{4}\frac{(\exp(\beta\omega)+1)}{(\exp(\beta\omega)-1)} \tag{19}$$

so that, asymptotically, the relative-disparity is

$$\frac{Z(\beta;N)-Z(\beta)}{Z(\beta)} \approx \frac{(\beta^3\omega^3/N^2)}{48}\frac{(\exp(\beta\omega)+1)}{(\exp(\beta\omega)-1)} \tag{20}$$

as $N \to \infty$.

The foregoing values of relative-disparity were determined for the linear harmonic oscillator dealt with by Schweizer *et al*., for which several truncated-path-integral partition functions were determined explicitly.[11] These values are listed in Table 1, for $N \geqslant 15$, and are compared there with the relative disparities determinable from the values actually obtained by the authors. It is evident that each pair of values for a given N appears to approach essential equality as N increases, ultimately conforming to the values given by Eq. (20). Since this behavior required no *ad hoc* fitting whatever to do so, it serves to give good support for the theoretical results which have been have obtained. In addition, the oscillation frequency and the temperature pertaining to the example had values for which $\beta\omega = 20$, corresponding to that of a vibrating H_2-molecule at 300 K or that of a vibrating I_2-molecule at 15 K, both species thereby being essentially in their vibrational ground-states. It is therefore to be emphasized that the essential asymptotic agreement which has been found has involved a system which can be regarded as markedly quantum mechanical, and has thus provided a rather significant test of the theory:

Although the analysis explicitly required the numbers of path integral to be half or twice that of others, as in Eq. (6), the values in Table 1 were not so restricted. It would thus seem that such a restriction actually is not

Table 1. Comparison of Actual Relative Disparities of Truncated-Path-Integral Partition Functions and Their Bounds[a]

Number of path integrals, N	15	20	40	75	100
Relative disparity, actual	0.865	0.456	0.106	0.029	0.017
Relative disparity, bound	0.741	0.417	0.104	0.030	0.017

[a] See text for details.

necessary. An evident limitation, however, which undoubtedly has made agreement impossible for the smaller N-values of the example, arises from the limited expansions of the series which have been employed. Indeed, the values of the asymptotic bound of the relative disparities turning out to be smaller than the actual values for smaller N's suggests that higher order terms which have been neglected actually may be negative so as to account for it. This limitation could be eased by determining the operators which correspond to higher order terms that have been neglected. For the present, however, this limitation can be mitigated if any estimates involving it were to be made only when the truncated-path-integral partition functions of interest have small relative disparities from their exact counterparts.

A final limitation of the theory appears to be the presence of the exact equilibrium distribution operators in order to evaluate the relative disparities. Inasmuch as having them explicitly would render entirely unnecessary any need of the Feynman path-integral procedure, it can be anticipated that ordinarily such would not be available. However, by Eq. (13)

$$\sum_{k=1}^{R} \frac{\mathrm{Tr}\{\nabla_k V \cdot \nabla_k V \exp(-\beta H)\}}{m_k \,\mathrm{Tr}\{\exp(-\beta H)\}} = \lim_{N\to\infty} \sum_{k=1}^{R} \frac{\mathrm{Tr}\{\nabla_k V \cdot \nabla_k V (P(\beta; N))^N\}}{m_k \,\mathrm{Tr}\{(P(\beta; N))^N\}} \tag{21}$$

so that the various truncated-path-integral densities which arise in determining the corresponding partition functions make it possible to estimate the requisite bound without any knowledge of the exact equilibrium distribution, albeit as approximations to the ultimate ones.

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