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QUANTUM CORRECTIONS FOR THERMODYNAMICS*

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ABSTRACT

We generalize an expression for the trace of an operator due to Nishijima and derive, without the use of tedious mathematics, the Kirkwood expansion for the quantum mechanical partition function. This expansion is applied to three simple systems, and its use for more complex systems is thereby made clear.

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I. INTRODUCTION

The thermodynamic properties of a system of N particles in thermal equilibrium can be derived from the quantum mechanical partition function, Z_q, for a canonical ensemble[1],

$$Z_q = \mathrm{Tr}\, e^{-\beta\hat{H}}$$

(1)
$$= \sum_n e^{-\beta E_n}$$

where $\beta = (k_B T)^{-1}$, k_B is Boltzmann's constant, T is absolute temperature, and $\hat{H}$ is the Hamiltonian operator of the system. (A representation in which $\hat{H}$ is diagonal is assumed). The energy levels E_n in eq. (1) are the eigenvalues of the Schrödinger equation

(2)
$$\hat{H}\Phi_n = E_n \Phi_n$$

where Φ_n are normalized stationary N-particle wave functions for the whole system. For a system of N identical spinless particles, the Hamiltonian operator is given by[2]

(3)
$$\hat{H} = \hat{K} + \hat{\Omega}$$

where the kinetic energy $\hat{K}$ and sum of two-body potential energy $\hat{\Omega}$ are respectively given by

(4) $$\hat{K} = -\frac{\hbar^2}{2m} \sum_{j=1}^{N} \nabla_j^2$$

and

(5) $$\hat{\Omega}(\underset{\sim}{r}_1, \ldots, \underset{\sim}{r}_N) = \sum_{i<j} v(|\underset{\sim}{r}_i - \underset{\sim}{r}_j|).$$

The position vector of the j^{th} particle is represented by $\underset{\sim}{r}_j$.

The canonical ensemble average of a physical quantity represented by the operator $\hat{\mathcal{O}}$ is given by[3]

(6) $$\langle \hat{\mathcal{O}} \rangle_q = \frac{\mathrm{Tr}\, e^{-\beta\hat{H}}\, \hat{\mathcal{O}}}{Z_q}.$$

The exact and direct evaluation of the right-hand side of eq. (1), the central problem in equilibrium statistical mechanics, for most systems of physical interest is extremely difficult since one must first solve the Schrödinger equation (with the appropriate potential energy) to obtain the E_n. It is therefore natural to develop methods for approximating the right-hand side of eq. (1). The various approximation schemes developed to evaluate the quantum mechanical partition function (a) all avoid a direct computation of the E_n and (b) all are high temperature[4] expansions for the quantum corrections for

systems with classical analogs. These approximation methods can (for the most part) be grouped into the following three categories: (1) series solution of the Wigner differential equation[5-9] (the quantum mechanical analog of Liouville's equation), (2) series solution of the Block differential equation for the density matrix,[10-17] and (3) the Feynman path-integral method.[18-20] In addition to these three classes of approximation methods, other approximation schemes have been developed.[21-29]

The obtained quantum corrections are of the following two kinds (1) the corrections neglecting the details required by the symmetry restrictions to be placed on the wave functions (Bose-Einstein or Fermi-Dirac statistics); these quantum corrections are called diffraction effects (or the Wigner corrections[5]) and (2) the corrections required by the symmetry restrictions to be placed on the wave functions due to statistics; these quantum corrections are referred to as symmetry effects (or Uhlenbeck-Gropper[30] or statistical potential corrections). The first term of the diffraction effects is just the expression for the corresponding classical partition function,

(7) $$Z_c = \frac{1}{N!h^{3N}} \int \cdots \int d^{3N}r\, d^{3N}p\; e^{-\beta H}$$

where H is the corresponding classical Hamiltonian, h^{3N} is the volume of each subdivision of phase space, and $d^{3N}r\,d^{3N}p = d\underset{\sim}{r}_1 \ldots d\underset{\sim}{r}_N d\underset{\sim}{p}_1 \ldots d\underset{\sim}{p}_N$. The momentum of the N^{th} particle is represented by $\underset{\sim}{p}_N$. The related classical ensemble average is given by

$$(8) \qquad \langle \mathcal{O} \rangle_c = \frac{\frac{1}{N! h^{3N}} \int \cdots \int d^{3N} r \, d^{3N} p \; e^{-\beta H}}{Z_c} .$$

A tremendous amount of effort has been devoted to the evaluation of the right-hand side of eq. (1) since Wigner's paper in 1932 as indicated by the partial list of references. However, these developments using Wigner's differential equation, Block's differential equation, and Feynman's path-integral method or the other more formal treatments are tedious mathematical processes.[31] In almost all cases, the final result is presented in a form which makes straightforward applications extremely difficult. The analyses found in the listed textbooks are (mainly) outlines of Kirkwood's or Wigner's work.

Since the evaluation of Z_q is the main problem in equilibrium statistical mechanics, a transparent development of the right-hand side of eq. (1) is essential. In this paper, we generalize a procedure for representing the trace of an operator developed by Nishijima[21] to obtain both kind of quantum corrections for thermodynamics in a simple and straightforward manner. The resulting expansion for Z_q is used to obtain the quantum corrections (in the high-temperature limit) for an N-body system where the interaction potential is given by (1) $\Omega = 0$ (ideal gas), (2) Ω = constant, and (3) $\Omega = a \sum_{i<j} r_{ij}^2$ (harmonic oscillator).

II. THE TRACE OF AN OPERATOR

We assume that the wave functions, $\Phi_{\{\alpha\}}(\{\underset{\sim}{r}\})$, of the N-particle system can be factorized into a product of single-particle wave functions, $U_{\alpha_i}(\underset{\sim}{r}_i)$, such that

$$\Phi_{\{\alpha\}}(\{\underset{\sim}{r}\}) = \frac{1}{(N!)^{1/2}} \sum_{\rho} \delta_{\rho} \prod_{i=1}^{N} U_{\alpha_i}(\rho \underset{\sim}{r}_i)$$

$$(9) \qquad = \frac{1}{(N!)^{1/2}} \sum_{\rho} \delta_{\rho} \prod_{i=1}^{N} U_{\rho\alpha_i}(\underset{\sim}{r}_i)$$

where $\alpha_1, \alpha_2, \ldots, \alpha_N = \{\alpha\}$ are quantum numbers labelling the states occupied by individual particles. The N-particle wave functions $\Phi_{\{\alpha\}}(\{\underset{\sim}{r}\})$ characterize the states of the system as a whole. Here $\{r\} = \underset{\sim}{r}_1, \ldots, \underset{\sim}{r}_N$. The permutation on the N particles that sends the ordered set $\{\underset{\sim}{r}_1, \ldots, \underset{\sim}{r}_N\}$ into the ordered set $\{\rho \underset{\sim}{r}_1, \ldots, \rho \underset{\sim}{r}_N\}$ is represented by ρ. The $(N!)^{-\frac{1}{2}}$ quantity is a normalization factor, and the signature, δ_ρ, has the following property:

$$\delta_\rho = 1 \quad \text{bosons}$$

$$(10) \qquad \delta_\rho = \begin{cases} +1, & \rho \text{ even} \\ -1, & \rho \text{ odd} \end{cases} \qquad \text{fermions}$$

A permutation is even if it corresponds to an even number of interchanges and is odd if it is equivalent to an odd number of interchanges.

The trace (sum of the diagonal elements) of an operator $\hat{\mathcal{O}}$ is given by

$$\text{(11)} \qquad \mathrm{Tr}\,\hat{\mathcal{O}} = \frac{1}{N!} \sum_{\{\alpha\}} \int \cdots \int d^{3N}r \; \Phi^*_{\{\alpha\}}(\{\underset{\sim}{r}\}) \; \hat{\mathcal{O}} \; \Phi_{\{\alpha\}}(\{\underset{\sim}{r}\}).$$

The sum on the right-hand side of eq. (11) is over each α_i independently, and $1/N!$ is required to prevent double counting since a permutation of the α_i should not be counted as a new term in the sum.

In terms of the single-particle wave functions $U_{\alpha_i}(\underset{\sim}{r}_i)$, we write the trace of $\hat{\mathcal{O}}$ as

$$\mathrm{Tr}\,\hat{\mathcal{O}} = \frac{1}{(N!)^2} \sum_{\{\alpha\}} \int \cdots \int d^{3N}r \sum_{\rho,\rho'} \delta_\rho \delta_{\rho'} \prod_{i=1}^{N} U^*_{\alpha_i}(\rho \underset{\sim}{r}_i) \; \hat{\mathcal{O}} U_{\alpha_i}(\rho' \underset{\sim}{r}_i)$$

$$= \frac{1}{N!} \sum_{\{\alpha\}} \int \cdots \int d^{3N}r \prod_{i=1}^{N} U^*_{\alpha_i}(\underset{\sim}{r}_i) \; \hat{\mathcal{O}} \; U_{\alpha_i}(\underset{\sim}{r}_i)$$

$$\text{(12)} \qquad + \frac{1}{(N!)^2} \sum_{\{\alpha\}} \int \cdots \int d^{3N}r \sum_{\rho \neq \rho'} \delta_\rho \delta_{\rho'} \prod_{i=1}^{N} U^*_{\alpha_i}(\rho \underset{\sim}{r}_i) \, \hat{\mathcal{O}} \, U_{\alpha_i}(\rho' \underset{\sim}{r}_i).$$

The first term in eq. (12) contains the $N!$ terms in which ρ and ρ' are the same permutations, and the second term contains all terms in which ρ and ρ' are different permutations. Treating the latter term as the permutations of the particles taken two at a time (in pairs), we write eq. (12) as

$$\mathrm{Tr}\,\hat{\mathcal{O}} = \frac{1}{N!} \sum_{\{\alpha\}} \int \cdots \int d^{3N}r \prod_{i=1}^{N} U^*_{\alpha_i}(\underset{\sim}{r}_i) \, \hat{\mathcal{O}} \, U_{\alpha_i}(\underset{\sim}{r}_i)$$

$$\pm \frac{1}{N!} \sum_{\{\alpha\}} \int \cdots \int d^{3N}r$$

$$\times \prod_{j<k}^{N} \Big\{ U^*_{\alpha_j}(\underset{\sim}{r}_j) \; \hat{\mathcal{O}}_j U_{\alpha_j}(\underset{\sim}{r}_k) U^*_{\alpha_k}(\underset{\sim}{r}_k) \; \hat{\mathcal{O}}_k U_{\alpha_k}(\underset{\sim}{r}_j)$$

$$\text{(13)} \qquad + U^*_{\alpha_j}(\underset{\sim}{r}_k) \; \hat{\mathcal{O}}_j U_{\alpha_j}(\underset{\sim}{r}_j) U^*_{\alpha_k}(\underset{\sim}{r}_j) \; \hat{\mathcal{O}}_k U_{\alpha_k}(\underset{\sim}{r}_k) \Big\}$$

where the plus sign applies to bosons and the negative sign applies to fermions.

Since the trace operation is independent of the representation,[32] we use normalized free-particle wave functions for the $U_{\alpha_i}(\underset{\sim}{r}_i)$ and write

$$U_{pj}(\underset{\sim}{r}_j) = \frac{1}{V^{1/2}} \exp\left(\frac{i}{\hbar}\, \underset{\sim}{p}_j \cdot \underset{\sim}{r}_j\right) \tag{14}$$

where V is the volume of the system. We impose periodic boundary conditions on the $U_{pj}(\underset{\sim}{r}_j)$ wave functions. On substituting eq. (14) into eq. (13) and taking the thermodynamic limit, we obtain

$$\mathrm{Tr}\ \hat{\mathcal{O}} = \frac{1}{N!h^{3N}} \int\cdots\int d^{3N}r\, d^{3N}p\, A(r)B(p)$$

$$\pm \frac{1}{N!h^{3N}} \int\cdots\int d^{3N}r d^{3N} \sum_{j<k}^{N} \left\{ \left(\exp\left[\frac{i}{\hbar}\, \underset{\sim}{p}_{jk} \cdot \underset{\sim}{r}_{kj}\right] \right.\right.$$

$$\left.\left. + \exp\left[-\frac{i}{\hbar}\, \underset{\sim}{p}_{jk} \cdot \underset{\sim}{r}_{kj}\right]\right) \mathcal{O}_j \mathcal{O}_k \right\} \tag{15}$$

where $\sum_{\{p\}} \rightarrow \frac{V}{h^3} \int\cdots\int d^3p_j$ for $V \rightarrow \infty$ (the thermodynamic limit),

$\underset{\sim}{p}_{jk} = \underset{\sim}{p}_j - \underset{\sim}{p}_k$, $\underset{\sim}{r}_{kj} = \underset{\sim}{r}_k - \underset{\sim}{r}_j$, and $\mathcal{O}_j \mathcal{O}_k = A(r_j)B(p_j)A(r_k)B(p_k)$.

The form for $\hat{\mathcal{O}}$ is taken to be $\hat{\mathcal{O}} = \hat{A}(\underset{\sim}{r}_j)\hat{B}(\underset{\sim}{p}_j)$.

III. THE EXPANSION FOR Z_q

Extreme care must be used when treating $Z_q = \mathrm{Tr}\{\exp - \beta(\hat{K} + \hat{\Omega})\}$ since $\hat{K}$ and $\hat{\Omega}$ do not commute. With this in mind, we develop a series expansion for $\mathrm{Tr}\{\exp - \beta(\hat{K} + \hat{\Omega})\}$ by use of the general relation,[33] $e^{\hat{A}}e^{\hat{B}} = e^{\frac{1}{2}[\hat{A},\hat{B}]}e^{\hat{A}+\hat{B}}$ where $\hat{A}$ and $\hat{B}$ commute with $[\hat{A},\hat{B}]$. We write the partition function as[21, 29]

$$Z_q = \mathrm{Tr}\left\{e^{-\beta(\hat{K} + \hat{\Omega})}\right\}$$

$$= \mathrm{Tr}\left\{e^{-\beta\hat{\Omega}}e^{-\beta\hat{K}}\left(e^{\beta\hat{K}}e^{\beta\hat{\Omega}}e^{-\beta(\hat{K} + \hat{\Omega})}\right)\right\}$$

$$= \mathrm{Tr}\left\{e^{-\beta\hat{\Omega}}e^{-\beta\hat{K}}\left(1 + \frac{\beta^2}{2}[\hat{K},\hat{\Omega}] + \ldots\right)\right\}$$

$$= \mathrm{Tr}\left(e^{-\beta\hat{\Omega}}e^{-\beta\hat{K}}\right) + \frac{\beta^2}{2}\mathrm{Tr}\left\{e^{-\beta\hat{\Omega}}e^{-\beta\hat{K}}[\hat{K},\hat{\Omega}] + \ldots\right\} \tag{16}$$

where

$$[K,\Omega] = -\frac{\hbar^2}{2m}\sum_{j=1}^{N}\left(\frac{2i}{\hbar}\nabla_j\Omega \cdot \underset{\sim}{p}_j + \nabla_j^2\Omega\right). \tag{17}$$

Substituting eq. (17) into eq. (16), we get

$$Z_q = \mathrm{Tr}\left\{e^{-\beta\hat{\Omega}}e^{-\beta\hat{K}}\right\} + \frac{\hbar\beta^2}{2mi}\sum_{j=1}^{N}\mathrm{Tr}\left\{e^{-\beta\hat{\Omega}}e^{-\beta\hat{K}}\nabla_j\Omega \cdot \underset{\sim}{p}_j\right\}$$

$$(18) \qquad - \frac{\hbar^2\beta^2}{4m} \sum_{j=1}^{N} \mathrm{Tr}\left\{ e^{-\beta\hat{\Omega}} e^{-\beta\hat{K}} \nabla_j^2 \Omega \right\} + \cdots \quad .$$

Comparing eqs. (15) and (18), we find that Z_q becomes

$$Z_q \approx \frac{1}{N!h^{3N}} \int\cdots\int d^{3N}r\, d^{3N}p\, e^{-\beta H}$$

$$\pm \frac{1}{N!h^{3N}} \int\cdots\int d^{3N}r\, d^{3N}p \sum_{j\neq k}^{N} (\exp[\tfrac{i}{\hbar} \underset{\sim}{p}_{jk} \cdot \underset{\sim}{r}_{kj}])$$

$$\times (e^{-\beta H})_j (e^{-\beta H})_k$$

$$+ \frac{\hbar\beta^2}{2miN!h^{3N}} \sum_{\ell=1}^{N} \left\{ \int\cdots\int d^{3N}r d^{3N}p\, e^{-\beta H} \nabla_\ell \Omega \cdot \underset{\sim}{p}_\ell \right.$$

$$\pm \sum_{j\neq k}^{N} \int\cdots\int d^{3N}r d^{3N}p (\exp[\tfrac{i}{\hbar} \underset{\sim}{p}_{jk} \cdot \underset{\sim}{r}_{kj}])(e^{-\beta H})_j (e^{-\beta H})_k$$

$$\left. \times \nabla_\ell \Omega \cdot \underset{\sim}{p}_\ell \right\}$$

$$- \frac{\hbar^2\beta^2}{4mN!h^{3N}} \sum_{\ell=1}^{N} \left\{ \int\cdots\int d^{3N}r d^{3N}p\, e^{-\beta H} \nabla_\ell^2 \Omega \right.$$

(19)

$$\left. \pm \sum_{j\neq k} \int\cdots\int d^{3N}r d^{3N}p (\exp[\tfrac{i}{\hbar} \underset{\sim}{p}_{jk} \cdot \underset{\sim}{r}_{kj}])(e^{-\beta H})_j (e^{-\beta H})_k \nabla_\ell^2 \Omega \right\} .$$

Consider eq. (19): (1) the first term in just the classical partition function, Z_c; (2) the momentum intergration in the third term yields zero since the integrand is an odd function of momentum; (3) the integral in the fifth term is $Z_c \langle \nabla_\ell^2 \Omega \rangle_c$. The remaining terms in eq. (19) may be reduced to simpler forms by use of straightforward vector algebra. The final result for Z_q is

$$Z_q \approx Z_c \left(1 - \frac{\hbar^2\beta^2}{4m} \sum_{j=1}^{N} \langle \nabla_j^2 \Omega \rangle_c \right)$$

$$\pm \frac{1}{N!\lambda^{3N}} \sum_{j\neq k}^{N} \int\cdots\int d^{3N}r\, e^{-\beta\Omega} e^{-2\pi r_{kj}^2/\lambda^2} \left\{ 1 \right.$$

$$(20) \qquad \left. + \underset{\sim}{r}_{kj} \cdot (\nabla_j \Omega - \nabla_k \Omega) - \nabla_j^2 \Omega \right\}$$

where $\lambda = h/(\frac{2\pi m}{\beta})^{\frac{1}{2}}$ and is called the de Broglie thermal wavelength. The first part of eq. (20) contains the diffraction effects (Wigner corrections)[5] and the second part represents the symmetry effects (Uhlenbeck-Gropper statistical correction).[30] The expansion in eq. (20) was first derived by Kirkwood by use of a series solution of the Block differential equation for the density matrix.[10] The high-temperature approximation, $\beta = (k_B T)^{-1} \rightarrow$ small, was used in deriving eq. (20). Additional correction terms can be included by extending the development used in eq. (16).

IV. APPLICATIONS

A. Ideal Gas, $\Omega = 0$

For an ideal gas $\Omega = 0$, the expression for Z_q, eq. (20), becomes

$$Z_q \approx Z_c \pm \frac{1}{N!\,\lambda^{3N}} \sum_{j\neq k}^{N} \int\cdots\int d^{3N}r\; e^{-2\pi r_{ij}^2/\lambda^2}$$

$$= Z_c \pm \frac{N(N-1)V^{N-1}}{N!\ {}^{3N}}\, 4\pi \int_0^\infty dr\; r^2 e^{-2\pi r^2/\lambda^2}$$

or

$$(21) \qquad Z_q \approx Z_c\left(1 \pm \frac{N^2\lambda^3}{2^{3/2}V}\right)$$

where $Z_c = V^N/(N!\lambda^{3N})$ (for an ideal gas). Equation (21) is the usual expression for the partition function for an ideal gas in the high-temperature limit; the second term in eq. (21) is the correction due to the symmetry restriction placed on the wave function (symmetry effect or Uhlenbeck-Gropper correction).

B. Constant Potential. Ω = constant.

When Ω = constant, Z_q becomes

$$(22) \qquad Z_q \approx Z_c\left(1 \pm \frac{N^2\lambda^3}{2^{3/2}V}\right)$$

where $Z_c = e^{-\beta\Omega}V^N/(N!\lambda^{3N})$ for Ω = constant.

C. Harmonic Oscillator. $\Omega = a\sum_{i<j} r_{ij}^2$

If the two-body interaction is represented by a harmonic oscillator-type potential, we have by use of straightforward vector algebra

$$(23) \qquad \nabla_\ell^2\,\Omega \approx 12aN$$

and

$$(24) \qquad \underset{\sim}{r}_{kj} \cdot (\nabla_j\Omega - \nabla_k\Omega) = 4aNr_{kj}^2 \ .$$

The partition function then becomes

$$Z_q \sim Z_c \left(1 - \frac{3\hbar^2\beta^2 aN^2}{m} \right)$$

(25)
$$\pm \frac{N^2 V^{N-1} \pi^{3/2}}{N! \lambda^{3N}} \left\{ \frac{1-12aN}{(\beta a + \frac{2\pi}{\lambda^2})^{3/2}} - \frac{3aN}{2(\beta a + \frac{2\pi}{\lambda})^{5/2}} \right\} .$$

REFERENCES AND FOOTNOTES

1. For example the average energy, entropy, and average pressure are respectively given by $\langle E \rangle = - \frac{\partial \ln Z_q}{\partial \beta}$, $S = k_\beta(\ln Z_q - \beta \frac{\partial \ln Z_q}{\partial \beta})$, and $\langle P \rangle = \beta^{-1} \frac{\partial \ln Z_q}{\partial V}$ where V is the volume of the system. These expressions for closed systems are developed in standard texbooks on statistical mechanics. See for example reference 24, Chapter 8.
2. The extension to the general case of mixed particles with spin is straightforward.
3. See reference 24, Chapter 9.
4. A formal low-temperature treatment was proposed in reference 7.

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31. References 21 and 29 are exceptions.

32. See reference 24 page 187.

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