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A SIMPLIFIED DERIVATION OF WIGNER'S QUANTUM CORRECTION FOR THERMODYNAMICS*

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ABSTRACT

A simplified derivation of Wigner's quantum-mechanical correction for thermodynamic equilbrium is presented. The analysis is restricted to the quantum statistics of systems with classical analogs.

1. INTRODUCTION

It is well known that (a) the canonical ensemble is an appropriate model for systems consisting of a large number of particles, N, in statistical equilibrium and (b) the thermodynamic properties of the system may be obtained from the partition function,[1] Z_{QM}. For example, the average energy, entropy, and average pressure are respectively given by

$$\bar{E} = -\frac{\partial \ln Z_{QM}}{\partial\beta}, \quad S = k_B\left(\ln Z_{QM} - \beta\frac{\partial \ln Z_{QM}}{\partial\beta}\right), \text{ and}$$

$$\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z_{QM}}{\partial V}, \tag{1}$$

where $\beta = (k_B T)^{-1}$; k_B, T, and V are Boltzmann's constant, absolute temperature, and volume respectively. The quantum-mechanical partition function (canonical ensemble) is defined by[1]

$$Z_{QM} = \mathrm{Tr}\, e^{-\beta H}. \tag{2}$$

Here H is the Hamiltonian operator of the system.

A direct evaluation of the right-hand side of Eq. (2) for most systems is very complicated.[2] However, the corresponding classical partition function,[1]

$$Z_{CM} = \frac{1}{N!\, h^{3N}}\int\cdots\int d^{3N}q\, d^{3N}p\, e^{-\beta H}, \tag{3}$$

can usually be found. Hence it is desirable to have a procedure for transforming the right-hand side of Eq. (2) into an integral over phase

space analogous to that in Eq. (3). Wigner[3] has developed such a transformation and shown that the resulting phase integral can be expanded in powers of Planck's constant for systems with nearly classical behavior. By use of a simpler method (Bloch equation), Kirkwood[4] presented a comprehensive treatment of the problem and obtained an expansion which contained all quantum corrections[5] to Z_{CM}. However, the mathematical prerequisites[6] for understanding Kirkwood's work are such that it is not usually presented in undergraduate statistical mechanics courses.

Sposito[7] has shown, in a relatively simple way, that the correspondence postulate is valid for Z_{QM}, but he was unable to obtain an expression for the related quantum-mechanical corrections. Recently, McLellan[8] developed a procedure for establishing the validity of the correspondence postulate for Z_{QM}. He extended the method to (a) obtain the Uhlenbeck-Gropper correction for a perfect gas, (b) treat a mixture of two chemical components (Gibb's paradox[1]), and (c) find the classical limit of Z_{QM} for a system composed of particles with spin. McLellan did not obtain the Wigner correction for thermodynamic equilibrium.

The present paper is devoted to a derivation of the Wigner correction at a mathematical level that is suitable for students in undergraduate statistical mechanics courses.

2. THE RELATION BETWEEN Z_{QM} AND Z_{CM}

We consider a system of N identical spinless particles. (The extension to the general case of mixed particles with spin is straightforward.) The Hamiltonian operator is given by

$$H = K + \Omega , \tag{4}$$

where K is the kinetic energy operator and Ω is a sum of two-body potentials. That is to say,

$$K = -\frac{\hbar^2}{2m} \sum_{j=1}^{N} \nabla_j^2 \tag{5}$$

and

$$\Omega(\underset{\sim}{r}_1, \cdots, \underset{\sim}{r}_N) = \sum_{i<j} v(|\underset{\sim}{r}_i - \underset{\sim}{r}_j|) . \tag{6}$$

For this system, the canonical ensemble average of a physical quantity represented by $\mathcal{O}$ is[1]

$$\langle \mathcal{O} \rangle_{CM} = \frac{\frac{1}{N!\, h^{3N}} \int \cdots \int d^{3N}q \; d^{3N}p \; e^{-\beta H} \, \mathcal{O}}{Z_{CM}} \tag{7}$$

or

$$\langle \mathcal{O} \rangle_{QM} = \frac{\mathrm{Tr}\; e^{-\beta H} \, \mathcal{O}}{Z_{QM}} , \tag{8}$$

where h^{3N} is the volume of each subdivision of phase space.

On substituting Eq. (4) into Eq. (2), we obtain

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

$$= \mathrm{Tr}(e^{-\beta\Omega}\, e^{-\beta K}) + \frac{\beta^2}{2}\mathrm{Tr}(e^{-\beta\Omega}\, e^{-\beta K}[K,\Omega]) + \cdots \quad . \qquad (9)$$

We have used the following basic relations[9] for two arbitrary operators, A and B, to obtain Eq. (9): (a) $e^A e^B = e^{A+B} e^{\gamma/2}$ or $e^{-(A+B)} = e^{\gamma/2} e^{-B} e^{-A}$, where $\gamma = [A,B]$; (b) Tr AB = Tr BA; (c) $e^{-A} e^A = I$, where I is the identity operator; (d) Tr(A + B) = Tr A + Tr B; and $e^A = \sum_{n=0}^{\infty} \frac{A^n}{n!}$.

The commutator in Eq. (9) reduces to[10]

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

$$= -\frac{1}{2m}\sum_{j=1}^{N}(2i\hbar\,\nabla_j\Omega\cdot\underset{\sim}{p}_j + \hbar^2\,\nabla_j^{\,2}\Omega)$$

$$= \frac{\hbar^2}{mi}\sum_{j=1}^{N}\underset{\sim}{p}_j\cdot\nabla_j\Omega + \frac{\hbar^2}{2m}\sum_{j=1}^{N}\nabla_j^{\,2}\Omega\ , \qquad (10)$$

where $[\underset{\sim}{p},\Omega] = -i\hbar\nabla\Omega$. Substituting Eq. (10) into Eq. (9), we find that Z_{QM} becomes

$$Z_{QM} = \mathrm{Tr}(e^{-\beta\Omega}\, e^{-\beta K}) + \frac{\hbar^2\beta^2}{2mi}\sum_{j=1}^{N}\mathrm{Tr}(e^{-\beta\Omega}\, e^{-\beta K}\,\underset{\sim}{p}_j\cdot\nabla_j\Omega)$$

$$+ \frac{\hbar^2\beta^2}{4m}\sum_{j=1}^{N}\mathrm{Tr}(e^{-\beta\Omega}\, e^{-\beta K}\,\nabla_j^{\,2}\Omega) + \cdots \quad . \qquad (11)$$

We will now express the right-hand side of Eq. (11) in terms of Z_{CM}. Consider the trace of an operator $\mathcal{O} \equiv A(Q)\, B(\underset{\sim}{P})$ where Q and $\underset{\sim}{P}$ are space and momentum operators respectively. This trace becomes[1]

$$\mathrm{Tr}\,\mathcal{O} = \frac{1}{N!}\sum_{\underset{\sim}{P}_1\cdots\underset{\sim}{P}_N}\int\cdots\int d^{3N}r\ \Phi^*(\underset{\sim}{r}_1,\cdots,\underset{\sim}{r}_N)\,\mathcal{O}\,\Phi(\underset{\sim}{r}_1,\cdots,\underset{\sim}{r}_N)$$

$$= \frac{1}{N!\,h^{3N}}\int\cdots\int d^{3N}r\ d^{3N}p\ A(r)\ B(p)\ , \qquad (12)$$

where

$$\sum_{\underset{\sim}{P}_1\cdots\underset{\sim}{P}_N} \to \frac{V}{h^{3N}}\int\cdots\int d^{3N}p \quad \text{for } V\to\infty \quad . \qquad (13)$$

For convenience, we have taken Φ to be the wave function of a free particle since the trace is independent of the representation.[9] On comparing Eq. (12) with the first term in Eq. (11), we note that this term is just Z_{CM}. Similarly, we find that

$$\frac{\hbar^2 \beta^2}{2mi} \sum_{j=1}^{N} \mathrm{Tr}(e^{-\beta\Omega} e^{-\beta K} \nabla_j \Omega \cdot \underset{\sim}{p}_j)$$

$$= \frac{\hbar^2 \beta^2}{2mi} \sum_{j=1}^{N} \frac{1}{N!\, h^{3N}} \int \cdots \int d^{3N}r\, \nabla_j \Omega\, e^{-\beta\Omega} \cdot \int \cdots \int d^{3N}p\, \underset{\sim}{p}_j\, e^{-\beta K}$$

$$= 0 \qquad (14)$$

and

$$\frac{\hbar^2 \beta^2}{4m} \sum_{j=1}^{N} \mathrm{Tr}(e^{-\beta\Omega} e^{-\beta K} \nabla_j^2 \Omega) = \frac{\hbar^2 \beta^2}{4m} \sum_{j=1}^{N} \langle \nabla_j^2 \Omega \rangle_{CM} Z_{CM} \,. \qquad (15)$$

Substituting Eqs. (15) and (14) into Eq. (11), we obtain

$$Z_{QM} = Z_{CM} \left(1 + \frac{\hbar^2 \beta^2}{4m} \sum_{j=1}^{N} \langle \nabla_j^2 \Omega \rangle_{CM} + \cdots \right) \,. \qquad (16)$$

Equation (16) is the required expansion of Z_{QM} in terms of Z_{CM} in powers of $\hbar^2$ (the Wigner correction). Unlike Kirkwood, we have not considered the correction related to the symmetry restrictions to be placed on the wave functions corresponding to Bose-Einstein or Fermi-Dirac statistics (statistical potential: the Uhlenbeck-Gropper correction).

FOOTNOTES AND REFERENCES

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2. The procedure consists of (a) determining the allowed energies by use of the Schrödinger equation and symmetry restrictions and (b) carrying out the required summation.
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4. J. G. Kirkwood, Phys. Rev. 44, 31 (1933). Also see Chapter 10 of Ref. 1.
5. The quantum corrections consists of (a) the Wigner correction (see Ref. 3) and (b) the Uhlenbeck-Gropper correction [see G. E. Uhlenbeck and L. Gropper, Phys. Rev. 41, 79 (1932)]. The latter correction is now known as the statistical potential (see Ref. 1).
6. The mathematical prerequisites include the following: (a) Fourier transforms and inversions, (b) closure relations, (c) Bloch's equation, and (d) the WKBJ expansion.
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