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# Quantum Virial Expansion*

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The usual quantum mechanical cluster expansion in the theory of imperfect gases involves the trace of operators of the form $\exp(-H_n/kT)$, where $H_n$ is the $n$-body Hamiltonian. It is shown here that this expansion is identical with the recently derived cluster expansion in terms of the collision lifetime matrices $\mathbf{Q}_n(E)$, in which the characteristic terms involve the expressions Tr $[\exp(-E/kT)\mathbf{Q}_n(E)]$.

THE quantum mechanical form of the virial expansion for the equation of state of fluids has long been studied, especially by Uhlenbeck and his associates.[1-3] In that theory the cluster functions play a role analogous to that of the cluster integrals in the classical Ursell-Mayer theory. Following an intuitive line of reasoning, I recently derived an alternative form of the cluster expansion in which the collision lifetimes play a central part.[4] That expansion is valid both quantally and classically, but the connection with the pre-existing form was proved only in the classical case. This note contains a proof of the connection in quantum mechanics, which may also shed some further light on the structure and properties of the lifetime matrix.

Pais and Uhlenbeck[3] give a concise exposition of the quantal cluster theory. From the $n$-body Hamiltonians $H_n$ one defines the operators in the volume $V$:

$$W_n=e^{-H_n/kT}, \tag{1}$$

which are combined to form the cluster operators $U_n$. The first few of these are

$$U_1=W_1(A_1),$$
$$U_2=W_2(A_1,A_2)-U_1(A_1)U_2(A_2),$$
$$U_3=W_3(A_1,A_2,A_3)-\sum_{i=1}^{3} U_1(A_i)U_2(A_{i+1},A_{i+2})-\prod_{i=1}^{3} U_1(A_i). \tag{2}$$

The cluster functions $b_n(V)$ can then be defined by

$$(2\pi mkT/h^2)^{3n/2}n!Vb_n(V)=\mathrm{Tr}U_n=\sum_\alpha \langle\boldsymbol{\alpha}|U_n|\boldsymbol{\alpha}\rangle, \tag{3}$$

where $\boldsymbol{\alpha}$ represents all the quantum numbers needed to specify the wave functions in $V$. At large $V$ the $b_n$ become independent of $V$,

$$b_n=\lim_{V\to\infty} b_n(V). \tag{4}$$

The $b_n$ can then be identified with a ratio of partition functions which represents the equilibrium constant for $n$-body clusters. [It is for this reason that the factor $(2\pi mkT/h^2)^{3n/2}$ is included in Eq. (3)—in Ref. (3) this factor is incorporated in $z$ as it appears in their Eq. (2).]

In the collision lifetime formulation, the ratio of partition functions $b_n$ for an $n$-body cluster is given by

$$n!b_n=G_n$$
$$=(h^2/2\pi\mu_n kT)^{3(n-1)/2}\,\mathrm{Tr}'\{R_n(E',\gamma')e^{-E'/kT}\}, \tag{5}$$

where the trace operation involves an integration over the energy as well as a summation,

$$\mathrm{Tr}'=\sum_{\gamma'} h^{-1}\int dE', \tag{6}$$

and the indices $\gamma'$ include the ordinary and generalized angular momenta needed to describe the relative motion of the $n$-body system; $E'$ is the energy of relative motion in the center-of-mass system when the $n$ particles are far apart plus the internal excitation energies of the colliding particles. The trace Tr′ thus runs over the labels describing the $3n-3$ coordinates of relative motion, whereas the trace in Eq. (3) includes the motion of the center of mass as well.

The cluster lifetimes $R_n(E',\gamma')$ used in Eq. (5) are the diagonal elements of the cluster lifetime matrix.[5] Physically the $n$-body cluster lifetime refers to the time during which all $n$ bodies are close together; the $n$-body collision lifetime, on the other hand, refers to a standard state in which all $n$ particles are moving freely, and so includes contributions due to clusters of fewer than $n$ particles. $R_n$ is therefore related to the $n$-body collision lifetime matrices $Q_n$ by a subtraction scheme with the same effect as Eq. (2) [see Eqs. (52) and (56) of Ref. 5], but the result is obtained more simply by postponing the subtraction until after the averaging represented by the trace Tr′. Thus we write

$$G_n^*=(h^2/2\pi\mu_n kT)^{3(n-1)/2}\,\mathrm{Tr}'\{Q_n)E',\gamma')e^{-E'/kT}\} \tag{7}$$

and

$$G_1(A_1)=G_1^*(A_1),$$
$$G_2(A_1,A_2)=G_2^*(A_1,A_2),$$

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[1] E. Beth and G. E. Uhlenbeck, Physica **3**, 729 (1936); 4, 915 (1937).
[2] B. Kahn and G. E. Uhlenbeck, Physica **5**, 399 (1938); B. Kahn, dissertation, Utrecht, 1938 (unpublished).
[3] A. Pais and G. E. Uhlenbeck, Phys. Rev. **116**, 250 (1959).
[4] F. T. Smith, J. Chem. Phys. **38**, 1304 (1963).
[5] F. T. Smith, Phys. Rev. **130**, 394 (1963), in which $R_n$ was called the "complete lifetime matrix" and designated $Q_{A_1\cdots,A_n}$.

$$G_3(A_1,A_2,A_3)=G_3^*(A_1,A_2,A_3)-\sum_{i=1}^{3} G_1(A_i)G_2(A_{i+1},A_{i+2}), \quad (8)$$

and so on.

The collision lifetimes $Q_n$ are defined for $n\geq 2$ as the matrices[5,6]

$$Q_n(E',\gamma',\gamma'')=\lim_{R\to\infty}\left\{\int^{r\leq R}\psi_{\gamma',E'}{}^*\psi_{\gamma'',E'}d^{3n-3}t-R\sigma_{\gamma'\gamma''},\right.$$

$$\sigma_{\gamma'\gamma''}=\lim_{R\to\infty}R^{-1}\int^{r\leq R}{}_\infty\psi_{\gamma',E'\infty}\psi_{\gamma'',E'}{}^*d^{3n-3}t$$

$$=v_{\gamma'}{}^{-1}\delta_{\gamma'\gamma''}+\sum_\gamma S_{\gamma'\gamma}v_\gamma{}^{-1}S_{\gamma''\gamma}{}^*. \quad (9)$$

Here ${}_\infty\psi$ is the asymptotic form of the total wave function for the collision, and $v_\gamma$ is the velocity in the channel $\gamma$. Only the diagonal elements, $Q_n(E',\gamma')$ are needed in this application. The lifetime function $Q_1(E')$ represents the spectrum of internal energy states available for a single particle. If these states are strictly stable with degeneracies $\omega_i$, we can write

$$Q_1(E')=\sum_i \omega_i\delta(E'-E_i); \quad (10)$$

if the levels have finite widths $\Gamma_i$ and corresponding lifetimes, the Dirac $\delta$'s can be replaced by Breit-Wigner distributions.

The scattering wave functions $\psi_{\gamma',E'}$ in Eq. (9) are defined in the $(3n-3)$-dimensional space of the relative motion; they are labeled by $\gamma'$ in accordance with their incoming parts at large $R$, which correspond (except in phase) with the functions $\psi_{\gamma',E'}{}^-$ that are defined with the assumption that the scattering interaction vanishes everywhere. These functions are normalized to unit current through the $(3n-3)$-dimensional sphere at large $R$; they are not orthogonal in the usual sense, but in such a way that cross terms in the integrated current matrix at large $R$ vanish. The wave functions $|\alpha\rangle$ of Eq. (3), in the limit of very large $V$, span the same space as the product of the functions $\psi_{\gamma',E'}$ and the wave functions $\psi_{\text{c.m.}}$ describing the motion of the center of mass.

In order to show the connection between the lifetime formulation and Eqs. (3) and (4), one may introduce the approximating lifetimes $Q_n(V;E',\gamma')$ for large but finite $V$ and $R$, and the corresponding functions $G_n^*(V)$ and $G_n(V)$. Further, we can introduce $(2\pi M_nkT/h^2)^{3/2}$ which is just the partition function per unit volume for the motion of the center of mass of the group of $n$ particles; if the subscript "0" refers to the center of mass, we have

$$(2\pi M_nkT/h^2)^{3/2}V=Z_0V=\text{Tr}^0\left\{e^{-E_0/kT}\int^V\psi_0{}^*(\alpha_0)\psi_0(\alpha_0)d^3t\right\}. \quad (11)$$

If we now write $|\beta\rangle=|\alpha_0\rangle|E',\gamma'\rangle$, and define

$$P_n(V)=\langle\beta_n|\beta_n\rangle_V, \quad (12)$$

we have

$$Z_0V\,\text{Tr}'(Q_n(V)e^{-E'/kT})=\text{Tr}\{P_ne^{-E/kT}\}-\text{Tr}\left\{\prod_{i=1}^{n}P_1(A_i)e^{-E/kT}\right\}. \quad (13)$$

Now, since

$$M_n(\mu_n)^{n-1}=m^n,$$

we can prove the equivalence of Eqs. (3) and (5) by showing that

$$\text{Tr}W_n=\text{Tr}\{P_ne^{-E/kT}\}. \quad (14)$$

This is easily done if we represent the matrix $P_n$ in terms of the vectors $|\alpha_n\rangle$ rather than $|\beta_n\rangle$ for then we have

$$e^{-E/kT}|\alpha_n\rangle=e^{-H_n/kT}|\alpha_n\rangle \quad (15)$$

as a direct consequence of the Schrödinger equation.

This completes the demonstration of the equivalence of the two forms of the quantal cluster expansion.

This deduction as given is suited to Boltzmann statistics. Pais and Uhlenbeck[3] give a useful review of the adjustments needed in order to go to Bose-Einstein or Fermi-Dirac statistics [Eq. (15) above is in essence their Eq. (7)]. The formalism, largely due to Lee and Yang,[7] can be applied without difficulty to the lifetime form of the expansion.

One value of the lifetime formulation lies in the connection between $Q$ and the scattering matrix $S$, which can be defined for $n$-body collisions as well as 2-body ones. In matrix form,

$$\mathbf{Q}=i\hbar\mathbf{S}\frac{d\mathbf{S}^\dagger}{dE}. \quad (16)$$

This makes it possible to compute $Q$ in favorable cases. By this means, the problem of computing the quantal third virial coefficient is reduced to the determination of the two- and three-body scattering matrices. Similarly, the $n$th virial coefficient requires the scattering matrices up to the $n$th.

On the other hand, in the limit of classical mechanics the collision lifetime can be expressed as an integral over the trajectory—the connection between this and the quantal forms of $Q$ can be obtained by a semiclassical (WKB) analysis. Through this integral form one can easily get to the Ursell-Mayer classical cluster expansion.[4] Thus the lifetime expansion provides a convenient bridge between the quantal and classical cluster theories.

I am grateful to Professor G. E. Uhlenbeck for pointing out the importance of connecting the lifetime expansion with the quantal cluster function theory.

[6] F. T. Smith, Phys. Rev. **118**, 349 (1960).

[7] See T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959).