Journal of Statistical Physics, Vol. 62, Nos. 3/4, 1991

Convergence of Spherical Harmonic Expansions for the Evaluation of Hard-Sphere Cluster Integrals

George D. J. Phillies[1]

Received November 21, 1989; final August 6, 1990

For N particles ($N>2$), by means of a spherical harmonic expansion of Silverstone and Moats, a $3N$-dimensional cluster may be reduced to $2N+1$ trivial integrals and $N-1$ interesting integrals. For hard spheres, the $N-1$ interesting integrals are products of polynomials integrated between binomial bounds. With simple clusters, closed forms are obtained; for more complex clusters, infinite series in l (of Y_{lm}) appear. It is here shown for representative cases that these series converge exponentially rapidly, the leading pair of terms accounting for all but a few tenths of a percent of the total cluster integral.

KEY WORDS: Mathematical methods; virial coefficients; cluster integrals.

1. INTRODUCTION

In a previous paper,[1] it was demonstrated that a specific spherical harmonic transformation allows one to reduce an N-particle cluster integral from $3N$ to $N-1$ nontrivial integrations. In some cases the reduction gives rise to infinite series rather than simple closed forms. The series are exact, in the sense that the full-infinite series gives the complete function that it represents, rather than being an asymptotic approximant. This note reports the use of symbolic integration methods to test the *practical* (though not absolute) convergence of several of these infinite series. To study the practical convergence of a series, one determines if evaluation of a reasonable number of low-order terms gives a good approximation of the exact value, thereby establishing the utility of the technique for evaluating higher-order virial coefficients. The expansion methods should also be effective for evaluating higher-order[2] pseudovirial coefficients that arise naturally in concentration expansions of solution transport properties.

[1] Department of Physics, Worcester Polytechnic Institute, Worcester, Massachusetts 01609.

0022-4715/91/0200-0577$06.50/0

The pressure of a neutral gas has an expansion

$$\frac{PV}{k_B T} = n(1 + B_2\rho + B_3\rho^2 + \cdots) \tag{1}$$

n being the number of particles in the system, V being the system volume, $\rho = n/V$, and the B_N being virial coefficients. For gases whose molecules interact via an orientation-independent pair potential U_{ij}, each B_N may be written[4] as a sum of cluster diagrams. A typical N-particle cluster diagram is an integral, over the positions of N particles, of a product of Mayer f-functions $f_{ij} = \exp(-\beta U_{ij})$. Therefore B_N can be written as a series of $3N$-dimensional integrals.

For $N > 2$, translational and rotational symmetry allows reduction of B_N from $3N$ to $3N-6$ dimensions. In a previous paper,[1] I demonstrated that a transformation, introduced by Silverstone and Moats[3] based on work of Sharma[5] for many-electron quantum mechanics, serves to reduce an arbitrary N-particle cluster integral from $3N$ dimensions to: (i) three entirely trivial integrals over the location of a first particle, (ii) $2N-2$ nearly trivial integrals over products of spherical harmonics $Y_{lm}(\Omega_i)$ (the Ω_i being the angular coordinates of particles 2,..., i,..., N as determined with the origin at particle 1), and (iii) $N-1$ significant integrals over scalar distances r, s, t,... from the first particle to each of the other particles. For hard spheres, the integrands are conventional polynomials, while the limits of integration are monomials or binomials in r, s, t, e.g., 0, r, $1-s$.

With relatively simple cluster diagrams (ref. 1 provides a more complete discussion), application of the Silverstone–Moats transformation gives simple closed forms which may be evaluated analytically. With more complex diagrams, one obtains from the Silverstone–Moats transformation an infinite series in l, l being the principal index of a spherical harmonic $Y_{lm}(\Omega)$. Infinite series arising from spherical harmonics are often described as "angular momentum" expansions (though the problem at hand is purely classical, and involves only position coordinates of the molecules). Angular momentum expansions are often viewed as being slow to converge. The objective here is to show that spherical harmonic expansions based on the Silverstone–Moats transform converge relatively rapidly, at least in representative cases.

2. GENERAL RESULTS

Consider a set of points $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_i, \ldots$, separated by vectors $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. Silverstone and Moats[3] expand a function $f(\mathbf{r}_{ij}) \equiv f(|\mathbf{r}_i - \mathbf{r}_j|)$ in terms of the scalar distances r_{1i} and r_{1j} from 1 to i and j, and the angular coordinates of i and j, as measured from point 1. Specifically, $F(\mathbf{r}) = f(r)\, Y_{LM}(\theta, \phi)$ may be expanded

$$F(\mathbf{r}-\mathbf{R}) = \sum_{l=0,\, l+L+\lambda \text{even}}^{\infty} \sum_{\lambda=|l-L|}^{l+L} v_{l\lambda L}(r, R) \times \sum_{m=-l}^{l} C_{\lambda LMlm}\, Y_{\lambda, M-m}(\theta_R, \phi_R)\, Y_{lm}(\theta_r, \phi_r) \tag{2}$$

$$C_{\lambda LMlm} = \int d\Omega\; Y^{*}_{\lambda, M-m}(\Omega)\, Y^{*}_{lm}(\Omega)\, Y_{LM}(\Omega) \tag{3}$$

$$v_{l\lambda L}(r, R) = \frac{2\pi(-1)^l}{R} \sum_{a=0}^{(L+l+\lambda)/2} \sum_{b=0}^{(L+l+\lambda-2a)/2} D_{l\lambda Lab} \left(\frac{r}{R}\right)^{2b-l-1} \times \int_{|r-R|}^{r+R} \left(\frac{r'}{R}\right)^{2a-L+1} f(r')\, dr' \tag{4}$$

$$D_{l\lambda Lab} = [(2a)!!\,(2a-2L-1)!!\,(2b-2l-1)!!\,(L+l+\lambda-2a-2b)!! \times (2b)!!\,(L+l-\lambda-2a-2b-1)!!]^{-1} \tag{5}$$

$$(2N)!! = 2^N N! \tag{6}$$

$$(2N-1)!! = (2N)!/(2N)!! \tag{7}$$

$$(-2N-1)!! = (-1)^N/(2N-1)!! \tag{8}$$

Here θ_R, ϕ_R are the angular parts of $\mathbf{R}$ in spherical polar coordinates. Following Edmonds,[6] the phase of the spherical harmonics is $Y^{*}_{lm}(\theta, \phi) = (-1)^m\, Y_{l,-m}(\theta, \phi)$. Equation (3) is essentially a 3-j symbol; to aid the reader in tracing the derivation of Eqs. (3)–(8), the notation $C_{\lambda LMlm}$ of ref. 3 has been retained here. Equation (4) looks potentially tricky near $R \to 0$. For spherical atoms, the $l=0$ case is well behaved; for $l>0$, one finds the well-converged behavior $v_{ll0}(r, R) \to 0$ as $R \to 0$.

A typical N-particle cluster integral has the form $\int d\mathbf{r}_1 \cdots d\mathbf{r}_i \cdots d\mathbf{r}_N$ [...product of f functions...], individual f functions depending on pairs of particle coordinates via $f_{ij} \equiv f(\mathbf{r}_i - \mathbf{r}_j)$. By applying the transformation of Eqs. (2)–(8) to all f_{ij} in which neither i nor j is unity, one obtains products of the $v_{l\lambda L}(r_{1i}, r_{1j})$ and spherical harmonics, all spherical harmonics being centered on particle 1. Angular integrals over products of spherical harmonics are fundamentally trivial, but serve to constrain the relative values of their indices.

For hard spheres, $L = M = 0$, while $l = \lambda$. A Mayer f-function has an expansion

$$f(\mathbf{r}_{ij}) = \sum_{l=0}^{\infty} v_{ll0}(r_{1i}, r_{1j}) \sum_{m=-l}^{l} C_{l00lm}\, Y_{l,-m}(\theta_{1i}, \phi_{1i})\, Y_{lm}(\theta_{1j}, \phi_{1j}) \tag{9}$$

where $r_{1i} = |\mathbf{r}_{1i}|$, other symbols being defined in Eqs. (2)–(8). Note that the $f(r')$ in Eq. (4) is related to the Mayer f-function by $f(\mathbf{r}_{ij}) = f(r')\, Y_{00}(\Omega)$. The previous work[1] used this expansion to evaluate the three- and four-particle ring diagrams B_3 and D_4, as well as the four-particle, five-f cluster D_5, getting complete agreement with previous results. For the fully-connected four-point cluster D_6, the spherical harmonic expansion gives an infinite series, the first term of which was previously evaluated.

3. EXEMPLARY SERIES

This section treats the evaluation of two heavily-connected clusters, namely D_6 (the fully connected four-particle cluster) and E_8 (a five-particle, eight-link cluster). Consider first D_6. Placing the first particle at the origin and denoting the vectors from the first particle to the second, third, fourth,..., particles by **r**, **s**, **t**, **u**,..., one obtains for D_6.

$$D_6 = M \int d\mathbf{r} \int d\mathbf{s} \int d\mathbf{t}\, f_r f_s f_t f_{rs} f_{st} f_{rt} \tag{10}$$

where f_r links the first and second particles, $f_{rs} \equiv f(|\mathbf{r}-\mathbf{s}|)$ links the second and third particles, etc. M is the multiplicity: the number of times the diagram contributes to B_4. For D_6, one has $M = 1$. The spherical harmonic transformation eliminates f-functions not involving the first particle, so that

$$\begin{aligned} D_6 = \int d\mathbf{r}\, d\mathbf{s}\, d\mathbf{t}\, f_r f_s f_t \sum_{l,l',l''=0}^{\infty} \sum_{m,m',m''} & v_{ll0}(r, s)\, v_{l'l'0}(s, t)\, v_{l''l''0}(r, t) \\ \times\, C_{l00lm} C_{l'00l'm'} C_{l''00l''m''} & Y^*_{lm}(\Omega_r)\, Y_{lm}(\Omega_s)\, Y^*_{l'm'}(\Omega_s) \\ \times\, Y_{l'm'}(\Omega_t)\, Y^*_{l''m''}(\Omega_r)\, Y_{l''m''}(\Omega_t) & \end{aligned} \tag{11}$$

In the above equation, the triple sum on l, l', l'' is collapsed to a single sum by the angular integrals. Namely, applying the orthogonality equation $\int d\Omega_r\, Y_{lm}(\Omega_r)\, Y_{l'-m'}(\Omega_r) = (-1)^m\, \delta_{ll'} \delta_{mm'}$ (and similarly for $\int d\Omega_s, \int d\Omega_t$) forces $l = l' = l''$ and $m = m' = m''$. For hard spheres, $f(r) = 0$ $(r > 1)$ and $f(r) = -1$ $(r < 1)$. Noting $C_{l00lm} = (-1)^m/(4\pi)^{1/2}$, we may define $D_6(l)$ by $D_6 = \sum_{l=0}^{\infty} D_6(l)$, with

$$D_6(l) = -\int_0^1 dr \int_0^1 ds \int_0^1 dt\, r^2 s^2 t^2 v_{ll0}(r, s)\, v_{ll0}(s, t)\, v_{ll0}(r, t) \frac{2l+1}{(4\pi)^{3/2}} \tag{12}$$

The factors $v_{ll0}(r, s)$ of the integral are all simple polynomials, whose length increases with increasing l. While evaluation of the resulting integrals by hand would be somewhat tedious, modern computer-algebraic programs make the integrations straightforward. Using *Mathematica* (386/Weitek Version 1.1a.1), $D_6(l)$ was obtained for $l = 0, 1, \ldots, 6$; results appear in Table I, column 2. Since the fourth virial coefficient B_4, and the other doubly-connected hard-sphere cluster integrals D_4 and D_5 which contribute to B_4, are known exactly, D_6 is analytically determined; its value $D_6(\infty)$ is the final line of Table I. The right-hand column of Table I gives

$$\Delta = \frac{D_6(\infty) - \sum_{i=0}^{l} D_6(i)}{D_6(\infty)} \tag{13}$$

which is the fractional error in estimating D_6 by truncating the spherical harmonic expansion at the indicated value of l. The $l = 0$ and $l = 1$ terms jointly get D_6 within 0.1%.

It should be emphasized that the numbers in the tables largely derive from analytic calculations, conversion from exact rational numbers to decimal approximations (initially performed to 20 significant figures) generally being made as the final step of the computation. For example,

$$D_6(1) = \left(\frac{2\pi}{3}\right)^3 \frac{21429}{89600} \approx 0.2391629 \left(\frac{2\pi}{3}\right)^3$$

In two cases, the outermost integral could not be performed in a simple way by the available computer program; in these cases, the final integration was performed numerically to a higher precision than indicated here. Roundoff errors in quoting the $D_6(l)$ are therefore not significant.

A slight variation on the above method gives the integral E_8,

$$E_8 = M \int d\mathbf{r} \int d\mathbf{s} \int d\mathbf{t} \int d\mathbf{u}\, f_r f_s f_t f_u f_{rs} f_{st} f_{tu} f_{su} \tag{14}$$

Table I. Evaluation of $D_6(l)$ [Eq. (12)] for Various l, Together with the Fractional Error in Computing D_6 Attendant to Terminating the Spherical Harmonic Expansion at the Current l

l	$D_6[l]$	Δ
0	1.025669	0.1904
1	0.239163	0.001635
2	0.004848	−0.002192
3	−0.001687	−0.000859
4	−0.001186	0.000077
5	−0.000092	0.000150
6	0.000119	0.000056
∞	1.266904	0

the value of M being determined by the cluster, so $M=30$. Applying the spherical harmonic transformation

$$E_8 = 30 \int d\mathbf{r}\, d\mathbf{s}\, dt\, d\mathbf{u}\, f_r f_s f_t f_u$$
$$\times \sum_{l,l',l'',l'''=0}^{\infty} \sum_{m,m',m'',m'''} v_{ll0}(r,s)\, v_{l'l'0}(s,t)\, v_{l''l''0}(t,u)\, v_{l'''l'''0}(s,u)$$
$$\times C_{l00lm} C_{l'00l'm'} C_{l''00l''m''} C_{l'''00l'''m'''} Y^*_{lm}(\Omega_r)\, Y_{lm}(\Omega_s)$$
$$\times Y^*_{l'm'}(\Omega_s)\, Y_{l'm'}(\Omega_t)\, Y^*_{l''m''}(\Omega_t)\, Y_{l''m''}(\Omega_u)\, Y^*_{l'''m'''}(\Omega_s)\, Y_{l'''m'''}(\Omega_u) \quad (15)$$

The angular integrals again constrain the l's and m's, namely $l=m=0$ and $l'=l''=l'''$, $m'=m''=m'''$. Using identities to eliminate the C_{l00lm}, and introducing $E_8(l)$ via $E_8=\sum_{l=0}^{\infty} E_8(l)$, Eq. (15) gives

$$E_8(l) = -30 \int_0^1 dr \int_0^1 ds \int_0^1 dt \int_0^1 du\, r^2 s^2 t^2 u^2 v_{000}(r,s)$$
$$\times v_{ll0}(s,t)\, v_{ll0}(t,u)\, v_{ll0}(s,u) \frac{2l+1}{(4\pi)^2} \quad (16)$$

Table II presents $E_8(l)$ for $l=0,\ldots,7$. The exact value of this integral (39.89421) is taken from Kilpatrick.[7] From the fractional error in the truncated series (Δ, right-hand column), the series for E_8 converges slightly more rapidly than does the series for D_6, Table I. Katsura and Abe[8] have estimated E_8 by means of series expansions and a Monte Carlo expansion. Their series expansion, terminated at fourth order, does not agree with the

Table II. Evaluation of $E_8(l)$ [Eq. (16)] for Various l, Together with the Total Contribution to E_8 of All Terms through to the Current l[a]

l	$E_8[l]$	Total	Δ
0	33.402736	33.4027	0.1627
1	6.455151	39.8579	9.10×10^{-4}
2	0.107285	39.9652	-1.78×10^{-3}
3	−0.046044	39.9192	-6.26×10^{-4}
4	−0.027167	39.8920	5.54×10^{-5}
5	−0.002128	39.8899	1.08×10^{-4}
6	0.002800	39.8927	3.78×10^{-5}
7	0.001919	39.8946	-9.78×10^{-6}
∞	39.894210	0	

expansion used here to the fourth order. While Katsura and Abe's series methods are related to those used here, the two methods are clearly not identical.

4. CONCLUSIONS

The primary conclusion here is that the Silverstone–Moats spherical harmonic transformation[3] leads to series which are relatively rapidly convergent. Both for D_6 and E_8, the first two terms of the expansion account for all but a fraction of a percent of the infinite series. Use of the transformation allows a facile, primarily algebraic, attack on functions which elsewise could only be evaluated by numerical means. Even if more complicated diagrams led to forms which could not be handled analytically, so that the final integrations needed numerical or Monte Carlo integration, effecting a substantial reduction in the dimensionality of the integration

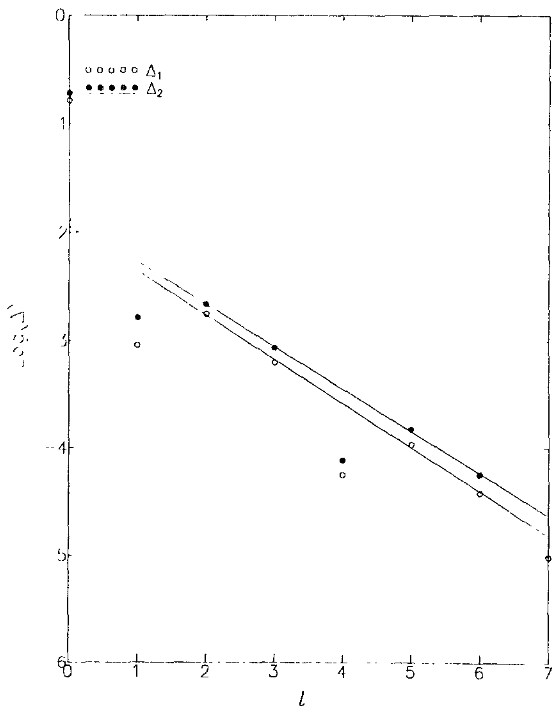

Fig. 1. Magnitude of the fractional error Δ in the spherical harmonic expansions for cluster diagrams as a function of the highest order l of included terms. Δ_1 is the error in D_6; Δ_2 is the error in E_8.

—for E_8, from 15 to 4 dimensions—may under some conditions improve both speed and accuracy of integration.

Figure 1 illustrates the convergence of the series for D_6 and E_8, plotting $\log(|\Delta|)$ against l. Evaluation of the $l=0$ and $l=1$ terms accounts for most of the value of each integral. $|\Delta|$ falls rapidly with increasing l. The solid lines, fit at large l to the outer envelope of Δ's nonmonotonic l dependence, correspond to $\log(|\Delta|)=a-bl$. For D_6, one finds $a=-1.94$, $b=-0.411$, while for E_8 one has $a=-1.873$, $b=-0.394$. The error in the fit thus improves tenfold if l is increased by $2\frac{1}{2}$.

Series treatments of virial coefficients of hard spheres have previously been used by Katsura, Kilpatrick, and collaborators.[8–11] The spherical harmonic transformation implicit in Eqs. (2)–(8) differs the series used previously in several respects. The most important is that the calculation of ref. 8 is a beautiful mathematical tour-de-force, a variety of clever methods being used to perform the computation. The method shown here hides the clever mathematics in the derivation of Eqs. (2)–(8), which for the user are a given. To apply the Silverstone–Moats transformation to hard-sphere systems, as demonstrated here, the user only needs to integrate polynomials and products of spherical harmonics.

There are expansions alternative to the Mayer graphs; Kratky,[12] proceeding from earlier partial results of Lesk,[13] introduced an expansion for the B_N in terms of overlap graphs. Also notable are the Ree–Hoover graphs,[14], in which some f_{ij} are replaced with terms $g_{ij}=f_{ij}+1$. By combining Mayer graphs with proper multiplicities into Ree–Hoover graphs, the number of distinct graphs needed in the evaluation of a given virial coefficient may be greatly reduced. For example, the diagrams D_4 and D_5 (each at multiplicity 1) combine as $D_4+D_5=\int f_r f_{rs} f_{st} f_t g_s$. Both D_4 and D_5 can be evaluated with the expansion procedure treated here, so the corresponding Ree–Hoover graph (obtained by summing the polynomials for D_4 and D_5) can also be evaluated. It is not necessary to generate D_4 and D_5 separately. Since $g_s=f_s+1$, g_s has a well-defined spherical harmonic expansion, differing from f_s in the value of v_{000}. Substitution of the spherical harmonic expansion for g_s into Ree–Hoover graphs allows their direct evaluation.

ACKNOWLEDGMENT

The material in this paper is based upon work supported by the NSF under grant DMR89-43885. The U.S. government has certain rights in this material.

REFERENCES

1. G. D. J. Phillies, *J. Stat. Phys.* **28**:673 (1989).
2. J. M. Carter and G. D. J. Phillies, *J. Phys. Chem.* **89**:5918 (1985).
3. H. J. Silverstone and R. K. Moats, *Phys. Rev. A* **16**:1731 (1977).
4. D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976).
5. R. R. Sharma, *Phys. Rev. A* **13**:517 (1976).
6. A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1974).
7. J. E. Kilpatrick, *Adv. Chem. Phys.* **20**:39 (1971).
8. S. Katsura and Y. Abe, *J. Chem. Phys.* **39**:2068 (1963).
9. J. E. Kilpatrick and S. Katsura, *J. Chem. Phys.* **45**:1866 (1966).
10. S. Katsura, *J. Chem. Phys.* **45**:3480 (1966).
11. J. E. Kilpatrick, S. Katsura, and Y. Inoue, *Math. Comput.* **21**:407 (1967).
12. K. W. Kratky, *J. Stat. Phys.* **27**:533 (1982).
13. A. M. Lesk, *J. Chem. Phys.* **63**:5048 (1975).
14. F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **46**:4181 (1967).