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# Delta-Function Expansion of Mayer Function with Application to Virial Coefficients

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The Mayer cluster integrals of a fluid with smooth, repulsive interactions are expanded in orders of a well-defined softness parameter. To first but not second order in softness, all virial coefficients are given by their hard-sphere forms with an effective diameter. A closed asymptotic expression is derived for the third virial coefficient which gives excellent results for the inverse power and exponential potentials.

**KEY WORDS:** Cluster expansion; exponential potential; inverse power potential; Mayer function; soft spheres; third virial coefficient.

## 1. INTRODUCTION

There are a variety of problems in statistical mechanics where numerical solutions for hard-sphere potentials are known with greater accuracy and rigor than those for soft potentials. Examples are the third and higher virial coefficients[(1)] and density-dependent contributions to transport coefficients.[(2)] It is thus of interest to find techniques by which these solutions for the hard sphere may be generalized to soft potentials.

One such technique, the subject of this paper, is the delta-function expansion of the Mayer function. Although such a method has been discussed by Kim,[(3)] it does not seem to have been recognized previously that this makes possible a *systematic* expansion in orders of the softness of the potential. The expansion is closely analogous to Sommerfeld's expression[(4)] for the derivative of the Fermi distribution; in the present case softness plays the same role as temperature in the Fermi problem.

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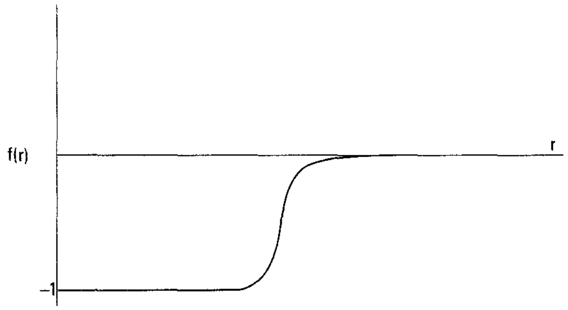


Fig. 1. The Mayer function $f(r)$.

The Mayer function is

$$f(r) = e^{-\phi(r)/kT} - 1 \tag{1}$$

where $\phi(r)$ is the two-body potential. For a sharply repulsive potential, $f(r)$ is displayed in Fig. 1. It is a step function for hard spheres. The derivative of the Mayer function, $h(r) = \partial f/\partial r$, is displayed in Fig. 2. For hard spheres, $h(r) = \delta(r - \sigma)$, where $\sigma$ is the hard-sphere diameter.

We consider integrals of the form

$$\int_0^\infty F(r)h(r)\,dr$$

where $F(r)$ is any function that varies slowly compared to the sharp spike $h(r)$. If $F(r)$ is expanded in a Taylor series about a point $r_0$, chosen near the peak of $F(r)$, the integral may be written as

$$\int_0^\infty F(r)h(r)\,dr = \sum_{m=0}^{\infty} \frac{1}{m!}\left(\frac{\partial^m F}{\partial r^m}\right)_{r=r_0} \int_0^\infty (r - r_0)^m h(r)\,dr \tag{2}$$

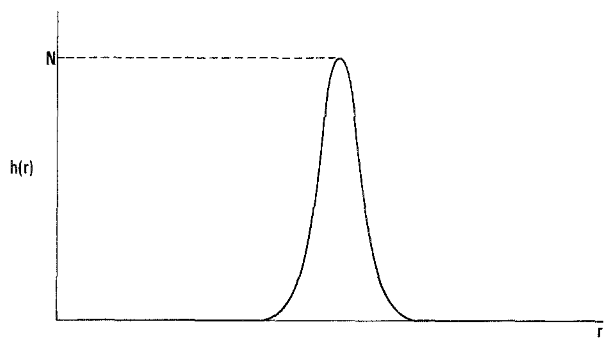


Fig. 2. The derivative of the Mayer function.

Upon defining the averages

$$\langle r^m \rangle = \int_0^\infty r^m h(r)\, dr \tag{3}$$

it is seen that a convenient choice of $r_0$ is $r_0 = \langle r \rangle$. Then Eq. (2) can be rewritten

$$\int_0^\infty F(r)h(r)\, dr = F(r_0) + \sum_{m=2}^{\infty} \frac{1}{m!} \left(\frac{\partial^m F}{\partial r^m}\right)_{r=r_0} \langle (r - \langle r \rangle)^m \rangle \tag{4}$$

and therefore $h(r)$ can effectively be written as an expansion in derivatives of Dirac $\delta$-functions,

$$h(r) = \delta(r - r_0) + \sum_{m=2}^{\infty} (-1)^m \langle (r - \langle r \rangle)^m \rangle \frac{1}{m!} \frac{\partial^m}{\partial r^m} \delta(r - r_0) \tag{5}$$

Formal integration of Eq. (5) yields a similar expansion for $f(r)$,

$$\begin{aligned} f(r) &= -1 + \int_0^r h(r')\, dr' \\ &= -\theta(r_0 - r) + \sum_{m=2}^{\infty} \frac{1}{m!} (-1)^m \langle (r - \langle r \rangle)^m \rangle \frac{\partial^{m-1}}{\partial r^{m-1}} \delta(r - r_0) \end{aligned} \tag{6}$$

where $\theta$ is the Heaviside step function.

The utility of Eqs. (5) and (6) is that, for steeply repulsive potentials, the successive coefficients of the $\delta$-function derivatives form a rapidly decreasing series. This can be seen from a qualitative examination of Fig. 2. If the potential is nearly a hard sphere, $h(r)$ has a large maximum value $N$. But since there is unit area under the curve, the width of the peak is $\sim N^{-1}$. Provided that the wings of the peak decay rapidly, the dispersion averages $\langle (r - \langle r \rangle)^m \rangle$ are of order $N^{-m}$, so Eqs. (5) and (6) are expansions in the small parameter $(r_0 N)^{-1}$.

More specifically, we may consider a class of potentials containing a parameter $n$ such that, in the limit $n \to \infty$, the potential becomes a hard sphere. Two examples are the inverse power potential

$$\phi(r) = \epsilon(\sigma/r)^n \tag{7}$$

and the exponential potential

$$\phi(r) = \phi_0 e^{-r/a} \tag{8}$$

which may be written in the alternate form

$$\phi(r) = \epsilon e^{n(\sigma - r)/\sigma} \tag{9}$$

When $n$ is large for either potential, $N \approx n/\sigma e$. It will be shown explicitly that the coefficients of Eqs. (5)–(6) for these potentials are $O(n^{-m})$.

The present choice of $r_0$ coincides with the effective temperature-dependent hard-sphere diameter proposed by Rowlinson[5] and utilized by Barker and Henderson.[6] This feature has been pointed out previously by Kim.[3]

This expansion in powers of a softness parameter is somewhat similar to that of the well-known liquid theory of Andersen, Weeks, and Chandler (AWC).[7] However, AWC generalize the above $r_0$ by constructing a temperature- *and density*-dependent effective diameter, and then relate the thermodynamics of a core fluid to that of a fluid of hard spheres with their effective diameter. In the present context, only a temperature-dependent effective diameter $r_0$ is introduced and higher order corrections are derived explicitly without reference to a further generalization of the effective diameter concept.

Sommerfeld's expression for the derivative of the Fermi distribution function is perhaps the best-known example of the delta-function expansion technique. The temperature of the Fermi fluid is assumed small compared to the degeneracy temperature $T_F$, and coefficients of the analog of Eq. (5) are proportional to successively higher powers of $(T/T_F)$. This method can be used to derive the thermodynamic properties of the ideal Fermi gas and, with some modifications, interacting Fermi fluids[8] in a series in the small parameter $T/T_F$. Zero temperature is analogous to the hard sphere, and finite temperature to the soft potential. One difference is that the derivative of the Fermi function is symmetric, so terms in odd powers of $(T/T_F)$ do not appear, whereas $h(r)$ in general is not symmetric [for the inverse power and exponential potential $h(r)$ is skewed right], so that terms of both even and odd $m$ are present in Eq. (5). It has been shown[9] that the Sommerfeld expansion of Fermi gas thermodynamic properties is not a convergent series in $(T/T_F)$ but is an asymptotic expansion, which, however, is in excellent agreement with the exact result for small temperature. We shall see that a similar situation holds for the virial coefficients of steeply repulsive potentials.

The remainder of this paper is devoted to a study of virial coefficients of such potentials. A closed algebraic expression is derived for the third virial coefficient which gives excellent agreement with previous numerical results.

## 2. INVERSE POWER POTENTIAL

For convenience we denote the dispersion averages in Eqs. (5) and (6) by $R_m$, i.e.,

$$R_m = \langle (r - \langle r \rangle)^m \rangle \tag{10}$$

It is easily seen by using $\phi$ instead of $r$ as the integration variable in Eq. (3) that, for the inverse power potential,

$$\begin{aligned} \langle r^m \rangle &= \sigma^m (\epsilon/kT)^{m/n} \Gamma(1 - m/n) \\ r_0 &= \sigma(\epsilon/kT)^{1/n} \Gamma(1 - 1/n) = \sigma(\epsilon/kT)^{1/n}[1 + (\gamma/n) + O(1/n^2)] \end{aligned} \tag{11}$$

where $\gamma$ is Euler's constant, and therefore

$$R_m = \sigma^m \left(\frac{\epsilon}{kT}\right)^{m/n} \sum_{j=0}^{m} \binom{m}{j} (-1)^j \Gamma\left(1 - \frac{m-j}{n}\right)\left[\Gamma\left(1 - \frac{1}{n}\right)\right]^j \tag{12}$$

It is shown in the appendix that $R_m$ is $O(n^{-m})$, so that the inverse power potential explicitly satisfies the criteria described below Eq. (6), and hence Eq. (6) is a power series with $n^{-1}$ as the expansion parameter.

We immediately have an interesting result concerning the general virial coefficients. The virial coefficients are linear sums of cluster integrals, which in general have the form

$$\int \cdots \int d\mathbf{r}_i \, d\mathbf{r}_j \, d\mathbf{r}_k \cdots f_{ij} f_{jk} \cdots$$

These are known through the seventh virial coefficient for hard spheres.[1] Now Eq. (10) may be substituted for the $f$'s in the integral. The leading term contains only products of $\theta(r_0 - r)$. Now $r_0$ is temperature- and $n$-dependent but otherwise constant, so this leading term is simply the (known) virial coefficient for a hard sphere with the temperature-dependent diameter $r_0$.

The next-to-leading terms in the product of $f_{ij}$ are the cross products containing one factor of $R_2 \, \delta'(r - r_0)$ with all other factors being step functions. But these terms are $O(n^{-2})$ and all additional terms are at least $O(n^{-3})$. Therefore, through $O(n^{-1})$, the correct virial coefficients are obtained immediately by means of the hard-sphere virial formulas with an effective $T$-dependent diameter $r_0$. Rowlinson[10] has shown that the third virial coefficient is given correctly through $O(n^{-1})$ by the above effective diameter replacement method, and has devised an approximation scheme[5] for the fourth and higher virial coefficients along similar lines. But it appears not to have been previously recognized that the *exact* virial coefficients, through $O(n^{-1})$, may be found with such a simple replacement.

The effective diameter alone does not give the correct result through $O(n^{-2})$, because of the terms in $R_2$. In general these terms will resemble the cluster integrals of the hard-sphere problem, but with one of the volume integrals replaced by a surface integral.

## 3. EXPONENTIAL POTENTIAL

The exponential potential is given by Eq. (7). The second[11] and third[12] virial coefficients for this potential have been analyzed by Bruch. Again it is convenient to use $\phi$ as the integration variable, and it is easily found that

$$\langle r^m \rangle = a^m \int_0^{\phi_0/kT} [\ln(\phi_0/kT) - \ln x]^m \, dx \, e^{-x} \tag{13}$$

For reasonably large $\phi_0/kT$, the upper limit can, to excellent approximation, be replaced by infinity. The error is of order $\exp(-\phi_0/kT)$; in the alternate form for $\phi$, Eq. (8), the error is $\sim\exp(-e^n)$, which is extremely small for large or moderate $n$.

It is easy to show that, if $2 \leqslant m \leqslant 6$,

$$R_m = a^m \sum_{j=0}^{m} \binom{m}{j} (-1)^j I_j I_1^{m-j} \tag{14}$$

where

$$I_j = \int_0^\infty \ln^j x \, dx \, e^{-x} \tag{15}$$

From Eq. (8), $a = \sigma/n$, so that $R_m$ is $O(n^{-m})$ and the criteria described below Eq. (6) are again satisfied.

The $I_j$ may be found from the following properties of the gamma and psi functions.[13]

$$\Gamma(1 + x) = \sum_{m=0}^{\infty} \frac{x^m}{m!} I_m \tag{16}$$

so that $-I_1 = \gamma =$ Euler's constant, and $r_0 = a[\ln(\phi_0/kT) + \gamma]$; and

$$\psi(x) = \frac{d}{dx} \ln \Gamma(x) \tag{17}$$

$$\frac{d^m}{dx^m} \psi(x)|_{x=1} = (-1)^{m+1} m! \, \zeta(m + 1) \tag{18}$$

where $\zeta$ is the Riemann zeta function.[13] Manipulation of the Taylor series expansions of $\Gamma(1 + x)$ and $\psi(1 + x)$ yields a set of simultaneous equations for the $I_j$ and we eventually find, after a straightforward calculation,

$$\begin{aligned} &R_2 = a^2\zeta(2), \qquad R_3 = 2a^3\zeta(3), \qquad R_4 = a^4\{6\zeta(4) + 3[\zeta(2)]^2\} \\ &R_5 = a^5\{24\zeta(5) + 20\zeta(2)\zeta(3)\} \\ &R_6 = a^6\{120\zeta(6) + 90\zeta(2)\zeta(4) + 40[\zeta(3)]^2 + 15[\zeta(2)]^3\} \end{aligned} \tag{19}$$

Note that $\zeta(2) = \pi^2/6$, $\zeta(4) = \pi^4/90$, and $\zeta(6) = \pi^6/945$.

## 4. SECOND VIRIAL COEFFICIENT

The second virial coefficient $B$ provides an almost trivial but nevertheless instructive example of the present technique. The expression for $B$ is

$$B = \frac{2\pi}{3} \int_0^\infty r^3 \frac{d}{dr} f(r) \, dr \tag{20}$$

We substitute the delta-function expansion, Eq. (6), for $f(r)$. Although Eq. (6) is an infinite series, when applied to Eq. (20) the series can be truncated since fourth and higher derivatives of the integrand vanish. The result is

$$B = B^{(0)} + B^{(2)} + B^{(3)} \tag{21}$$

where

$$B^{(0)} = \tfrac{2}{3}\pi r_0^3, \qquad B^{(2)} = 2\pi r_0 R_2 = O(n^{-2}), \qquad B^{(3)} = \tfrac{2}{3}\pi R_3 = O(n^{-3}) \tag{22}$$

For example, for the inverse power potential $B^{(0)} = (2\pi\sigma^3/3)(\epsilon/kT)^{3/n} \times [1 + (3\gamma/n) + O(n^{-2})]$, which agrees with the exact $B$ through $O(n^{-1})$.

However, since $\langle r \rangle = r_0$, the above expressions can be added explicitly to give

$$B = \tfrac{2}{3}\pi\langle r^3 \rangle \tag{23}$$

which recovers Eq. (20). Thus, although in general the delta-function expansion of $f(r)$ is valid only for large $n$, here it gives a closed result valid for all $n$ (such that $B$ exists). We shall see that for the third virial coefficient a similar closed form results.

## 5. THIRD VIRIAL COEFFICIENT

The third virial coefficient has been examined for the inverse power potential by Rowlinson[10] and for the exponential potential by Bruch.[12] A useful expression for the third virial coefficient is

$$C = -(8\pi^2/3)\int_0^\infty r_{12}\,dr_{12}\int_0^\infty r_{13}\,dr_{13} \times \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} r_{23}\,dr_{23} f(r_{12})f(r_{13})f(r_{23}) \tag{24}$$

We now substitute the delta-function expansion for $f(r)$, Eq. (6), into Eq. (24). The result is

$$C = -\frac{8\pi^2}{3}\Bigg[C_{000} + \frac{1}{2!}R_2(C_{200} + C_{020} + C_{002}) - \frac{1}{3!}R_3(C_{300} + C_{030} + C_{003}) + \frac{1}{4!}R_4(C_{400} + C_{040} + C_{004}) - \frac{1}{(2!)^2}R_2^2(C_{220} + C_{202} + C_{022}) + \cdots\Bigg] \tag{25}$$

where

$$C_{ijk} = \int_0^\infty r_{12}\,dr_{12}\int_0^\infty r_{13}\,dr_{13}\int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} r_{23}\,dr_{23} f^{(i)}(r_{12})f^{(j)}(r_{13})f^{(k)}(r_{23}) \tag{26}$$

$$f^{(0)}(r) = -\theta(r_0 - r) \tag{27}$$

$$f^{(m)}(r) = \frac{d^{m-1}}{dr^{m-1}}\,\delta(r - r_0) \qquad (m \geqslant 2) \tag{28}$$

Although the series in Eq. (25) appears to be infinite, in fact a natural truncation occurs. First, since the integration region of Eq. (26) is symmetric in $r_{12} - r_{13} - r_{23}$ space, $C_{ijk}$ is invariant under permutation of its indices. Second, when $r_{12} < 2r_0$,

$$\int_0^\infty r_{13}\,dr_{13}\int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} r_{23}\,dr_{23}\,\theta(r_0 - r_{13})\theta(r_0 - r_{23})$$
$$= (1/24)r_{12}^4 - \tfrac{1}{2}r_{12}^2 r_0{}^2 + \tfrac{2}{3}r_{12}r_0{}^3 \tag{29}$$

This is a fourth-degree polynomial in $r_{12}$, so $C_{m00}$ vanishes for $m > 6$. Similarly, since

$$-\int_0^\infty r_{13}\,dr_{13}\,\delta'(r_{13} - r_0)\int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} r_{23}\,dr_{23}\,\theta(r_0 - r_{23})$$
$$= -\tfrac{1}{2}r_{12}^2 + 2r_0 r_{12} - r_0{}^2 \tag{30}$$

it follows that $C_{m20}$ vanishes for $m > 4$. The only remaining nonzero integral is $C_{222}$. The calculation of the $C_{ijk}$ is straightforward; the results are

$$\begin{aligned} &C_{000} = -(5/48)r_0{}^6, \quad C_{200} = -(1/24)r_0{}^4, \quad C_{300} = -\tfrac{5}{6}r_0{}^3 \\ &C_{220} = -\tfrac{3}{2}r_0{}^2, \quad C_{400} = \tfrac{1}{2}r_0{}^2, \quad C_{320} = r_0, \quad C_{500} = 5r_0 \\ &C_{600} = -5, \quad C_{402} = 3, \quad C_{222} = -1 \end{aligned} \tag{31}$$

Therefore, the final result for $C$ is

$$\begin{aligned} C = \pi^2[&(5/18)r_0{}^6 + \tfrac{1}{6}r_0{}^4R_2 - (10/9)r_0{}^3R_3 - \tfrac{1}{6}r_0{}^2R_4 + 3r_0{}^2R_2{}^2 + \tfrac{1}{3}r_0R_5 \\ &+ \tfrac{4}{3}r_0R_2R_3 + (1/18)R_6 - R_4R_2 + \tfrac{1}{3}R_2{}^3] \end{aligned} \tag{32}$$

For an inverse power potential with very large $n$, the first term dominates and $C = (5\pi^2\sigma^6/18)(\epsilon/kT)^{6/n}[1 + (6\gamma/n) + O(n^{-2})]$.

Unlike the second virial coefficient, this method does not give an *exact* expression for $C$, as a counterexample can be found. However, Eq. (32) provides an asymptotic expansion for steep potentials which remains an excellent approximation over a fairly large range of the steepness parameter.

Rowlinson[10] has derived the following expression for $C$ for an inverse power potential:

$$C = C^{(1)} + C^{(2)} \tag{33}$$

with

$$\begin{aligned} C^{(1)} = \pi^2\sigma^6\left(\frac{\epsilon}{kT}\right)^{6/n}&\left\{\frac{4}{3}\left[\Gamma\left(1 - \frac{2}{n}\right)\right]^3 - \frac{1}{2}\Gamma\left(1 - \frac{2}{n}\right)\Gamma\left(1 - \frac{4}{n}\right)\right. \\ &\left. + \left[\Gamma\left(1 - \frac{3}{n}\right)\right]^2\right\} \end{aligned} \tag{34}$$

$$\begin{aligned} C^{(2)} = 8\pi^2 n\left(\frac{\epsilon}{kT}\right)^{6/n} z^{-6/n}\sum_{j=1}^{q}\sum_{k=1}^{q}\frac{(-z)^{j+k}}{j!\,(k-1)!} \\ \times [(nj-2)(nj-3)(nj-4)(nj-6)(nj+nk-6)]^{-1} \end{aligned} \tag{35}$$

Table I. Values of $c_0$ for Inverse Power Potential

| $n$ | Eq. (32) | Rowlinson | Kihara and Hikita |
|---|---|---|---|
| 9 | 0.9798351 | — | 0.9756 |
| 10 | 0.9296451 | 0.9297 | — |
| 12 | 0.8643722 | 0.86439 | 0.8644 |
| 15 | 0.8061341 | 0.80613 | 0.8069 |
| 18 | 0.7704327 | 0.77044 | 0.7706 |
| 20 | 0.7534600 | 0.75346 | — |
| 25 | 0.7243374 | 0.72434 | — |
| 28 | 0.7124060 | 0.71239 | — |
| 50 | 0.6856234 | — | — |

In Eq. (35), $q$ is a large, odd integer and $z$ is the root of the equation

$$\sum_{k=0}^{q} (-z)^{-k}/k! = 0 \tag{36}$$

Rowlinson gives his results in terms of a parameter $c_0$ defined such that

$$C = c_0 b_0^2 (\epsilon/kT)^{6/n} \tag{37}$$

where $b_0 = \frac{2}{3}\pi\sigma^3$. For hard spheres, $c_0 = 5/8$. Table I shows a comparison of Rowlinson's results, numerical results due to Kihara and Hikita,[14] and our results obtained by substituting Eq. (12) into Eq. (32).

The agreement with Rowlinson is excellent. However, Eq. (32) predicts an infinite $C$ for $n = 6$ (because of the term in $R_6$), whereas $C$ remains finite for all $n > 3$. Thus the asymptotic series, Eq. (32), breaks down near $n = 6$. Note that Rowlinson's formulas, Eqs. (33)–(35), suffer from a similar defect. The disagreement with Kihara and Hikita at $n = 9$ may reflect the onset of instability in our series.

It is interesting to look at Eq. (32) in a bit more detail. Table II gives

Table II. Values of the Dispersion Averages $R_i$

| | $n = 7$ | $n = 9$ | $n = 12$ | $n = 28$ | $n = 50$ |
|---|---|---|---|---|---|
| $R_2$ | 0.0532719 | 0.0285871 | 0.0146085 | 0.0023149 | 0.0006944 |
| $R_3$ | 0.0298178 | 0.0098020 | 0.0030896 | 0.0001526 | 0.0000231 |
| $R_4$ | 0.0497596 | 0.0099937 | 0.0020263 | 0.0000357 | 0.0000029 |
| $R_5$ | 0.1359816 | 0.0131592 | 0.0014670 | 0.0000073 | 0.0000003 |
| $R_6$ | 0.9042642 | 0.0285213 | 0.0015646 | 0.0000021 | $4 \times 10^{-8}$ |

**Table III. Values of the Terms in Eq. (32)**

| Term in (32) | $n = 7$ | $n = 9$ | $n = 12$ | $n = 28$ | $n = 50$ | Order |
|---|---|---|---|---|---|---|
| 1 | 1.1425151 | 0.9795116 | 0.8644590 | 0.7118359 | 0.6711623 | $n^0$ |
| 2 | 0.0298665 | 0.0144640 | 0.0068006 | 0.0009467 | 0.0002731 | $n^{-2}$ |
| 3 | −0.1007875 | −0.0306775 | −0.0090839 | −0.0004072 | −0.0000599 | $n^{-3}$ |
| 4 | −0.0228158 | −0.0043531 | −0.0008443 | −0.0000140 | −0.0000011 | $n^{-4}$ |
| 5 | 0.0234222 | 0.0064075 | 0.0016050 | 0.0000378 | 0.0000033 | $n^{-4}$ |
| 6 | 0.1127730 | 0.0106368 | 0.0011613 | 0.0000056 | 0.0000002 | $n^{-5}$ |
| 7 | 0.0052694 | 0.0009060 | 0.0001429 | 0.0000011 | 0.0000001 | $n^{-5}$ |
| 8 | 0.1130330 | 0.0035652 | 0.0001956 | 0.0000003 | $5.3 \times 10^{-9}$ | $n^{-6}$ |
| 9 | −0.0059643 | −0.0006428 | −0.0000664 | −0.0000002 | $-4.5 \times 10^{-9}$ | $n^{-6}$ |
| 10 | 0.0001134 | 0.0000175 | 0.0000023 | $9.3 \times 10^{-9}$ | $2.5 \times 10^{-10}$ | $n^{-6}$ |
| Total | 1.2974248 | 0.9798351 | 0.8643722 | 0.7124060 | 0.6713779 | — |

values of $R_m$, and Table III gives the contribution of the successive terms in Eq. (32) to $c_0$ for various exponents. The order in $(n^{-1})$ of each term is indicated; recall that $R_m$ is $O(n^{-m})$. For large values of $n$ the terms are clearly separated into different orders. But as $n$ becomes smaller, the higher order terms become more important until, for $n = 7$, the fifth- and sixth-order terms are dominant. (When $n = 6$, $R_6$ and the contribution of term 8 in Table III become infinite.) Upon comparing Tables I–III, it is seen that a reasonable criterion for the accuracy of the present method is that the terms as ordered in powers of $n^{-1}$ form a decreasing series, with some allowances made for parity considerations.

It may also be shown, by means of the Taylor series for the gamma function, that the first three terms of Eq. (32) agree with Rowlinson's $C^{(1)}$ through $O(n^{-3})$, as they should, since both the remainder of Eq. (32) and Rowlinson's $C^{(2)}$ are $O(n^{-4})$.

Equation (32) may also be applied to the exponential potential. On substituting Eq. (19), we find that

$$C = \frac{5}{18}\pi^2 a^6 \left\{ \left(\ln\frac{\phi_0}{kT} + \gamma\right)^6 + \frac{\pi^2}{10}\left(\ln\frac{\phi_0}{kT} + \gamma\right)^4 - 8\zeta(3)\left(\ln\frac{\phi_0}{kT} + \gamma\right)^3 + \frac{21\pi^4}{100}\left(\ln\frac{\phi_0}{kT} + \gamma\right)^2 + \left[\frac{144}{5}\zeta(5) + \frac{28\pi^2}{5}\zeta(3)\right]\left(\ln\frac{\phi_0}{kT} + \gamma\right) + 8[\zeta(3)]^2 - \frac{149\pi^6}{12{,}600} \right\} \tag{38}$$

Numerically, this equation is

$$C = \frac{5}{18}\pi^2 a^6\left[\left(\ln\frac{\phi_0}{kT}+\gamma\right)^6 + 0.98696\left(\ln\frac{\phi_0}{kT}+\gamma\right)^4 - 9.61646\left(\ln\frac{\phi_0}{kT}+\gamma\right)^3 + 20.4559\left(\ln\frac{\phi_0}{kT}+\gamma\right)^2 + 96.3009\left(\ln\frac{\phi_0}{kT}+\gamma\right) + 0.1907\right] \tag{39}$$

The first three terms of Eq. (39) agree with results derived by Bruch.[12] The fourth and fifth terms coincide with Bruch's upper limit [see his Eq. (18)], while the sixth term lies between Bruch's upper and lower limits.

The numerical calculations of Sherwood and Mason[15] are compared with Eq. (39) in Table IV. Agreement is excellent over the entire range. Here the parameter $C^*$ is defined by the equation

$$C = C^* b_0^2[\ln(\phi_0/kT) + \gamma]^6 \tag{40}$$

where $b_0 = \frac{2}{3}\pi a^3$. As $\phi_0/kT$ becomes infinite, $C^*$ approaches 5/8.

Kim[3] has employed the delta-function expansion method to derive the third virial coefficient, but instead of using the Mayer cluster integrals, he uses the Percus–Yevick[16] approximation to the radial distribution function. In particular, he obtains an incorrect expression for the third virial coefficient for a gas of exponentially repulsive molecules. Since the Percus–Yevick radial distribution is known to yield the correct third virial coefficient, the reason for Kim's discrepancy is not clear.

**Table IV. Values of $C^*$ for Exponential Potential**

| $\phi_0/kT$ | $C^*$ [Eq. (39)] | $C^*$ (Ref. 15) |
|---|---|---|
| $10^{12}$ | 0.6255310 | 0.62553 |
| $10^{11}$ | 0.6256070 | 0.62561 |
| $10^{10}$ | 0.6256996 | 0.62570 |
| $10^{9}$ | 0.6258135 | 0.62581 |
| $10^{8}$ | 0.6259550 | 0.62596 |
| $10^{7}$ | 0.6261325 | 0.62613 |
| $10^{6}$ | 0.6263573 | 0.62636 |
| $10^{5}$ | 0.6266505 | 0.62665 |
| $10^{4}$ | 0.6270924 | 0.62710 |
| $10^{3}$ | 0.6283135 | 0.62829 |

## 6. DISCUSSION

The delta-function expansion method has been shown to provide a *systematic* expansion of the thermodynamic properties of a "nearly hard-sphere" gas in orders of the softness of the potential. As an explicit example, an expression for the third virial coefficient, Eq. (32), has been derived. The complicated three-body cluster integrals have been replaced by the simpler dispersion averages $R_m$, Eq. (10). The expression holds for *any* sufficiently steep potential, while the $R_m$ are analytically solvable for the special cases of inverse power and exponential potentials. The resulting numerical values agree very well with previous studies over a wide range of softness. The method can also be applied to higher virial coefficients, quantum corrections to the virial coefficients, density expansions of pair distribution functions, and related problems.

The present technique may also prove valuable in the study of the density dependence of gas transport properties,[17–19] and particularly to those theories that depend in some way on the equilibrium properties of the fluid.[19] The latter topic is presently under investigation.

## APPENDIX

Here we prove the result for inverse power potentials that $R_m$ is $O(n^{-m})$. This result is to be expected from the qualitative considerations discussed below Eq. (6).

Let $x = n^{-1}$. Then Eq. (12) is

$$R_m = \sigma^m(\epsilon/kT)^{m/n} \sum_{j=0}^{m} \binom{m}{j}(-1)^j \Gamma[1-(m-j)x][\Gamma(1-x)]^j \tag{A1}$$

Now the gamma function is analytic about $x = 1$ [cf. Eq. (16)], so

$$\Gamma(1-x) = \sum_{l=0}^{\infty} \Gamma_l x^l \tag{A2}$$

where $\Gamma_0 = 1$. Therefore,

$$R_m = \sigma^m(\epsilon/kT)^{m/n} \sum_{j=0}^{m} \binom{m}{j}(-1)^j \sum_{k=0}^{\infty} \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \cdots \sum_{l_j=0}^{\infty}$$
$$\times (m-j)^k x^k x^{l_1} x^{l_2} \cdots x^{l_j} \Gamma_k \Gamma_{l_1} \Gamma_{l_2} \cdots \Gamma_{l_j} \tag{A3}$$

The sums may be rearranged so that identical powers of $x$ are grouped together,

$$R_m = \sigma^m(\epsilon/kT)^{m/n} \sum_{j=0}^{m} \binom{m}{j}(-1)^j \sum_{p=0}^{\infty} x^p \sum_{k=0}^{p} (m-j)^k \sum_{\{l_i\}} \prod_{l_i} \Gamma_{l_i} \tag{A4}$$

where $\{l_i\}$ is a set of positive integers (including zero) such that $\sum_i l_i = k - p$.

We may now hold $k$ and $p$ fixed and sum over $j$. But

$$\sum_{j=0}^{m} \binom{m}{j}(-1)^j(m-j)^k = \left(x\frac{d}{dx}\right)^k \sum_{j=0}^{m} \binom{m}{j}(-1)^j x^{m-j}\Big|_{x=1}$$

$$= \left(x\frac{d}{dx}\right)^k (x-1)^m\Big|_{x=1} \tag{A5}$$

which vanishes if $k < m$. But $k \leqslant p$, so the coefficient of $x^p$ vanishes if $p < m$. Hence the first nonvanishing term in $R_m$ is $O(x^m)$, or $O(n^{-m})$.

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