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Virial coefficients for the square-well potential

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Abstract. The aim of the present work is to derive exact expressions for the second and third virial coefficients $B(T)$ and $C(T)$ for fluids of molecules interacting according to the square-well potential of arbitrary well width and arbitrary dimensionality d. General expressions for the terms of the fourth virial coefficient $D(T)$, where $D(T)=D_1(T)+D_2(T)+D_3(T)$ are obtained when the width of the attractive well is equal to the radius of the hard sphere. For $d=3$ and 1, the values of D_1, D_2 are analytically obtained, whereas D_3 is computed numerically.

1. Introduction

The virial coefficients B, C, D, ... are defined as the coefficients in the equation of state for fluids

$$\frac{P}{KT}=\rho+B\rho^2+C\rho^3+D\rho^4+\ldots \tag{1.1}$$

where P is the pressure, K is the Boltzmann constant, T is the absolute temperature and ρ is the density.

For the square-well potential, the virial coefficients up to the third have been calculated by Kihara [1] for the attractive well for all values of the range parameter g (see equation (2.3)). The fourth virial coefficient has been calculated for $g=2$ by Katsura [2, 3] and Barker and Monaghan [4]. Hauge [5] gave expressions, valid for arbitrary g, for the integrals contributing to the fourth virial coefficient.

In d dimensions, Luban and Baram [6] derived exact expressions for the third virial coefficient and two of the three terms contributing to the fourth virial coefficient for an assembly of hard hypersphere (d is arbitrary). Ree and Hoover [7] calculated the fourth virial coefficient for a hard sphere ($1\leqslant d\leqslant 9$). Kreimer *et al* [8] calculated the third virial coefficient for the Lennard-Jones potential ($d=2, 3$).

In this paper we use the method of Luban and Baram [6], which is based on re-expressing the configuration multiple integrals as multiple integrals in k-space with integrands involving products of Bessel functions and the method of Katsura [2, 3] which is based on Fourier transforms and the addition theorem of Bessel functions.

2. Calculation of $B(T)$ and $C(T)$

The second and third virial coefficients are given by

$$B(T)=-\tfrac{1}{2}\int f(r)\,\mathrm{d}\boldsymbol{r} \tag{2.1}$$

$$C(T) = -\tfrac{1}{3} \int f(r_1) f(r_2) f(|\boldsymbol{r}_2 - \boldsymbol{r}_1|)\, \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2 \tag{2.2}$$

where

$$f(r) = \exp\left(\frac{-U(r)}{KT}\right) - 1$$

and $U(r)$ is the intermolecular potential between two molecules separated by a distance r.

For the square-well potential, the function $f(r)$ is given by

$$f(r) = \begin{cases} -1 & r < \sigma \\ f = \exp(\varepsilon/KT) - 1 & \sigma < r < g\sigma \\ 0 & g\sigma < r \end{cases} \tag{2.3}$$

where σ is the diameter of the hard sphere, g is the range of the attractive well and ε is the well depth.

When the integrand of a d-dimensional integral possesses spherical symmetry [6], we have

$$\int H(r)\, \mathrm{d}^d r = C_d \int_0^\infty H(r) r^{d-1}\, \mathrm{d}r \tag{2.4}$$

whereas if H is a function of r and a single polar angle θ,

$$\int H(r, \theta)\, \mathrm{d}^d r = C_{d-1} \int_0^\infty r^{d-1}\, \mathrm{d}r \int_0^\infty H(r, \theta) \sin^{d-2}\theta\, \mathrm{d}\theta. \tag{2.5}$$

The quantity C_d is defined by

$$C_d = \frac{2\pi d/2}{\Gamma(d/2)}. \tag{2.6}$$

The d-dimensional Fourier transform $F_d(k)$ of $f(r)$ is defined by

$$\begin{aligned} F_d(k) &= \int f(r) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} \\ &= \int f(r) \exp(\mathrm{i}kr\cos\theta)\, \mathrm{d}r. \end{aligned} \tag{2.7}$$

From (2.7), (2.5) and (2.3), we get

$$\begin{aligned} F_d(k) = C_{d-1} \Bigg[&-\int_0^\sigma r^{r-1}\, \mathrm{d}r \int_0^\pi \exp(\mathrm{i}kr\cos\theta) \sin^{d-2}\theta\, \mathrm{d}\theta \\ &+ f \int_\sigma^{g_\sigma} r^{d-1}\, \mathrm{d}r \int_0^\pi \exp(\mathrm{i}kr\cos\theta) \sin^{d-2}\theta\, \mathrm{d}\theta \Bigg]. \end{aligned} \tag{2.8}$$

Using the following standard identities for Bessel functions,

$$J_\nu(x) = \frac{(x/2)^\nu}{\pi^{1/2}\Gamma(\nu + \frac{1}{2})} \int_0^\pi \exp(\mathrm{i}x\cos\theta) \sin^{2\nu}\theta\, \mathrm{d}\theta \qquad (\mathrm{Re}\ \nu > -\tfrac{1}{2}) \tag{2.9}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}(x^\nu J_\nu(x)) = x^\nu J_{\nu-1}(x) \tag{2.10}$$

we have

$$F_d(k)=\left(\frac{2\pi\sigma}{k}\right)^{d/2}[g^{d/2}fJ_{d/2}(g\sigma k)-(1+f)J_{d/2}(\sigma k)]. \tag{2.11}$$

The calculation of $B(T)$ is quite trivial. Using (2.1), (2.3) and (2.4), one obtains

$$B(T)=\frac{C_d}{2^d}\sigma^d[1-(g^d-1)f]. \tag{2.12}$$

To evaluate the multiple integral in (2.2), giving rise to $C(T)$, we replace the third factor in the integrand by the Fourier representation

$$f(r)=(2\pi)^{-d}\int \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})F_d(k)\,\mathrm{d}\boldsymbol{k} \tag{2.13}$$

so that

$$C(T)=-\tfrac{1}{3}(2\pi)^{-d}\int (E_d(k))^3\,\mathrm{d}\boldsymbol{k}. \tag{2.14}$$

Substitution of (2.11) in (2.14) yields

$$C(T)=\frac{-C_d}{3}(2\pi)^{d/2}\sigma^{2d}$$
$$\times\{[g^{2d}f^3-(1+f)^3]I_1-3g^df^2(1+f)I_2+3g^{d/2}f(1+f)^2I_3\} \tag{2.15}$$

where

$$x=\sigma k$$
$$I_1=\int_0^\infty (J_{d/2}(x))^3x^{-(1+d/2)}\,\mathrm{d}x$$
$$I_2=\int_0^\infty (J_{d/2}(gx))^2(J_{d/2}(x))x^{-(1+d/2)}\,\mathrm{d}x$$
$$I_3=\int_0^\infty (J_{d/2}(gx))(J_{d/2}(x))^2x^{-(1+d/2)}\,\mathrm{d}x$$

where I_1 is given as in Luban and Baram [6].

The integrals I_2 and I_3 can be expressed using the following standard formula ([9], p 231, equation (21)),

$$\int_0^\infty x^{\alpha-1}J_\lambda(bx)J_\mu(bx)J_\nu(cx)\,\mathrm{d}x$$
$$=\frac{2^{-2}c^{1-\alpha}}{b}\Gamma\left[\begin{matrix}\frac{\nu+\alpha-1}{2}\\ \frac{1+\mu-\lambda}{2},\frac{1+\lambda-\mu}{2},\frac{\nu+3-\alpha}{2}\end{matrix}\right]$$
$$\times{}_4F_3\left(\frac{1-\lambda-\mu}{2},\frac{1+\lambda-\mu}{2},\frac{1-\lambda+\mu}{2},\frac{1+\lambda+\mu}{2};\right.$$
$$\left.\frac{1}{2},\frac{3-\alpha-\nu}{2},\frac{3-\alpha+\nu}{2};\frac{C^2}{4b^2}\right)+2^{\alpha-1}b^{-\alpha-\nu}c^{\nu}$$

$$\times\Gamma\begin{bmatrix} 1-\alpha-\nu, \dfrac{\alpha+\lambda+\mu+\nu}{2} \\ 1+\dfrac{\mu+\lambda+\alpha+\nu}{2}, 1+\dfrac{\mu-\lambda-\alpha-\nu}{2}, 1+\dfrac{\lambda-\mu-\alpha-\nu}{2}, 1+\nu \end{bmatrix}$$

$$\times{}_4F_3\left(\frac{\alpha+\nu-\mu-\lambda}{2}, \frac{\alpha+\nu-\mu+\lambda}{2}, \frac{\alpha+\nu+\mu-\lambda}{2}, \frac{\alpha+\nu+\mu+\lambda}{2};\right.$$

$$\left.\times\frac{1+\alpha+\nu}{2}, \frac{\alpha+\nu}{2}, 1+\nu; \frac{C^2}{4b^2}\right)$$

$$-\frac{2^{\alpha-3}C^{2-\alpha}(\mu+\lambda)}{b^2}\Gamma\begin{bmatrix} \dfrac{\nu+\alpha}{2-1} \\ \dfrac{\mu-\lambda}{2}, \dfrac{\lambda-\mu}{2}, 2+\dfrac{\nu-\alpha}{2} \end{bmatrix}$$

$$\times{}_4F_3\left(1-\frac{\mu+\lambda}{2}, 1+\frac{\lambda-\mu}{2}, 1+\frac{\mu-\lambda}{2}, 1+\frac{\mu+\lambda}{2};\right.$$

$$\left.\frac{3}{2}, 2-\frac{\nu+\alpha}{2}, 2+\frac{\nu-\alpha}{2}; \frac{C^2}{4b}\right) \tag{2.16}$$

which applies as long as $(0<c<2b;\ -\mathrm{Re}(\mu+\nu+\lambda)<\mathrm{Re}\,\alpha<\frac{5}{2})$. Thus we have

$$I_2 = \frac{2^{-(d/2+2)}\Gamma(-\frac{1}{2})}{g(\Gamma(\frac{1}{2}))^2\Gamma((3+d)/2)}\,{}_4F_3\left(\frac{1-d}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1+d}{2}; \frac{1}{2}, \frac{3}{2}, \frac{3+d}{2}; \frac{1}{4g^2}\right)$$

$$+\frac{2^{-(1+d/2)}\Gamma(d/2)}{[\Gamma(1+d/2)]^2}\,{}_4F_3\left(-\frac{d}{2}, 0, 0, \frac{d}{2}; \frac{1}{2}, 0, 1+\frac{d}{2}; \frac{1}{4g^2}\right)$$

$$+\frac{2^{-(d/2+3)}d}{g^2}\,\frac{\Gamma(-1)}{(\Gamma(0))^2\Gamma(2+d/2)}$$

$$\times{}_4F_3\left(1-\frac{d}{2}, 1, 1, 1+\frac{d}{2}; \frac{3}{2}, 2, 2+\frac{d}{2}; \frac{1}{4g}\right). \tag{2.17}$$

The function is usually referred to as a generalized hypergeometric function, where the function ${}_4F_3$ is the usual hypergeometric function which admits the power series representation of the general form

$${}_4F_3(\alpha_1, \alpha_2, \alpha_3, \alpha_4;\ B_1, B_2, B_3;\ x)$$

$$= \sum_{n=0} \frac{(\alpha_1)_n(\alpha_2)_n(\alpha_3)_n(\alpha_4)_n}{n!(B_1)_n(B_2)_n(B_3)_n}x^n \qquad (|x|<1). \tag{2.18}$$

It must be noted that, in the above function, when the number of α_is which are equal to zero is more than the number of B_is which are equal to zero, then ${}_4F_3=1$. When $\alpha_i=B_j$, for any i, j, ${}_4F_3$ becomes equal to ${}_3F_2$. When zero or negative integer occurs in the denominator of the constant factor of any term containing ${}_4F_3$, then this must be equal to zero. Using the above properties of ${}_4F_3$, and the properties of a gamma function ([10], vol I, pp 3, 4, equations (1), (10)) we get

$$I_2 = \frac{-2^{-(d/2+1)}}{g\pi^{1/2}\Gamma((3+d)/2)}\,{}_3F_2\left(\frac{1-d}{2}, \frac{1}{2}, \frac{1+d}{2}; \frac{3}{2}, \frac{3+d}{2}; \frac{1}{4g^2}\right)$$

$$+\frac{2^{(1-d/2)}}{d^2\Gamma(d/2)} \qquad \text{for } 0.5\leqslant g. \tag{2.19}$$

Also, using (2.16), we have

$$I_3=\left(\frac{g}{2}\right)^{d/2}\frac{2}{d^2\Gamma(d/2)}-\frac{1}{\pi^{1/2}\Gamma((3+d)/2)}$$
$$\times {}_3F_2\left(\frac{1-d}{2},\frac{1}{2},\frac{1+d}{2};\frac{3}{2},\frac{3+d}{2};\frac{g^2}{4}\right)\qquad \text{for } g\leqslant 2. \tag{2.20}$$

For $g\geqslant 2$, we use the following standard formula ([9], p 231, equation (20)),

$$\int_0^\infty x^{\alpha-1}J_\lambda(bx)J_\mu(bx)J_\nu(cx)\,\mathrm{d}x$$
$$=2^{\alpha-1}b^{\mu+\lambda}c^{-\alpha-\mu-\lambda}\Gamma\left[\begin{matrix}\dfrac{\alpha+\mu+\lambda+\nu}{2}\\ 1+\mu,\,1+\lambda,\,1+\dfrac{\nu-\alpha-\mu-\lambda}{2}\end{matrix}\right]$$
$$\times {}_4F_3\left(\frac{\alpha+\mu+\lambda-\nu}{2},\frac{\alpha+\mu+\lambda+\nu}{2},\frac{1+\mu+\lambda}{2},1+\frac{\mu+\lambda}{2};\right.$$
$$\left.\times 1+\mu+\lambda,\,1+\mu,\,1+\lambda;\frac{4b^2}{c^2}\right)$$

which applies as long as ($0<2b<c$; $-\mathrm{Re}(\mu+\nu+\lambda)$ Re $\alpha<\frac{5}{2}$). Then

$$I_3=\frac{2(2g)^{-d/2}}{d^2\Gamma(d/2)}\qquad g\geqslant 2. \tag{2.21}$$

From (2.20) and (2.21), we have

$$I_3=\begin{cases}\dfrac{2(2g)^{-d/2}}{d^2\Gamma(d/2)} & g\geqslant 2\\ \dfrac{2}{d^2\Gamma(d/2)}\left(\dfrac{g}{2}\right)^{d/2}-\dfrac{(g/2)^{d/2+1}}{\pi^{1/2}\Gamma((3+d)/2)} & \end{cases}$$
$$\times {}_3F_2\left(\frac{1-d}{2},\frac{1}{2},\frac{1+d}{2};\frac{3}{2},\frac{3+d}{2};\frac{g^2}{4}\right)\qquad g\leqslant 2. \tag{2.22}$$

Substituting (2.16), (2.19) and (2.20) into (2.15), we get

$$\frac{C(T)}{b}=2\left\{[(1+f)^3-g^{2d}f^3]\left[1-\frac{1}{B(\frac{1}{2},(1+d)/2)}\,{}_2F_1\left(\frac{1}{2},\frac{1-d}{2},\frac{3}{2},\frac{1}{4}\right)\right]\right.$$
$$-\frac{2dg^{d-1}f^2(1+f)}{(d+1)B(\frac{1}{2},(1+d)/2)}\,{}_3F_2\left(\frac{1-d}{2},\frac{1}{2},\frac{1+d}{2}T;\frac{3}{2},\frac{3+d}{2};\frac{1}{4g^2}\right)$$
$$-\frac{2}{d}g^d f(1+f)+\frac{2dg^{d+1}}{(d+1)B(\frac{1}{2},(1+d)/2)}f(1+f)^2$$
$$\left.\times {}_3F_2\left(\frac{1-d}{2},\frac{1}{2},\frac{1+d}{2};\frac{3}{2},\frac{3+d}{2};\frac{g^2}{4}\right)\right\}\qquad 1\leqslant g\leqslant 2$$

$$= 2\Big\{[(1+f)^3 - g^{2d}f^3]\Big[1 - \frac{1}{B(\frac{1}{2},(1+d)/2)}\,{}_2F_1\Big(\frac{1}{2},\frac{1-d}{2};\frac{3}{2};\frac{1}{4}\Big)\Big]$$

$$-\frac{2dg^{d-1}f^2(1+f)}{(d+1)B(\frac{1}{2},(1+d)/2)}\,{}_3F_2\Big(\frac{1-d}{2},\frac{1}{2},\frac{1+d}{2};\frac{3}{2},\frac{3+d}{2};\frac{1}{4g^2}\Big)$$

$$-2f(1+f)[1-(g^d-1)f]\Big\} \qquad g \geqslant 2 \tag{2.23}$$

where

$$b = \frac{\sigma^d}{2d}c_d \tag{2.24}$$

is the value of the second virial coefficient of the hard hypersphere.

For odd integer dimensionalities, each of the hypergeometric series in (2.23) terminates after $(d+1)/2$ terms. For even-integer dimensionalities, each of the hypergeometric series in (2.23) does not terminate.

If $d = 2N$ (see [6]), we have

$$2\Big[1 - \frac{1}{B(\frac{1}{2},(1+d)/2)}\,{}_2F_1\Big(\frac{1}{2},\frac{1-d}{2};\frac{3}{2};\frac{1}{4}\Big)\Big]$$

$$= \frac{4}{3} - \frac{N!}{\pi^{1/2}\Gamma(N+\frac{1}{2})}\Big(\frac{3}{4}\Big)^{N-1/2}\,{}_2F_1(1, N+1; \tfrac{3}{2}; \tfrac{1}{4})_N \tag{2.25}$$

where the subscript on ${}_2F_1$ denotes the parital sum of the first N terms of the infinite series of ${}_2F_1$. For $N = 0$ this partial sum is zero.

Thus, for even integer dimensionalities, we obtain

$$\frac{C(T)}{b} = [(1+f)^3 - 2^{4N}f^3]\Big(\frac{4}{3} - \frac{N!}{\pi^{1/2}\Gamma(N+\frac{1}{2})}\Big(\frac{3}{4}\Big)^{(N-1)/2}\Big)\,{}_2F_1(1, N+1; \tfrac{3}{2}; \tfrac{1}{4})_N$$

$$-\frac{8Ng^df^2(1+f)}{g(2N+1)B(\frac{1}{2},(1+2N)/2)}\,{}_3F_2\Big(\frac{1-2N}{2},\frac{1}{2},\frac{1+2N}{2};\frac{3}{2},\frac{3+2N}{2};\frac{1}{4g^2}\Big)$$

$$-\frac{4}{N}g^{2N}f(1+f) + \frac{8Ng^{2N+1}}{(2N+1)B(\frac{1}{2},(1+2N)/2)}f(1+f)^2$$

$$\times\,{}_3F_2\Big(\frac{1-2N}{2},\frac{1}{2},\frac{1+2N}{2};\frac{3}{2},\frac{3+2N}{2};\frac{g^2}{4}\Big) \qquad 1 \leqslant g \leqslant 2$$

$$= [(1+f)^3 - 2^{4N}f^3]\Big(\frac{4}{3} - \frac{N}{\pi^{1/2}\Gamma(N+\frac{1}{2})}\Big(\frac{3}{4}\Big)^{(N-1)/2}\Big)\,{}_3F_1(1, N+1; \tfrac{3}{2}; \tfrac{1}{4})_N$$

$$-\frac{8Ng^{d-1}f^2(1+f)}{(2N+1)B(\frac{1}{2},(1+2N)/2)}\,{}_3F_2\Big(\frac{1-2N}{2},\frac{1}{2},\frac{1+2N}{2};\frac{3}{2},\frac{3+2N}{2};\frac{1}{4g^2}\Big)$$

$$-4f(1+f)[1-(g^d-1)f] \qquad g \geqslant 2. \tag{2.26}$$

For non-integral values of d, the hypergeometric series in (2.23) can be easily evaluated on a computer, since these converge very rapidly.

In table 1 we have listed closed-form results of $C(T)/b^2$ for assorted odd-integer dimensionalities d and numerical results with good approximations for even-integer dimensionalities d. It is interesting to observe that all of the first terms of our results

Table 1. The values of $C(T)/b^2$ for $g=2$ for assorted integer dimensionalities.

d	$\dfrac{C(T)}{b^2}$
0	$\dfrac{4}{3}$
1	$1-f+2f^2$
2	$\dfrac{4}{3}-\dfrac{\sqrt{3}}{\pi}-1.653\,98f+6.972f^2-3.104f^3$
3	$\dfrac{1}{2^3}{}^3(5-17f+136f^2-162f^3)$
4	$\dfrac{4}{3}-\dfrac{3\sqrt{3}}{2\pi}-2.486\,94f+40.743\,47f^2-86.023f^3$
5	$\dfrac{1}{2^7}(53-353f+9316f^2-445\,50f^3)$
6	$\dfrac{4}{3}-\dfrac{9\sqrt{3}}{5\pi}-2.977\,17f+141.7718f^2-1253.6065f^3$
7	$\dfrac{1}{2^{10}}(289-3229f+328\,416f^2-440\,3042f^3)$
8	$\dfrac{4}{3}-\dfrac{279\sqrt{3}}{140\pi}-3.2961f+517.694\,98f^2-148\,89.327f^3$
9	$\dfrac{1}{2^{15}}(6413-111\,833f+321\,663\,17f^2-164\,884\,490f^3)$

for odd- and even-integer dimensionalities d, which are the values corresponding to the hard hyperspheres, are the same as those obtained by Luban and Baram [6].

3. The fourth virial coefficient for the square-well potential

3.1. Calculation of $D_1(T)$

It is well known that the fourth virial coefficient $D(T)$ is given by

$$D(T)=D_1(T)+D_2(T)+D_3(T) \tag{3.1.1}$$

where

$$D_1(T)=-\tfrac{3}{8}\iiint f(r_1)f(r_2)f(|\boldsymbol{r}_3-\boldsymbol{r}_2|)f(|\boldsymbol{r}_1-\boldsymbol{r}_3|)\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\,\mathrm{d}\boldsymbol{r}_3 \tag{3.1.2}$$

$$D_2(T)=-\tfrac{3}{4}\iiint f(r_1)f(r_2)f(r_3)f(|\boldsymbol{r}_1-\boldsymbol{r}_2|)f(|\boldsymbol{r}_2-\boldsymbol{r}_3|)\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\,\mathrm{d}\boldsymbol{r}_3 \tag{3.1.3}$$

$$D_3(T)=-\tfrac{1}{8}\iiint f(r_1)f(r_2)f(r_3)f(|\boldsymbol{r}_1-\boldsymbol{r}_2|)f(|\boldsymbol{r}_2-\boldsymbol{r}_3|)\times f(|\boldsymbol{r}_3-\boldsymbol{r}_1|)\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\,\mathrm{d}\boldsymbol{r}_3. \tag{3.1.4}$$

To evaluate the multiple integral in (3.1.2) giving $D_1(T)$, we replace the third and fourth factors in the integrand representation, so that

$$D_1(T) = -\tfrac{3}{8}(2\pi)^{-2d}\Bigg(\Bigg[\iint f(r_1)f(r_2)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_2 - \mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}_1)\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\Bigg]$$
$$\times\Bigg\{\int \exp[-\mathrm{i}\boldsymbol{r}\cdot(\boldsymbol{k}-\boldsymbol{k}')]\,\mathrm{d}\boldsymbol{r}_3\,F_d(k)F_d(k')\,\mathrm{d}\boldsymbol{k}\,\mathrm{d}\boldsymbol{k}'\Bigg\}\Bigg)$$
$$= -\tfrac{3}{8}(2\pi)^{-2d}\Bigg[\iint (F_d(k))^2(F_d(k'))^2\delta(|\boldsymbol{k}-\boldsymbol{k}'|)\,\mathrm{d}\boldsymbol{k}\,\mathrm{d}\boldsymbol{k}'\Bigg] \tag{3.1.5}$$

where $\delta(a-b)$ is the Dirac δ-function. Then

$$D_1(T) = -\tfrac{3}{8}(2\pi)^{-d}\int (F_d(k))^4\,\mathrm{d}\boldsymbol{k}.$$

Using (2.4), we get

$$D_1(T) = -\tfrac{3}{8}(2\pi)^{-d}C_d\int_0^\infty (F_d(k))^4 k^{d-1}\,\mathrm{d}k. \tag{3.1.6}$$

Inserting (2.11), when $g=2$ for $F_d(k)$, in (3.1.6),

$$D_1(T) = -\tfrac{3}{8}(2\pi)^d\sigma^{2d}C_d\int_0^\infty [2^{d/2}fJ_{d/2}(2\sigma k) - (1+f)J_{d/2}(\sigma k)]^4 k^{-(d+1)}\,\mathrm{d}k. \tag{3.1.7}$$

Using (2.24) and (2.6), we have

$$\frac{D_1(T)}{b^3} = -3d2^d\left(\Gamma\left(\frac{d}{2}+1\right)\right)^2\int_0^\infty [2^{d/2}fJ_{d/2}(2x) - (1+f)J_{d/2}(x)]^4 x^{-(d+1)}\,\mathrm{d}x$$
$$= -3d2^d\left[\Gamma\left(\frac{d}{2}+1\right)\right]^2\Bigg\{2^{3d}f^4\int_0^\infty (J_{d/2}(2x))^4(2x)^{-(d+1)}\,\mathrm{d}(2x)$$
$$-4\times 2^{3d/2}f^3(1+f)\int_0^\infty (J_{d/2}(2x))^3(J_{d/2}(x))x^{-(d+1)}\,\mathrm{d}x$$
$$+3\times 2^{d+1}f^2(1+f)^2\int_0^\infty (J_{d/2}(2x))^2(J_{d/2}(x))^2x^{-(d+1)}\,\mathrm{d}x$$
$$-2^{d/2+2}f(1+f)^3\int_0^\infty (J_{d/2}(2x))(J_{d/2}(x))^3x^{-(d+1)}\,\mathrm{d}x$$
$$+(1+f)^4\int_0^\infty (J_{d/2}(x))^4x^{-(d+1)}\,\mathrm{d}x\Bigg\}. \tag{3.1.8}$$

From [6], we have

$$\int_0^\infty (J_{d/2}(x))^4x^{-(d+1)}\,\mathrm{d}x = \int_0^\infty (J_{d/2}(2x))^4(2x)^{-(d+1)}\,\mathrm{d}(2x)$$
$$= \frac{2}{3\pi}\,\frac{\Gamma(d/2)\Gamma(d)}{\Gamma(3d/2)(\Gamma((d+3)/2))^2}\,{}_3F_2\left(\frac{1}{2}, 1, \frac{1-d}{2}; \frac{d+3}{2}, \frac{d+3}{2}; 1\right).$$

Thus,

$$\frac{D_1(T)}{b^3} = -3d2^{d+1}\left(\Gamma\left(\frac{d}{2}+1\right)\right)^2\left[\frac{\Gamma(d/2)\Gamma(d)}{3\pi\Gamma(3d/2)(\Gamma((d+3)/2))^2}[2^{3d}f^4+(1+f)^4]\right.$$
$$\times {}_3F_2\left(\frac{1}{2}, 1, \frac{1-d}{2}; \frac{d+3}{2}, \frac{d+3}{2}; 1\right) - 2^{3d/2+1}f^3(1+f)$$
$$\times \int_0^\infty (J_{d/2}(2x))^3(J_{d/2}(x))x^{-(d+1)}\,\mathrm{d}x + 3[2^d f^2(1+f)^2]$$
$$\times \int_0^\infty (J_{d/2}(2x))^2(J_{d/2}(x))^2 x^{-(d+1)}\,\mathrm{d}x - 2^{d/2+1}f(1+f)^3$$
$$\left.\times \int_0^\infty (J_{d/2}(2x))(J_{d/2}(x))^3 x^{-(d+1)}\,\mathrm{d}x\right]. \tag{3.1.9}$$

For $d=3$ we have

$$\left[\frac{D_1(T)}{b^3}\right]_{d=3} = -\tfrac{1}{560}(544 - 4075f - 350\,07f - 996\,87f^3 + 139\,215f^4) \tag{3.1.10}$$

which was obtained by Katsura [2].

To evaluate the integrals in (3.1.9), when $d=1$, we use the standard identity for a Bessel function,

$$J_{1/2}(x) = \left(\frac{2}{\pi x}\right)^{1/2} \sin x. \tag{3.1.11}$$

Then

$$\left[\frac{D_1(T)}{b^3}\right]_{d=1} = -3\pi\left(\frac{2}{3\pi}[8f^4+(1+f)^4] - \frac{8}{\pi^2}f^3(1+f)\right.$$
$$\times \int_0^\infty (\sin 2x)^3(\sin x)x^{-4}\,\mathrm{d}x + \frac{12}{\pi^2}f^2(1+f)^2$$
$$\times \int_0^\infty (\sin 2x)^2(\sin x)^2 x^{-4}\,\mathrm{d}x - \frac{8}{\pi^2}f(1+f)^3$$
$$\left.\times \int_0^\infty (\sin 2x)(\sin x)^3 x^{-4}\,\mathrm{d}x\right). \tag{3.1.12}$$

Using the following standard identities ([11], p 451, equations (10), (12)),

$$\int_0^\infty (\sin ax)^3(\sin 3bx)x^{-4}\,\mathrm{d}x = \frac{9b\pi}{8}(a^2-b^2) \qquad (3b \leqslant a)$$
$$= \frac{\pi}{16}[8a^3 - 9(a-b)^3] \qquad (a \leqslant 3b \leqslant 3a)$$
$$\int_0^\infty (\sin ax)^2(\sin bx)^2 x^{-4}\,\mathrm{d}x = \frac{\pi b^2}{6}(3a-b) \qquad (0 \leqslant b \leqslant a)$$

one finds that

$$\left[\frac{D_1(T)}{b^3}\right]_{d=1} = -\tfrac{1}{2}(4 - 7f + 15f^2 - 3f^3 + 3f^4). \tag{3.1.13}$$

The first term, −2, which is the value that corresponds to the hard sphere, agrees with that obatined by Luban and Baram [6].

3.2. Calculation of $D_2(T)$

Applying the Fourier transformation to the fourth and fifth factors in the integrand of (3.1.3), we get

$$D_2(T)=-\tfrac{3}{4}(2\pi)^{-2d}\left\{\int\int\left[\int\int f(r_1)f(r_3)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_1-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}_3)\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_3\right]\right.$$
$$\left.\times\left[\int f(r_2)\exp(\mathrm{i}r_2)|\boldsymbol{k}'-\boldsymbol{k}|)\,\mathrm{d}r_2\right]F_d(k)F_d(k')\,\mathrm{d}\boldsymbol{k}\,\mathrm{d}\boldsymbol{k}'\right\}. \quad (3.2.1)$$

Integration (2.7), (2.3) for $f(r)$ when $g=2$, and using (2.4) for the integration over r, in (3.2.1), then

$$D_2(T)=-\tfrac{3}{4}(2\pi)^{-2d}C_d\left\{-\int_0^{\sigma}[(F_d(k))^2\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})\,\mathrm{d}\boldsymbol{k}]^2r^{d-1}\,\mathrm{d}r+f\right.$$
$$\left.\times\int_{\sigma}^{2\sigma}\left[\int(F_d(k))^2\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})\,\mathrm{d}\boldsymbol{k}\right]^2r^{d-1}\,\mathrm{d}r\right\}. \quad (3.2.2)$$

Using (2.6) and (2.5) for the integration over k, we obtain

$$D_2(T)=\frac{-3\times2^{-2d+1}\pi^{-(d/2+1)}}{\Gamma(d/2)(\Gamma((d-1)/2))^2}$$
$$\times\left\{-\int_0^{\sigma}\left[\int_0^{\infty}k^{d-1}\,\mathrm{d}k\int_0^{\pi}(F_d(k))^2\sin^{d-2}\theta\exp(\mathrm{i}kr\cos\theta)\,\mathrm{d}\theta\right]^2r^{d-1}\,\mathrm{d}r\right.$$
$$+f\int_{\sigma}^{2\sigma}\left[\int_0^{\infty}(F_d(k))^2k^{d-1}\,\mathrm{d}k\right.$$
$$\left.\left.\times\int_0^{\pi}\sin^{d-2}\theta\exp(\mathrm{i}kr\cos\theta)\,\mathrm{d}\theta\right]^2r^{d-1}\,\mathrm{d}r\right\}. \quad (3.2.3)$$

Using (2.9) for the integration over θ and inserting (2.11) for $F_d(k)$ when $g=2$, putting $r=\sigma y$, $k=x/\sigma$ and using (2.24), we obtain

$$\frac{D_2(T)}{b^3}=-3d2^{d+1}\left(\Gamma\left(\frac{d}{2}+1\right)\right)^2\left\{-\int_0^1\left[2^{(3d-2)/2}f^2\right.\right.$$
$$\times\int_0^{\infty}(J_{d/2}(2x))^2(J_{d/2-1}(yx))(2x)^{-d/2}\,\mathrm{d}(2x)-2^{d/2+1}f(1+f)$$
$$\times\int_0^{\infty}J_{d/2}(2x)J_{d/2}(x)J_{(d/2)-1}(yx)x^{-d/2}\,\mathrm{d}x+(1+f)^2$$
$$\left.\left.\times\int_0^{\infty}(J_{d/2}(x))^2(J_{d/2-1}(yx))x^{-d/2}\,\mathrm{d}x\right]^2y\,\mathrm{d}y+f\int_1^2[\quad]^2y\,\mathrm{d}y\right\}. \quad (3.2.4)$$

where the contents of the second square bracket are the same as that in the first one.

From [6] and equation (3.2.4), we obtain

$$\frac{D_2(T)}{b^3} = -3d2^{d+1}\left(\Gamma\left(\frac{d}{2}+1\right)\right)^2\left(-\int_0^1\left\{2^{d/2}f\frac{y^{d/2-1}}{\Gamma(d/2+1)}\right.\right.$$
$$\times\left[1-\frac{y\Gamma(d/2+1)}{2^{1/2}\Gamma((d+1)/2)}\,{}_2F_1\left(\frac{1}{2},\frac{1-d}{2};\frac{3}{2};\frac{y^2}{16}\right)\right]$$
$$+(1+f)^2\frac{y^{d/2-1}}{2^{d/2}\Gamma(d/2+1)}$$
$$-\left[1-\frac{y\Gamma(d/2+1)}{\pi^{1/2}\Gamma((d+1)/2)}\,{}_2F_1\left(\frac{1}{2},\frac{1-d}{2};\frac{3}{2};\frac{y^2}{16}\right)\right]-2^{d/2+1}f(1+f)$$
$$\times\left.\int_0^\infty J_{d/2}(2x)J_{d/2}(x)J_{(d/2)-1}(yx)x^{-d/2}\,\mathrm{d}x\right\}^2 y\,\mathrm{d}y$$
$$\left.+f\int_1^2[\quad]^2 y\,\mathrm{d}y\right). \tag{3.2.5}$$

The last integral inside the first square bracket in (3.2.5) can be expressed by using the following standard formula ([11], p 695, equation (4)):

$$\int_0 x^{\lambda-\mu-\nu-1}J_\nu(ax)J_\mu(bx)J_\lambda(cx)\,\mathrm{d}x=\frac{2^{\lambda-\mu-\nu-1}}{c^\lambda\Gamma(\mu+1)\Gamma(\nu+1)}$$

which applies as long as $\mathrm{Re}\,\lambda>0$, $\mathrm{Re}(\lambda-\mu-\nu)<\frac{5}{2}$, $c>b>0$, $0<a<c-b$. Thus

$$\int_0^\infty x^{-d/2}J_{d/2}(x)J_{(d/2)-1}(yx)J_{d/2}(2x)\,\mathrm{d}x=\frac{y^{d/2-1}}{z^d\Gamma(d/2+1)}\qquad 0<y<1. \tag{3.2.6}$$

Substitution of (3.2.6) into (3.2.5) yields

$$\frac{D_2(T)}{b^3}=6b\left(\int_0^1\left\{2^d f^2\left[1-\frac{y\Gamma(d/2+1)}{2\pi^{1/2}\Gamma((d+1)/2)}\,{}_2F_1\left(\frac{1}{2},\frac{1-d}{2};\frac{3}{2};\frac{y^2}{16}\right)\right]+(1+f)^2\right.\right.$$
$$\times\left.\left[1-\frac{y\Gamma(d/2+1)}{\pi^{1/2}((d+1)/2)}\,{}_2F_1\left(\frac{1}{2},\frac{1-d}{2};\frac{3}{2};\frac{y^2}{4}\right)\right]+2f(1+f)\right\}^2 y^{d-1}\,\mathrm{d}y$$
$$\left.-2^d\left(\Gamma\left(\frac{d}{2}+1\right)\right)^2 f\int_1^2\{\ldots+\ldots-2^{d/2+1}f(1+f)I\}^2 y\,\mathrm{d}y\right) \tag{3.2.7}$$

where the first and second terms of the second set of braces are the same as those in the first set of braces and I is given by

$$I=\int_0^\infty J_{d/2}(2x)J_{d/2}(x)J_{(d/2)-1}(yx)x^{-d/2}\,\mathrm{d}x\qquad 1\leqslant y\leqslant 2.$$

The value of the preceeding integral is obtained (see the appendix) with the result for $\nu>0$ of

$$\int_0^\infty J_\nu(2x)J_\nu(x)J_{\nu-1}(yx)x^{-\nu}\,\mathrm{d}x$$
$$=\frac{(10y^2-y^4-9)^{\alpha/2}}{2^{2\alpha+4}\nu^2\pi^{1/2}y^{1/2}}(10y^2-y^4-9)^{1/2}$$
$$\times\left[\nu P_\alpha^{1-\alpha}\left(\frac{y^2-3}{2y}\right)+\nu 2^{\alpha+2}P_\alpha^{-1-\alpha}\left(\frac{y^2+3}{4y}\right)\right]$$
$$+4\left(\frac{y}{2}\right)^{-\alpha}P_{\alpha+2}^{-\alpha}\left(\frac{5-y^2}{4}\right)-4P_{\alpha+3}^{-\alpha}\left(\frac{y^2-3}{2y}\right)\qquad 1\leqslant y\leqslant 2 \tag{3.2.8}$$

where $\alpha=(2\nu-3)/2$ and $P_{\mu}^{\nu}(x)$ is the Legendre function of degree ν and order μ of the first kind.

Substituting (3.2.8) into (3.2.7) we obtain

$$\frac{D_2(T)}{b^3}=6d\Bigg(\int_0^1\Bigg\{2^d f^2\Bigg[1-\frac{y\Gamma(d/2+1)}{2\pi^{1/2}\Gamma((d+1)/2)}\,{}_2F_1\Big(\frac{1}{2},\frac{1-d}{2};\frac{3}{2};\frac{y^2}{16}\Big)\Bigg]+(1+f)^2$$
$$\times\Bigg[1-\frac{y^{(d/2+1)}}{\pi^{1/2}\Gamma((d+1)/2)}\,{}_2F_1\Big(\frac{1}{2},\frac{1-d}{2};\frac{3}{2};\frac{y^2}{4}\Big)\Bigg]-2f(1+f)\Bigg\}^2 y^{d-1}\,\mathrm{d}y$$
$$-3d2^{d+1}f\Big(\Gamma\Big(\frac{d}{2}+1\Big)\Big)^2\int_1^2\Bigg\{2^{(d/2)+1}f^2\frac{y^{(d/2)-1}}{d\Gamma(d/2)}$$
$$\times\Bigg[1-\frac{y\Gamma(d/2+1)}{2\pi^{1/2}\Gamma((d+1)/2)}\,{}_2F_1\Big(\frac{1}{2},\frac{1-d}{2};\frac{3}{2};\frac{y^2}{16}\Big)\Bigg]+2^{-d/2}(1+f)^2$$
$$\times\frac{y^{(d/2)-1}}{\Gamma(d/2+1)}\Bigg[1-\frac{y\Gamma(d/2+1)}{\pi^{1/2}\Gamma((d+1)/2)}\,{}_2F_1\Big(\frac{1}{2},\frac{1-d}{2};\frac{3}{2};\frac{y^2}{4}\Big)\Bigg]$$
$$-\frac{2^{(1-(d/2))}}{d^2\pi^{1/2}y^{1/2}}(10y^2-y^4-9)^{(d-3)/4}f(1+f)$$
$$\times\Bigg\{\Bigg[dP_{(d-3)/2}^{(1-d)/2}\Big(\frac{y^2-3}{2y}\Big)+d2^{(d+1)/2}P_{(d-3)/2}^{(1-d)/2}\Big(\frac{y^2+3}{4y}\Big)\Bigg]$$
$$\times(10y^2-y^4-9)^{1/2}-8P_{(d-3)/2}^{(3-d)/2}\Big(\frac{y^2-3}{2y}\Big)+8\Big(\frac{y}{2}\Big)^{(3-d)/2}$$
$$\times P_{(d+1)/2}^{(3-d)/2}\Big(\frac{5-y^2}{4}\Big)\Bigg\}\Bigg)^2 y\,\mathrm{d}y. \qquad (3.2.9)$$

To calculate the values of $D_2(T)/b^3$ for $d=3$ and 1, we use the properties of the Legendre function (see [12]) and of the hypergeometric function ${}_2F_1$. Then, we have

$$\left[\frac{D_2(T)}{b^3}\right]_{d=3}=-\tfrac{1}{4480}(-6347+273\,69f-184\,156f^2$$
$$+594\,27f^3-151\,8980f^4+918\,540f^5). \qquad (3.2.10)$$

This result is the same as that obtained by Katsura [2],

$$\left[\frac{D_2(T)}{b^3}\right]_{d=1}=\tfrac{1}{2}(7-9f+36f^2-184f^3-292f^4-112f^5). \qquad (3.2.11)$$

The first term, $\frac{7}{2}$, which is the value corresponding to the hard sphere, agrees with that obtained by Luban and Baram [6].

3.3. *Calculation of $D_3(T)$*

Applying the Fourier transformation to the fourth, fifth and sixth factors in the integrand of (3.1.4), we get

$$D_3(T) = -\tfrac{1}{8}(2\pi)^{-3d} \int \ldots \int f(r_1)f(r_2)f(r_3)$$
$$\times \exp\{i[\boldsymbol{r}_1\cdot(\boldsymbol{k}-\boldsymbol{k}'') + r_2\cdot(\boldsymbol{k}'-\boldsymbol{k}) + r_3\cdot(\boldsymbol{k}''-\boldsymbol{k}')]\}$$
$$\times F_d(k)F_d(k')F_d(k'')\,\mathrm{d}\boldsymbol{k}\,\mathrm{d}\boldsymbol{k}'\,\mathrm{d}\boldsymbol{k}''$$
$$= -\tfrac{1}{8}(2\pi)^{-3d} \iiint F_d(k)F_d(k')F_d(k'')F_d(|\boldsymbol{k}-\boldsymbol{k}''|)$$
$$\times F_d(|\boldsymbol{k}'-\boldsymbol{k}|)F_d(|\boldsymbol{k}''-\boldsymbol{k}'|)\,\mathrm{d}\boldsymbol{k}\,\mathrm{d}\boldsymbol{k}'\,\mathrm{d}\boldsymbol{k}''. \tag{3.3.1}$$

Inserting (2.11) for $F_d(k)$, we obtain

$$D_3(T) = -\tfrac{1}{8}\sigma^{3d} \sum_{a_1\ldots a_6} (1+f)^{n_1}(-2^d f)^{n_2} I_{d/2}(a_1, a_2, a_3; a_4, a_5, a_6) \tag{3.3.2}$$

where

$$I_{d/2}(a_1, a_2, a_3; a_4, a_5, a_6)$$
$$= \iiint h_{d/2}(a_1 x)h_{d/2}(a_2 x')h_{d/2}(a x'')h_{d/2}(a_4|x-x''|)h_{d/2}(a_5|x'-x|)$$
$$\times h_{d/2}(a_6|x''-x'|)\,\mathrm{d}x\,\mathrm{d}x'x'' \tag{3.3.3}$$

$$h_{d/2}(t) = -\frac{J_{d/2}(t)}{t^{d/2}} \qquad \sigma k = x \qquad \sigma k' = x' \qquad \sigma k'' = x''.$$

The summation in (3.3.2) is taken over all combinations $\{a_1, \ldots, a_6\}$ where a_i takes the values 1, 2 amounting to $2 = 64$ terms, n_1 and n_2 represent the number of a_i which take the values 1 and 2, respectively, $(n_1 + n_2 = 6)$:

$$D_3(T) = -\tfrac{1}{8}\sigma^{3d}\{(1+f)^6 I_{d/2}(1,1,1;1,1,1) - 3(1+f)^5(2^d f)I_{d/2}(2,1,1;1,1,1)$$
$$+ I_{d/2}(1,1,1;2,1,1) + 3(1+f)^4(2^d f)^2[I_{d/2}(1,2,2;1,1,1)$$
$$+ I_{d/2}(1,1,1;1,2,2) + 2I_{d/2}(2,1,1;1,2,1) + I_{d/2}(2,1,1;2,1,1)]$$
$$-(1+f)^3(2^d f)^3[I_{d/2}(1,1,1;2,2,2) + 3I_{d/2}(1,2,2;2,1,1)$$
$$+ 6I_{d/2}(2,1,1;2,1,2) + 6I_{d/2}(1,2,2;1,2,1) + 3I_{d/2}(2,1,1;1,2,2)$$
$$+ I_{d/2}(2,2,2;1,1,1)] + 3(1+f)^2(2^d f)^4[I_{d/2}(1,2,2;1,2,2)$$
$$+ 2I_{d/2}(1,2,2;2,1,2) + I_{d/2}(2,2,2;2,1,1)$$
$$+ I_{d/2}(2,1,1;2,2,2)] - 3(1+f)(2^d f)^5[I_{d/2}(2,2,2;1,2,2)$$
$$+ I_{d/2}(1,2,2;2,2,2)] + (2^d f)^6 I_{d/2}(2,2,2;2,2,2)\}. \tag{3.3.4}$$

To decompose $h_{d/2}(a|x-x'|)$ in (3.3.3), we use the addition theorem of the Bessel function ([10], vol II, p 101, equation (30)):

$$w^{-\mu}J(w) = (\tfrac{1}{2}zZ)^{-\mu}\Gamma(\mu)\sum_{n=0}(\mu+n)C_n^{\mu}(\cos\phi)J_{\mu+n}(z)J_{\mu+n}(Z)$$
$$\mu \neq 0, -1, -2, \ldots,$$

where $w=(z^2+Z^2-2zZ\cos\phi)^{1/2}$, and $C_n^{\mu}(z)$ is Gegenbauer's polynomial ([10], vol I, p 175, equation (4)), which is defined by

$$C_n^{\mu}(z)=2^{\mu-1/2}\left(\frac{\Gamma(n+2\mu)\Gamma(\mu+\frac{1}{2})}{n!\Gamma(2\mu)}\right)(z^2-1)^{1/4-\mu/2}P_{n+\mu-1/2}^{1/2-\mu}(Z). \quad (3.3.5)$$

Then

$$-h_{d/2}(a|x-x'|)$$
$$=\frac{J_{d/2}[a(x^2+x'^2-2xx'\cos\nu)]^{1/2}}{[a(x^2+x'^2-2xx'\cos\nu)]^{d/2}}$$
$$=(2)^{d/2}\Gamma\left(\frac{d}{2}\right)\sum_{n=0}\left(\frac{d}{2}+n\right)\frac{J_{(d/2)+m}(ax)J_{d/2}(ax')}{(ax)^{d/2}(ax')^{d/2}}C_n^{d/2}(\cos\nu) \quad (3.3.6)$$

where ν is the angle between x and x'. Substituting (3.3.6) into (3.3.3) we get

$$I_{d/2}(a_1, a_2, a_3; a_4, a_5, a_6)$$
$$=\left[(2)^{d/2}\Gamma\left(\frac{d}{2}\right)\right]^3(a_1a_2a_3)^{-d/2}(a_4a_5a_6)^{-d}$$
$$\times\sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\left(\frac{d}{2}+l\right)\left(\frac{d}{2}+m\right)\left(\frac{d}{2}+n\right)$$
$$\times\iiint J_{d/2}(a_1x)J_{d/2}(ax')J_{d/2}(a_3x'')J_{(d/2)+l}(a_4x')J_{(d/2)+l}(a_4x'')$$
$$\times J_{(d/2)+m}(a_5x'')J_{(d/2)+m}(a_5x)J_{(d/2)+n}(a_6x)J_{(d/2)+n}(a_6x')$$
$$\times C_l^{d/2}(\cos\nu)C_m^{d/2}(\cos\nu)C_n^{d/2}(\cos\nu'')$$
$$\times(x)^{-3d/2}(x')^{-3d/2}(x'')^{-3d/2}\,dx\,dx'\,dx'' \quad (3.3.7)$$

where ν, ν', ν'' are the angles between x and x', x' and x'', x'' and x, respectively.

Using (2.25), equation (3.3.2) becomes

$$\frac{D_3(T)}{b^3}=-\left(\frac{d^3}{c_d}\right)\sum_{a_1\ldots a_6}(1+f)^{n_1}(-2^df)^{n/2}I_{d/2}(a_1, a_2, a_3; a_4, a_5, a_6). \quad (3.3.8)$$

The polar coordinates of x, x' and x'' are denoted by (x, α', B), (x', α', B') and (x'', α'', B''), respectively, their solid angle elements are denoted by $d\Omega$, $d\Omega'$ and $d\Omega''$, respectively ($d\Omega=\sin\alpha\, d\alpha\, dB$). Then for $d=3$,

$$I_{3/2}(a_1, a_2, a_3; a_4, a_5, a_6)$$
$$=(2\pi)^{3/2}(a_1a_2a_3)^{-3/2}(a_4a_5a_6)^{-3}\sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}(\tfrac{3}{2}+l)$$
$$\times(\tfrac{3}{2}+m)(\tfrac{3}{2}+n)\int\ldots\int J_{3/2}(a_1x)J_{3/2}(a_2x')J_{3/2}(a_3x'')$$
$$\times J_{(3/2)+l}(a_4x')J_{(3/2)+l}(a_4x'')J_{(3/2)+m}(a_5x'')J_{(3/2)+m}(a_5x)$$
$$\times J_{(3/2)+n}(a_6x)J_{(3/2)+n}(a_6x')C^{3/2}(\cos\nu)C_m^{3/2}(\cos\nu')$$
$$\times C_n^{3/2}(\cos\nu'')(x)^{-5/2}(x')^{-5/2}(x'')^{-5/2}\,dx\,dx'\,dx''\,d\Omega\,d\Omega'\,d\Omega'' \quad (3.3.9)$$

where $dx\,d\Omega=x^{-2}\,dx$ and $\cos\nu=\cos\alpha\cos\alpha'+\sin\alpha\sin\alpha'\cos(B-B')$, etc.

Equation (3.3.9) is equivalent to (2.17) in Katsura's paper [2]. Applying his technique used in [3], we obtain the same results. It may be noted that

$$\left[\frac{D_3(T)}{b^3}\right]_{d=3} = -\tfrac{1}{8}(1.266\,904 - 3.7325f + 15.105f^2 - 74.283f^3 + 157.64f^4 - 294.65f^5 + 101.97f^6). \tag{3.3.10}$$

The values of $D_1(T)$, $D_2(T)$ and $D_3(T)$ obtained in (3.1.10), (3.2.10) and (3.3.10) can be used to evaluate the fourth virial coefficient $D(T)$, given by (3.1), which is found to agree with Katsura [3], as follows,

$$\left[\frac{D(T)}{b^3}\right]_{d=3} = 0.286\,95 + 1.6342f - 23.294f^2 + 54.648f^3 + 70.754f^4 - 168.20f^5 - 12.747f^6. \tag{3.3.11}$$

For $d = 1$, (3.3.7) becomes

$$I_{1/2}(a_1, a_2, a_3; a_4, a_5, a_6) = 8(a_1a_2a_3)^{-1/2}(a_4a_5a_6)^{-1}\sum_l\sum_m{}'\sum_n{}'(\tfrac{1}{2}+l)(\tfrac{1}{2}+m)(\tfrac{1}{2}+n) \times N_{mn}(a_1, a_5, a_6)N_{ln}(a_2, a_4, a_6)N_{lm}(a_3, a_4, a_5) \tag{3.3.12}$$

where

$$N_{mn}(a, b, c) = (2\pi)^{1/2}\int_0^\infty J_{1/2}(a_ix)J_{1/2+m}(a_jx)J_{1/2+n}(a_kx)x^{-3/2}\,dx. \tag{3.3.13}$$

The triple sum in (3.3.12) indicates summation over l, m and n, where l, m, n are zero, all positive even integers, and all positive odd integers.

The necessary integrals of $N_{mn}(a_i, a_j, a_k)$ can be calculated by using $N_{mn}(a, b, b)$ given by (3.3.13) for $a, b = 1, 2$. These integrals are calculated one by one. In the numerical calculation, we truncate the triple infinite summation $\sum_l'$, $\sum_m'$, $\sum_n'$ to the finite summation in which (l, m, n) is taken to be (0, 0, 0), (0, 0, 2), (0, 2, 2), (0, 0, 4), (2, 2, 2), (1, 1, 1), (1, 1, 3), (1, 3, 3), and their permutations. These values are listed in table 2. Then we have

$$\left[\frac{D_3(T)}{b^3}\right]_{d=1} = -(0.481\,68 + 2.927\,82f + 7.772\,11f^2 - 38.009\,78f^3 - 125.470\,66f^4 - 137.008\,34f^5 - 51.538\,97f^6). \tag{3.3.14}$$

Hence by using (3.1.13), (3.2.11) and (3.3.14), we get

$$\left[\frac{D(T)}{b^3}\right]_{d=1} = 1.018\,32 - 3.9282f + 2.727\,89f^2 - 52.490\,22f^3 - 22.029\,34f^4 + 81.008\,34f^5 - 51.538\,97f^6. \tag{3.3.15}$$

Table 2. The values of $N_{mn}(a, b, c)$, $a, b, c = 1$ or 2.

a, b, c	1, 1, 1	2, 1, 1	1, 2, 2	2, 2, 2	1, 2, 1	2, 1, 2	1, 1, 2	2, 2, 1
N_{00}	$\frac{3}{2}$	0	$\frac{7}{4}$	$\frac{3\sqrt{2}}{2}$	0	$\frac{7}{4}$	0	$\frac{7}{4}$
N_{22}	$\frac{1}{80}$	0	$\frac{423}{512}$	$\frac{\sqrt{2}}{80}$	$\frac{\sqrt{2}}{20}$	$\frac{293}{20\,480}$	$\frac{\sqrt{2}}{20}$	$\frac{293}{20\,480}$
N_{20}	$\frac{1}{8}$	0	$\frac{9}{16}$	$\frac{\sqrt{2}}{8}$	0	$\frac{1}{16}$	0	$\frac{9}{16}$
N_{02}	$\frac{1}{8}$	0	$\frac{9}{16}$	$\frac{\sqrt{2}}{8}$	0	$\frac{9}{16}$	0	$\frac{1}{16}$
N_{40}	$\frac{1}{48}$	0	$\frac{27}{256}$	$\frac{\sqrt{2}}{48}$	0	$\frac{1}{96}$	0	$\frac{27}{256}$
N_{04}	$\frac{1}{48}$	0	$\frac{27}{256}$	$\frac{\sqrt{2}}{48}$	0	$\frac{27}{256}$	0	$\frac{1}{96}$
N_{11}	$\frac{5}{24}$	0	$\frac{27}{64}$	$\frac{5\sqrt{2}}{24}$	$\frac{\sqrt{2}}{6}$	$\frac{13}{96}$	$\frac{2}{6}$	$\frac{13}{96}$
N_{33}	$\frac{-19}{896}$	0	$\frac{15\,057}{229\,376}$	$\frac{-19\sqrt{2}}{896}$	$\frac{2}{56}$	$\frac{1093}{114\,688}$	$\frac{2}{56}$	$\frac{1093}{114\,688}$
N_{13}	$\frac{1}{48}$	$\frac{-\sqrt{2}}{12}$	$\frac{371}{12\,288}$	$\frac{\sqrt{2}}{48}$	0	$\frac{-45}{256}$	$\frac{\sqrt{2}}{24}$	$\frac{125}{6144}$
N_{31}	$\frac{1}{48}$	$\frac{-\sqrt{2}}{12}$	$\frac{371}{12\,288}$	$\frac{\sqrt{2}}{48}$	$\frac{\sqrt{2}}{24}$	$\frac{125}{6144}$	0	$\frac{-45}{256}$

Appendix

This appendix is devoted to the evaluation of the integral

$$I = \int_0^\infty J_\nu(2x) J_\nu(x) J_{\nu-1}(yx) x^{-\nu} \, dx \qquad 1 \leqslant y \leqslant 2. \tag{A1}$$

Applying the recurrence formula for the Bessel function ([10], vol II, p 12, equation (56))

$$J_\nu(x) = \frac{x}{2\nu} J_{\nu-1}(x) + J_{\nu+1}(x) \tag{A2}$$

to the first and second factors in (A1), we get

$$\begin{aligned} I = \frac{1}{2\nu^2} \bigg(\int_0 J_{\nu-1}(x) J_{\nu-1}(2x) J_{\nu-1}(yx) x^{2-\nu} \, dx + \int_0^\infty J_{\nu-1}(x) J_{\nu+1}(2x) J_{\nu-1}(yx) x^{2-\nu} \, dx \\ + \int_0^\infty J_{\nu+1}(x) J_{\nu-1}(2x) J_{\nu-1}(yx) x^{2-\nu} \, dx \\ + \int_0^\infty J_{\nu+1}(x) J_{\nu+1}(2x) J_{\nu-1}(yx) x^{2-\nu} \, dx \bigg). \end{aligned} \tag{A3}$$

Applying (A2) to the second and third integrals in (A3), we obtain

$$I=\frac{1}{2\nu^2}\left(\nu\int_0^\infty J_{\nu-1}(x)J_\nu(2x)J_{\nu-1}(yz)x^{1-\nu}\,\mathrm{d}x-\int_0^\infty J_{\nu-1}(x)J_{\nu-1}(2x)J_{\nu-1}(yx)x^{2-\nu}\,\mathrm{d}x\right.$$
$$+2\nu\int_0^\infty J_\nu(x)J_{\nu-1}(2x)J_{\nu-1}(yx)x^{1-\nu}\,\mathrm{d}x$$
$$\left.+\int_0^\infty J_{\nu+1}(x)J_{\nu+1}(2x)J_{\nu-1}(yx)x^{2-\nu}\,\mathrm{d}x\right). \tag{A4}$$

The four integrals in (A4) can be obtained from the standard formula ([11], p 695, equation (9.8))

$$\int_0^\infty J_\mu(ax)J_\mu(bx)J_\nu(cx)x^{1-\nu}\,\mathrm{d}x=\frac{(ab)^{\nu-1}}{(2\pi)^{1/2}c^\nu}\sin^{\nu-1/2}VP_{\mu-1/2}^{1/2-\nu}(\cos V)$$

which applies as long as ($|a-b|<c,\ a+b;\ a,\ b>0,\ 2ab\cos v=a^2+b^2-c^2$; Re $\mu>-1$, Re $\nu>-\frac{1}{2}$).

Therefore,

$$I=\frac{(10y^2-y^4-9)^{\alpha/2}}{2^{2\alpha+4}\nu^2\pi^{1/2}y^{1/2}}\left\{(10y^2-y^4-9)^{1/2}\left[\nu P_\alpha^{-1-\alpha}\left(\frac{y^2-3}{2y}\right)\right.\right.$$
$$\left.+\nu 2^{\alpha+2}P_\alpha^{-1-\alpha}\left(\frac{y^2+3}{4y}\right)\right]+4\left(\frac{y}{2}\right)^{-\alpha}P_{\alpha+2}^{-\alpha}\left(\frac{5-y^2}{4}\right)\Bigg]$$
$$\left.-4P_\alpha^{-\alpha}\left(\frac{y^2-3}{2y}\right)\right\} \tag{A5}$$

where $\alpha=(2\nu-3)/2$.

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