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1997 J. Phys. A: Math. Gen. 30 445

(http://iopscience.iop.org/0305-4470/30/2/012)

J. Phys. A: Math. Gen. **30** (1997) 445–465. Printed in the UK PII: S0305-4470(97)66230-7

The first quantum correction to the fourth virial coefficient for fluids in d-dimensionality for the square-well potential at the classical limit

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Received 3 July 1995, in final form 3 January 1996

Abstract. The aim of the present work is to derive the first quantum correction to the fourth virial coefficient for fluids of molecules interacting according to the square-well potential of arbitrary dimensionality d. In this paper, we show that the basic method of Hemmer and Jancovici, which was followed by Gibson, can be extended to cover more general intermolecular potentials. The extension of the formalism is straightforward, but some consideration has to be given to the problem of how to truncate the resulting expansion to get all the quantum corrections to a given order in λ. The first quantum correction to the fourth virial coefficient is obtained in arbitrary dimensionality ($d = 1, 3$).

1. Introduction

The quantum corrections to the equation of state are usually calculated by using the Wigner–Kirkwood (WK) method [1, 2] when the potential is analytic and by the Hemmer–Jancovici (HJ) method [3, 4] when the potential is a hard-sphere one. The WK method fails in the case of nonanalytic potentials. Gibson [5] has extended the method of Hemmer and Jancovici to cover more general intermolecular potentials and calculated the first quantum correction to the virial coefficients for the square-well plus hard-core potential.

Another possible method is the ‘modified’ WK expansion developed by Derdeian and Steele [6] and further extended by Singh and Sinha [7], in which the hard-sphere potential is used as a reference potential and the hard-sphere wavefunctions as a basis set. Singh and Sinha [7] used this method to calculate the quantum corrections to the third virial coefficient for hard-core fluids. Singh and Sinha [8] have used the modified WK series to calculate the quantum corrections to the third virial coefficient for a fluid with a square-well plus hard-core potential. Nilsen [9] calculated the first quantum correction to the classical value of the second virial coefficient for the square-well potential.

In arbitrary dimensionality d, Luban and Baram [10] derived exact expressions for the third virial coefficient and two of the three terms contributing to the fourth virial coefficient. Ree and Hoover [11] calculated the fourth virial coefficient for a hard sphere ($1 \leqslant d \leqslant 9$). Hussien and Ahmed [12] used the method of Luban and Baram [10] to derive exact expressions for the second and third virial coefficients, and they calculated a general expression for the terms of the fourth virial coefficient for fluids to the square-well potential of arbitrary well width and arbitrary dimensionality d. Recently, Sinha and Sinha [13] calculated the quantum corrections to the properties of a dense d-dimensional fluid of hard d-spheres.

0305-4470/97/020445+21\$19.50

In this paper, we generalize the method given by Gibson [5] using the basic method of Hemmer and Jancovici [3, 4] to calculate the first quantum correction to the fourth virial coefficient for the square-well potential of arbitrary dimensionality. In section 2, we review the work of Gibson [5]. In section 3, we present a calculation for the square-well plus hard-core potential in d-dimensionality. The paper ends with numerical results in some special cases and the figures.

2. Expansion of the partition function

Gibson [5] showed that the basic method of Hemmer and Jancovici [3, 4] can be extended to cover more general intermolecular potentials. The extension of the formalism is straightforward, but some consideration has to be given to the problem of how to truncate the resulting expansion to get all the quantum corrections to a given order in λ. It should be noted that in his work he considered only the direct part of the virial coefficients—the effects of quantum statistics are completely neglected. If the potential is strongly repulsive at small distances (as is the case for all realistic potentials), it is expected that statistical effects will be negligible at temperatures where a series in powers of λ is useful. This has only been proved for the second virial coefficient [14], but it seems clear that higher coefficients will exhibit a similar behaviour, since the physical mechanism responsible for the rapid suppression of statistical effects with increasing temperature is present in all cases [15].

Gibson [5] considered a system of N identical particles each of mass m in a container of volume Ω. Let the Hamiltonian be

$$H_N = N_N^0 + V_N \tag{1}$$

where H_N^0 is the kinetic energy of the N particles, and V_N is the total potential energy. Let

$$W_N(1, 2, \ldots, N) = \lambda^{3N} \langle \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N | \mathrm{e}^{-\beta H_N} | \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N \rangle \tag{2}$$

where $\beta = 1/KT$ and $\lambda = (2\pi h^2 \beta/m)^{1/2}$. The classical limit of W_N is

$$W_N^C(1, 2, \ldots, N) = \mathrm{e}^{-\beta V_N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)}. \tag{3}$$

A 'modified' W function $W_N^m(1, 2, \ldots, N)$ is defined by the relation

$$W_N = W_N^C W_N^m. \tag{4}$$

(If the pair potential has a hard core, both W_N and W_N^C will vanish for particle configurations in which hard cores overlap. In this case, W_N^m can be taken as zero also.) We note that since both W_N and W_N^C possess the 'product property', W_N^m will possess it too. This means that when the particles split into two groups whose surfaces are separated by a distance that is large compared with the potential range and the thermal wavelength λ, W_N^m can be expressed as a product of two terms, one referring to each group.

In the usual treatment of a quantum gas, W_N is expressed in terms of Ursell functions U_l [14]. In an analogous way, we express W_N^m in terms of 'modified' Ursell functions U_l^m:

$$W_1^m(1) = U_1^m(1) = 1 \tag{5}$$

$$W_2^m(1, 2) = 1 + U_2^m(1, 2) \tag{6}$$

$$W_3^m(1, 2, 3) = 1 + U_2^m(2, 3) + U_2^m(3, 1) + U_2^m(1, 2) + U_3^m(1, 2, 3) \tag{7}$$

$$\begin{aligned} W_N^m(1, \ldots, N) = 1 &+ \sum U_2^m(i, j) + \sum U_3^m(i, j, k) + \sum U_4^m(i, j, k, l) \\ &+ \sum U_2^m(i, j) U_2^m(k, l) + \cdots. \end{aligned} \tag{8}$$

Equation (8) is obtained by taking a partition of the N particles in groups, making the corresponding product of U_l^m functions, and summing over all possible partitions. These equations can be solved successively for $U_1^m, U_2^m, \ldots$:

$$U_2^m(1,2) = W_2^m(1,2) - 1 \tag{9}$$

$$U_3^m(1,2,3) = W_3^m(1,2,3) - W_2^m(2,3) - W_2^m(3,1) - W_2^m(1,2) + 2 \tag{10}$$

etc. Since the W_l^m possess the 'product property', it follows that U_l^m will possess the 'cluster property'. This means that U_l^m approaches zero for a configuration in which the l particles are separated into two or more groups sufficiently distant from each other.

We define

$$Q = \int W_N(1,\ldots,N)\,\mathrm{d}^{3N}r \tag{11}$$

$$Q^C = \int W_N^C(1,\ldots,N)\,\mathrm{d}^{3N}r \tag{12}$$

$$g_l(1,\ldots,l) = (\Omega^l/Q^c)\int W_N^c(1,\ldots,N)\,\mathrm{d}^3r_{l+1},\ldots\mathrm{d}^3r_N. \tag{13}$$

Note that g_l is a classical correlation function. Inserting the expansion (8) into (4), and integrating over the coordinates, gives

$$Q = Q^c\Big\{1 + \Omega^{-2}\sum\int g_2(i,j)U_2^m(i,j)\,\mathrm{d}^6r + \Omega^{-3}\sum\int g_3(i,j,k)U_3^m(i,j,k)\,\mathrm{d}^9r$$
$$+\Omega^{-4}\sum\int g_4(i,j,k,l)[U_4^m(i,j,k,l) + U_2^m(i,j)U_2^m(k,l)]\,\mathrm{d}^{12}r + \cdots\Big\}. \tag{14}$$

We wish to use (14) to calculate quantum corrections to Q at moderately high temperatures, where λ is small. In general, these corrections will take the form of a series in powers of λ. The expansion (14) will be useful only if it can be truncated in some well defined way, to give the total correction to a specified order in λ. The λ contribution from a factor U_l^m depends on the potential, and we now consider various cases.

The simplest case is that of hard spheres, for which U_l^m is identical to the usual Ursell function U_l. The contribution from U_l to a term in (14) is determined by two factors. First, the correlation functions vanish for a particle configuration in which hard cores overlap, and second, U_l vanishes whenever the particles separate into two groups with a distance $\gg \lambda$ between surfaces. This means that the entire contribution comes from configurations in which the distance between centres of neighbouring spheres is r, where $a < r < a + \lambda$ (a is the sphere diameter). It follows that the contribution from U_l to an integral in (14) is of order λ^{l-1}.

Turning now to more general potentials, we note first that, by their construction, the U_l^m vanish except for configurations in which the particle separations are such that quantum effects are present. For example, for a pure square-well potential [$v(r) = -\epsilon,\ r < b$, $v(r) = 0,\ r > b$], quantum effects are negligible unless neighbouring particles are separated by a distance r, where $|r - b| \leqslant \lambda$. In this case, the contribution from U_l^m is of order λ^{l-1}. This result can be extended to a potential which is a finite chain of rectangular wells, with or without a hard core; again the contribution from U_l^m will be of order λ^{l-1}.

The situation becomes less clear when we go beyond these simple potentials. Consider a potential which is analytic and sufficiently repulsive at the origin, so that the WK expansion exists. The quantum corrections to Q will then be given as a series in powers of λ^2. It is necessary to include contributions from both U_2^m and U_3^m in order to get the first-order correction term.

Finally, consider a potential which is analytic except at a finite number of points. One might argue that the dominant quantum effects occur in the neighbourhoods of these points, and that U_l^m will contribute to order λ^{l-1}, as in the rectangular well case, but this conclusion is only tentative. However, it seems fairly certain that the first-order correction (of order λ) will come entirely from U_2^m and since this is about all one would be able to calculate in practice, the method is applicable.

Let us now assume that the potential is such that the first-order correction is contained entirely in the U_2^m term. Then (14) gives

$$Q = Q^c[1 + N(N-1)A_2/\Omega + 0(\lambda^2)] \tag{15}$$

where

$$A_2 = \frac{1}{2\Omega}\int g_2(1,2)U_2^m(1,2)\,\mathrm{d}^6r. \tag{16}$$

For a spherically symmetric pair potential, this can be written

$$A_2 = 2\pi\int_0^\infty g(r)U_2^m(r)r^2\,\mathrm{d}r \tag{17}$$

where $g(r)$ is the (classical) radial distribution function. The pressure is given by

$$P = P^c - \frac{\rho^2}{\beta}\frac{\partial}{\partial\rho}(\rho A_2) + 0(\lambda^2). \tag{18}$$

Expanding the pressure in a virial series,

$$\beta P = \rho + \sum_{n\geqslant 2} B_n\rho^n. \tag{19}$$

$U_2^m(r)$ can be found from the solution of the quantum-mechanical two-body problem. From (9), it can be written in the form

$$U_2^m(r) = 2^{3/2}\mathrm{e}^{\beta v(r)}\lambda^3 G(\boldsymbol{r},\boldsymbol{r};\beta) - 1 \tag{20}$$

where $v(r)$ is the two-body potential and

$$G(\boldsymbol{r},\boldsymbol{r};\beta) \equiv \langle\boldsymbol{r}|\mathrm{e}^{-\beta H_2^{rel}}|\boldsymbol{r}\rangle \tag{21}$$

where H_2^{rel} is the Hamiltonian for the relative motion of the two particle system.

3. Square-well potential with hard core

The potential is

$$v(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma < r < a_1\sigma \\ 0 & r > a_1\sigma \end{cases} \tag{22}$$

where σ is the diameter of the hard sphere, a_1 is the range of the attractive well and is usually taken to be 1 and 2, and ϵ is the well depth.

The function $\lambda^3 G(\boldsymbol{r}, \boldsymbol{r}; \beta)$, to first order in λ, was calculated [5]. Then, we find

$$U_2^m(r) = -\sqrt{2}\lambda e^{-\beta\epsilon} L_\alpha^{-1}\left[\frac{1}{4\Gamma^2}\delta(r-\sigma+) - \frac{1}{4\Gamma^2}\frac{\Gamma-\gamma}{\Gamma+\gamma}\delta(r-a_1\sigma-) + 0\left(\frac{1}{\Gamma^3}\right)\right]$$

$$\sigma < r < a_1\sigma \tag{23}$$

$$U_2^m = -\sqrt{2}\lambda L_\alpha^{-1}\left[\frac{1}{4\gamma^2}\frac{\Gamma-\gamma}{\Gamma+\gamma}\delta(r-a_1\sigma+) + 0\left(\frac{1}{\gamma^3}\right)\right] \qquad r > a_1\sigma$$

where L_α^{-1} is the inverse Laplace transform operator defined as

$$L_\alpha^{-1} \equiv \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} dp\, e^{\alpha p}$$

$\alpha = \lambda^2/2\pi$, $\gamma = p^{1/2}$ and $\Gamma^2 = \gamma^2 - m\epsilon/h^2$. Substituting in (17), doing the r integration and then the inverse transform, gives

$$A_2 = -2^{1/2}\pi[e^{\beta\epsilon}\sigma^2 Y(\sigma) + \Theta(\beta\epsilon)(a_1\sigma)^2 Y(a_1\sigma)]\lambda + 0(\lambda^2) \tag{24}$$

where

$$\Theta(x) \equiv 1 + e^x - 2e^{x/2} I_0(\tfrac{1}{2}x). \tag{25}$$

I_0 is the modified Bessel function of the first kind and order zero. We have also introduced $Y(r)$, which is related to the radial distribution function $g(r)$ by

$$Y(r) = g(r)e^{\beta v(r)}. \tag{26}$$

In the case where the hard core is present, one can obtain explicit expressions for the first few virial coefficients by making use of the density expansion of the radial distribution [16]. We write

$$Y(r) = Y_0(r) + \rho Y_1(r) + \rho^2 Y_2(r) + \cdots \tag{27}$$

which leads to

$$B_n = B_n^c + (n-1)2^{1/2}\pi\sigma^2[e^{\beta\epsilon}Y_{n-2}(\sigma) + \Theta(\beta\epsilon)a_1^2 Y_{n-2}(a_1\sigma)]\lambda + 0(\lambda^2). \tag{28}$$

3.1. The first quantum correction to the fourth virial coefficient

We evaluate the first quantum correction to the fourth virial coefficient in arbitrary dimensionality. From Luban and Baram [10], if the integrand of a d-dimensional integral possesses spherical symmetry, then

$$\int H(r)\, dr = C_d \int_0^\infty H(r) r^{d-1}\, dr \tag{29}$$

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

$$\int H(r,\theta)\, dr = C_{d-1}\int_0^\infty r^{d-1}\, dr \int_0^\infty H(r,\theta)\sin^{d-2}\theta\, d\theta. \tag{30}$$

The quantity C_d is the surface area of a unit sphere in R^d, defined by

$$C_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}. \tag{31}$$

By using (29), equation (16) can be written as

$$A_2 = \frac{C_d}{2}\int_0^\infty g(r) U_2^m(r) r^{d-1}\, dr. \tag{32}$$

Then equation (24) becomes

$$A_2 = -\frac{C_d}{2^{(d+1)/2}}[\mathrm{e}^{\beta\epsilon}\sigma^{d-1}Y^d(\sigma) + \Theta(\beta\epsilon)(a_1\sigma)^{d-1}Y^d(a_1\sigma)]\lambda + 0(\lambda^2) \tag{33}$$

where Y^d means that Y is d-dimensional. By using (28) and (33), we get

$$B_n^q = B_n^c + (n-1)\frac{C_d\sigma^d}{2^{(d+2)/2}}[\mathrm{e}^{\beta\epsilon}Y^d_{n-2}(\sigma) + \Theta(\beta\epsilon)a_1^{d-1}Y^d_{n-2}(a_1\sigma)](\lambda/\sigma) + 0(\lambda^2). \tag{34}$$

In cases of $(n = 2, 3)$ this work is at press [17] and the results are

$$B_2^q = B_2^c + \frac{C_d\sigma^d}{2^{(d+2)/2}}[\mathrm{e}^{\beta\epsilon} + \Theta(\beta\epsilon)a_1^{d-1}](\lambda/\sigma) + 0(\lambda/\sigma)^2 \tag{35}$$

and

$$\begin{aligned} B_3^q = B_3^c + \frac{2\pi^d\sigma^{\frac{3d}{2}+1}}{\Gamma(\frac{d}{2})}\{&\mathrm{e}^{\beta\epsilon}[(1+f)^2W^{d/2}_{d/2,d/2,d/2-1}(\sigma,\sigma,\sigma) \\ &-2a_1^{d/2}f(f+1)W^{d/2}_{d/2,d/2,d/2-1}(\sigma,a_1\sigma,\sigma) \\ &+a_1^d f^2W^{d/2}_{d/2,d/2,d/2-1}(a_1\sigma,a_1\sigma,\sigma)] \\ &+a_1^{d/2}\Theta(\beta\epsilon)[(1+f)^2W^{d/2}_{d/2,d/2,d/2-1}(\sigma,\sigma,a_1\sigma) \\ &-2g^{d/2}f(f+1)W^{d/2}_{d/2,d/2,d/2-1}(\sigma,a_1\sigma,a_1\sigma) \\ &+a_1^d f^2W^{d/2}_{d/2,d/2,d/2-1}(a_1\sigma,a_1\sigma,a_1\sigma)]\}(\lambda/\sigma) + 0(\lambda/\sigma)^2 \end{aligned} \tag{36}$$

where

$$W^{d/2}_{d/2,d/2,d/2-1}(\sigma,\sigma,r) = \begin{cases} 2^{-d/2}r^{d/2-1}\Bigg[\dfrac{1}{\Gamma(1+d/2)} \\ \quad -\dfrac{r}{\sigma\Gamma(1/2)\Gamma(d+1)/2)} \\ \quad \times {}_2F_1\left(\dfrac{1-d}{2},\dfrac{1}{2},\dfrac{3}{2},\dfrac{r^2}{4\sigma^2}\right)\Bigg] & 0 \leqslant r \leqslant 2\sigma \\ 0 & r \geqslant 2\sigma \end{cases} \tag{37}$$

$$W^{d/2}_{d/2,d/2,d/2-1}(a_1\sigma,a_1\sigma,r) = \begin{cases} 2^{-d/2}r^{d/2-1}\Bigg[\dfrac{1}{\Gamma(1+d/2)} \\ \quad -\dfrac{r}{a_1\sigma\Gamma(1/2)\Gamma(d+1)/2)} \\ \quad \times {}_2F_1\left(\dfrac{1-d}{2},\dfrac{1}{2},\dfrac{3}{2},\dfrac{r^2}{4a_1^2\sigma^2}\right)\Bigg] & 0 \leqslant r \leqslant 2a_1\sigma \\ 0 & r \geqslant 2a_1\sigma \end{cases} \tag{38}$$

and

$$W^{d/2}_{d/2,d/2,d/2-1}(\sigma,a_1\sigma,r) = \begin{cases} \dfrac{2^{-d/2}r^{d/2-1}}{a_1^{d/2}\Gamma(1+d/2)} & 0 \leqslant r \leqslant \sigma(a_1-1) \\ I & \sigma \leqslant r \leqslant \sigma(a_1+1) \\ 0 & r \geqslant \sigma(a_1+1) \end{cases} \tag{39}$$

where

$$I = \frac{a_1\sigma^2}{d^2}\left\{\frac{d}{a_1\sigma}\left[\frac{(r\sigma)^{d/2-1}}{(2\pi)^{1/2}(a_1\sigma)^{d/2}}(1-x_1^2)^{\frac{d-1}{4}}P^{\frac{1-d}{2}}_{\frac{d-3}{2}}(x_1)\right.\right.$$
$$\left.-\frac{(r\sigma)^{d/2-2}}{(2\pi)^{1/2}(a_1\sigma)^{d/2-1}}(1-x_1^2)^{\frac{d-3}{4}}P^{\frac{3-d}{2}}_{\frac{d-3}{2}}(x_1)\right.$$
$$+\frac{d(ra_1\sigma)^{d/2-1}}{(2\pi)^{1/2}\sigma^{d/2}}(1-x_2^2)^{\frac{d-1}{4}}P^{\frac{1-d}{2}}_{\frac{d-3}{2}}(x_2)$$
$$\left.+\frac{(a_1\sigma^2)^{d/2-2}}{(2\pi)^{1/2}r^{d/2-1}}(1-x_3^2)^{\frac{d-3}{4}}P^{\frac{3-d}{2}}_{\frac{d+1}{2}}(x_3)\right\} \tag{40}$$

and

$$x_1 = \frac{r^2+\sigma^2(1-a_1^2)}{2r\sigma} \qquad x_2 = \frac{r^2+\sigma^2(1+a_1^2)}{2a_1r\sigma} \qquad x_3 = \frac{\sigma^2(1+a_1^2)-r^2}{2a_1\sigma}.$$

3.2. Calculation of $B_4^q(T)$

When $n = 4$ in equation (34), we get

$$B_4^q = B_4^c + \frac{3C_d\sigma^d}{2^{(d+2)/2}}[\mathrm{e}^{\beta\epsilon}Y_2^d(\sigma) + \Theta(\beta\epsilon)g^{d-1}Y_2^d(a_1\sigma)](\lambda/\sigma) + 0(\lambda^2) \tag{41}$$

where Y_2^d means that Y_2 is d-dimensional, but Y_2 is

$$Y_2(r) = Y_{21}(r) + Y_{22}(r) + Y_{23}(r) \tag{42}$$

where

$$Y_{21}(r) = \tfrac{1}{2}\iint f(r_{12})f(r_{13})f(r_{24})f(r_{34})\,\mathrm{d}r_3\,\mathrm{d}r_4 \tag{43}$$

$$Y_{22}(r) = \iint f(r_{12})f(r_{23})f(r_{34})\,\mathrm{d}r_3\,\mathrm{d}r_4 \tag{44}$$

and

$$Y_{23}(r) = 2\iint f(r_{12})f(r_{13})f(r_{23})f(r_{34})\,\mathrm{d}r_3\,\mathrm{d}r_4 \tag{45}$$

where $f(r)$ is the Mayer function which is defined as

$$f(r) = \exp\left[\frac{-v(r)}{KT}\right] - 1. \tag{46}$$

By using equation (22) we get

$$f(r) = \begin{cases} -1 & r < \sigma \\ f = \exp(\beta\epsilon) - 1 & \sigma < r < a_1\sigma \\ 0 & r > a_1\sigma. \end{cases} \tag{47}$$

3.2.1. Calculation of $Y_{21}(r)$. By using the techniques of Katsura [18] we can evaluate $Y_{21}(r)$ analytically. The d-dimensional Fourier transform $F_d(k)$ of $f(r)$ is defined by

$$F_d(k) = \int f(r)\exp(\mathrm{i}kr)\,\mathrm{d}r$$
$$F_d(k) = \int f(r)\exp(\mathrm{i}kr\cos\theta)\,\mathrm{d}r. \tag{48}$$

From (30), (47) and (48) we get

$$F_d(k) = C_{d-1}\left\{ -\int_0^{\sigma} r^{d-1}\,\mathrm{d}r \int_0^{\pi} \exp(\mathrm{i}kr\cos\theta)\sin^{d-2}\theta\,\mathrm{d}\theta \right. \\ \left. + f\int_{\sigma}^{a_1\sigma} r^{d-1}\,\mathrm{d}r \int_0^{\pi} \exp(\mathrm{i}kr\cos\theta)\sin^{d-2}\theta\,\mathrm{d}\theta \right\}. \tag{49}$$

Using the following standard identities for the Bessel function:

$$J_\nu(x) = \frac{\frac{x}{2}}{\pi^{1/2}\Gamma\left(\nu+\frac{1}{2}\right)} \int_0^{\infty} \exp(\mathrm{i}x\cos\theta)\sin^{2\nu}\theta\,\mathrm{d}\theta \qquad (\mathrm{Re}\,\nu > \tfrac{1}{2}) \tag{50}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}[x^\nu J_\nu(x)] = x^\nu J_{\nu-1}(x) \tag{51}$$

one can find that

$$F_d(k) = \left(\frac{2\pi\sigma}{k}\right)^{d/2} [g^{d/2} f J_{d/2}(a_1\sigma k) - (1+f)J_{d/2}(\sigma k)]. \tag{52}$$

Following the technique used by Katsura [18] to evaluate the fourth virial coefficient for square-well.

We let

$$\begin{aligned} &\rho_i = r_i - r_1 \qquad i = 2, 3, 4 \\ &f(|\rho|) = h(|\rho|) = h(\rho) \\ &Y_{21}(r) = \tfrac{1}{2}\iint h(\rho_2)h(\rho_3)h(\rho_4-\rho_2)h(\rho_4-\rho_3)\,\mathrm{d}\rho_3\,\mathrm{d}\rho_4. \end{aligned} \tag{53}$$

Let the Fourier transform of $h(\rho)$ be $F_d(k)$, which is defined in equation (52)

$$Y_{21}(r) = \tfrac{1}{2}(2\pi)^{-d}\iint [F_d(k)]^4\,\mathrm{d}k. \tag{54}$$

Using (29), we get

$$Y_{21}(r) = \tfrac{1}{2}(2\pi)^{-d} C_d \int_0^{\infty} [F_d(k)]^4 k^{d-1}\,\mathrm{d}k. \tag{55}$$

Inserting (48) with $a_1 = 2$ for $F_d(k)$,

$$Y_{21}(r) = \frac{(2\pi)^d\sigma^{2d}C_d}{2}\int_0^{\infty} [2^{d/2} f J_{d/2}(2\sigma k) - (1+f)J_{d/2}(\sigma k)]^4 k^{-(d+1)}\,\mathrm{d}k. \tag{56}$$

To evaluate the first and the last integrals in (56) using the standard identity, see appendix A. Thus, we have

$$\begin{aligned} \frac{Y_{21}(r)}{b^3} = d2^{(d-2)}\left[\Gamma\left(\frac{d}{2}+1\right)\right]^2 &\left\{ \frac{\Gamma\left(\frac{d}{2}\right)\Gamma(d)}{3\pi\Gamma\left(\frac{3d}{2}\right)\left[\Gamma\left(\frac{d+3}{2}\right)\right]^2} [2^{3d} f^4 + (1+f)^4] \right. \\ &\times {}_3F_2\left(\frac{1}{2}, 1, \frac{1-d}{2}; \frac{d+3}{2}, \frac{d+3}{2}; 1\right) \\ &-2^{\frac{3d+2}{2}} f^3(1+f)\int_0^{\infty} [J_{d/2}(2x)]^3 J_{d/2}(x) x^{-(d+1)}\,\mathrm{d}x \\ &+32^d f^2(1+f)^2 \int_0^{\infty} [J_{d/2}(2x)]^2 [J_{d/2}(x)]^2 x^{-(d+1)}\,\mathrm{d}x \\ &\left. -2^{\frac{d+2}{2}} f(1+f)^3 \int_0^{\infty} [J_{d/2}(2x)][J_{d/2}(x)]^3 x^{-(d+1)}\,\mathrm{d}x \right\} \end{aligned} \tag{57}$$

where

$$b = \frac{\sigma^d}{2d} C_d. \tag{58}$$

3.2.2. Calculation of $Y_{22}(r)$

$$Y_{22}(r) = \iint f(r_{12}) f(r_{23}) f(r_{34})\, \mathrm{d}r_3\, \mathrm{d}r_4$$
$$= \iint h(\rho_2) h(\rho_3 - \rho_2) h(\rho_4 - \rho_3)\, \mathrm{d}\rho_3\, \mathrm{d}\rho_4 \tag{59}$$

$$Y_{22}(r) = \frac{(2\pi)^{-d/2}}{r^{d/2-1}} \int_0^\infty [F_d(k)]^3 J_{d/2-1}(rk) k^{d/2}\, \mathrm{d}k. \tag{60}$$

Inserting (52) with $a_1 = 2$ for $F_d(k)$,

$$Y_{22}(r) = \frac{(2\pi)^2 \sigma^{3d/2}}{r^{d/2-1}} \left\{ \int_0^\infty 2^{3d/2} f^3 [J_{d/2}(2\sigma k)]^3 J_{d/2-1}(rk) k^{-d}\, \mathrm{d}k \right.$$
$$-3(2)^d f^2 (1+f) \int_0^\infty [J_{d/2}(2\sigma k)]^2 J_{d/2}(\sigma k) J_{d/2-1}(rk) k^{-d}\, \mathrm{d}k$$
$$+3(2)^{d/2} f (1+f)^2 \int_0^\infty J_{d/2}(2\sigma k) [J_{d/2}(\sigma k)]^2 J_{d/2-1}(rk) k^{-d}\, \mathrm{d}k$$
$$\left. -(1+f)^3 \int_0^\infty [J_{d/2}(\sigma k)]^3 J_{d/2-1}(rk) k^{-d}\, \mathrm{d}k \right\}. \tag{61}$$

3.2.3. Calculation of $Y_{23}(r)$

$$Y_{23}(r) = \iint f(r_{12}) f(r_{13}) f(r_{23}) f(r_{34})\, \mathrm{d}r_3\, \mathrm{d}r_4$$
$$= \iint h(\rho_2) h(\rho_3) h(\rho_3 - \rho_2) h(\rho_4 - \rho_3)\, \mathrm{d}\rho_3\, \mathrm{d}\rho_4 \tag{62}$$
$$= \frac{2^{(1-d/2)}}{\Gamma\left(\frac{d}{2}\right)} \left\{ -\int_0^\sigma r^{d/2} I\, \mathrm{d}r + f \int_\sigma^{2\sigma} r^{d/2}\, \mathrm{d}r \right\} \tag{63}$$

where

$$I = \int_0^\infty [F_d(k)]^3 J_{\frac{d}{2}-1}(rk) k^{\frac{d}{2}}\, \mathrm{d}k.$$

Inserting (52) $F_d(k)$ with $a_1 = 2$,

$$I = (2\pi\sigma)^{3d/2} \int_0^\infty [2^{d/2} f J_{d/2}(2\sigma k) - (1+f) J_{d/2}(\sigma k)]^3 J_{d/2-1}(rk) k^{-d}\, \mathrm{d}k. \tag{64}$$

3.2.4. Special cases.

For $d = 1$. When $d = 1$, we will evaluate these integrals in (57), (61) and (63) in the following sub-section. Putting $d = 1$ in (57), we get

$$\frac{Y_{21}(r)}{b^3} = \frac{\pi}{8} \left\{ \frac{2}{3\pi} [8 f^4 + (1+f)^4] - (2)^{\frac{5}{2}} f^3 (1+f) \int_0^\infty [J_{1/2}(2x)]^3 [J_{1/2}(x)] x^{-2}\, \mathrm{d}x \right.$$
$$+6 f^2 (1+f)^2 \int_0^\infty [J_{1/2}(2x)]^2 [J_{1/2}(x)]^2 x^{-2}\, \mathrm{d}x$$
$$\left. -(2)^{\frac{3}{2}} f (1+f)^3 \int_0^\infty [J_{1/2}(2x)] [J_{1/2}(x)]^3 x^{-2}\, \mathrm{d}x \right\}. \tag{65}$$

To evaluate the integrals in (65), we use the standard identity for the Bessel function, see appendix A, equations (A2) and (A3).

$$\frac{Y_{21}(r)}{b^3} = \frac{\pi}{8}\left\{\frac{2}{3\pi}[8f^4 + (1+f)^4] - \frac{8}{\pi^2}f^3(1+f)\int_0^\infty [\sin(2x)]^3[\sin x]x^{-4}\,\mathrm{d}x \right.$$
$$+\frac{12}{\pi^2}f^2(1+f)^2\int_0^\infty [\sin(2x)]^2[\sin x]^2x^{-4}\,\mathrm{d}x$$
$$\left. -\frac{8}{\pi^2}f(1+f)^3\int_0^\infty [\sin(2x)][\sin x]^3x^{-4}\,\mathrm{d}x\right\}. \qquad (66)$$

Using the standard identity in appendix A, see equations (A4), (A5) and (A6), we have

$$\left[\frac{Y_{21}(r)}{b^3}\right]_{d=1} = \frac{1}{48}[4 - 7f + 15f^2 - 3f^3 + 3f^4].$$

When $\sigma = 1$, then

$$[Y_{21}(r)]_{d=1} = \tfrac{1}{48}[4 - 7f + 15f^2 - 3f^3 + 3f^4]. \qquad (67)$$

Putting $d = 1$ in equation (61),

$$Y_{22}(r) = \frac{(2\pi)\sigma^{3/2}}{r^{-1/2}}\left\{\int_0^\infty 2^{3/2}f^3[J_{1/2}(2\sigma k)]^3 J_{-1/2}(rk)k^{-1}\,\mathrm{d}k\right.$$
$$-6f^2(1+f)\int_0^\infty [J_{1/2}(2\sigma k)]^2 J_{1/2}(\sigma k)J_{-1/2}(rk)k^{-1}\,\mathrm{d}k$$
$$+3(2)^{1/2}f(1+f)^2\int_0^\infty J_{1/2}(2\sigma k)[J_1(\sigma k)]^2 J_{-1/2}(rk)k^{-1}\,\mathrm{d}k$$
$$\left.-(1+f)^3\int_0^\infty [J_{1/2}(\sigma k)]^3 J_{-1/2}(rk)k^{-1}\,\mathrm{d}k\right\}. \qquad (68)$$

To evaluate the integrals in (68), we use the standard identity for the Bessel functions, see appendix A, equations (A2) and (A3). Inserting (A2) and (A3) in (68), we get

$$Y_{22}(r) = \frac{8}{\pi}\left\{f^3\int_0^\infty [\sin(2\sigma k)]^3\cos(rk)k^{-3}\,\mathrm{d}k\right.$$
$$-3f^2(1+f)\int_0^\infty [\sin(2\sigma k)]^2\sin(\sigma k)\cos(rk)k^{-3}\,\mathrm{d}k$$
$$+3f(1+f)^2\int_0^\infty \sin(2\sigma k)[\sin(\sigma k)]^2\cos(rk)k^{-3}\,\mathrm{d}k$$
$$\left.-(1+f)^3\int_0^\infty [\sin(\sigma k)]^3\cos(rk)k^{-3}\,\mathrm{d}k\right\} \qquad (69)$$

$$Y_{22}(r) = \frac{8}{\pi}[f^3 I_1 - 3f^2(1+f)I_2 + 3f(1+f)^2 I_3 - (1+f)^3 I_4] \qquad (70)$$

where

$$I_1 = \int_0^\infty [\sin(2\sigma k)]^3\cos(rk)k^{-3}\,\mathrm{d}k \qquad (71a)$$

$$I_4 = \int_0^\infty [\sin(\sigma k)]^3\cos(rk)k^{-3}\,\mathrm{d}k \qquad (71b)$$

$$I_2 = \int_0^\infty [\sin(2\sigma k)]^2\sin(\sigma k)\cos(rk)k^{-3}\,\mathrm{d}k \qquad (71c)$$

and

$$I_3 = \int_0^\infty [\sin(2\sigma k)][\sin(\sigma k)]^2 \cos(rk)k^{-3}\,\mathrm{d}k. \tag{71d}$$

The integrals I_1 and I_4 can be expressed using the standard formula, see appendix B. Thus, by using (B1), we can obtain I_1 and I_4 as

$$I_1 = \begin{cases} \frac{\pi}{8}(12\sigma^2 - r^2) & r < 2\sigma \\ \frac{\pi r^3}{4} & r = 2\sigma \\ \frac{\pi}{6}(6\sigma - r)^2 & 2\sigma < r < 6\sigma \\ 0 & 6\sigma < r \end{cases} \tag{72}$$

and

$$I_4 = \begin{cases} \frac{\pi}{8}(3\sigma^2 - r^2) & r < \sigma \\ \frac{\pi r^3}{4} & r = \sigma \\ \frac{\pi}{6}(3\sigma - r)^2 & \sigma < r < 3\sigma \\ 0 & 3\sigma < r. \end{cases} \tag{73}$$

The value of the integrals I_2 and I_3 is obtained as

$$I_2 = 4I_4 - 4I_{22} \tag{74}$$

where

$$I_{22} = \int_0^\infty \sin^5(\sigma k)\cos(rk)k^{-3}\,\mathrm{d}k. \tag{75}$$

The value of the preceding integral is obtained in appendix B, see equation (B2), and the result is

$$I_{22} = \begin{cases} \frac{\pi}{128}(20\sigma^2 - 12r^2) & r < \sigma \\ \frac{\pi}{64}(15\sigma^2 - 10r\sigma - r^2) & r = \sigma \\ \frac{\pi}{16}(5\sigma^2 - 5r\sigma + r^2) & \sigma < r < 3\sigma \\ -\frac{\pi}{128}(5\sigma^2 + 10r\sigma - 3r^2) & r = 3\sigma \\ -\frac{\pi}{64}(25\sigma^2 - 10r\sigma + 16r^2) & 3\sigma < r < 5\sigma \\ 0 & r \geqslant 5\sigma \end{cases} \tag{76}$$

and

$$\begin{aligned} I_3 &= \int_0^\infty \sin(2\sigma k)\sin^2(\sigma k)\cos(rk)k^{-3}\,\mathrm{d}k \\ &= 2I_4 - 4I_{32} \end{aligned} \tag{77}$$

where

$$I_{32} = \int_0^\infty \sin^3(\sigma k)\sin^2\left(\frac{\sigma k}{2}\right)\cos(rk)k^{-3}\,\mathrm{d}k. \tag{78}$$

The value of the preceding integral is obtained in appendix B, see equation (B3), and the result is

$$I_{32} = \begin{cases} \frac{\pi}{64}(4\sigma^2 - 6r^2) & r < \sigma \\ \frac{\pi}{64}(7\sigma^2 - 6r\sigma) & r = \sigma \\ \frac{\pi}{64}(10\sigma^2 - 12r\sigma + 3r^2) & \sigma < r < 2\sigma \\ \frac{\pi}{64}(6\sigma^2 - 8r\sigma + 2r^2) & r = 2\sigma \\ \frac{\pi}{64}(2\sigma^2 - 4r\sigma + r^2) & 2\sigma < r < 3\sigma \\ -\frac{\pi}{64}(7\sigma^2 - 2r\sigma) & r = 3\sigma \\ -\frac{\pi}{64}(16\sigma^2 - 8r\sigma - r^2) & 3\sigma < r < 4\sigma \\ 0 & r \geqslant 4\sigma. \end{cases} \tag{79}$$

Substituting from (72), (73), (76) and (79) into (70), we get

$$Y_{22}(r) = b_1(r) + b_2(r) f + b_3(r) f^2 + b_4(r) f^3 \tag{80}$$

where

$$b_1(r) = -\frac{8}{\pi} I_4 = -4 \begin{cases} \frac{1}{4}(3\sigma^2 - r^2) & r < \sigma \\ \frac{1}{2}r^3 & r = \sigma \\ \frac{1}{3}(3\sigma - r)^2 & \sigma < r < 3\sigma \\ 0 & 3\sigma < r. \end{cases} \tag{81}$$

$$b_2(r) = \frac{8}{\pi}[3I_3 - 3I_4] = 12 \begin{cases} \frac{1}{4}(\sigma^2 + 2r^2) & r < \sigma \\ \frac{1}{8}(4r^3 - 7\sigma^2 + 6r\sigma) & r = \sigma \\ \frac{1}{24}(42\sigma^2 - 12r\sigma + 5r^2) & \sigma < r < 2\sigma \\ \frac{1}{12}(27\sigma^2 - 12r\sigma - r^2) & r = 2\sigma \\ \frac{1}{24}(66\sigma^2 - 36r\sigma + 5r^2) & 2\sigma < r < 3\sigma \\ \frac{1}{8}(7\sigma^2 - 2r\sigma) & r = 3\sigma \\ \frac{1}{8}(16\sigma^2 - 8r\sigma - r^2) & 3\sigma < r < 4\sigma \\ 0 & r \geqslant 4\sigma \end{cases} \tag{82}$$

$$b_3(r) = \frac{8}{\pi}[-3I_2 + 6I_3 - 3I_4] = 12 \begin{cases} \frac{1}{2}[2r^2 - \sigma^2] & r < \sigma \\ \frac{1}{8}[\sigma^2 + 2r\sigma - r^2 - 4r^3] & r = \sigma \\ -\frac{1}{12}(36\sigma^2 - 30r\sigma + 7r^2) & \sigma < r < 2\sigma \\ -\frac{1}{6}[12\sigma^2 - 9r\sigma + 2r^2] & r = 2\sigma \\ -\frac{1}{12}[12\sigma^2 + 6r\sigma + r^2] & 2\sigma < r < 3\sigma \\ \frac{1}{16}[23\sigma^2 - 18r\sigma + 3r^2] & r = 3\sigma \\ \frac{1}{8}[7\sigma^2 - 6r\sigma - 18r^2] & 3\sigma < r < 4\sigma \\ -\frac{1}{8}[25\sigma^2 - 10r\sigma + 16r^2] & 4\sigma < r < 5\sigma \\ 0 & r \geqslant 5\sigma \end{cases} \tag{83}$$

and

$$b_4(r) = \frac{8}{\pi}[I_1 - 3I_2 + 3I_3 - I_4] = 4\begin{cases} \frac{21}{8}r^2 & r < \sigma \\ \frac{1}{8}[48\sigma^2 - 12r\sigma - 5r^2 - 28r^3] & r = \sigma \\ -\frac{53}{4}\sigma^2 + 11r\sigma - \frac{53}{24}r^2 & \sigma < r < 2\sigma \\ -\frac{1}{2}[\frac{63}{2}\sigma^2 - 19r\sigma + \frac{19}{6}r^2 - r^3] & r = 2\sigma \\ -\frac{1}{24}[54\sigma^2 - 96r\sigma + 91r^2] & 2\sigma < r < 3\sigma \\ \frac{1}{16}[219\sigma^2 - 106r\sigma + 15r^2] & r = 3\sigma \\ \frac{1}{4}[\frac{69}{2}\sigma^2 - 13r\sigma - \frac{77}{3}r^2] & 3\sigma < r < 4\sigma \\ \frac{21}{8}\sigma^2 - \frac{1}{4}r\sigma - \frac{17}{3}r^2 & 4\sigma < r < 5\sigma \\ \frac{1}{3}(6\sigma - r)^2 & 5\sigma < r < 6\sigma \\ 0 & r > 6\sigma. \end{cases} \quad (84)$$

Then we get

$$\begin{aligned} Y_{22}(\sigma) &= b_1(\sigma) + b_2(\sigma)f + b_3(\sigma)f^2 + b_4(\sigma)f^3 \\ &= -2\sigma^3 + \tfrac{3}{2}\sigma^2(4\sigma - 1)f + 3\sigma^2(1 - 2\sigma)f^2 + \tfrac{1}{2}\sigma^2(31 - \sigma)f^3. \end{aligned}$$

When $\sigma = 1$ then

$$Y_{22}(1) = \tfrac{1}{2}[-4 + 9f - 6f^2 + 3f^3] \quad (85)$$

and so

$$Y_{22}(2) = -\tfrac{1}{3}[4 + 3f + 12f^2 - 11f^3]. \quad (86)$$

Putting $d = 1$ in (64) and (63), we get

$$Y_{23}(r) = 4\pi\sigma^{3/2}\left\{ -\int_0^{\sigma} r^{1/2} I\,\mathrm{d}r + f\int_{\sigma}^{2\sigma} r^{1/2} I\,\mathrm{d}r \right\} \quad (87)$$

where

$$I = \int_0^{\infty} [2^{1/2} f J_{1/2}(2\sigma k) - (1+f)J_{1/2}(\sigma k)]^3 J_{-1/2}(rk)k^{-1}\,\mathrm{d}k.$$

Substituting from (60) we get

$$Y_{23}(r) = 2\left\{ -\int_0^{\sigma} Y_{22}(r)\,\mathrm{d}r + f\int_{\sigma}^{2\sigma} Y_{22}(r)\,\mathrm{d}r \right\}. \quad (88)$$

Inserting $Y_{22}(r)$ we can write

$$Y_{23}(r) = E_1(r) + E_2(r)f + E_3(r)f^2 + E_4(r)f^3 + E_5(r)f^4. \quad (89)$$

As before, we get

$$\begin{aligned} &E_1 = \tfrac{16}{3}\sigma^3 \qquad E_2 = -14\sigma^3 \qquad E_3 = \tfrac{119}{3}\sigma^3 \\ &E_4 = -\tfrac{1}{3}\sigma^3 \qquad \text{and} \qquad E_5 = -7\sigma^3. \end{aligned} \quad (90)$$

Substituting from (90) in (89), we get

$$Y_{23}(\sigma) = \frac{\sigma^3}{3}[16 - 52f + 119f^2 - f^3 - 21f^4] \quad (91)$$

and

$$Y_{23}(2\sigma) = \frac{(2\sigma)^3}{3}[16 - 52f + 119f^2 - f^3 - 21f^4]. \quad (92)$$

3.2.5. Calculation of $B_4^q(T)$ in one-dimension. Putting ($d = 1$ and $\sigma = 1$) in equation (41), we get

$$B_4^q|_{d=1} = B_4^c|_{d=1} + \frac{6}{2^{3/2}}[\mathrm{e}^{\beta\epsilon} Y_2^1(1) + \theta(\beta\epsilon) Y_2^1(2)](\lambda) + 0(\lambda^2) \tag{93}$$

where $Y_2^1(r)$ is the radial distribution function in one dimension and

$$Y_2^1 = Y_{21}^1 + Y_{22}^1 + Y_{23}^1. \tag{94}$$

From equations (67), (85), (86), (91) and (92), we get

$$\frac{Y_2(1)}{b^3}|_{d=1} = \frac{1}{48}[164 - 623f + 1775f^2 + 53f^3 - 333f^4] \tag{95}$$

and

$$\frac{Y_2(2)}{b^3}|_{d=1} = \frac{1}{48}[1988 - 6711f + 15\,055f^2 + 45f^3 - 2685f^4]. \tag{96}$$

Substituting in (93)

$$B_4^{*q} = B_4^{*c} + \frac{3}{\sqrt{2}}\left\{\frac{1}{48}\mathrm{e}^{\beta\epsilon}[164 - 623f + 1775f^2 + 53f^3 - 333f^4] + \tfrac{1}{48}\theta(\beta\epsilon)[1988 - 6711f + 15\,055f^2 + 45f^3 - 2685f^4]\right\} \tag{97}$$

where B_4^{*c} from [12] can be written in the following as

$$B_4^{*c}|_{d=1} = \frac{B_4^c}{b^3}|_{d=1} = 1.018\,32 - 3.927\,82f + 2.727\,89f^2 - 52.490\,22f^3 - 22.029\,34f^4 + 81.008\,34f^5 + 51.538\,97f^6. \tag{98}$$

For $d = 3$. When $d = 3$, we will evaluate these integrals in (57), (61) and (63) in the following sub-section.

Putting $d = 3$ in (57)

$$\frac{Y_{21}(r)}{b^3} = \frac{27\pi}{16}\left\{\frac{8}{315\pi}[8f^4 + (1+f)^4]\,{}_3F_2\left(\frac{1}{2}, 1, -1; 3, 3; 1\right) - (2)^{13/2} f^3(1+f)\int_0^\infty [J_{3/2}(2x)]^3[J_{3/2}(x)]x^{-4}\,\mathrm{d}x + 3(2)^4 f^2(1+f)^2\int_0^\infty [J_{3/2}(2x)]^2[J_{3/2}(x)]^2 x^{-4}\,\mathrm{d}x - (2)^{7/2} f(1+f)^3\int_0^\infty [J_{3/2}(2x)][J_{3/2}(x)]^3 x^{-4}\,\mathrm{d}x\right\}. \tag{99}$$

Katsura [18] has evaluated the integrals in (99), see appendix A (equations (A7), (A8), (A9) and (A10)); we get

$$\frac{Y_{21}(r)}{b^3} = \frac{3}{2240}[544 - 4075f + 35\,007f^2 - 9968f^3 + 139\,215f^4].$$

When $\sigma = 1$, then we get

$$Y_{21}(r) = \frac{\pi^3}{2520}[544 - 4075f + 35\,007f^2 - 9968f^3 + 139\,215f^4]. \tag{100}$$

Putting $d = 3$ in (61), we get

$$Y_{22}(r) = \frac{(2\pi)^3\sigma^{9/2}}{r^{1/2}}\{2^{9/2} f^3 W^3_{\frac{3}{2},\frac{3}{2},\frac{3}{2},\frac{1}{2}}(2\sigma, 2\sigma, 2\sigma, r) - 24 f^2(1+f) W^3_{\frac{3}{2},\frac{3}{2},\frac{3}{2},\frac{1}{2}}(2\sigma, 2\sigma, \sigma, r) \\ +3(2)^{3/2} f(f+1)^2 W^3_{\frac{3}{2},\frac{3}{2},\frac{3}{2},\frac{1}{2}}(2\sigma, \sigma, \sigma, r) - (1+f)^3 W^3_{\frac{3}{2},\frac{3}{2},\frac{3}{2},\frac{1}{2}}(\sigma, \sigma, \sigma, r)\} \tag{101}$$

where

$$W^{\lambda}_{\alpha,\beta,\gamma,\ldots}(a, b, c, \ldots) = \int X^{-\lambda} J_\alpha(ax) J_\beta(bx) \cdots \, \mathrm{d}x.$$

The integrals in (101) have been obtained by McQuarrie [22] when $\sigma = 1$, see appendix B (equations (B4), (B5), (B6) and (B7)); we get when $\sigma = 1$

$$Y_{22}(r) = \frac{(2\pi)^3}{r^{1/2}}\{2^{9/2} f^3 W^3_{\frac{3}{2},\frac{3}{2},\frac{3}{2},\frac{1}{2}}(2, 2, 2, r) - 24 f^2(1+f) W^3_{\frac{3}{2},\frac{3}{2},\frac{3}{2},\frac{1}{2}}(2, 2, 1, r) \\ +3(2)^{3/2} f(f+1)^2 W^3_{\frac{3}{2},\frac{3}{2},\frac{3}{2},\frac{1}{2}}(2, 1, 1, r) - (1+f)^3 W^3_{\frac{3}{2},\frac{3}{2},\frac{3}{2},\frac{1}{2}}(1, 1, 1, r)\}. \tag{102}$$

Substituting from (B4), (B5), (B6) and (B7) into (102), we get

$$\frac{Y_{22}(1)}{b^3} = \frac{3}{2\pi}\left[-\frac{136}{315} + \frac{467}{140} f - \frac{683}{42} f^2 + \frac{2159}{84} f^3\right]. \tag{103a}$$

When $\sigma = 1$ then we get

$$Y_{22}(1) = \pi^2\left[-\frac{136}{315} + \frac{467}{140} f - \frac{683}{42} f^2 + \frac{2159}{84} f^3\right] \tag{103b}$$

and so

$$\frac{Y_{22}(2)}{b^3} = \frac{3}{2\pi}\left[-\frac{91}{2250} + \frac{13}{7} f - \frac{1829}{210} f^2 + \frac{715}{42} f^3\right]. \tag{104a}$$

When $\sigma = 1$ then we get

$$Y_{22}(2) = \pi^2\left[-\frac{91}{2250} + \frac{13}{7} f - \frac{1829}{210} f^2 + \frac{715}{42} f^3\right]. \tag{104b}$$

Putting $d = 3$ in (63) and (64), we get

$$Y_{23}(r) = \sqrt{\frac{2}{\pi}}\left\{\left[-\int_0^{\sigma} r^{3/2} I + f \int_{\sigma}^{2\sigma} r^{3/2} I\right] \mathrm{d}r\right\} \tag{105}$$

where

$$I = (2\pi\sigma)^{9/2}\int_0^{\infty} [2^{3/2} f J_{3/2}(2\sigma k) - (1+f) J_{3/2}(\sigma k)]^3 J_{1/2}(rk) k^{-3} \, \mathrm{d}k. \tag{106}$$

The integrals in (106) have been obtained when $\sigma = 1$. Then we can write $Y_{23}(r)$ as follows:

$$Y_{23}(r) = 4\pi \int_0^1 r^2 Y_{22}(r) \, \mathrm{d}r + f \int_1^2 r^2 Y_{22}(r) \, \mathrm{d}r. \tag{107}$$

Substituting from (104) and integrating, we get

$$\frac{Y_{23}(r)}{b^3} = 12\left[\frac{272}{2835} - \frac{8095}{12\,090} f + \frac{663\,581}{273\,880} f^2 - \frac{4\,703\,417}{11\,503\,296} f^3 - \frac{409\,243}{36\,288} f^4\right]. \tag{108a}$$

When $\sigma = 1$ then we get

$$Y_{23}(r) = (2\pi)^3\left[\frac{272}{2835} - \frac{8095}{12\,090} f + \frac{663\,581}{273\,880} f^2 - \frac{4\,703\,417}{11\,503\,296} f^3 - \frac{409\,243}{36\,288} f^4\right]. \tag{108b}$$

3.2.6. Calculation of $B_4^q(T)$ in three dimensions. Putting $d = 3$ and $\sigma = 1$ in equation (41), we get

$$B_4^q = B_4^c + \frac{3C_3}{2^{5/2}}[\mathrm{e}^{\beta\epsilon} Y_2^3(1) + 4\theta(\beta\epsilon) Y_2^3(2)](\lambda) + 0(\lambda^2).$$

Substituting from (31)

$$C_3 = \frac{2\pi^{3/2}}{\Gamma\left(\frac{3}{2}\right)} = 4\pi$$

then

$$B_4^q = B_4^c + \frac{3\pi}{\sqrt{2}}[\mathrm{e}^{\beta\epsilon} Y_2^3(1) + 4\theta(\beta\epsilon) Y_2^3(2)](\lambda) + 0(\lambda^2) \tag{109}$$

where $Y_2^3(r)$ is the radial distribution function in three dimensions and

$$Y_2 = Y_{21} + Y_{22} + Y_{23}. \tag{110}$$

From equations (100), (104) and (108), we get

$$\frac{Y_2(1)}{b^2} = 1.673\,834 - 11.900\,28 f + 68.197\,69 f^2 + 3.236\,28 f^3 + 51.116\,99 f^4 \tag{111a}$$

and

$$\frac{Y_2(2)}{b^3} = 1.860\,591 - 12.605\,94 f + 71.802\,23 f^2 - 10.605 f^3 + 51.116\,99 f^4. \tag{111b}$$

Inserting (111) in (109)

$$\begin{aligned} B_4^{*q} = B_4^{*c} + \frac{3\pi}{\sqrt{2}}\{&\mathrm{e}^{\beta\epsilon}[1.673\,834 - 11.900\,28 f + 68.197\,69 f^2 \\ &+ 3.236\,28 f^3 + 51.116\,99 f^4] \\ &+ 4\theta(\beta\epsilon)[1.860\,591 - 12.605\,94 f + 71.802\,23 f^2 \\ &- 10.605 f^3 + 51.116\,99 f^4]\} \end{aligned} \tag{112}$$

where

$$B_4^{*c} = 0.286\,95 + 1.6342 f - 23.294 f^2 + 54.648 f^3 + 70.754 f^4 - 168.20 f^5 - 12.747 f^6. \tag{113}$$

4. Discussion

The values obtained for the first quantum correction to the fourth virial coefficient $B_4^{*q}(T)$ in $d = 1$, with $a_1 = 2$, are shown in figure 1. We see that the first quantum effects to $B_4(T)$ appear up to $\frac{T}{T_B} = 0.5$ for all values of λ, where $\frac{T}{T_B} = \frac{KT}{\epsilon} \ln 2$ and T_B is the Boyle temperature. Up to this range the first quantum effect decreases with a decrease of λ.

The classical $B_4(T)$ for the square-well potential (SW) is also shown in the figures for comparison.

The values obtained for the first quantum correction to B_4^{*q} in $d = 3$, with $a_1 = 2$, are reported in figure 2. We see that the first quantum effects to $B_4(T)$ appear up to $\frac{T}{T_B} = 0.75$ for all values of λ, where $\frac{T}{T_B} = \frac{KT}{\epsilon} \ln \frac{8}{7}$. Up this range the first quantum effect decreases with a decrease of λ.

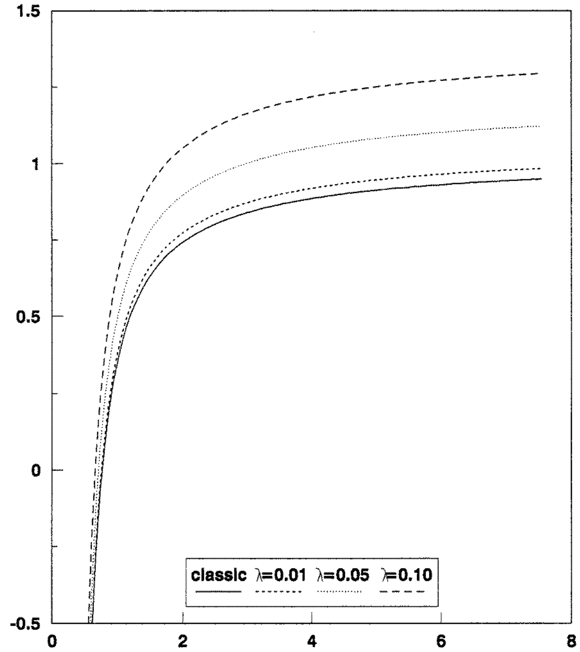

Figure 1. The reduced fourth virial coefficient $B_4^{*q} = \frac{B_4^q}{b^3}$ in one dimension as a function of the temperature $\left(\frac{T}{T_B}\right)$.

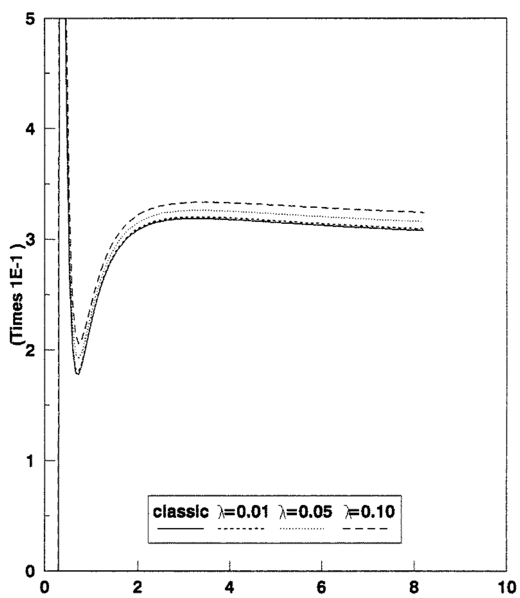

Figure 2. The reduced fourth virial coefficient $B_4^{*q} = \frac{B_4^q}{b^3}$ in three dimensions as a function of the temperature $\left(\frac{T}{T_B}\right)$.

Appendix A

From Loban and Baram [10],

$$\int_0^\infty [J_\nu(x)]^4 x^{-(2\nu+1)}\,\mathrm{d}x = \int_0^\infty [J_\nu(2x)]^4 (2x)^{-(2\nu+1)}\,\mathrm{d}(2x)$$
$$= \frac{2\Gamma(\nu)\Gamma(2\nu)}{3\pi\Gamma(3\nu)\left[\Gamma\left(\nu+\frac{3}{2}\right)\right]^2}\,{}_3F_2\left(\frac{1}{2}, 1, \frac{1}{2}-\nu; \nu+\frac{3}{2}, \nu+\frac{3}{2}; 1\right) \quad \text{(A1)}$$

see [19] vol II, p 79, equation (14)

$$J_{1/2}(x) = \sqrt{\frac{2}{\pi x}}\sin x \quad \text{(A2)}$$
$$J_{-1/2}(x) = \sqrt{\frac{2}{\pi x}}\cos x. \quad \text{(A3)}$$

To evaluate the integrals in (61) using the following standard identities, see [20] (p 451, equations (10), (12))

$$\int_0^\infty [\sin ax]^3[\sin 3bx]x^{-4}\,\mathrm{d}x = \begin{cases} \frac{9b\pi}{8}(a^2-b^2) & 3b \leqslant a \\ \frac{\pi}{16}[8a^3 - 9(a-b)^3] & a \leqslant 3b \leqslant 3a. \end{cases} \quad \text{(A4)}$$
$$\int_0^\infty [\sin ax]^2[\sin bx]^2 x^{-4}\,\mathrm{d}x = \frac{\pi b^2}{6}(3a-b) \qquad 0 \leqslant b \leqslant a \quad \text{(A5)}$$

so that

$$\int_0^\infty [\sin 2x]^3[\sin x]x^{-4}\,\mathrm{d}x = \tfrac{35}{24}\pi$$
$$\int_0^\infty [\sin 2x]^2[\sin x]^2 x^{-4}\,\mathrm{d}x = \tfrac{5}{6}\pi$$
$$\int_0^\infty [\sin 2x]^2[\sin x]^3 x^{-4}\,\mathrm{d}x = \tfrac{23}{48}\pi. \quad \text{(A6)}$$

Katsura [18] has evaluated the integrals in (94) as follows:

$$\int_0^\infty [J_{3/2}(2x)]^3[J_{3/2}(x)]x^{-4}\,\mathrm{d}x = \frac{\sqrt{2}}{\pi}\frac{92\,051}{2835}(2)^{-9} \quad \text{(A7)}$$
$$\int_0^\infty [J_{3/2}(2x)]^2[J_{3/2}(x)]^2 x^{-4}\,\mathrm{d}x = \frac{1}{2\pi}\frac{263}{2835} \quad \text{(A8)}$$
$$\int_0^\infty [J_{3/2}(2x)][J_{3/2}(x)]^3 x^{-4}\,\mathrm{d}x = \frac{1}{\sqrt{2}\pi}\frac{6251}{2835}(2)^{-6} \quad \text{(A9)}$$

also,

$${}_3F_2 = \tfrac{17}{8}. \quad \text{(A10)}$$

Appendix B

To evaluate the integrals in (66*a*) and (66*b*) using the following standard identity, see [20]

$$\int_0^\infty \frac{\sin^3 ax \cos bx}{x^3}\,\mathrm{d}x = \begin{cases} \frac{\pi}{8}(3a^2 - b^2) & b < a \\ \frac{\pi b^3}{4} & a = b \\ \frac{\pi}{6}(3a - b)^2 & a < b < 3a \\ 0 & 3a < b. \end{cases} \tag{B1}$$

To calculate the integrals in (70) and (73) using the software Mathematica [21] we get

$$\begin{aligned}\int_0^\infty \frac{\sin^5(ax)\cos(rx)}{x^3}\,\mathrm{d}x = &-\frac{5a^2\pi\ \mathrm{sign}[a-r]}{64} + \frac{5ar\pi\ \mathrm{sign}[a-r]}{32} - \frac{5r^2\pi\ \mathrm{sign}[a-r]}{64}\\ &+\frac{45a^2\pi\ \mathrm{sign}[3a-r]}{128} - \frac{15ar\pi\ \mathrm{sign}[3a-r]}{64} + \frac{5r^2\pi\ \mathrm{sign}[3a-r]}{128}\\ &-\frac{25a^2\pi\ \mathrm{sign}[5a-r]}{128} + \frac{5ar\pi\ \mathrm{sign}[5a-r]}{64} - \frac{r^2\pi\ \mathrm{sign}[5a-r]}{128}\\ &-\frac{5a^2\pi\ \mathrm{sign}[a+r]}{64} - \frac{5ar\pi\ \mathrm{sign}[a+r]}{32} - \frac{5r^2\pi\ \mathrm{sign}[a+r]}{64}\\ &+\frac{45a^2\pi\ \mathrm{sign}[3a+r]}{128} + \frac{15ar\pi\ \mathrm{sign}[3a+r]}{64} + \frac{5r^2\pi\ \mathrm{sign}[3a+r]}{128}\\ &-\frac{25a^2\pi\ \mathrm{sign}[5a+r]}{128} - \frac{5ar\pi\ \mathrm{sign}[5a+r]}{64} - \frac{r^2\pi\ \mathrm{sign}[5a+r]}{128}\end{aligned} \tag{B2}$$

$$\begin{aligned}\int_0^\infty \frac{\sin^3(ax)\sin^2\left(\frac{ax}{2}\right)\cos(rx)}{x^3}\,\mathrm{d}x = &-\frac{3a^2\pi\ \mathrm{sign}[a-r]}{64} + \frac{3ar\pi\ \mathrm{sign}[a-r]}{32}\\ &-\frac{3r^2\pi\ \mathrm{sign}[a-r]}{64} + \frac{a^2\pi\ \mathrm{sign}[2a-r]}{16} - \frac{ar\pi\ \mathrm{sign}[2a-r]}{16}\\ &+\frac{r^2\pi\ \mathrm{sign}[2a-r]}{64} + \frac{9a^2\pi\ \mathrm{sign}[3a-r]}{64} - \frac{3ar\pi\ \mathrm{sign}[3a-r]}{32}\\ &+\frac{r^2\pi\ \mathrm{sign}[3a-r]}{64} - \frac{a^2\pi\ \mathrm{sign}[4a-r]}{8} + \frac{ar\pi\ \mathrm{sign}[4a-r]}{16}\\ &-\frac{r^2\pi\ \mathrm{sign}[4a-r]}{128} - \frac{3a^2\pi\ \mathrm{sign}[a+r]}{64} - \frac{3ar\pi\ \mathrm{sign}[a+r]}{32}\\ &-\frac{3r^2\pi\ \mathrm{sign}[a+r]}{64} + \frac{a^2\pi\ \mathrm{sign}[2a+r]}{16} + \frac{ar\pi\ \mathrm{sign}[2a+r]}{16}\\ &+\frac{r^2\pi\ \mathrm{sign}[2a+r]}{64} + \frac{9a^2\pi\ \mathrm{sign}[3a+r]}{64} + \frac{3ar\pi\ \mathrm{sign}[3a+r]}{32}\\ &+\frac{r^2\pi\ \mathrm{sign}[3a+r]}{64} - \frac{a^2\pi\ \mathrm{sign}[4a+r]}{8} - \frac{ar\pi\ \mathrm{sign}[4a+r]}{16}\\ &-\frac{r^2\pi\ \mathrm{sign}[4a+r]}{128}\end{aligned} \tag{B3}$$

where

$$\operatorname{sign} x = \begin{cases} -1 & x < 0 \\ 0 & x = 0 \\ 1 & x > 0. \end{cases}$$

McQuarrie [22] has evaluated the integrals in (97) as follows:

$$W^{3}_{\frac{3}{2},\frac{3}{2},\frac{3}{2},\frac{1}{2}}(1,1,1,r) = \begin{cases} \dfrac{1}{4\pi r^{1/2}}\left(-\dfrac{r^7}{1260}+\dfrac{r^5}{20}-\dfrac{r^3}{4}+\dfrac{5}{12}r\right) & 0 \leqslant r \leqslant 1 \\ \dfrac{1}{4\pi r^{3/2}}\left(\dfrac{r^7}{2520}-\dfrac{r^5}{40}+\dfrac{r^4}{12}+\dfrac{r^3}{8}\right. & \\ \quad \left. -\dfrac{9}{10}r^2+\dfrac{9}{8}r-\dfrac{27}{140}\right) & 1 \leqslant r \leqslant 3 \\ 0 & r \geqslant 3 \end{cases} \tag{B4}$$

$$W^{3}_{\frac{3}{2},\frac{3}{2},\frac{3}{2},\frac{1}{2}}(1,1,2,r) = \begin{cases} \dfrac{1}{4\pi (2r)^{1/2}}\left(-\dfrac{r^7}{5040}+\dfrac{r^5}{40}-\dfrac{r^4}{12}+\dfrac{4}{9}r\right) & 0 \leqslant r \leqslant 2 \\ \dfrac{1}{4\pi r^{1/2}}\left(\dfrac{r^7}{5040}-\dfrac{r^5}{40}+\dfrac{5r^4}{36}\right. & \\ \quad \left. -\dfrac{8}{5}r^2+\dfrac{32}{9}r-\dfrac{64}{35}\right) & 2 \leqslant r \leqslant 4 \\ 0 & r \geqslant 4 \end{cases} \tag{B5}$$

$$W^{3}_{\frac{3}{2},\frac{3}{2},\frac{3}{2},\frac{1}{2}}(1,2,2,r) = \begin{cases} \dfrac{1}{8\pi r^{1/2}}\left(-\dfrac{r^7}{5040}+\dfrac{3r^5}{80}-\dfrac{5r^3}{16}+\dfrac{185}{144}r\right) & 0 \leqslant r \leqslant 1 \\ \dfrac{1}{8\pi r^{1/2}}\left(\dfrac{r^4}{72}-\dfrac{13r^2}{20}+\dfrac{16}{9}-\dfrac{37}{240}\right) & 1 \leqslant r \leqslant 3 \\ \dfrac{1}{8\pi r^{1/2}}\left(\dfrac{r^7}{10\,080}-\dfrac{3r^5}{160}-\dfrac{17r^4}{144}+\dfrac{5r^3}{32}\right. & \\ \quad \left. -\dfrac{25r^2}{8}+\dfrac{2375}{288}r-\dfrac{625}{142}\right) & 3 \leqslant r \leqslant 5 \\ 0 & r \geqslant 5 \end{cases} \tag{B6}$$

$$W^{3}_{\frac{3}{2},\frac{3}{2},\frac{3}{2},\frac{1}{2}}(2,2,2,r) = \begin{cases} \dfrac{1}{8\pi (2r)^{1/2}}\left(-\dfrac{r^7}{10\,080}+\dfrac{r^5}{40}-\dfrac{r^3}{2}+\dfrac{10}{3}r\right) & 0 \leqslant r \leqslant 2 \\ \dfrac{1}{8\pi (2r)^{1/2}}\left(\dfrac{r^7}{20\,160}-\dfrac{r^5}{80}+\dfrac{r^4}{12}\right. & \\ \quad \left. +\dfrac{r^3}{4}-\dfrac{18r^2}{5}+9r-\dfrac{108}{35}\right) & 2 \leqslant r \leqslant 6 \\ 0 & r \geqslant 6. \end{cases} \tag{B7}$$

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