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A simple method of generating equations of state for hard sphere fluid

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Abstract

We present in this paper a simple method of obtaining various equations of state for hard sphere fluid in a simple unifying way. Using the first several virial coefficients of hard sphere fluid, we will guess equations of state by using the *asymptotic expansion* method. Among the equations of state obtained in this way are Percus–Yevick, Scaled Particle Theory, and Carnahan–Starling equations of state. Also by combining the Monte Carlo results on hard sphere fluid with the *asymptotic expansion* method many other equations of state for hard sphere fluid can be found where all of them give essentially similar results in the region of isotropic hard sphere liquid, i.e., up to $\eta < 0.5$, in which η is the packing fraction. In addition we have found a simple equation of state for the hard sphere fluid in the metastable region which represents the simulation data accurately.

Keywords: Equation of state; Hard sphere fluid

1. Introduction

Hard sphere fluid plays a central role in almost all theories of liquid state chemical physics, for example, in perturbation theories [1–3], in statistical associating fluid theories [4], etc. For this reason its thermodynamic properties has been studied by various methods; scaled particle theory [5], integral equation theories, especially Percus–Yevick equation [6,7], and calculation of its virial coefficients [8]. By these methods one can obtain the most important quantity of interest; the equation of state, by which one can calculate all thermodynamic properties. Scaled particle theory generates the following equation of state:

$$Z = \frac{1+\eta+\eta^2}{(1-\eta)^3} \tag{1}$$

where $Z(=P/\rho kT)$ is the compressibility factor, $\eta\left(=\frac{\pi}{6}\rho\sigma^3\right)$ is the packing fraction, ρ is the number density, P is the pressure, T is the absolute temperature, σ is the diameter of hard sphere, and k is the Boltzmann constant.

Wertheim and Thiele solved the Percus–Yevick [6,7] equation and obtained two equations of state; one form which is obtained through compressibility route is Eq. (1) and the second one originated from virial route is

$$Z = \frac{1+2\eta+3\eta^2}{(1-\eta)^2} \tag{2}$$

When expanding Eqs. (1) anf (2) in terms of η, one can find:

$$Z = 1+4\eta+10\eta^2+19\eta^3+31\eta^4+46\eta^5+64\eta^6+85\eta^7+\mathrm{O}(\eta^8) \tag{3}$$

and

$$Z = 1+4\eta+10\eta^2+16\eta^3+22\eta^4+28\eta^5+34\eta^6 + 40\eta^7+\mathrm{O}(\eta^8) \tag{4}$$

It is seen that both equations produce exact virial coefficients up to third term only. As we may know the first several virial coefficients of the hard sphere fluid are [9]: $B_2 = 4$, $B_3 = 10$, $B_4 = 18.36$, $B_5 = 28.23$, $B_6 = 39.54$,

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$B_7 = 53.54$ and $B_8 = 70.78$. Carnahan and Starling used the first three virial coefficients (of course they adopted $B_4 = 18$) and approximated the virial coefficients to be $B_n = n^2 + 3n$ and summed the virial coefficients, then reached to their famous equation [10]:

$$Z = \frac{\eta^3 - \eta^2 - \eta - 1}{(\eta - 1)^3} \tag{5}$$

Another route to obtain hard sphere fluid equations of state stems from virial expansion. Summing the known first several virial coefficients of the hard sphere fluid by, say, Padé approximation method, one may obtain some equations of state. For example, Ree and Hoower found the following equation [11]:

$$Z = \frac{1 + 1.75399\eta + 2.31704\eta^2 + 1.108928\eta^3}{1 - 2.246004\eta + 1.301056\eta^2} \tag{6}$$

Also one can employ the so-called rescaled virial expansion to obtain equations of state for hard spheres [12,13].

Here we present a simple method to generate many equations of state (among them are Eqs. (1), (2) and (5)) for hard sphere fluid.

2. The asymptotic expansion method

We start from known virial coefficients of hard sphere fluid and write

$$Z = 1 + B_2\eta + B_3\eta^2 + B_4\eta^3 + \cdots \tag{7}$$

We may notice that if Eq. (7) should represent the properties of a real fluid, it must be convergent. Suppose the radius of convergence of the virial expansion is b; therefore η must be less than b, because for $\eta \geqslant b$ the virial expansion becomes divergent, i.e., it can not represent a real system. Since we are unable to obtain and calculate all virial coefficients, we can only hope to obtain an approximation. By now, all that we know besides knowing first several virial coefficients is that it must be divergent at $\eta \geqslant b$. So one can deduce that b is a pole for the compressibility factor $Z = Z(\eta)$. Taking this fact into account we may write the *asymptotic expansion* of Z, which is of the form:

$$Z = a_0 + \frac{a_1}{\eta - b} + \frac{a_2}{(\eta - b)^2} + \frac{a_3}{(\eta - b)^3} + \ldots \tag{8}$$

Adopting this form for the asymptotic expansion of Z, then expanding into virial form and comparison with known first several virial coefficients, one can easily arrive at much many equations of state for hard sphere fluid, all of them are in fact asymptotic forms of Z.

3. Some equations of state for hard sphere fluid

Since we are not aware of the exact value of b at which the virial expansion, Eq. (7), becomes divergent, we are free to choose it conveniently. Because hard spheres crystallize at $\eta = 0.7405$ [9], hence one may assume any value for b greater than 0.7405, say, $b = 3/4$, $b = 1$, or $b = 2$, besides this we can not say anymore. In addition to this, the number of terms in asymptotic expansion, Eq. (8), is another degree of freedom we have. For example, if we restrict ourselves to use only three known virial coefficients, we should select those asymptotic forms with only three unknowns. But if one would like to find more rigorous representations for equation of state, (s)he should know and use more virial coefficients, hence more possibilities for the form of asymptotic expansion are there to be tried. As we may see, virial coefficients are all related to b, the pole (see for example Eq. (10)). As soon as selecting a definite value for b, one is able to obtain the desired coefficients. Different b's produce different coefficients, but up to third order of course, they are all the same. They approximate different values for the remainder terms. Among them one must be the best, but this method can not achieve this important goal alone. At the best we can resort to approximate theories like Scaled Particle Theory which asserts that $b = 1$, or approximately determine it by the known virial coefficients as done in Section 4.

(A) Suppose that the asymptotic form of the compressibility factor Z to be:

$$Z = a_0 + \frac{a_1}{\eta - b} + \frac{a_2}{(\eta - b)^2} \tag{9}$$

Expanding Eq. (9) in powers of η gives:

$$Z = \left(a_0 - \frac{a_1}{b} + \frac{a_2}{b^2}\right) + \left(-\frac{a_1}{b^2} + \frac{2a_2}{b^3}\right)\eta + \left(-\frac{a_1}{b^3} + \frac{3a_2}{b^4}\right)\eta^2 + \mathrm{O}(\eta^3) \tag{10}$$

By equating these coefficients with known second and third virial coefficients gives:

$$\begin{cases} a_0 - a_1/b + a_2/b^2 = 1 \\ -a_1/b^2 + 2a_2/b^3 = B_2 \\ -a_1/b^3 + 3a_2/b^4 = B_3 \end{cases} \tag{11}$$

Which its solution is:

$$\begin{cases} a_0 = 1 - 2B_2b + B_3b^2 \\ a_1 = -3B_2b^2 + 2B_3b^3 \\ a_2 = -B_2b^3 + B_3b^4 \end{cases} \tag{12}$$

Inserting these values in Eq. (9) and collecting we finally obtain:

$$Z = \frac{(1 - 2B2b + B3b^2)\eta^2 + (B2b^2 - 2b)\eta + b^2}{(\eta - b)^2} \tag{13}$$

Now we may put $b = 1$(together with $B_2 = 4$ and $B_3 = 10$) in Eq. (13) which gives:

$$Z = \frac{3\eta^2 + 2\eta + 1}{(\eta - 1)^2} \tag{14}$$

This is the well-known equation of state of Wertheim and Thiele, Eq. (2), obtained from the analytical solution of the Percus–Yevick equation by the virial route.

(B) Now we suppose that the asymptotic form of the compressibility factor Z to be (while retaining the unknowns to be three again since we want to use only first two virial coefficients as in previous example):

$$Z = \frac{a_1}{\eta - b} + \frac{a_2}{(\eta - b)^2} + \frac{a_3}{(\eta - b)^3} \tag{15}$$

By taking similar steps one finds:

$$Z = -\frac{b((3 - 3B2b + B3b^2)\eta^2 + (B2b^2 - 3b)\eta + b^2)}{(\eta - b)^3} \tag{16}$$

Now putting $b = 1$ (together with $B_2 = 4$ and $B_3 = 10$) in Eq. (16) gives:

$$Z = \frac{\eta^2 + \eta + 1}{(1 - \eta)^3} \tag{17}$$

This is the well-known equation of state of Scaled Particle Theory, Eq. (1) and also obtained from the analytical solution of the Percus–Yevick equation by the compressibility route.

(C) In order to obtain another (proposed originally in [14]) equation of state we suppose that the asymptotic form of Z is:

$$Z = a_0 + \frac{a_1}{\eta - 3/4} + \frac{a_2}{\eta - 1} \tag{18}$$

where we have used two values for b; i.e., $b = 1$ and $b = 3/4$ that come from Scaled Particle Theory and close packing fraction of hard spheres [9], respectively. Proceeding as before we will find the following equation:

$$Z = \frac{6\eta^2 + 5\eta + 3}{(4\eta - 3)(\eta - 1)} \tag{19}$$

This equation has been used for simplification of SAFT equation of state for hard sphere chains [15,16].

(D) Now we proceed one step further and suppose that the asymptotic form of Z is:

$$Z = a_0 + \frac{a_1}{\eta - b} + \frac{a_2}{(\eta - b)^2} + \frac{a_3}{(\eta - b)^3} \tag{20}$$

We have this time four unknowns, hence need to employ up to fourth virial coefficients. For simplicity we set $B_4 = 18$ as Carnahan and Starling did and proceed as before to obtain:

$$\begin{aligned} Z = {} & ((28b^4 + 1 - 16b + 60b^2 - 72b^3)\eta^3 + (20b^3 - 3b \\ & - 54b^4 + 28b^5 + 8b^2)\eta^2 + (3b^2 - 54b^5 + 28b^6 \\ & + 30b^4 - 8b^3)\eta - b^3 - 4b^4 + 30b^5 - 54b^6 \\ & + 28b^7)/(\eta - b)^3 \end{aligned} \tag{21}$$

Now if we set $b = 1$ in Eq. (21) we arrive at the well-known Carnahan–Starling equation:

$$Z_{22} = \frac{\eta^3 - \eta^2 - \eta - 1}{(\eta - 1)^3} \tag{22}$$

(E) In this stage we would like to improve the Carnahan–Starling equation a bit further by taking the exact value of the fourth virial coefficient, i.e., $B_4 = 18.36$ and employ Eq. (20) to obtain a new approximation for Z. Doing as before we obtain:

$$Z = \frac{(-30b^2 + 12b - 1 + 18.36b^3)\eta^3 + (10b^3 - 12b^2 + 3b)\eta^2 + (4b^3 - 3b^2)\eta + b^3}{(-\eta + b)^3} \tag{23}$$

Now if we set $b = 1$ in Eq. (23) we arrive at the following equation:

$$Z_{24} = \frac{0.64\eta^3 - \eta^2 - \eta - 1}{(\eta - 1)^3} \tag{24}$$

(F) It is obvious that if we take some other values for b we will find another set of equations for hard sphere fluid. For example, by inserting $b = 3/4$ in Eqs. (13), (16), (21), and (23), respectively, one finds:

$$Z_{25} = \frac{10\eta^2 + 12\eta + 9}{(4\eta - 3)^2} \tag{25}$$

$$Z_{26} = \frac{9(2\eta^2 - 3)}{(4\eta - 3)^3} \tag{26}$$

$$Z_{27} = \frac{82\eta^3 + 18\eta^2 - 27}{(4\eta - 3)^3} \tag{27}$$

$$Z_{28} = \frac{72.28\eta^3 + 18\eta^2 - 27}{(4\eta - 3)^3} \tag{28}$$

(G) One may also prefer another choice for the asymptotic expansion of Z, for instance, we may suppose the following form:

$$Z = a_0 + \frac{a_1}{\eta - \frac{3}{4}} + \frac{a_2}{(\eta - b)^2} + \frac{a_3}{(\eta - b)^3} \tag{29}$$

We therefore will need to have four virial coefficients where we take $B_4 = 18$ for simplicity. Proceeding as before we find the following equation:

$$\begin{aligned} Z = -\big(& 81b^3 - 144b^4 + 72b^5 - 81\eta^3 - 216\eta^4 - 243b^2\eta \\ & + 648b^3\eta - 600b^4\eta + 243b\eta^2 + 888b\eta^4 - 2358b^2 \\ & + 1746b^3\eta^2 + 792b\eta^3 - 1080b^2\eta^2 - 1137b^2\eta^4 + 2970b^3\eta^3 \\ & - 1248b^4\eta^2 + 192b^5\eta + 588b^3\eta^4 - 1680b^4\eta^3 + 336b^5\eta^2 \\ & - 112b^4\eta^4 + 336b^5\eta^3\big) / \Big(3\big(8b^2 - 16b + 9\big)(4\eta - 3)(-\eta + b)^3\Big) \end{aligned} \tag{30}$$

Now we set, say, $b = 3/2$ to obtain the following equation:

$$Z_{31} = -\frac{22\eta^4 + 114\eta^3 - 54\eta^2 - 54\eta - 81}{(4\eta - 3)(2\eta - 3)^3} \tag{31}$$

4. Determination of the radius of convergence from the virial coefficients

Until now, the choice of the radius of convergence (b) was arbitrary. But we can determine b from the virial coefficients; hence there is indeed no need to assume it freely. It is obvious that if we take b as another unknown, we are able to find it. Also we would like to work with only three known virial coefficients, i.e., $B_2 = 4$, $B_3 = 10$, $B_4 = 18.36$, hence we prefer to work with Eqs. (9) and (15).

I. First we work with Eq. (9) and write it:

$$Z = a_0 + \frac{a_1}{\eta - b} + \frac{a_2}{(\eta - b)^2} \tag{32}$$

which may be expanded in powers of η up to fourth order:

$$Z = \left(a_0 - \frac{a_1}{b} + \frac{a_2}{b^2}\right) + \left(\frac{2a_2}{b^3} - \frac{a_1}{b^2}\right)\eta + \left(\frac{3a_2}{b^4} - \frac{a_1}{b^3}\right)\eta^2 + \left(\frac{4a_2}{b^5} - \frac{a_1}{b^4}\right)\eta^3 + O(\eta^4) \tag{33}$$

Equating these coefficients with known first three virial coefficients gives:

$$\begin{cases} a_0 - a_1/b + a_2/b^2 = 1 \\ 2a_2/b^3 - a_1/b^2 = 4 \\ 3a_2/b^4 - a_1/b^3 = 10 \\ 4a_2/b^5 - a_1/b^4 = 18.36 \end{cases} \tag{34}$$

This system of equations has two set of solutions.The first set is:

$$b = 0.26, \quad a_0 = -0.41, \quad a_1 = -0.47, \quad a_2 = -0.03$$

and the second one:

$$b = 0.83, \quad a_0 = 1.21, \quad a_1 = 3.07, \quad a_2 = 2.39 \tag{35}$$

Since we would like to have b as large as possible we must choose the second set. Inserting these values in Eq. (32) and collecting them gives the desired equation:

$$Z_{36} = \frac{1.21\eta^2 + 1.07\eta + 0.68}{(\eta - 0.83)^2} \tag{36}$$

II. As the second step we invoke Eq. (15) and write it:

$$Z = \frac{a_1}{\eta - b} + \frac{a_2}{(\eta - b)^2} + \frac{a_3}{(\eta - b)^3} \tag{37}$$

which may be expanded in powers of η up to fourth order:

$$Z = \left(-\frac{a_1}{b} + \frac{a_2}{b^2} - \frac{a_3}{b^3}\right) + \left(-\frac{3a_3}{b^4} - \frac{a_1}{b^2} + \frac{2a_2}{b^3}\right)\eta + \left(-\frac{6a_3}{b^5} + \frac{3a_2}{b^4} - \frac{a_1}{b^3}\right)\eta^2 + \left(\frac{4a_2}{b^5} - \frac{10a_3}{b^6} - \frac{a_1}{b^4}\right)\eta^3 + O(\eta^4) \tag{38}$$

Equating these coefficients with known first three virial coefficients gives:

$$\begin{cases} -a_1/b + a_2/b^2 - a_3/b^3 = 1 \\ -3a_3/b^4 - a_1/b^2 + 2a_2/b^3 = 4 \\ -6a_3/b^5 + 3a_2/b^4 - a_1/b^3 = 10 \\ 4a_2/b^5 - 10a_3/b^6 - a_1/b^4 = 18.36 \end{cases} \tag{39}$$

This system of equations has three set of solutions.The first two sets are:

$$a_2 = -0.01, \quad a_3 = 0, \quad b = 0.11, \quad a_1 = -0.20$$
$$a_3 = 0.05, \quad a_2 = 0.39, \quad b = 0.45, \quad a_1 = 0.17$$

These are rejected in favor of the third set:

$$a_2 = -5.20, \quad a_3 = -4.81, \quad b = 1.07, \quad a_1 = -1.74 \tag{40}$$

This is our desired solution because b in this solution has the greatest value. Inserting these values in Eq. (37) and collecting them gives the desired equation:

$$Z_{41} = \frac{1.74\eta^2 + 1.48\eta + 1.23}{(\eta - 1.07)^3} \tag{41}$$

III. As our final example we use Eq. (20):

$$Z = a_0 + \frac{a_1}{\eta - b} + \frac{a_2}{(\eta - b)^2} + \frac{a_3}{(\eta - b)^3} \tag{42}$$

which may be expanded in powers of η up to fifth order:

$$Z = \left(a_0 - \frac{a_1}{b} + \frac{a_2}{b^2} - \frac{a_3}{b^3}\right) + \left(-\frac{a_1}{b^2} + \frac{2a_2}{b^3} - \frac{3a_3}{b^4}\right)\eta + \left(-\frac{a_1}{b^3} + \frac{3a_2}{b^4} - \frac{6a_3}{b^5}\right)\eta^2 + \left(\frac{a_1}{b^4} + \frac{4a_2}{b^5} - \frac{10a_3}{b^6}\right)\eta^3 + \left(-\frac{a_1}{b^5} + \frac{5a_2}{b^6} - \frac{15a_3}{b^7}\right)\eta^4 + O(\eta^5) \tag{43}$$

Equating these coefficients with known virial coefficients (where for simplicity we set $B_4 = 18$ and $B_5 = 28$ as Carnahan and Starling did) gives:

$$\begin{cases} a_0 - a_1/b + a_2/b^2 - a_3/b^3 = 1 \\ -a_1/b^2 + 2a_2/b^3 - 3a_3/b^4 = 4 \\ -a_1/b^3 + 3a_2/b^4 - 6a_3/b^5 = 10 \\ -a_1/b^4 + 4a_2/b^5 - 10a_3/b^6 = 18 \\ -a_1/b^5 + 5a_2/b^6 - 15a_3/b^7 = 28 \end{cases} \tag{44}$$

This system of equations has two set of solutions, the first set reads:

$$b = 0.19, \quad a_0 = -0.33, \quad a_1 = -0.40, \quad a_2 = -0.03, \quad a_3 = 0$$

that should be rejected in favor of the following one:

$$a_0 = 1, \quad b = 1, \quad a_1 = 2, \quad a_2 = 0, \quad a_3 = -2$$

Not surprisingly, when putting them in Eq. (42) the famous Carnahan–Starling equation (Eq. (5)) will be recovered.We may compare the obtained equations of state for hard sphere fluid to computer simulation data, too. For this pur-

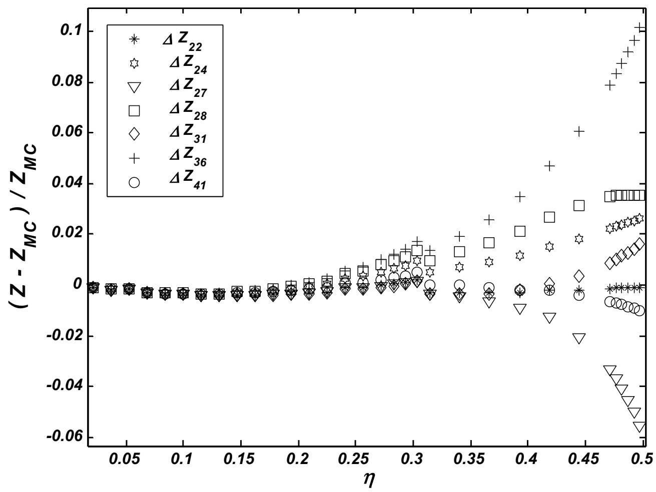

Fig. 1. Relative deviation curves of the obtained hard sphere equations of state based on known virial coefficients with computer simulation data.

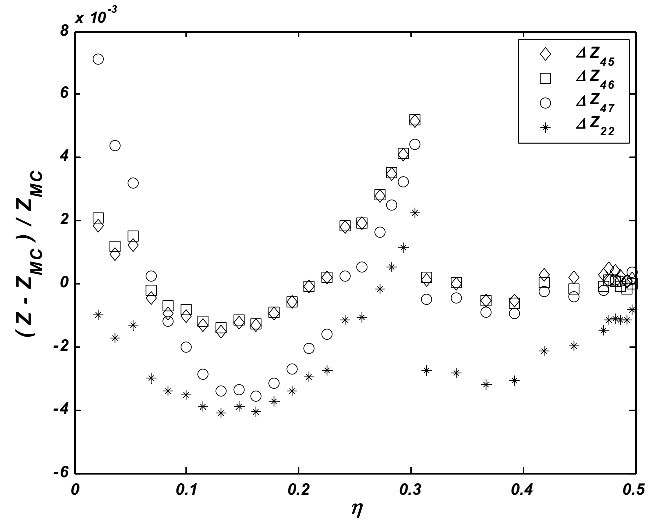

Fig. 2. Relative deviation curves of the obtained hard sphere equations of state based on Monte Carlo results with Carnahan–Starling and computer simulation data.

pose we have used the computer simulation data from [17]. The results are shown in Fig. 1. We may easily observe that all obtained equations can essentially well represent the hard sphere fluid properties in the isotropic liquid range, i.e., when $\eta \leqslant 0.5$. In addition we have compared the virial coefficients of the obtained equations of state with the exact values in Table 1.

5. Equations of state based on computer simulation data

In previous sections one restricted to use only known virial coefficients. Suppose we have access to computer simulation data. Since asymptotic expansion method produce as essentially accurate results as the original function, we may expect that (the various forms of) Eq. (8) can be used to accurately represent the original data. For this purpose we may use the recent Monte Carlo reported in Ref. [17] for hard sphere fluid in two cases; i.e., isotropic liquid and metastable fluid regions.

5.1. The isolated liquid region

We choose the asymptotic form of the compressibility factor Z to be like Eq. (20). Fitting the MC data by that equation and collecting, one finds:

$$Z_{45} = \frac{1.714\eta^3 + 0.014\eta^3 - 0.161\eta - 0.542}{(\eta - 0.814)^3} \tag{45}$$

One may also suppose in Eq. (20) that $b = 1$, and then perform fitting to obtain:

$$Z_{46} = \frac{1.151\eta^3 - 1.088\eta^2 - 0.990\eta - 1.003}{(\eta - 1)^3} \tag{46}$$

It is interesting to notice the very similarity between this equation with the Carnahan–Starling's.

Another suitable choice is to use Eq. (9), which after fitting with MC data gives:

$$Z_{47} = \frac{2.508\eta^2 + 1.326\eta + 0.825}{(\eta - 0.903)^2} \tag{47}$$

A comparison of these equations and Carnahan–Starling equation with MC data in the isotropic liquid region has been made in Fig. 2. As can be seen they are all essentially the same in this region. In addition we have compared the virial coefficients of the obtained equations of state with the exact values in Table 1.

Table 1
Comparison of the virial coefficients of the obtained hard sphere equations of state with computer simulation data

Virial coefficients	Z_{MD}[a]	Z_{22}	Z_{24}	Z_{27}	Z_{28}	Z_{31}	Z_{36}	Z_{41}	Z_{45}	Z_{46}	Z_{47}
B_2	4	4	4	4	4	4	4	4	3.99	3.99	3.87
B_3	10	10	10	10	10	10	10	10	10.143	10.08	10.40
B_4	18.36	18	18.36	18	18.36	18	18.36	18.36	17.99	18.08	18.28
B_5	28.23	28	29.08	28.15	29.59	27.63	29.81	28.53	27.78	28.02	27.74
B_6	39.54	40	42.16	40.30	44.14	39.26	45.28	40.03	39.75	39.89	39.02
B_7	53.54	54	57.60	53.73	62.26	53.73	65.97	52.45	54.06	53.69	52.40
B_8	70.78	70	75.40	66.72	83.79	72.25	93.38	65.45	70.79	69.41	68.21
B_9	93.06	88	96.56	75.85	107.71	96.44	129.44	78.73	89.83	87.07	86.80
B_{10}	123.21	108	118.08	74.9	131.55	128.38	176.59	92.06	110.79	106.66	108.59

[a] Taken from Ref. [9].

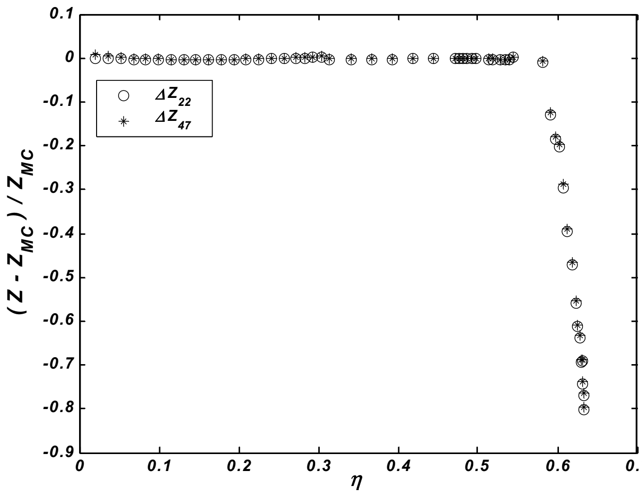

Fig. 3. Relative deviation curves of Eqs. (47) and (22) with computer simulation data in the whole liquid region of hard sphere fluid.

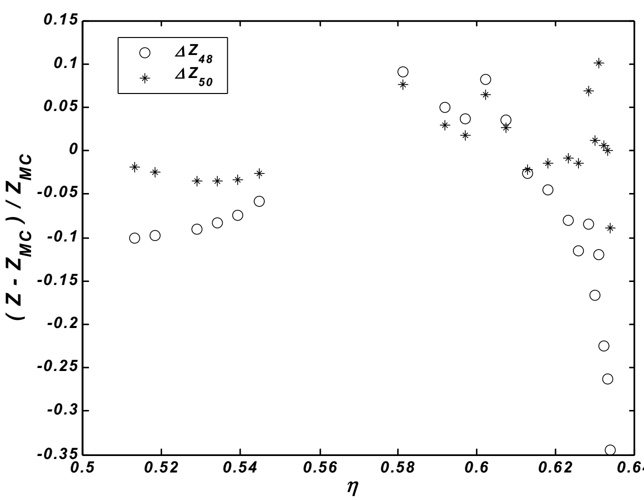

Fig. 4. Relative deviation curves of Eqs. (48) and (50) with computer simulation data in the metastable region of hard sphere fluid.

Eq. (47) appears to be interesting, because it is simpler than the others. In Fig. 3 a comparison has been made between Eq. (47) and Carnahan–Starling equation in the whole liquid region of hard sphere fluid which indicate that they give essentially the same results in the liquid region of hard sphere fluid.

5.2. The metastable fluid region

Speedy [18] has given a purely empirical equation for the metastable fluid region:

$$Z_{48} = \frac{2.67}{1 - 1.543\eta} \tag{48}$$

So we choose the simplest form of asymptotic expansion to represent this region; i.e.,

$$Z = a_0 + \frac{a_1}{\eta - b} \tag{49}$$

Fitting the MC data in this region and collecting, one finds:

$$Z_{50} = \frac{3.730\eta - 3.712}{\eta - 0.642} \tag{50}$$

Comparison between these two equations in Fig. 4 reveals that Eq. (50) represents MC data in the metastable region even better than Eq. (48). Of course, if one wants, it is possible to obtain more accurate equation by using, say, Eq. (9), but it will not be as simple as Eq. (50).

6. Conclusion

We have presented in this paper a simple method of obtaining various equations of state for hard sphere fluid in a simple unifying way. Using the first several virial coefficients of hard sphere fluid, we will guess equations of state by using the *asymptotic expansion* method. Among the equations of state obtained in this way are Percus–Yevick, Scaled Particle Theory, and Carnahan–Starling equations of state. Also by combining the Monte Carlo results on hard sphere fluid with the *asymptotic expansion* method many other equations of state for hard sphere fluid can be found where all of them give essentially similar results in the region of isotropic hard sphere liquid, i.e., up to $\eta < 0.5$, in which η is the packing fraction. In addition we have found a simple equation of state for the hard sphere fluid in the metastable region which represents the simulation data accurately.

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