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# Equations of State for Fused-Hard-Sphere Fluids

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Analytical equations of state for fused-hard-sphere fluids are developed from a generalization of the Carnahan–Starling method for obtaining the equation of state of the hard-sphere fluid. The results are in good agreement with existing simulation data.

**KEY WORDS:** Carnahan–Starling equation; equations of state; fused hard spheres.

## 1. INTRODUCTION

In perturbation theories of real fluids composed of spherical molecules, it is necessary to know an accurate analytical equation of state for the reference fluid, usually the hard-sphere fluid. The most widely-used equation of state for this fluid is the Carnahan–Starling (CS) equation [1], which combines simplicity and accuracy.

For real fluids composed of nonspherical molecules, it is convenient to use as a reference system a hard-body fluid with molecules of similar shape to those of the real fluid, if one wishes the perturbation expansion to converge rapidly [2]. This requires knowledge of accurate analytical equations of state for hard-body fluids. This can be achieved by means of a class of generalized approximants proposed recently [3, 4]. However, the CS method provides a simple way to obtain an accurate equation of state for the hard-sphere fluid and it is tempting to try to extend it to other hard-body fluids.

Some attempts have been made to derive equations of state for these fluids similar to the CS equation for hard spheres [5–7]. In this paper we

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first generalize the CS method and then apply it to obtain equations of state for fluids of fused hard spheres (FHS). These fluids seem suitable as reference systems in a perturbative treatment for many real fluids.

## 2. GENERALIZATION OF THE CARNAHAN–STARLING METHOD

In terms of the packing fraction $y = \rho v_{\mathrm{m}} = \pi \rho \sigma^3/6$, the virial expansion [8] of the compressibility factor $Z = pV/NkT$ of the hard-sphere fluid can be expressed in the form

$$Z = 1 + 4y + 10y^2 + 18.3648y^3 + 28.224512y^4 + 39.8336y^5 + \cdots \tag{1}$$

When the coefficients in this expansion are approached to their nearest integers, they can be obtained from the recurrence formula,

$$B_n^* = B_n / v_m^{n-1} = n^2 + n - 2 \tag{2}$$

for $n \geqslant 2$. Thus, rewriting Eq. (1) in the form

$$Z = \sum_{n=2}^{\infty} B_n^* \, y^{n-1} \tag{3}$$

with $B_n^*$ given by Eq. (2), the summations involved in this expression can be evaluated from the sum of the geometrical series and their derivatives. This leads to the well-known Carnahan–Starling equation [1]:

$$Z = \frac{1 + y + y^2 - y^3}{(1 - y)^3} \tag{4}$$

It is obvious from Eq. (1) that in approaching the virial coefficients to their nearest integers, none of them beyond the third is reproduced exactly by the recurrence formula, Eq. (2). This suggests the possibility of improving the method by obtaining expressions equivalent to Eq. (2) which exactly reproduce a certain number of the true virial coefficients, since the CS method does not necessarily require the virial coefficients to be integers. Then, postulating that the recursion formula thus obtained is valid for any value of $n$, substituting in Eq. (3), and adding the series, we obtain an equation of state of the form

$$Z = \frac{1 + \sum_{n=1}^{k-1} a_n y^n}{(1 - y)^{k-1}} \tag{5}$$

where $k$ is the number of virial coefficients to be reproduced exactly.

However, when this is done, the resulting equations of state do not provide better agreement with the simulation data for either the stable [9] or the metastable [10] fluid regions than the CS equation, Eq. (4). This is because Eq. (2) reproduces the true virial coefficients above $B_3$ sometimes by excess and sometimes by default. This leads to a fortunate cancellation of errors, which does not occur when we impose the condition that a greater number of virial coefficients must be exactly reproduced.

It is to be expected that this modification of the CS method would be particularly appropriate when virial coefficients are small, in which case the approach to their nearest integers can involve considerable errors. To illustrate this, we consider in some detail the hard-disk fluid case.

In terms of the packing fraction $y = \pi\rho\sigma^2/4$, the known virial coefficients for the hard-disk fluid are [11]

$$\begin{gathered} B_2 = 2, \qquad B_3 = 3.128018, \qquad B_4 = 4.257854, \qquad B_5 = 5.336898, \\ B_6 = 6.36576 \pm 0.00768, \qquad B_7 = 7.3472 \pm 0.0320 \end{gathered} \tag{6}$$

By approximating these coefficients to their nearest integers, the compressibility factor $Z$ can be expressed in the form

$$Z = 1 + 2y + 3y^2 + 4y^3 + 5y^4 + 6y^5 + 7y^6 + \cdots \tag{7}$$

The coefficients in this expansion can be obtained from the recurrence formula

$$B_n = n \tag{8}$$

and consequently, Eq. (7) can be put in the form

$$Z = 1 + \sum_{n=2}^{\infty} n y^{n-1} \tag{9}$$

Summation of this series, making use of the properties of the geometrical series, results in the expression

$$Z = \frac{1}{(1-y)^2} \tag{10}$$

which can be considered [12] as the two-dimensional ($D = 2$) equivalent of the CS equation.

Table I compares predictions for this equation with simulation data [13] for the hard-disk system. It can be seen that Eq. (10), as is to be expected, systematically underestimates simulation data since, in approximating the virial coefficients, Eq. (6), to their nearest integers, these are always lower than the true virial coefficients beyond $B_3$, in contrast to

**Table I.** Equation of State for a Hard-Disk Fluid ($D=2$): Here, Obviously, the "Volume" is a Surface and $V_0 = N\sigma^2\sqrt{3}/2$

| $V/V_0$ | $Z_{\text{sim}}$ | $Z\,(10)$ | $Z\,(12)$ |
|---|---|---|---|
| 30 | 1.064 | 1.063 | 1.063 |
| 20 | 1.097 | 1.097 | 1.098 |
| 10 | 1.211 | 1.209 | 1.211 |
| 5 | 1.498 | 1.492 | 1.499 |
| 3 | 2.077 | 2.054 | 2.078 |
| 2 | 3.42 | 3.35 | 3.44 |
| 1.8 | 4.17 | 4.06 | 4.19 |
| 1.6 | 5.50 | 5.33 | 5.55 |
| 1.5 | 6.61 | 6.40 | 6.70 |
| 1.4 | 8.31 | 8.06 | 8.49 |

what happens in three dimensions ($D=3$). Thus, for $D=2$ we can expect that the imposition of the condition that more virial coefficients be reproduced exactly will improve the quality of the resulting equation of state.

Consequently, if we impose the condition that the third virial coefficient must be reproduced exactly, we obtain

$$B_n = 1.128018n - 0.256035 \qquad (n \geqslant 2) \tag{11}$$

This expression furnishes $B_4 = 4.2560$, $B_5 = 5.3841$, $B_6 = 6.5121$, and $B_7 = 7.6401$, which, in general, are much closer to the correct values (6) than those predicted by (8). Using expression (11) and adding the corresponding virial expansion, we obtain the equation of state

$$Z = \frac{1 + 0.128018y^2}{(1-y)^2} \tag{12}$$

which, as we can see in Table I, constitutes a noticeable improvement with respect to Eq. (10).

It is possible to reproduce exactly up to the fourth virial coefficient, by means of the expression

$$B_n = 0.0009090n^2 + 1.123473n - 0.250582 \qquad (n \geqslant 2) \tag{13}$$

The values of $B_5$, $B_6$, and $B_7$ remain virtually unchanged from those given by Eq. (11) and lead to the equation of state,

$$Z = \frac{1 - y + 0.128018y^2 - 0.126198y^3}{(1-y)^3} \tag{14}$$

which provides results practically indistinguishable from those of Eq. (12).

Any attempt to increase the number of virial coefficients exactly reproduced results in progressive worsening of the equation of state.

Thus, to some extent, the modified CS method can improve not only the predictions of the equation of state, but also those of the virial coefficients. We can go further and generalize the CS method to nonspherical hard-body fluids, for which the virial coefficients are function of the shape. In these circumstances the coefficients $a_i$ in Eq. (5) would be functions of a suitable shape-defining parameter, such as the shape factor $\alpha = RS/3v_m$, where $R$ is the mean radius of curvature, $S$ the surface of the molecule, and $v_m$ the molecular volume.

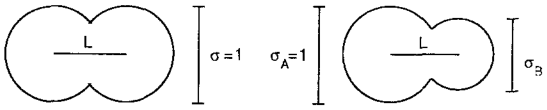
## 3. EQUATIONS OF STATE FOR FHS FLUIDS FROM THE GENERALIZED CS METHOD

### 3.1. Hard Dumbbells

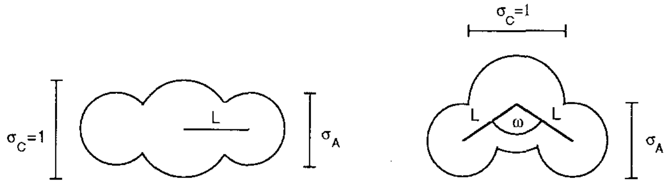
Homonuclear dumbbells (HMND) are characterized by the bond length-to-diameter ratio $L$, whereas heteronuclear dumbbells (HTND) are defined by $L$ and $\sigma_B$, the bond length and minor diameter, both in terms of the major diameter $\sigma_A$ (Fig. 1). However, we are interested in using a single parameter to define the shape of both types of molecules in order to obtain unified expressions for the virial coefficients and the equation of state.

For hard convex body fluids, the dependency of the reduced second virial coefficient $B_2^* = B_2/v_m$ on the shape factor $\alpha$ is given exactly by

$$B_2^* = 1 + 3\alpha \tag{15}$$



Homonuclear dumbbell Heteronuclear dumbbell



Linear symmetric triatomics Non-linear symmetric triatomics

Fig. 1. Several of the molecular shapes considered in the paper.

whereas for nonconvex hard-body fluids, such as FHS fluids, the second virial coefficients, determined exactly from theoretical methods, can be used to determine an effective shape factor by using Eq. (15).

The known reduced virial coefficients $B_n^* = B_n/v_m^{n-1}$, third to fifth, for both homonuclear dumbbells [14, 15] and heteronuclear dumbbells [15] are very well reproduced by means of the following polynomials in the shape factor $\alpha$ [3, 4]:

$$\begin{aligned} B_3^* &= 0.24 + 6.74\alpha + 3.02\alpha^2 \\ B_4^* &= -4.22 + 15.41\alpha + 7.17\alpha^2 \\ B_5^* &= 26.62 - 36.41\alpha + 38.01\alpha^2 \end{aligned} \tag{16}$$

These expressions reproduce to two decimal figures the hard-sphere fluid virial coefficients for $\alpha = 1$, and from them we can obtain a recurrence formula similar to Eq. (2), which is now expressed as

$$B_n^* = \sum_{i=0}^{k-2} f_i(\alpha) n^i, \qquad n \geqslant 2 \tag{17}$$

Then the summation given by Eq. (3) can be performed to give an expression similar to Eq. (5) with coefficients $a_n(\alpha)$ depending on $\alpha$.

We have obtained equations of state of the form of Eq. (5), with $\alpha$-dependent coefficients, reproducing exactly three, four, or five virial coefficients of HMND and HTND fluids as given by Eq. (16). The best results in comparison with simulation data [16–18] are obtained on the condition that four virial coefficients must be reproduced, that is, $k = 4$ in Eqs. (5) and (17). The latter expression now becomes

$$B_n^* = f_0(\alpha) + f_1(\alpha) n + f_2(\alpha) n^2 \tag{18}$$

with

$$\begin{aligned} f_0(\alpha) &= -8.58 + 10.31\alpha - 2.65\alpha^2 \\ f_1(\alpha) &= 8.49 - 8.585\alpha + 0.195\alpha^2 \\ f_2(\alpha) &= -1.85 + 2.465\alpha + 0.565\alpha^2 \end{aligned} \tag{19}$$

which lead to the equation of state,

$$Z = \frac{1 + a_1(\alpha)\, y + a_2(\alpha)\, y^2 + a_3(\alpha)\, y^3}{(1-y)^3} \tag{20}$$

with

$$a_1(\alpha) = -2 + 3\alpha$$
$$a_2(\alpha) = 0.24 - 2.26\alpha + 3.02\alpha^2 \qquad (21)$$
$$a_3(\alpha) = -2.94 + 4.19\alpha - 1.89\alpha^2$$

As we can see in Figs. 2 and 3, agreement between calculated and simulation data is very good for both HMND and HTND.

From the recurrence formula, Eq. (18), combined with Eq. (19), the expression for the fifth virial coefficient is

$$B_5^* = -12.38 + 29.01\alpha + 12.45\alpha^2 \qquad (22)$$

This expression gives values of $B_5^*$ which differ from those given by the last one in Eq. (16) by only a few percent in the range of $\alpha$ in which we are interested (roughly $1 \leqslant \alpha \leqslant 1.5$).

### 3.2. Symmetric Triatomics

Linear symmetric triatomics (LST) are characterized by the parameters $L$ and $\sigma_A$, where $L$ is the distance between the centers of the central sphere and one of the two equal outer spheres denoted $A$, and $\sigma_A$ is the diameter of the outer spheres, both expressed in terms of the diameter of the central

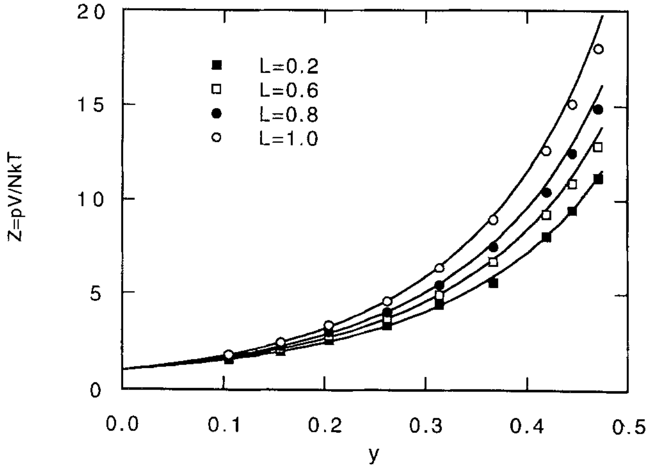


**Fig. 2.** Equation of state for HMND. Continuous lines: Eqs. (20) and (21). Points: simulation data from Ref. 16.

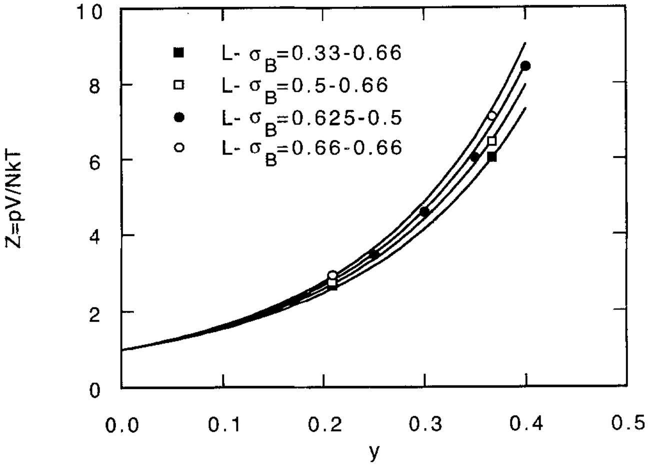


**Fig. 3.** Equation of state for HTND. Continuous lines: Eqs. (20) and (21). Points: simulation data from Refs. 17 and 18.

sphere. Nonlinear symmetric triatomics (NLST) are defined by the parameters $L$, $\sigma_A$, and $\omega$, where $L$ and $\sigma_A$ have the same meaning as for LST and $\omega$ is the valency angle (Fig. 1).

The simulation data for the equation of state of LST and NLST are scarce. For LST, to our knowledge, the only shape for which there are simulation data for several densities is for $L$–$\sigma_A = 0.8$–$1.0$ [19]. The corresponding reduced virial coefficients [15] are listed in Table II. From these we can apply the modified CS method to obtain equations of state reproducing exactly three to five virial coefficients. The best results are obtained when four virial coefficients are reproduced. The recurrence formula for this case is

$$B_n^* = -4.734 + 0.3765n + 2.4405n^2 \tag{23}$$

For the fifth virial coefficient, this expression gives $B_5^* = 58.16$, somewhat higher than the value listed in Table II.

**Table II.** Virial Coefficients for Symmetric Triatomics and Tetrahedral Penta-Atomics (See References in the Text)

| Fluid | $B_2^*$ | $B_3^*$ | $B_4^*$ | $B_5^*$ |
|---|---|---|---|---|
| LST ($L$–$\sigma_A = 0.8$–$1.0$) | 5.781 | 18.36 | 35.82 | 53.5 |
| NLST ($L$–$\sigma_A$–$\omega = 0.8$–$0.6$–$105$) | 6.069 | 20.91 | 44.66 | 64.2 |
| TPA ($L$–$\sigma_A = 0.8$–$1.0$) | 5.024 | 15.26 | 31.94 | 51.9 |

The resulting equation of state is then

$$Z = \frac{1 + 2.781y + 4.017y^2 - 2.917y^3}{(1-y)^3} \tag{24}$$

which, as we can see in Fig. 4, provides excellent agreement with simulation data [19].

For NLST there is also, to our knowledge, a single shape for which there are simulation data for the equation of state at several densities, namely, for $L$–$\sigma_A$–$\omega = 0.8$–$0.6$–$105$ [20]. The virial coefficients of this shape [15] are listed in Table II. Applying the modified CS method, we find that the best results as compared with simulation CS method, we find that the best results as compared with simulation data are also obtained when four virial coefficients are reproduced. The recurrence formula for the virial coefficients is then

$$B_n^* = 3.1140 - 7.4315n + 4.4545n^2 \tag{25}$$

which, for the fifth virial coefficient, gives 77.32, appreciably higher than that listed in Table II.

The equation of state resulting from the summation of the series given by Eq. (3) with $B_n^*$ given by Eq. (25) is

$$Z = \frac{1 + 3.069y + 5.703y^2 - 0.863y^3}{(1-y)^3} \tag{26}$$

which, as Fig. 4 shows, agrees very well with simulation data [20].

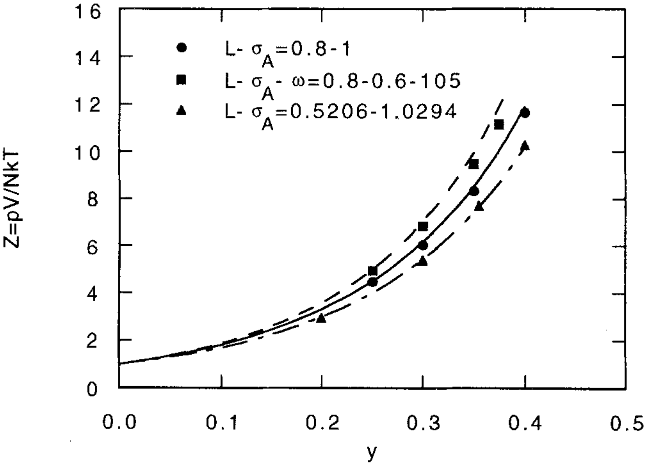


**Fig. 4.** Equations of state for LST, NLST, and TPA. Continuous line: Eq. (24). Dashed line: Eq. (26). Dashed-dotted line: Eq. (28). Points: simulation data from Refs. 19 (circles), 20 (squares), and 21 (triangles).

### 3.3. Tetrahedral Penta-Atomics

Hard tetrahedral penta-atomics is a model consisting of a central sphere and four other equal-sized spheres placed at the vertices of a tetrahedron. The virial coefficients up to $B_5^*$ are known [15] for the shape defined by $L$–$\sigma_A = 0.5206$–$1.0294$, where $L$ and $\sigma_A$ have the same meaning as for LST. They are listed in Table II. From the application of the modified CS method, the best results as compared with the simulation data [21] for the equation of state are obtained, in contrast with the preceding cases, when the five virial coefficients are reproduced exactly. The recurrence formula is

$$B_n^* = 16.54000 - 19.58467n + 7.96800n^2 - 0.52733n^3 \tag{27}$$

and the resulting equation of state,

$$Z = \frac{1 + 1.024y + 1.164y^2 - 2.956y^3 - 3.396y^4}{(1-y)^4} \tag{28}$$

which, as we can see in Fig. 4, provides excellent agreement with simulation data.

## 4. CONCLUSIONS

From the above results, we may conclude that the generalization of the Carnahan–Starling method introduced in this work allows us to obtain in a fairly simple and systematic way accurate equations of state for fused-hard-sphere fluids. For most of the cases considered it is sufficient to know only four virial coefficients to obtain the equation of state since, except for TPA, the most accurate results are obtained under the condition that the first four virial coefficients must be reproduced exactly. However, this may be due to insufficient accuracy in the fifth virial coefficients given in the literature.

## REFERENCES

1. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**:635 (1969).
2. W. A. Steele and S. I. Sandler, *J. Chem. Phys.* **61**:1315 (1974).
3. M. J. Maeso, J. R. Solana, and J. Amorós, *Mol. Phys.* **76**:1269 (1992).
4. M. J. Maeso, J. R. Solana, and J. Amorós, *Mater. Chem. Phys.* (in press).
5. T. Boublik, *J. Chem. Phys.* **63**:4084 (1975).
6. T. Boublík, *J. Chem. Phys.* **53**:471 (1970).
7. T. Boublík and I. Nezbeda, *Chem. Phys. Lett.* **46**:315 (1977).
8. K. W. Kratky, *Physica A* **87**:584 (1977).
9. J. J. Erpenbeck and W. W. Wood, *J. Stat. Phys.* **35**:321 (1984).

10. L. V. Woodcock, *Ann. N.Y. Acad. Sci.* **371**:274 (1981).
11. K. W. Kratky, *J. Chem. Phys.* **69**:2251 (1978).
12. D. Henderson, *Mol. Phys.* **30**:971 (1975).
13. J. J. Erpenbeck and E. Luban, *Phys. Rev. A* **32**:2920 (1985).
14. T. Boublík and I. Nezbeda, *Colln. Czech. Chem. Commun.* **51**:2301 (1986).
15. I. Nezbeda, B. Tríska, and A. Malijevsky, *Czech. J. Phys. B* **38**:1234 (1988).
16. D. J. Tildesley and W. B. Streett, *Mol. Phys.* **41**:85 (1980).
17. D. Jolly, B. C. Freasier, and R. Bearman, *Chem. Phys. Lett.* **46**:75 (1977).
18. W. B. Streett and D. J. Tildesley, *J. Chem. Phys.* **68**:1275 (1978).
19. I. Nezbeda, M. R. Reddy, and W. R. Smith, *Mol. Phys.* **55**:447 (1985).
20. S. Labik and I. Nezbeda, *Mol. Phys.* **48**:97 (1983).
21. I. Nezbeda and H. L. Vörtler, *Mol. Phys.* **57**:909 (1986).