

Bonded hard-sphere theory and computer simulation of the equation of state of linear fused–hard-sphere fluids

J. Largo, M. J. Maeso, and J. R. Solana^{a)}

Departamento de Física Aplicada, Universidad de Cantabria, 39005 Santander, Spain

C. Vega and L. G. MacDowell

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria, 28040 Madrid, Spain

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The bonded hard-sphere (BHS) theory is extended to fluids consisting of rigid, linear, homonuclear molecules, each of them formed by n fused hard spheres. The theory shows excellent agreement with the Monte Carlo NpT simulation data which are also reported for reduced bond lengths $l^*=0.5$ and $n=2, 3, 4, 6, 8,$ and 10 . The accuracy of the BHS prediction in comparison to simulation is similar to that of generalized Flory-dimer theory and superior to that of thermodynamic perturbation theory. © 2003 American Institute of Physics.

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I. INTRODUCTION

Much attention has been devoted in the last two decades to the study of fluids consisting of flexible molecules formed by tangent hard spheres. Now, a number of successful theories are available as well as a considerable amount of simulation data. Two of the most popular theories are the Wertheim's thermodynamic perturbation theory (TPT)¹ and the generalized Flory-dimer (GFD) theory.² The former of these two theories, although first developed for flexible molecules made up of tangent hard spheres, has been further extended^{3,4} to molecules consisting of fused hard spheres. Many refinements have been introduced since then.

Polyatomic fluids containing rigid molecules have received less theoretical attention. Nevertheless, both TPT and GFD theories can be modified in order to extend their applicability to rigid linear molecules consisting of either tangent hard spheres (LTHS) or fused hard spheres (LFHS).

A successful theory for molecular fluids consisting of chains of tangent hard spheres is the bonded hard-sphere (BHS) theory. This theory was first developed for hard-body fluids consisting of tangent hard spheres^{5,6} and later extended to fused hard-sphere (FHS) fluids.⁷ However, apart from tetrahedral pentatomic FHS molecules, only short linear FHS molecules, containing up to three spheres, were considered. The aim of this paper is to test the BHS theory for fluids consisting of linear FHS molecules with up to 10 monomers. To this end, Monte Carlo NpT simulations have been performed for LFHS fluids consisting of n spheres of equal diameter σ , with $n=2, 3, 4, 6, 8,$ and 10 , and center-to-center reduced distance $l^*=l/\sigma=0.5$. These data are used to test the performance of the BHS theory in comparison with GFD and the modified TPT (MTPT) theories for these kinds of fluids. In addition, second to fifth virial coefficients have been calculated numerically for the same fluids and compared with the corresponding values predicted by these theo-

ries. The MC simulation method and the calculation of the virial coefficients are presented in the next section. In Sec. III the foundations of the BHS theory and its implementation for LFHS fluids are described. In the last section, results from BHS theory are compared with those obtained from MTPT and GFD theories and from simulations.

II. MONTE CARLO SIMULATIONS

NpT Monte Carlo simulations have been performed for systems consisting of 256 particles, each of them formed by n hard spheres, with reduced bond length $l^*=0.5$. The pressure of the system, which is initially arranged in a regular configuration, was increased step by step. After each increase in pressure, the system was allowed to equilibrate for 1.2×10^5 cycles, each of them consisting of an attempt of translation plus an attempt of rotation per particle, and an attempted volume change, after which the density was determined by averaging over 1.2×10^5 additional cycles. No signal of ordering of the particles was observed in systems with $n \leq 6$, but molecules in systems with $n=8$ or $n=10$ showed tendency to align their axes along a given direction at high densities forming a nematic phase. For these two cases, the nematic order parameter was obtained from the largest eigenvalue of the second rank orientational tensor of the system (see Ref. 8 for further details), according to

$$S_2 = \langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \rangle. \quad (1)$$

Results for the equation of state are listed in Tables I–VI. The tables $n=8$ and $n=10$ include the values of the nematic order parameter S_2 .

On the other hand, second to fifth virial coefficients for the same fluids have been numerically determined in the usual way,^{9,10} using 10^7 to 3×10^8 trial configurations. A hundred intermediate calculations, each of them with the same number of trial configurations, were used to estimate the uncertainty as the standard deviation of the mean. Results are listed in Table VII.

^{a)}Author to whom correspondence should be addressed. Electronic mail: solanajr@unican.es

TABLE I. Monte Carlo simulation data for the equation of state of a LFHS fluid with $n=2$. $\rho^* = \rho\sigma^3$ is the reduced density, $\eta = \rho v_m$ is the packing fraction, where v_m is the molecular volume, $p^* = p\sigma^3/kT$ is the reduced pressure, and $Z = p^*/\rho^*$ is the compressibility factor. The number in parentheses in the density represents the statistical uncertainty in the last decimal place.

p^*	ρ^*	η	Z
0.10	0.074(3)	0.065	1.351
0.25	0.142(5)	0.125	1.761
0.35	0.173(6)	0.153	2.023
0.50	0.209(6)	0.185	2.392
0.75	0.256(6)	0.226	2.930
1.00	0.290(7)	0.256	3.448
1.25	0.319(6)	0.282	3.918
1.50	0.341(6)	0.301	4.399
1.75	0.359(6)	0.317	4.875
2.00	0.378(6)	0.334	5.291
2.25	0.392(5)	0.346	5.740
2.50	0.410(6)	0.362	6.098
2.75	0.419(6)	0.370	6.563
3.00	0.430(6)	0.380	6.977
3.25	0.441(5)	0.390	7.370
3.50	0.451(5)	0.399	7.761
4.00	0.468(5)	0.414	8.547
4.50	0.483(6)	0.427	9.317
5.00	0.498(4)	0.440	10.04
5.50	0.510(4)	0.451	10.78
6.00	0.523(5)	0.462	11.47
7.00	0.541(5)	0.478	12.94

III. BHS THEORY FOR LINEAR FUSED-HARD-SPHERE FLUIDS

A. Linear tangent-hard-sphere fluids

Let us first summarize the BHS theory for LTHS fluids. In this theory, the compressibility factor of a fluid consisting

TABLE II. As in Table I for $n=3$.

p^*	ρ^*	η	Z
0.10	0.067(3)	0.083	1.493
0.25	0.119(4)	0.148	2.101
0.35	0.143(4)	0.178	2.448
0.50	0.170(5)	0.211	2.941
0.75	0.203(4)	0.252	3.695
1.00	0.229(4)	0.285	4.367
1.25	0.247(4)	0.307	5.061
1.50	0.262(4)	0.326	5.725
1.75	0.276(4)	0.343	6.341
2.00	0.290(3)	0.361	6.897
2.25	0.301(4)	0.374	7.475
2.50	0.311(3)	0.387	8.039
2.75	0.319(4)	0.397	8.621
3.00	0.327(4)	0.407	9.174
3.25	0.335(3)	0.417	9.701
3.50	0.343(3)	0.427	10.20
4.00	0.353(3)	0.439	11.33
4.50	0.366(3)	0.455	12.30
5.00	0.373(3)	0.464	13.40
5.50	0.383(3)	0.476	14.36
6.00	0.390(3)	0.485	15.38
6.50	0.397(2)	0.494	16.37

TABLE III. As in Table I for $n=4$.

p^*	ρ^*	η	Z
0.10	0.060(2)	0.096	1.670
0.25	0.103(3)	0.165	2.440
0.35	0.121(3)	0.194	2.886
0.50	0.143(3)	0.229	3.489
0.75	0.170(3)	0.273	4.411
1.00	0.186(3)	0.298	5.382
1.25	0.203(3)	0.326	6.167
1.50	0.217(3)	0.348	6.919
1.75	0.225(2)	0.361	7.768
2.00	0.235(2)	0.377	8.528
2.25	0.244(2)	0.391	9.215
2.50	0.253(3)	0.406	9.889
2.75	0.259(2)	0.415	10.64
3.00	0.264(2)	0.423	11.36
3.25	0.272(2)	0.436	11.95

of N linear molecules, each of them formed by n tangent hard spheres with diameters σ_i , is considered to consist of two contributions in the form^{5,6}

$$Z^{\text{BHS}} = Z_{\text{mix}}^{\text{HS}} + Z^{\text{bond}}, \quad (2)$$

where $Z_{\text{mix}}^{\text{HS}}$ is the compressibility factor of a mixture of the nN unbonded spheres and Z^{bond} is the contribution of the bonds. The first contribution is accurately given by the Boublík–Mansoori–Carnahan–Starling–Leland (BMCSL)^{11,12} equation of state

$$Z_{\text{mix}}^{\text{HS}} = \frac{6}{\pi\rho} \left(\frac{\xi_0}{1-\xi_3} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{3\xi_2^3}{(1-\xi_3)^3} - \frac{\xi_3\xi_2^3}{(1-\xi_3)^3} \right), \quad (3)$$

where ρ is the number density and

$$\xi_l = \frac{\pi}{6} \rho \sum_i x_i \sigma_i^l, \quad (4)$$

where x_i is the mole fraction of spheres of diameter σ_i in the mixture.

On the other hand, the bonding contribution can be expressed in the form^{5,6}

TABLE IV. As in Table I for $n=6$.

p^*	ρ^*	η	Z
0.10	0.049(2)	0.114	2.041
0.25	0.080(2)	0.186	3.125
0.50	0.109(2)	0.253	4.587
0.75	0.127(2)	0.295	5.906
1.00	0.138(2)	0.321	7.246
1.25	0.147(2)	0.342	8.503
1.50	0.159(1)	0.369	9.434
1.75	0.165(1)	0.383	10.606
2.00	0.173(1)	0.402	11.561
2.25	0.177(1)	0.411	12.712
2.50	0.183(1)	0.425	13.661
2.75	0.188(1)	0.439	14.628
3.00	0.193(1)	0.448	15.544
3.25	0.197(2)	0.458	16.497
3.50	0.200(1)	0.464	17.544

TABLE V. As in Table I for $n=8$. S_2 is the nematic order parameter.

p^*	ρ^*	η	Z	S_2
0.10	0.042(1)	0.129	2.381	0.05
0.25	0.065(1)	0.198	3.846	0.06
0.50	0.087(1)	0.265	5.747	0.06
0.75	0.101(1)	0.307	7.426	0.07
1.00	0.110(1)	0.335	9.091	0.07
1.25	0.119(1)	0.362	10.504	0.08
1.50	0.125(1)	0.380	12.000	0.07
1.75	0.133(1)	0.405	13.158	0.10
2.00	0.138(1)	0.420	14.493	0.12
2.25	0.142(1)	0.432	15.845	0.15
2.50	0.148(1)	0.450	16.892	0.14
2.75	0.153(1)	0.466	17.974	0.34
3.00	0.159(1)	0.484	18.868	0.41
3.25	0.162(1)	0.493	20.062	0.40
3.50	0.167(1)	0.508	20.958	0.60

$$Z^{\text{bond}} = - \sum_{\text{bonds}} \left\{ 1 + \frac{\rho}{g_{ij}^{\text{HS}}(\sigma_{ij})} \left[\frac{\partial g_{ij}^{\text{HS}}(\sigma_{ij})}{\partial \rho} \right]_{T,N} \right\}, \quad (5)$$

where the sum extends over all bonds, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ is the contact distance for the pair ij in the HS mixture, and $g_{ij}^{\text{HS}}(\sigma_{ij})$ is the contact value of the radial distribution function for the same pair. The expression of $g_{ij}^{\text{HS}}(\sigma_{ij})$ which corresponds to the BMCSL equation of state (3) is¹¹

$$g_{ij}^{\text{HS}}(\sigma_{ij}) = \frac{1}{1 - \xi_3} + \frac{3\xi_2}{(1 - \xi_3)^2} \frac{\sigma_i \sigma_j}{\sigma_i + \sigma_j} + \frac{2\xi_2^2}{(1 - \xi_3)^3} \left(\frac{\sigma_i \sigma_j}{\sigma_i + \sigma_j} \right)^2. \quad (6)$$

This completes the BHS equation of state for LTHS.

B. Linear fused-hard-sphere fluids

In the case of fused-hard-sphere fluids, the BHS theory⁷ replaces the real molecule by an equivalent one formed by tangent hard spheres. This equivalent molecule is determined from the conditions that it must have both molecular volume

TABLE VI. As in Table I for $n=10$. S_2 is the nematic order parameter.

p^*	ρ^*	η	Z	S_2
0.10	0.036(1)	0.135	2.778	0.06
0.25	0.055(1)	0.207	4.545	0.06
0.50	0.073(1)	0.275	6.849	0.07
0.75	0.084(1)	0.316	8.929	0.08
1.00	0.093(1)	0.350	10.753	0.10
1.25	0.101(1)	0.380	12.376	0.09
1.50	0.107(1)	0.403	14.019	0.28
1.75	0.114(1)	0.429	15.351	0.36
2.00	0.121(1)	0.455	16.529	0.47
2.25	0.130(1)	0.489	17.308	0.70
2.50	0.140(1)	0.527	17.857	0.80
2.75	0.145(1)	0.546	18.966	0.82
3.00	0.156(1)	0.587	19.231	0.84
3.25	0.159(1)	0.598	20.440	0.84
3.50	0.163(1)	0.613	21.472	0.84

TABLE VII. Reduced virial coefficients $B_i^* = B_i / (v_m)^{i-1}$ for LFHS fluids with reduced bond length $l^* = 0.5$. Numbers in parentheses represent the estimated statistical uncertainty in the last digit.

n	B_2^*	B_3^*	B_4^*	B_5^*
2	4.327(1)	11.439(8)	21.62(6)	32.3(4)
3	4.778(1)	13.352(9)	25.09(9)	37.5(6)
4	5.266(2)	15.462(9)	28.6(1)	39.5(8)
6	6.287(2)	20.12(1)	34.3(1)	44(1)
8	7.330(2)	25.11(2)	37.5(1)	48(2)
10	8.384(3)	30.37(2)	37.2(2)	58(3)

v_m and nonsphericity parameter α equal to those corresponding to the real molecule. The nonsphericity parameter for a hard convex molecule is defined in the form

$$\alpha = \frac{RS}{3v_m}, \quad (7)$$

where S is the surface of the molecule and R is $(1/4\pi)$ times the mean curvature integrated over the whole surface of the convex body.^{13,14} However, for a nonconvex molecule the latter quantity is not well defined. A successful criterion proposed by Boublík and Nezbeda (BN)¹⁵ in this case consists of determining the R that corresponds to the convex envelope of the molecule. Using this criterion, BHS theory was applied⁷ to FHS fluids consisting of hard diatomic, triatomic, and tetrahedral pentatomic molecules.

For linear molecules with $n > 3$, the nonsphericity parameter generally must be determined numerically.¹⁶ In the BHS theory, it is suggested⁷ to apply the above-mentioned procedure to each of the diatomic segments which form the polyatomic molecule. An alternative way to define the nonsphericity parameter for homonuclear FHS molecules is¹⁷

$$\alpha = \frac{1}{3\pi} \frac{(\partial v_m / \partial \sigma)(\partial^2 v_m / \partial \sigma^2)}{v_m}, \quad (8)$$

where σ is the diameter of the spheres. For homonuclear FHS molecules, this expression gives the same result as the BN procedure. The generalization of Eq. (8) to heteronuclear LFHS molecules is straightforward¹⁷

$$\alpha = \frac{1}{3\pi} \frac{\sum_i (\partial v_m / \partial \sigma_i) \sum_{i,j} (\partial^2 v_m / \partial \sigma_i \partial \sigma_j)}{v_m}. \quad (9)$$

This definition is particularly suitable for our purposes as we will see shortly.

Let us consider now a linear heteronuclear molecule consisting of n fused hard spheres in which sphere i has diameter σ_i and the center-to-center distance between two adjacent spheres j and k is l_{jk} . The volume of this molecule can be obtained exactly in the form

$$v_m = \sum_{i=1}^n v_i, \quad (10)$$

where

$$v_i = \frac{4}{3} \pi (\sigma_i/2)^3 - v_{i,i-1} - v_{i,i+1}, \quad (11)$$

with $v_{i,0} = v_{n,n+1} = 0$,

$$v_{j,k} = \frac{1}{3} \pi h_{jk}^2 \left(\frac{3}{2} \sigma_j - h_{jk} \right), \quad (12)$$

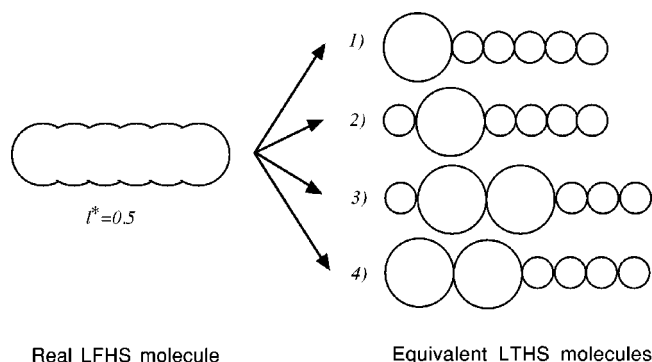


FIG. 1. LTHS molecules equivalent to an homonuclear LFHS molecule with $l^*=0.5$ and $n=6$.

$$h_{jk} = \sigma_j/2 - x_{jk}, \quad (13)$$

and

$$x_{jk} = \frac{(\sigma_j/2)^2 - (\sigma_k/2)^2 + l_{jk}^2}{2l_{jk}}. \quad (14)$$

Using Eq. (10) for v_m , together with Eqs. (11)–(14), in the definition Eq. (9), the nonsphericity parameter α for LFHS molecules can be readily obtained. For diatomic and triatomic molecules this gives the same results as the BN procedure outlined above.

The procedure that we will use to apply the BHS theory to rigid LFHS molecules will consist of replacing the real molecule with an equivalent LTHS molecule with the diameters σ_i of the spheres determined from the conditions that the molecular volume v_m and the nonsphericity parameter α , as determined from Eqs. (10) and (9), respectively, must be equal for the two molecules. Notice that the total number of spheres is kept identical in both models, the LFHS and the equivalent LTHS models. For $n=2$, the result will be the same as that obtained from the original procedure.⁷ However, for $n>2$ more than one solution is possible. This is illustrated in Fig. 1 for $n=6$. Note that, as we have only two conditions, only two different diameters σ_1 and σ_2 for the spheres can be determined. But still we may have one or more spheres of diameter σ_1 , where we consider that $\sigma_1 > \sigma_2$ for convenience, and the values of σ_1 and σ_2 obtained may depend on the relative positions of the spheres in the molecule, as Fig. 1 shows. Moreover, note that for fixed values of σ_1 and σ_2 , and fixed number of spheres of each kind, the BHS equation of state depends on the relative positions of the two kinds of spheres through the dependency on bonds in Eq. (5). However, for the molecules considered here there are only two solutions which arise in all cases. They correspond to solutions (1) and (2) in Fig. 1. Of course, for $n=2$ the two solutions are equal. Both solutions differ only slightly and, when implemented in the BHS theory, give nearly the same results. Therefore, we have considered the solution (1) for all values of n considered.

Alternatively, we could have considered the equivalent LTHS molecule to consist of an effective number of monomers $n_{\text{eff}} \neq n$, all of them with the same diameter d . Again we would have two parameters that could be determined from the two above-mentioned conditions. However, apart from

TABLE VIII. Parameters in the BHS theory for the homonuclear LFHS fluids considered. l^* is the center-to-center distance. Lengths are in units of σ , the diameter of one of the spheres of the homonuclear LFHS molecules, and volumes are in units of σ^3 . The equivalent LTHS molecule consists of one sphere of diameter σ_1 and $n-1$ spheres of diameter σ_2 .

n	v_m	α	σ_1	σ_2
$l^*=0.5$				
2	0.8836	1.1111	1.1830	0.3170
3	1.2435	1.2632	1.3224	0.3151
4	1.6035	1.4286	1.4345	0.3330
6	2.3235	1.7746	1.6127	0.3651
8	3.0434	2.1290	1.7545	0.3888
10	3.7634	2.4870	1.8740	0.4068
$l^*=0.6$				
11	4.6705	3.1390	1.9680	0.5063
15	6.3293	4.0437	2.1550	0.5297

the fact that this eventually would give noninteger values of n_{eff} , we have found that this yields poorer results for the equation of state than those obtained from the procedure we propose.

IV. RESULTS AND DISCUSSION

The parameters relevant to the BHS theory obtained as described in the preceding section are listed in Table VIII. Results obtained from the BHS theory for the equation of state are compared in Figs. 2–7 with the simulation data listed in Tables I–VI for $l^*=0.5$. For $n=8$ and $n=10$ only the data corresponding to the isotropic phase have been included in the figures. This corresponds roughly to packing fractions below 0.45 for $n=8$ and 0.40 for $n=10$. For higher packing fractions, the nematic order parameter starts to increase abruptly, as shown in Tables V and VI. In addition, in Figs. 8 and 9 the theoretical results are compared with the simulation data from Refs. 18 and 19 for $l^*=0.6$ and $n=11$ and 15. We have not considered here the simulation data of Ref. 20 because they were reported only in graphical form. The predicted virial coefficients are compared with the numerical values of Table VII and of Ref. 21 in Figs. 10–13. For comparison, we have included in these figures also the

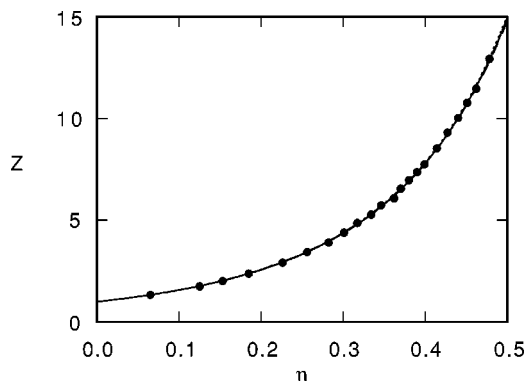


FIG. 2. Equation of state for a LFHS with $l^*=0.5$ and $n=2$. Points, simulation data from this work. Continuous curve, BHS theory. Dashed curve, GFD theory. Dotted curve, MTPT1 theory. The curves are nearly indistinguishable with respect to each other at the scale of the figure.

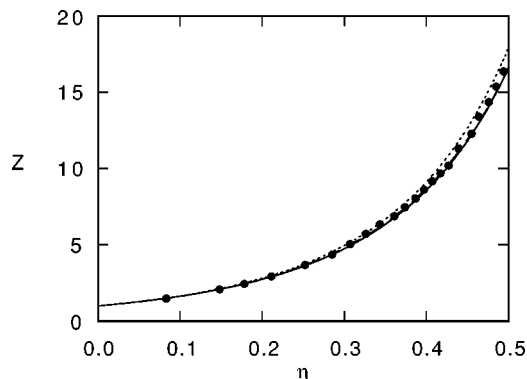


FIG. 3. As in Fig. 2 for $n=3$. BHS and GFD curves are nearly indistinguishable to each other at the scale of the figure.

results we have obtained from the generalized Flory-dimer (GFD) theory as well as from the first-order thermodynamic perturbation theory appropriately modified, as shown later, for these kind of fluids.

The GFD equation of state for homonuclear LTHS is expressed in the form²

$$Z^{\text{GFD}} = (Y_n + 1)Z_2 - Y_n Z_1, \quad (15)$$

where Z_1 is the compressibility factor of the monomers, that is, the hard-sphere fluid, and is given accurately by the Carnahan-Starling²² equation

$$Z_1 = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \quad (16)$$

Z_2 is the compressibility factor of a hard dumbbell fluid, given by²³

$$Z_2 = \frac{1 + F(l^*)\eta + G(l^*)\eta^2 - H(l^*)\eta^3}{(1 - \eta)^3} \quad (17)$$

with $l^* = 1$ for tangent spheres,

$$F(l^*) = 1 + 0.37836l^* + 1.07860l^{*3}, \quad (18)$$

$$G(l^*) = 1 + 1.30376l^* + 1.80010l^{*3}, \quad (19)$$

$$H(l^*) = 1 + 2.39803l^* + 0.35700l^{*3}, \quad (20)$$

and

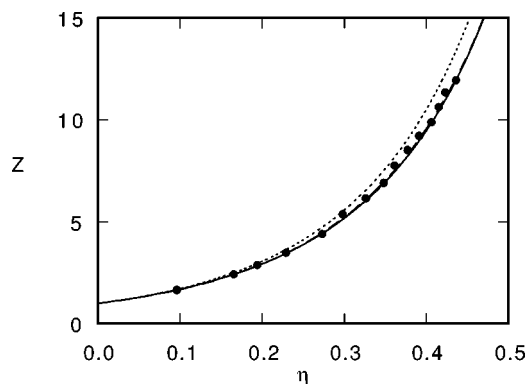


FIG. 4. As in Fig. 2 for $n=4$. BHS and GFD curves are nearly indistinguishable to each other at the scale of the figure.

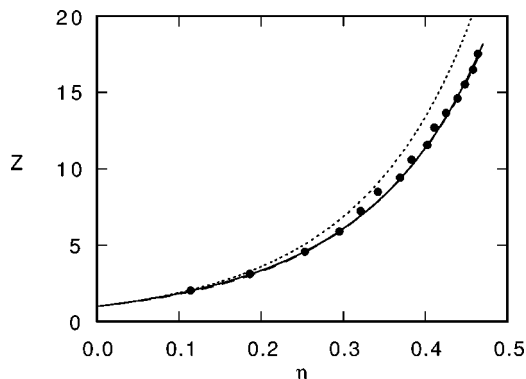


FIG. 5. As in Fig. 2 for $n=6$. BHS and GFD curves are nearly indistinguishable to each other at the scale of the figure.

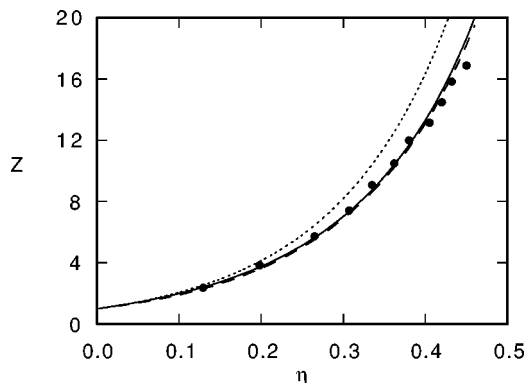


FIG. 6. As in Fig. 2 for $n=8$. Simulation results are presented only for the isotropic phase.

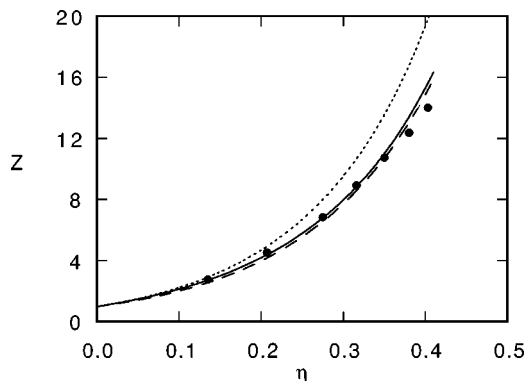


FIG. 7. As in Fig. 2 for $n=10$. Simulation results are presented only for the isotropic phase.

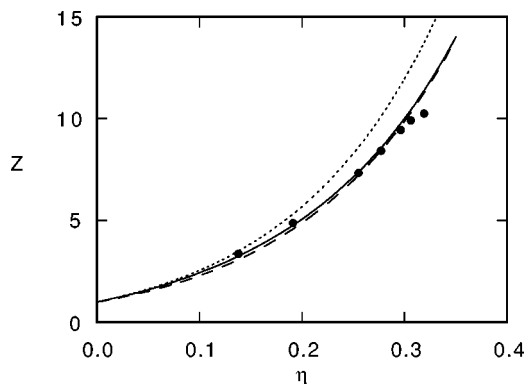


FIG. 8. As in Fig. 2 for $l^*=0.6$ and $n=11$. Simulation data are from Refs. 18 and 19.

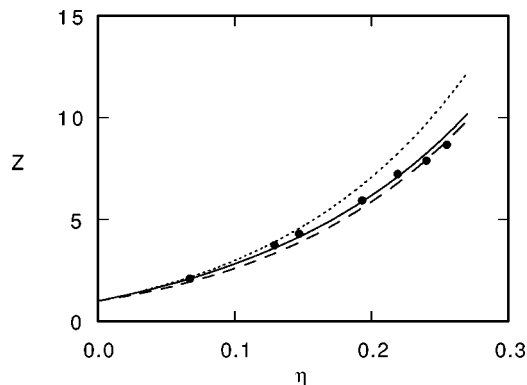


FIG. 9. As in Fig. 2 for $l^*=0.6$ and $n=15$. Simulation data are from Refs. 18 and 19.

$$Y_n = \frac{v_e(n) - v_e(2)}{v_e(2) - v_e(1)}, \quad (21)$$

where $v_e(1)$, $v_e(2)$, and $v_e(n)$ are the excluded volumes of the monomer, dimer, and n -mer molecules, respectively. For rigid linear molecules these excluded volumes are given by²⁴

$$v_e(1) = \frac{4}{3} \pi \sigma^3, \quad (22)$$

$$v_e(2) = \frac{4}{3} \pi \sigma^3 \left[1 + \frac{3}{2} \frac{l^*}{2} - \frac{1}{2} \left(\frac{l^*}{2} \right)^2 \right], \quad (23)$$

$$v_e(n) = v_e(1) + (n-1)[v_e(2) - v_e(1)], \quad (24)$$

which gives

$$Y_n = n - 2. \quad (25)$$

On the other hand, the Wertheim's TPT1 equation of state for LTHS molecules is expressed in the form¹

$$Z^{\text{TPT1}} = n \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - (n-1) \frac{1 + \eta - \eta^2/2}{(1 - \eta)(1 - \eta/2)}. \quad (26)$$

The theory has been modified in order to extend its applicability to LFHS^{3,4} fluids. The modified Wertheim's or modified TPT1 (MTPT1) equation of state is expressed in the form

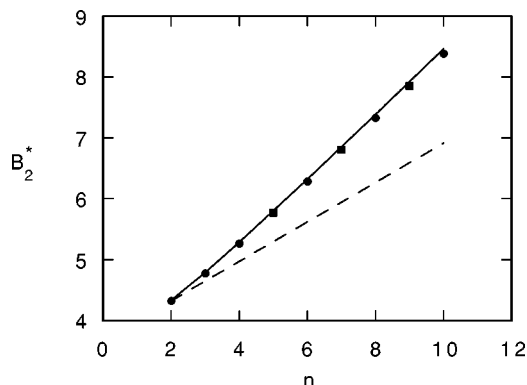


FIG. 10. Second virial coefficient for LFHS fluids with $l^*=0.5$. Points, exact results from Table VII (circles) and from Ref. 21 (squares). Continuous, dashed, and dotted curves are the results from BHS, GFD, and MTPT1 theories, respectively.

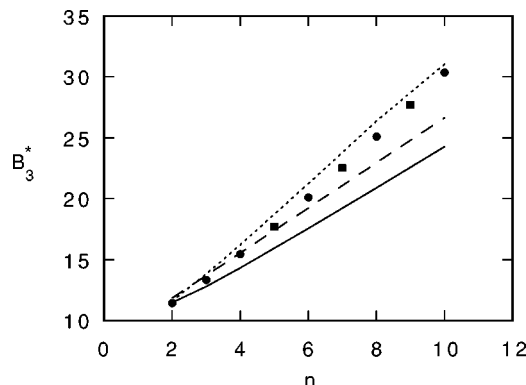


FIG. 11. As in Fig. 10 for the third virial coefficient.

$$Z^{\text{MTPT1}} = (2\alpha - 1) \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - (2\alpha - 2) \frac{1 + \eta - \eta^2/2}{(1 - \eta)(1 - \eta/2)}. \quad (27)$$

In Figs. 2–9 one can see that both, the BHS and the GFD theories, have nearly the same accuracy as compared with simulation data for the equation of state at low values of n . In fact the curves corresponding to these two theories are nearly indistinguishable to each other at the scale of the figures but for $n \geq 8$, when the BHS theory is perhaps a bit more accurate at moderate densities. By contrast, the MTPT1 theory considerably overestimates the simulation data in most cases.

Figure 10 shows that second virial coefficient is much better predicted by the BHS and MTPT1 theories than by the GFD theory. Figure 11 shows that the third virial coefficient is more accurately given by the GFD and MTPT1 theories than by the BHS theory. Fairly good accuracy up to $n=8$ is achieved from the GFD and BHS theories (Fig. 12) in predicting the fourth virial coefficient, whereas it is considerably overestimated by the MTPT1 theory. Finally, none of these theories are capable of accurately reproducing the fifth virial coefficient for high values of n although again GFD and BHS theories are more satisfactory, as Fig. 13 shows.

In summary, we have extended the BHS theory to fluids consisting of rigid linear fused hard spheres. For the com-

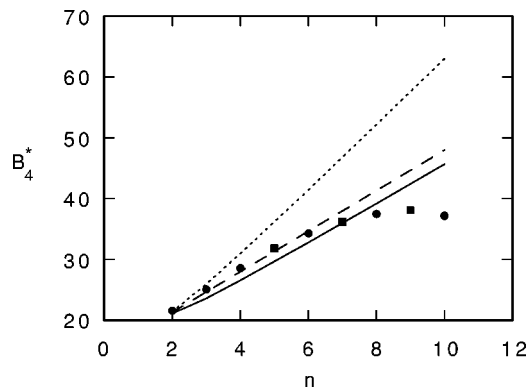


FIG. 12. As in Fig. 10 for the fourth virial coefficient.

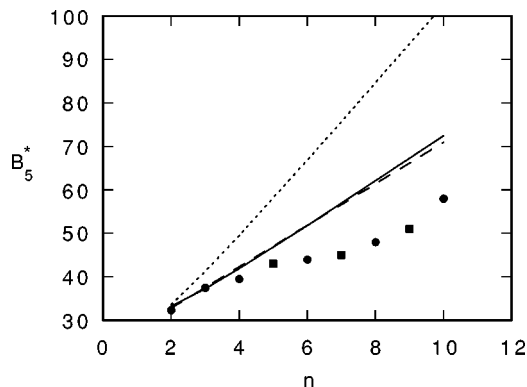


FIG. 13. As in Fig. 10 for the fifth virial coefficient.

compressibility factor the theory shows, on the whole, at least similar accuracy to the generalized Flory-dimer theory when compared with the reported simulation data. Regarding the virial coefficients, comparison with the numerical values also reported reveals that the BHS theory is more accurate than the GFD theory for the second virial coefficient, less accurate for the third, and of similar accuracy for the fourth and fifth. Therefore, the BHS theory seems to be appropriate for dealing with fluids consisting of elongated polyatomic molecules as well as fluids having shorter molecules. Research along these lines is continuing in our laboratory.

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