Geometrical Characteristics of the Enlarged Fused Hard Sphere Models of Simple Molecules

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The enlarged fused hard sphere model represents a compromise between fused hard sphere- and hard convex body models of repulsive interactions of nonspherical molecules. Geometric functionals of the enlarged fused hard sphere models, i.e., the hard body volume, surface area, and "mean radius" for 25 molecules of the linear and approximately planar shapes (cycloalkanes and aromatic compounds), neopentane and cyclohexane were determined from the bond lengths and bond angles and expressed in the dimensionless form. The hard sphere diameters, first approximated by the values found from the correlation of the second virial coefficients, were then adjusted to heats of vaporization of the studied compounds. Parameters of nonsphericity and molar volumes, evaluated from these characteristics, are compared with parameters of modern semiempirical equations of state (BACK, BACKONE, SAFT). The calculated geometric quantities for a series of compounds make it possible to improve methods of determining the characteristic parameters of the modern semiempirical equations of state, as well as those from the perturbation approaches.

1. Introduction

For the rational design of separation units and large containers or transport lines the accurate equations of state are essential. Modern equations of state (EOS) are composed of the repulsive part, which, besides density, reflects the size and shape of the considered molecules, and one or several attractive terms characterizing different types of intermolecular interactions among molecules. Proper knowledge of the size and shape (surface area and volume) is also important in studies of biomolecules.[1] The simplest characterization of the short-range interactions among nonspherical molecules is via interaction of the representative hard bodies. Two types of the hard body models are considered most often: fused hard sphere (FHS) bodies,[2] where repulsive interactions of atoms or groups of atoms are characterized by the interaction of hard spheres which remain in contact (forming tangential chains) or mutually overlap. In the other case, a hard convex core is ascribed to the given molecule and the parallel hard convex body[3] (HCB), with constant thickness relative to the core, models the repulsive interactions. Advantages of the FHS model are proximity to our intuitive view of the structure of molecules and simplicity of determination of the molecular overlapping in simulation experiments; cusps at the intersection of neighboring spheres cause problems in theoretical expressions. Hard convex body models describe the molecular structure often in a rather simple way; however, the convex body geometry offers some exact relations such as relationships for the mean volume or mean surface area of a couple of HCBs. The enlarged fused hard sphere (EFHS) bodies, which originate when a probe hard sphere moves in contact with hard spheres of the FHS body, retain advantages of both of the previously mentioned approaches. Moreover, in comparison with the fused hard body, it reflects better the electron-density contours of molecules. The EFHS model of repulsive interactions of molecules is not new; it was considered in the seventies[1] for interpretation of the behavior

of water−protein systems. Abascal and Lago[4] considered an enlarged volume when dealing with hard dumbbells (cf. also ref 5). Determination of surface area and volume of FHS models was studied by several authors,[6−9] a general method to determine the EFHS volumes and surface areas (of large organic molecules) was given by Connolly.[10,11] Recently we have shown[12] that the EFHS model allows the calculation of the second and third virial coefficients of linear hard chain molecules, employing the relationships derived within hard convex body geometry. For the series of the linear chains with number of segments $m = 1-10$ and the reduced lengths $L^* = 0.5$ and 1, we found values of both the second and third virial coefficients in rather good agreement with the numerical data.

Quite recently we apply the EFHS model to a series of *n*-alkanes, C_1-C_7. In our paper[13] we employed values of the hard sphere diameter, C−C bond length, bond angles in different rotamers (for higher members of series), as considered previously by Vega et al.[14,15] We determined the EFHS reduced molecular volume, surface area and "mean radius" (exactly the mean curvature integral divided by 4π); from these geometric quantities we calculated the nonsphericity parameter and packing fraction. After substitution into an entropic cycle, we determined the heat of vaporization, ΔH^{vap}, of the individual rotamers at the normal boiling point. A fair agreement was found of the average vaporization heats with experimental values of ΔH_{expt}^{vap}.

In this paper we (i) give a brief review of the expressions employed in the determination of the geometric characteristics of the EFHS bodies, (ii) determine the *representative* reduced volumes, surface areas, and mean radii of *n*-alkanes, (iii) evaluate the reduced geometric quantities of diatomic- and cyclic polyatomic molecules − cycloalkanes and aromatic compounds plus neopentane, and (iv) determine the hard sphere diameters from the experimental heats of vaporization. Next, we determine HB molar volumes and nonsphericity parameters of the single compounds and compare them with the parameters of the modern semiempirical equations of state: BACK,[16] BACK-

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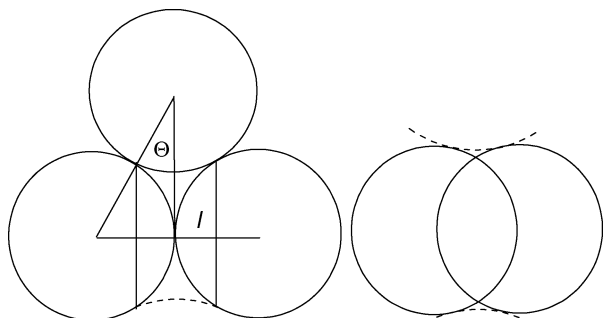
Figure 1. Enlarged fused hard sphere model of diatomics of $L^* = 1$ and $L^* = 0.5$.
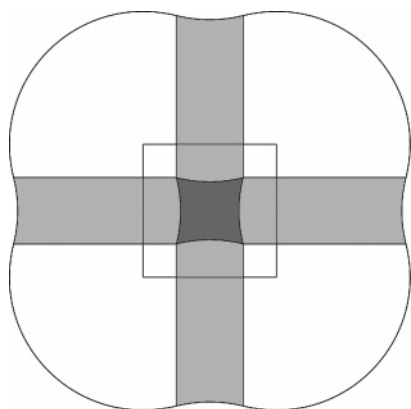
Figure 2. Enlarged fused hard sphere model of cyclobutane. Convex facets − open; saddle facets − gray; concave facets − black.

ONE[17,18] and SAFT.[19,20] In conclusion, we discuss possible further applications of the EFHS geometric characteristics.

2. Theory

As was mentioned in the introductory part, an advantage of the enlarged fused hard sphere (EFHS) model relies on the fact that it represents more closely than the corresponding hard convex body the structure of the considered molecule, but, in comparison with the fused hard body (FHS), it avoids cusps at the hard sphere intersections.

The geometry of the EFHS body, corresponding to the hard dumbbell of the reduced length $L^* = l/\sigma = 1$ and 0.5 is depicted in Figure 1. For the evaluation of the respective geometric quantities (volume, V^e, surface area, S^e, and mean radius, R^e) of the above EFHS body, the angle $\theta = \arcsin(L^*/2)$ is essential. It can be found that for all the linear chains

$$V^e = 1 + (m-1)\left(3L^* - \frac{1}{2}L^{*3} - 3\theta\cos(\theta)\right)(\pi\sigma^3/6) \quad (1)$$

$$S^e = [1 + 2(m-1)\theta\cos(\theta)]\pi\sigma^2 \quad (2)$$

$$R^e = [1 + (m-1)\theta](\sigma/2) \quad (3)$$

where m stands for the number of segments; in our example (see Figure 1), $m = 2$.

For the more complex EFHS bodies we turn to the expressions proposed by Connolly.[10,11] He considered surface area (and similarly volume) to be composed of convex, saddle, and concave facets. For example, the model of cyclobutane, shown in Figure 2, consists of four convex, four saddle, and two concave facets. The surface area and volume of the facets are functions of three angles, θ, ϕ, and β, where ϕ denotes the angle between normals of the neighboring facets and β − an angle of

the spherical triangle on the surface of the probe sphere. If the radius of the probe sphere is r_p, and of the i-site r_i, the convex (+), saddle (±) and concave (−) contributions follow from expressions

$$V_+ = \frac{1}{3}r_iS_+V_- = \frac{1}{6}hS_b - \frac{1}{3}r_pS_-$$

$$V_\pm = (V_{ci} + V_{cj}) + (V_{si} + V_{sj})$$

where in the case $r_i = r_j$

$$V_{ci} = \frac{\phi_s}{6}r_i^3\sin(\theta)\cos^2(\theta)$$

$$V_{si} = \frac{\phi_s}{2}r_p\left\{r_{ij}^2\sin(\theta_i) - r_{ij}r_p(\sin(\theta_i)\cos(\theta_i) + \theta_i) + \frac{1}{3}r_p^2(\sin(\theta_i)\cos^2(\theta_i) + 2\sin(\theta_i))\right\}$$

The total EFHS volume, V^e, is given by three sums of the convex, saddle, and concave contributions,

$$V^e = \sum V_+ + \sum V_\pm + \sum V_- \quad (4)$$

Similarly

$$S^e = \sum S_+ + \sum S_\pm + \sum S_- \quad (5)$$

with

$$S_+ = r_i^2[2\pi\chi + \sum\phi_i\sin(\theta_i) - \sum\beta_v]$$

$$S_\pm = \phi_s r_p[r_{ij}(\theta_i + \theta_j) - r_p(\sin(\theta_i) + \sin(\theta_j))]$$

$$S_- = r_p^2[\sum\beta_v - \pi]; \quad S_b = \frac{1}{2}d_{ij}d_{ik}\sin(\omega)$$

In the above expressions, the single sums are prescribed over all the sites (e.g., atoms), saddle strips, or all the vertices.

For the mean radius, R^e, we were unable to write a general expression of the form of eq 3; instead, we determined it as the $(1/8\pi)$-multiple of the derivative of surface area, S^e, with respect to $r_p(= r_i)$. It appears that for the enlarged hard dumbbell of $L^* = 0.5$ the difference amounts only 0.2%. In the case of planar molecules of cyclobutane, cyclopentane and aromatic compounds, the original expressions for S_- and V_- were modified for the symmetric spherical figure, i.e., spherical square, spherical pentagon or hexagon, and the corresponding angles.

2.1. Reduced Geometric Quantities. Within this study we first determined the reduced geometric quantities, defined as

$$V^* = V^e/\sigma^3; \quad S^{e*} = S^e/\sigma^2; \quad R^{e*} = R^e/\sigma$$

from the bond angles and the reduced bond lengths, $L^* = l/\sigma$. In the case of n-alkanes we used $\sigma = 0.37$ nm and $L^* = 0.4123$ (cf. studies of Vega et al.[14,15]); in the other cases, the σ values found in the correlation of the second virial coefficient to the Kihara expression[3] and values of the bond lengths and angles from the literature were employed. With the exception of cyclopropane, all of the cycloalkanes possess Baeyer tension resulting for cyclobutane and cyclopentane in a departure from the planar arrangement. However, for the determination of volume and surface area, this departure is not significant; in the case of cyclohexane with the chair and boot structures, we determined the geometric quantities for both forms and calcu-

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TABLE 1: Geometric Functionals of the Enlarged Fused Hard Sphere Models of *n*-Alkanes

compound	σ/nm	R^e/σ	S^e/σ^2	V^e/σ^3	σ_H/nm
methane	0.37	0.5000	3.1416	0.5236	0.378
ethane	0.37	0.6038	4.4182	0.8337	0.378
propane	0.37	0.6897	5.5980	1.1455	0.373
butane	0.37	0.7676	6.7181	1.4565	0.373
pentane	0.37	0.8502	7.8577	1.7685	0.373
hexane	0.37	0.9314	9.0056	2.0839	0.373
heptane	0.37	1.0108	10.1482	2.4010	0.373

TABLE 2: Geometric Functionals of the Enlarged Fused Hard Sphere Models of Cyclic and Other Simple Compounds

compound	σ/nm	R^e/σ	S^e/σ^2	V^e/σ^3	σ_H/nm
argon	0.34	0.5000	3.1416	0.5236	0.340
krypton	0.37	0.5000	3.1416	0.5236	0.367
xenon	0.40	0.5000	3.1416	0.5236	0.399
nitrogen	0.32	0.5868	4.2107	0.7856	0.316
oxygen	0.30	0.5868	4.2107	0.7856	0.299
fluorine	0.28	0.6316	4.7207	0.9011	0.282
chlorine	0.34	0.6516	4.9595	0.9513	0.335
carbon monoxide	0.32	0.5908	4.2583	0.7968	0.323
carbon dioxide	0.32	0.6806	5.3746	1.0699	0.310
ethylene	0.36	0.5929	4.2888	0.8039	0.362
cyclopropane	0.37	0.6567	5.2052	1.0599	0.373
cyclobutane	0.37	0.7084	6.0398	1.3065	0.378
cyclopentane	0.37	0.7593	6.9309	1.5441	0.378
cyclohexane	0.37	0.8261	7.7173	1.8813	0.378
neopentane	0.37	0.8168	7.6554	1.7724	0.373
acetylene	0.35	0.5866	4.2080	0.7850	0.358
benzene	0.35	0.8001	7.7159	1.7323	0.348
toluene	0.35	0.8785	8.6596	2.1296	0.358
naphthalene	0.35	0.9757	10.9414	2.8196	0.348

lated the representative values similarly as in the case of higher *n*-alkanes, *n*-butane up to *n*-heptane. For all the rotamers (different combinations of the trans and gauche orientations) of *n*-alkanes C_1-C_7, the corresponding geometric quantities together with the ideal gas population ratios were referred to in our previous paper.[13] Here we consider the average, *representative* functionals, obtained as a sum of the reduced values X_r^e* for the individual rotamers (r) multiplied by the relative populations, $\mathscr{P}_r$ in the given compound; thus

$$V^e* = \sum V_r^e* \mathscr{P}_r; \quad S^e* = \sum S*_r^e \mathscr{P}_r; \quad R^e* = \sum R*_r^e \mathscr{P}_r \quad (6)$$

Values of R^e*, S^e*, and V^e* for *n*-alkanes C_1-C_7 are listed in Table 1.

Examining the tabulated values of the geometric functionals, we observed (with the exception of methane) linear dependence of V^e*, S^e*, and R^e* on the number of CH_n groups, *m*, i.e.,

$$V^e* = 0.5183 + 0.3133(m - 1)$$

$$S^e* = 3.2896 + 1.1433(m - 1)$$

$$R^e* = 0.5250 + 0.0811(m - 1)$$

This linear dependence enables extrapolation to higher *n*-alkanes, where the number of rotamers of the single alkane increases dramatically.

In Table 2. we list values of the geometric functionals of the newly studied compounds (Ar, Kr, Xe, N_2, O_2, F_2, Cl_2, CO, and CO_2), series of cycloalkanes (cyclopropane, cyclobutane, cyclopentane, and cyclohexane (plus ethylene), neopentane), and series of aromates (benzene, toluene, and naphthalene (plus acetylene)). In the second column of this table the estimates of the hard sphere diameters, considered for the evaluation of the reduced bond lengths are given. In the series of cycloalkanes,
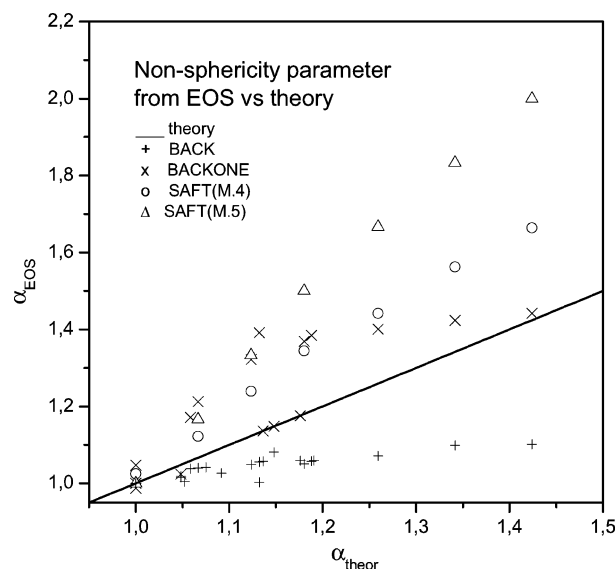
Figure 3. The nonsphericity parameter, α, from theory and several equations of state.

similar regularities as for *n*-alkanes can be observed (an exception is the molecule of cyclohexane). Thus, for cycloalkanes it holds approximately

$$V^e* = 0.8193 + 0.2421(m - 2)$$

$$S^e* = 4.3329 + 0.8628(m - 2)$$

$$R^e* = 0.6055 + 0.0513(m - 2)$$

Unfortunately, the extrapolation for $m > 5$ (giving geometric quantities of higher cycloalkanes) is not correct due to the different (spatial) structures of C_mH_{2m} in comparison with roughly planar $C_3H_6 - C_5H_{10}$. On the other hand, geometric functionals of the linear molecule of ethylene suit well to the above prescriptions, see Figure 3.

2.2. Hard Sphere Diameter from ΔH^{vap}. In our previous paper we used heats of vaporization to verify accuracy of the geometric quantities, determined for single *n*-alkanes from the considered structures and the hard sphere diameter $\sigma = 0.37$ nm. The fair agreement[13] of the calculated and experimental data of ΔH^{vap} led us to a conclusion that ΔH^{vap} and liquid density, at temperatures close to the normal boiling point, can be employed to determine the diameter(s) of hard spheres which form the EFHS body. To this end we used the formula

$$\frac{\Delta H^{vap}}{RT} = \ln\frac{RT}{P^oV_l} - \frac{dB}{dT}\frac{P^o}{R} + \frac{1}{RT}\int_{V_l}^{V*} P^{hb}\, dV \quad (7)$$

where P^o and P^{hb} stand for the saturated vapor and hard body pressures, B denotes the second virial coefficient, and V_l and $V*$ stand for liquid and ideal gas volumes (taken from ref 21). Equation 7 was derived from the thermodynamic entropy cycle, see ref 13.

To evaluate the last term of eq 7 we considered the expression[22]

$$\frac{PV}{RT} = \frac{1}{1-y} + \frac{3\alpha y}{(1-y)^2} + \frac{y^2[3\alpha^2\xi - \alpha^3 y - (\alpha^3 - 1)y^2]}{(1-y)^2} \quad (8)$$

with $y = \rho d^3 V^e*$ denoting the packing fraction and $\xi = (S^e/4\pi R^{e2})^{1/2}$, which predicts with high accuracy the hard body simulation results up to quite large values of the nonsphericity

parameter $\alpha = R^{e*}S^{e*}/3V^{e*}$. In the process of optimization we considered the Barker−Henderson method[23] of determination of the representative hard sphere diameter $d = c(T)\sigma$. The refined values of σ are given in the last columns of Tables 1 and 2.

3. Applications

One of the possible applications of the refined EFHS geometric characteristics of individual compounds is their use in the modern equations of state (EOS). Alternatively, these quantities can be used to judge, from the agreement of the theoretical and experimental values of α and characteristic volumes, V, adjusted within the frame of the respective method, on the correctness of the derivation of the semiempirical equations of state.

Here we will discuss two semiempirical equations, namely BACK and BACKONE, and the perturbation approach, called SAFT. The first two EOS belong to "the augmented van der Waals" equations,[16,17] which make it possible to determine very precisely the P−V−T behavior of fluids in a broad range of independent variables (two-phase and supercritical regions). They contain repulsive and attractive parts, the former expressed by the hard convex body compressibility factor,[24] whereas the latter is given by expansions in the reciprocal reduced temperature and reciprocal molar volume or density. (The considered expansions include 20−30 nonspecific constants, D, adjusted to the chosen reference fluids).

For BACK (Boublík-Alder-Chen-Kreglewski),[16] it holds that

$$\left(\frac{PV}{RT}\right)_{\text{BACK}} = Z_{\text{B}}^{\text{hb}} + Z_{\text{BACK}}^{\text{att}} \tag{9}$$

where

$$Z_{\text{B}}^{\text{hb}} = \frac{1}{1-y} + \frac{3\alpha y}{(1-y)^2} + \frac{\alpha^2 y^2(3-y)}{(1-y)^3} \tag{10}$$

$$Z_{\text{BACK}}^{\text{att}} = \sum\sum mD_{mn}\left(\frac{u}{kT}\right)^m\left(\frac{V^0}{V}\right)^n \tag{11}$$

Here $u/k = (u^0/k)(1 + \eta/kT)$ is the energy parameter and

$$\mathscr{V}^0 = \mathscr{V}^{00}\left[1 - C\exp\left(\frac{-3u^0}{kT}\right)\right]^3 \tag{12}$$

stands for the volumetric parameter; $\eta = 0$ for spherical nonpolar molecules, C is often taken $C = 0.12$. The packing fraction is then $y = \rho\mathscr{V}^0$.

In 1996 Müller et al.[17] proposed a modification of the BACK EOS, called SIMBACK, in which the repulsive term, Z_{B}^{hb}, has been retained, but for the attractive term more complicated expansion (based on the theoretical studies of diatomic molecules) in the reduced density ρ/ρ^0 and reduced temperature was proposed. Later on, Wendland et al.[18] proposed further modifications in which contributions of the permanent quadrupole (QUABACK) and dipole moments (DIBACK) were taken explicitly into consideration. These equations form the BACKONE family; in all the equations, the above-mentioned repulsive term is considered. The nonsphericity parameter α in BACK and BACKONE has the same meaning, however, the packing fraction, y, is defined in BACKONE as

$$y = 0.1617\frac{\rho}{\rho_0}\left[a + (1-a)\left(\frac{T}{T_0}\right)^\gamma\right]^{-1} \tag{13}$$

where $a = 0.689$ and $\gamma \sim 1/3$.

TABLE 3: Parameters of Nonsphericity from the Present Theory, BACK(B), BACKONE(M), and SAFT(S) Equations of State

compound	α	α_B	α_M	α_S
argon	1.0000	1.0000	0.9876	
krypton	1.0000	1.0000		
xenon	1.0000		1.0471	
nitrogen	1.0484	1.0185		
oxygen	1.0484	1.0155	1.0244	
carbon monoxide	1.0525	1.0040		
carbon dioxide	1.1323	1.0560	1.3919	
fluorine	1.1029			
chlorine	1.1323	1.0030		
methane	1.0000	1.0000	1.0000	1.025
ethane	1.0666	1.0402	1.2126	1.122
propane	1.1235	1.0485	1.3215	1.239
n-butane	1.1802	1.0510	1.3693	1.344
n-pentane	1.2592	1.0712	1.4011	1.442
n-hexane	1.3417	1.0989	1.4230	1.562
n-heptane	1.4241	1.1014	1.4416	1.664
neopentane	1.1760	1.0590	1.1760	
ethylene	1.0544	1.0384	1.1716	
cyclopropane	1.0750	1.0415		
cyclobutane	1.0916	1.0267		
cyclopentane	1.1361	1.0569	1.1361	
cyclohexane	1.1479	1.0810	1.1479	
acetylene	1.0481	−	−	
benzene	1.1879	1.0580	1.3846	
toluene	1.1907	1.0590		
naphthalene	1.2621			

Because the nonsphericity parameter, α, is defined unambiguously in the present work, in BACK EOS, and in BACKONE EOS, the comparison of this characteristic parameter is simple; it is presented in Table 3, where in the second column we give the theoretical value, in third column the value α_B adjusted within BACK EOS, and in fourth column α_M from BACKONE EOS. From Table 3 and Figure 3 it is obvious that values of α_B are consistently lower than theoretical ones, but depend linearly on theoretical α. On the other hand, deviations of α_M (BACKONE EOS) from α exhibit a maximum at approximately $\alpha = 1.25$; for higher values of α deviations reduce in a step-by-step manner and for values $\alpha \sim 1.4$, α_M tends to α.

Comparison of the molar hard body volumes is more complicated: theoretical values, $\mathscr{V}$, are obtained as product of V^{e*}, d^3, and Avogadro's number, N_A. In BACK, $y = (\pi\sqrt{2}/6)\mathscr{V}^0$, from which it follows that $\mathscr{V}_B = 0.7405\ \mathscr{V}^0$. If we consider $T \to 0$, $\mathscr{V}_B = 0.7405\ \mathscr{V}^{00}$.

From the expression for the packing fraction in BACKONE EOS, it follows that $\mathscr{V}_M = (0.1617/\rho_0)[0.689 + (1-0.689)(T/T_0)^\gamma]^{-1}$. For simplification we assume $T = T_0$, i.e., temperatures close to the critical point. Theoretical and (to experiment) adjusted values within BACK and BACKONE EOSs are listed in Table 4 and depicted in Figure 4. The comparison reveals a fair agreement of the characteristic values $\mathscr{V}_B$ with those from theory; the same is true for $\mathscr{V}_M$ calculated from ρ_0 of BACKONE EOS.
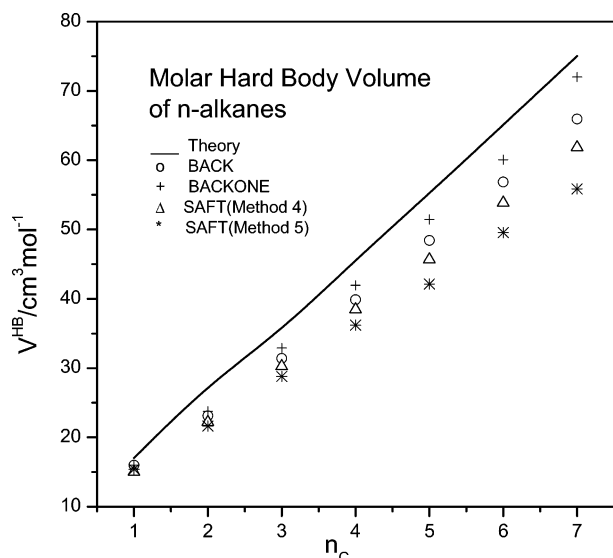
In addition to equations of the augmented van der Waals type, we studied also the SAFT (statistical associating fluid theory) EOS, which reads as

$$\frac{PV}{RT} = Z_{\text{S}}^{\text{rep}} + Z_{\text{S}}^{\text{att}}$$

where

$$Z^{\text{rep}} = Z^{\text{hs}} + Z^{\text{chain}} = mZ^{\text{CS}} - (m-1)\left(1 + y\frac{\partial\ln g(1)}{\partial y}\right) \tag{14}$$

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Figure 4. Molar hard body volume, $\mathcal{V}$, of *n*-alkanes from theory and several equations of state.

TABLE 4: Hard Body Molar Volumes (cm³ mol⁻¹) from the Present Theory and from BACK(B), BACKONE(M), and SAFT(S) Equations of State

| compound	$\mathcal{V}$	$\mathcal{V}_B$	$\mathcal{V}_M$	$\mathcal{V}_S$
argon	12.39	12.06	11.99	
krypton	15.59	15.18		
xenon	20.03		18.90	
nitrogen	14.28		14.52	
oxygen	12.52	11.81	11.85	
carbon monoxide	16.17	14.66		
carbon dioxide	19.19	14.66	15.33	
fluorine	12.17			
chlorine	21.54	19.86		
methane	17.03	15.98	15.98	15.02
ethane	27.12	23.01	23.78	22.21
propane	35.80	31.40	32.89	30.27
n-butane	45.52	39.88	41.94	38.47
n-pentane	55.27	48.43	51.48	45.69
n-hexane	65.13	56.86	60.07	53.86
n-heptane	75.04	65.95	72.02	61.86
neopentane	55.39	48.51	51.61	
ethylene	22.97	20.64	21.38	
cyclopropane	33.12	19.66		
cyclobutane	42.49	34.18		
cyclopentane	50.22	40.84		
cyclohexane	60.94	48.25	51.41	53.60
acetylene	21.69			
benzene	43.96	40.50	42.39	42.82
toluene	58.84			
naphthalene	71.56			

Here Z^{CS} stands for the Carnahan−Starling[25] expression (most frequently used) and $g(1)$ is the corresponding contact value of the HS radial distribution function; m is the number of segments in a chain molecule.

From the expression for the second virial coefficient we conjecture that

$$\alpha = (m+1)/2 \qquad (15)$$

Adidharma and Radosz[26] studied six methods (models) of determining parameters m, $\mathcal{V}_S$, and T_0 of SAFT EOS for series of *n*-alkanes; they concluded that from all the considered approaches methods 4 and 5 (based on the analytic distribution function and temperature dependent u/k) yielded the most reliable parameters. Values of α_S determined on the basis of m from method 4 are listed in the fifth column of Table 3 and
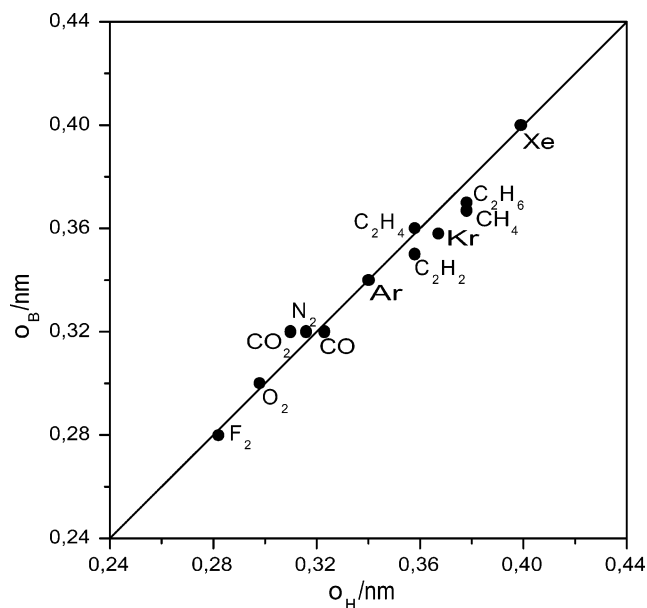
Figure 5. Hard sphere diameters from the correlation of the second virial coefficients vs values from the heats of vaporization.

values of $\mathcal{V}_S$ in the last column of Table 4. As expected, values of α_S in comparison with theoretical α are systematically larger but linearly dependent; the corresponding $\mathcal{V}_S$ are linearly dependent on $\mathcal{V}$, too, but are consistently lower. On the other hand, values of the nonsphericity parameter of *n*-alkanes determined within method 5 [taking the linear dependence of m on the number of C atoms, n_C, so that $\alpha_S = 1 + (n_C - 1)/6$], differ considerably from theoretical α values, see Figure 3. The characteristic volumes from method 5 are even smaller than those from method 4. Thus, parameters found within method 4 are more reliable than those from method 5.

From these examples it follows that the theoretical geometric quantities determined in this work make it possible to discern between sets of parameters and, more generally, between different methods/equations used for correlation of the *P-V-T* behavior of fluids.

In Figure 5 we compare σ-values obtained in this work for low-molecular compounds with the same parameter determined in the correlation of the second virial coefficient to an expression proposed for the Kihara pair interaction potential.[3] A fair agreement for all the low-molecular compounds indicates a possibility to estimate the σ parameter of the Kihara pair potential in the expression for B on the basis of ΔH^{vap}; this might be important in the case of higher molecular compounds where often insufficient B vs T data are available.

4. Conclusion

In this paper we refer to the EFHS geometric characteristics of some compounds with linear, planar, and spatial molecules. We analyzed our previous results for models of *n*-alkanes and found regularities, linear dependence of the reduced "mean radius", surface area and volume on the number of C atoms in the molecule. These three quantities make it possible to calculate the nonsphericity parameter. To determine the hard body molar volume we determined the HS diameters from the heat of vaporization in the temperature range near to the normal boiling point of the studied compounds. The calculated theoretical quantities R^e, S^e, and V^e reduce the number of necessary parameters in the formulas to correlate the second virial coefficient or the *P-V-T* data; they can be used also for prediction of the hard body free energy and isotropic−nematic transition.

When we compared theoretical values of α and $\mathscr{V}$ with those adjusted to experiments within the augmented van der Waals equations of state, BACK and BACKONE, we have found certain discrepancies, probably due to the insufficient dependence of the attractive term on the nonsphericity of the nonspherical molecules in the former and too large value of α_M for one of the reference fluids (ethane) in the latter cases. Similarly, theoretical α and $\mathscr{V}$ values enable us to discern between sets of parameters from different approaches, as demonstrated on the comparison of methods developed for the SAFT equation of state.

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