

Virial coefficients and equation of state of hard alkane models

C. Vega, S. Lago, and B. Garzón

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

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The virial coefficients up to the fifth of hard conformers of alkanes have been evaluated numerically. The conformers were selected by using the rotational isomeric state approximation. The effect of branching and length of the chain on the anisotropy of alkanes is discussed and a relation between the nonsphericity parameter α and the acentric factor ω for this kind of molecule is proposed. We modified the equation of state for tangent hard spheres first proposed by Wertheim [M. S. Wertheim, *J. Chem. Phys.* **87**, 7323, (1987)] to allow for overlapping of the constituting hard spheres. This modified version predicts with high accuracy the virial coefficient of the hard conformers of alkanes. Moreover comparison of this equation of state with simulation results of repulsive models of n -alkanes reveals very good agreement. The effect of condensed phase effect on the conformational equilibria of n -alkanes up to n -octane is analyzed.

I. INTRODUCTION

The statistical mechanics of spherical and linear molecules have received much attention during the last two decades so that a fairly good understanding of the liquid behavior of this kind of molecule has been achieved.^{1,2} Among the techniques used, perturbation theory³⁻⁵ seems one of the most promising. In perturbation theory the pair potential is split into a reference part containing all the repulsive forces and a perturbation part which includes the attractive ones. The knowledge of the thermodynamic and structural properties of purely repulsive models appears as crucial in this kind of treatment. During the last decade a great amount of effort has been devoted to the study of molecules possessing internal flexibility. Computer simulation studies of flexible chain models either by Monte Carlo⁶⁻⁹ (MC) or by molecular dynamics¹⁰⁻¹⁴ (MD) techniques have appeared, and also several theoretical treatments for this kind of molecule have been proposed. At this stage it seems reasonable to try to extend perturbation theory to flexible models and some recent work points to that direction.^{15,16} A key ingredient in that extension is a knowledge of the thermodynamic and structural properties of hard chain models which constitute the natural reference system for this kind of molecule. In a series of papers Wertheim¹⁷⁻²¹ has proposed a theory for associated fluids (i.e., hydrogen bonded fluids). The Wertheim approach also allows the study of behavior of chain molecules since in the limit of infinitely strong association, chain molecules are obtained from the initial monomer liquid.²¹ As a consequence, Wertheim and independently Chapman *et al.*²² have proposed an equation of state (EOS) for chain molecules made up of tangent spheres. This EOS arises from a first order perturbation expansion of the properties of the chain fluid around those of the hard sphere reference system. The results obtained from this EOS for different flexible chains seems to be satisfactory. The ability of this EOS for describing simple flexible hard models, as for instance, a hard model of an n -alkane, remains to be tested. In particular, a problem to be solved is how to extend Wertheim EOS which was originally derived for tangent spheres to

the physically more interesting case of overlapping spheres. In that respect Boublik has illustrated a relationship between m , the number of monomer units that make up the chain and α the nonsphericity parameter of hard convex bodies.^{23,24}

In this work we shall focus on the study of hard models of n -alkanes from butane up to octane. We shall use the rotational isomeric state approximation²⁵ (RIS) so that we shall regard the n -alkane as a multicomponent mixture of conformers in chemical equilibrium. In order to gain some insight into the differences of each of the conformers that make up the n -alkane, we shall evaluate numerically the virial coefficients up to the fifth for each of the conformers separately. Then, we shall compare the predictions for the virial coefficients of different proposed theoretical EOS with those obtained numerically. We shall show how a modification of Wertheim EOS allowing for overlapping of the constituent hard spheres successfully predicts the virial coefficients of all the studied conformers. This modification of Wertheim EOS exhibits also very good agreement with computer simulation data of butane, pentane, and octane repulsive models so that it may be used as an EOS for the reference system of n -alkanes. Finally, we shall analyze the role of packing effects on conformational equilibria of short (up to octane) n -alkanes hard models.

II. VIRIAL COEFFICIENTS OF HARD n -ALKANES

We shall present the model that will be used throughout this work. The methyl CH_3 and methylene groups CH_2 of the alkanes are represented as hard spheres of equal diameter d . The bond length and bond angle will be denoted as l and θ , respectively. We fix θ to its tetrahedral value so that $\theta = 109.5$ degrees. Once θ is fixed only two variables are needed to define the geometry of the model, namely, the number of spheres and $L^* = l/d$ which is the reduced bond length. In Fig. 1 we illustrate the geometry of the model for $n=4$ (n -butane). For L^* we adopt the value $L^* = 0.4123$. This value appears as reasonable since it is very close to the one obtained by taking $l = 1.53$ Å (the C-C bond length) and $d = 3.70$ Å. As we shall show below,

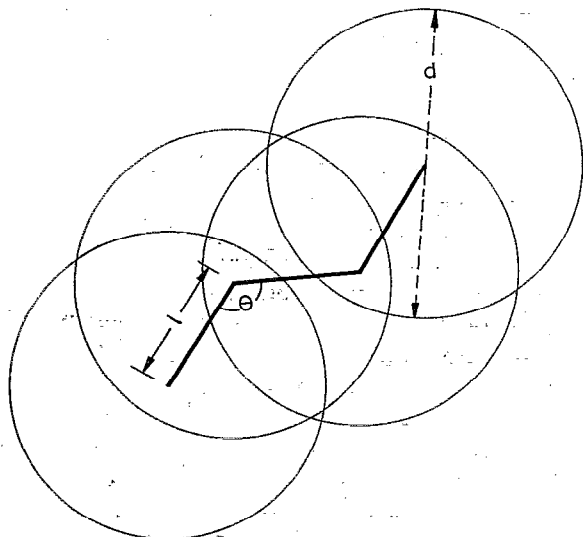


FIG. 1. Geometry of the hard n -alkane model. The bond length is denoted as l and the bond angle is θ . The diameter of the hard sphere associated with the site is d .

$d \approx \sigma$, the length parameter in a site-site Lennard-Jones interaction model. Furthermore, with similar choices of l and σ a fairly good description of the second virial coefficient of n -alkanes have been achieved using this model.²⁶ Our choice of L^* is then physically meaningful. For each bond (excluding the last and the first) we shall assume the existence of a torsional potential with three relative minima, $\phi=0$ which correspond to the *trans* conformer (t), $\phi=120$ which correspond to the *gauche*⁺ (g^+), and $\phi=-120$ which is the *gauche*⁻ (g^-) conformer. Following Flory,²⁵ we shall assume that each bond spends most of the time close to one of these relative minima. We substitute in this way the continuum of torsional angles by a discrete set. For instance, n -pentane is regarded as a mixture of $tt, tg^+, tg^-, g^+g^+, g^+g^-, g^-g^-$ conformers or grouping together similar species tt, tg, gg, gg' . As illustrated by Flory,²⁵ the gg' conformation is highly improbable due to a steric hindrance and this fact receives the name of pentane effect.²⁵ In this work we shall suppress all the conformers including a gg' (or $g'g$) sequence since their probability of occurrence is very small.

We evaluate the molecular volume for each conformer, V , by using a MC procedure with 10^7 sampling points as described by Alejandro *et al.*²⁷ The virial coefficients up to the fifth, B_2 to B_5 , were evaluated for each conformer by using the method of Ree and Hoover.²⁸ We typically generate 10^7 independent configurations for their evaluation. Results with the obtained virial coefficients are shown in Table I for butane to heptane and in Table II for octane. In the last column we show the value of the nonsphericity parameter α obtained from the equation²⁹ (see discussion below)

$$B_2^* \equiv B_2/V = 1 + 3\alpha. \quad (1)$$

For a hard body B_2 is a measure of the averaged excluded volume so that α is a measure of the quotient of the

TABLE I. Reduced virial coefficients $B_i^* = B_i/V^{i-1}$ of hard alkanes conformers. We present the results for the conformers of n -butane, n -pentane, isopentane, neopentane, n -hexane, and n -heptane. The value of L^* is $L^*=0.4123$. We used 10^7 MC independent configurations to determine B_i^* . V stands for the molecular volume.

Conformer	V/d^3	B_2^*	B_3^*	B_4^*	B_5^*	α
<i>n</i> -butane						
<i>t</i>	1.430 85	4.6924	13.097	25.16	38.64	1.2308
<i>g</i>	1.424 77	4.5514	12.580	24.48	38.27	1.1838
<i>n</i> -pentane						
<i>tt</i>	1.731 19	4.9791	14.383	27.59	42.20	1.3264
<i>tg</i>	1.725 87	4.8393	13.879	27.16	42.09	1.2798
<i>gg</i>	1.719 23	4.6791	13.269	26.35	41.24	1.2264
Isopentane ^a						
syn	1.715 24	4.6267	13.035	25.83	41.11	1.2089
anti	1.721 18	4.7323	13.461	26.57	41.76	1.2441
Neopentane	1.71725	4.6540	13.221	26.47	42.22	1.2180
<i>n</i> -hexane						
<i>ttt</i>	2.032 47	5.2760	15.716	29.92	44.45	1.4253
<i>ttg</i>	2.026 14	5.1384	15.325	30.12	45.60	1.3795
<i>tgt</i>	2.026 02	5.1421	15.256	29.77	45.14	1.3807
<i>tgg</i>	2.021 14	4.9646	14.649	29.46	46.52	1.3215
<i>gtg</i>	2.020 31	4.9845	14.735	29.59	45.92	1.3282
<i>gtg'</i>	2.020 49	5.0113	14.746	29.19	45.07	1.3371
<i>ggg</i>	2.014 56	4.8275	14.013	28.23	44.93	1.2758
<i>n</i> =7						
<i>n</i> -heptane						
<i>tttt</i>	2.332 33	5.5862	17.156	32.26	46.34	1.5287
<i>tttg</i>	2.327 54	5.4463	16.738	32.59	47.80	1.4821
<i>ttgt</i>	2.327 19	5.4438	16.771	32.75	47.48	1.4813
<i>tggg</i>	2.320 45	5.2682	16.166	32.72	50.01	1.4227
<i>tggt</i>	2.321 18	5.2930	16.145	32.16	48.56	1.4310
<i>gttg'</i>	2.320 62	5.3237	16.164	31.78	47.75	1.4412
<i>gttg</i>	2.321 89	5.2496	16.123	32.86	50.77	1.4165
<i>gttg'</i>	2.320 37	5.3079	16.345	32.95	49.71	1.4360
<i>gttg'</i>	2.320 16	5.2574	16.186	33.16	51.27	1.4191
<i>tggtg</i>	2.315 16	5.1234	15.467	31.46	49.91	1.3745
<i>gttg</i>	2.314 68	5.0269	15.106	31.15	49.98	1.3423
<i>gtg'g'</i>	2.315 13	5.1518	15.578	31.53	49.34	1.3839
<i>gggg</i>	2.309 53	4.9922	14.811	30.12	48.75	1.3307

^aThe notation anti-syn in isopentane refers to the antiperiplane and synclinal conformers, respectively. Furthermore, synclinal corresponds to conformer I of Ref. 9.

excluded volume to the molecular volume. For a sphere $\alpha=1$ and for a nonspherical body $\alpha>1$. We shall take Eq. (1) as our definition of α . This definition was first proposed by Rigby.²⁹ The estimated uncertainty in B_2^* , B_3^* , B_4^* , B_5^* is of about 0.02%, 0.05%, 0.3%, and 2%, respectively. For each n -alkane the all-*trans* conformer is always the most anisotropic one (i.e., with the highest value of α) whereas the all-*gauche* conformer is usually the most spherical (i.e., with the lowest value of α). That corresponds to the intuitive idea that a folded chain is more spherical than an extended chain.

In general, as the number of *gauche* bonds in the molecule increases α decreases. Moreover, α seems to be a very sensitive parameter. Thus the differences in volume among the conformers of each n -alkane amounts to about 1%, whereas the differences in α range from 4% in n -butane to 23% in n -octane. In other words, differences in volume between conformers of a given alkane are small whereas

TABLE II. As in Table I for the conformers of *n*-octane.

Conformer	V/d^3	B_2^*	B_3^*	B_4^*	B_5^*	α
<i>n</i> -octane						
ttttt	2.635 17	5.8953	18.592	34.36	47.12	1.6318
ttttg	2.627 37	5.7609	18.252	35.08	49.54	1.5870
tttgt	2.628 70	5.7558	18.235	35.14	49.78	1.5853
ttgtt	2.627 74	5.7428	18.412	36.19	49.68	1.5809
ttggg	2.623 66	5.5765	17.629	35.30	51.15	1.5255
ttggt	2.621 29	5.5428	17.717	36.61	55.01	1.5143
gtttg	2.620 55	5.6231	17.837	35.47	50.61	1.5410
gtttg'	2.622 96	5.6241	17.764	35.13	51.30	1.5413
gttgt	2.620 50	5.6161	17.887	35.96	51.31	1.5387
gttgt'	2.620 60	5.5637	17.715	36.19	54.13	1.5212
gttgt	2.622 06	5.5954	17.750	35.54	51.23	1.5318
gtg'tt	2.623 02	5.6290	17.705	34.74	50.16	1.5430
tgtgt	2.622 92	5.6041	17.600	34.75	51.20	1.5347
tgtgt'	2.622 11	5.6362	17.601	34.18	50.26	1.5454
gggtt	2.617 60	5.4260	16.984	34.65	52.71	1.4753
ggttg	2.615 42	5.4442	17.197	35.51	53.96	1.4814
ggttg'	2.615 03	5.3570	16.899	35.71	57.42	1.4523
tgggt	2.616 03	5.4403	17.065	34.92	54.01	1.4801
tggtg	2.616 24	5.2941	16.560	34.81	55.54	1.4314
tggtg'	2.616 41	5.4403	17.065	34.92	54.01	1.4801
tgtgg	2.615 64	5.3408	16.601	34.04	52.60	1.4469
tgtg'g'	2.615 89	5.4668	17.058	34.30	52.01	1.4889
gttgt	2.615 95	5.4551	17.072	34.62	52.55	1.4850
gtg'tg	2.616 44	5.5125	17.115	33.64	50.11	1.5042
gtg'tg'	2.616 52	5.4810	17.114	34.28	51.70	1.4937
ggggt	2.611 46	5.2900	16.265	33.21	52.33	1.4300
gggtg	2.610 83	5.1833	15.963	33.44	54.42	1.3944
gggtg'	2.610 07	5.3157	16.447	33.63	52.08	1.4386
gg'tgg	2.610 70	4.9760	14.923	31.10	51.22	1.3253
gg'tg'g'	2.611 14	5.2999	16.412	33.84	53.28	1.4333
ggggg	2.605 23	5.1644	15.639	31.89	51.55	1.3882

differences in α (excluded volume) are large and these differences increase dramatically with the chain length. The behavior of B_3^* , B_4^* , B_5^* is highly correlated with that of B_2^* and in general the larger B_2^* is the larger are B_3^* , B_4^* , B_5^* . For pentane we have calculated the virial coefficients for several isomers (not to confuse with conformers) so that the effect of branching on virial coefficients could be evaluated. In Table I we have results for *n*-pentane, iso-pentane (2 methyl butane), and neopentane (2,2 dimethylpropane). Branching decreases the value of α confirming that branched alkanes tend to be more spherical than *n*-alkanes.

One can see from Table II that the number of conformers rapidly increases with the length of the chain so that an exhaustive enumeration of conformers beyond *n*-octane becomes cumbersome. We now compare the predictions of different EOS for B_i^* with the numerical results. One possible EOS is the improved scaled particle theory³⁰ (ISPT). This EOS writes

$$Z = \frac{p}{\rho kT} = \frac{1 + (3\alpha - 2)y + (3\alpha^2 - 3\alpha + 1)y^2 - \alpha^2 y^3}{(1 - y)^3}, \quad (2)$$

where ρ is the number density, y is the packing fraction defined as $y = \rho V$ with V being the molecular volume, and α is the nonsphericity parameter. For hard convex bodies

the second virial coefficient can be evaluated analytically³⁰ and therefore α can be obtained from Eq. (1) so that α is given by

$$\alpha = RS/3V, \quad (3)$$

where R is the mean radius of curvature and S is the molecular surface.³⁰

For hard convex bodies Eq. (1) and Eq. (3) provide identical values of α . When the molecule is not convex then R is ill-defined and therefore Eq. (3) cannot be considered as a definition of α . In some cases good results have been obtained for nonconvex bodies taking Eq. (3) as a definition of α with R taken from a convex body of similar shape to that of the molecule.³⁰ However, for some of the conformers of Tables I and II it is hard to visualize any convex body of shape close to that of the real molecule and because of that we shall abandon this route to α . Equation (1), however, provides a reliable and well defined route to α for convex and nonconvex bodies. We shall therefore take Eq. (1) as our definition of α . Wertheim²¹ and Chapman *et al.*²² have recently proposed an EOS for chain models made up of tangent hard spheres. This equation reads

$$Z = m \frac{(1 + y + y^2 - y^3)}{(1 - y)^3} - (m - 1) \frac{(1 + y - y^2/2)}{(1 - y)(1 - y/2)}, \quad (4)$$

where m is the number of hard spheres of the chain. The problem with Eq. (4) is that as written it is not directly applicable to our hard *n*-alkane model (see Fig. 1) since our chain is not made up of tangent spheres. A way to overcome this problem was proposed by Boublik²³ and Walsh and Gubbins.³¹ The second virial coefficient of Eq. (2) and Eq. (4) reads

$$B_2^* = (1 + 3\alpha) \quad (\text{ISPT}), \quad (5)$$

$$B_2^* = 1.5m + 2.5 \quad (\text{Wertheim}). \quad (6)$$

By equating Eq. (5) and Eq. (6) we obtain

$$m = 2\alpha - 1, \quad (7)$$

so that substituting Eq. (7) into Eq. (4) we obtain

$$Z = (2\alpha - 1) \frac{(1 + y + y^2 - y^3)}{(1 - y)^3} - (2\alpha - 2) \frac{(1 + y - y^2/2)}{(1 - y)(1 - y/2)}. \quad (8)$$

Equations (1) and (8) constitute our modified version of Wertheim EOS (MW). We should emphasize that the MW EOS differs in a few aspects of the original Eq. (4). First Eq. (8) is valid not only for tangent spheres ($L^* = 1$) but also when $L^* < 1$ where Eq. (4) is not valid. Second, Eq. (4) (which arises from a first order perturbation theory) predicts that for an m -mer with bond angle θ , Z is independent of θ . In Eq. (8) the dependence of Z with θ in an m -mer is established through Eq. (1), that is, through the differences in the second virial coefficient. One interesting feature of Eq. (8) is that it predicts that all the virial coefficients from B_2^* to B_5^* are linear functions²³ of α . Be-

TABLE III. Average deviation ΔB_k [see Eq. (9) of the text] over all the conformers between the theoretical predictions and the numerical values of the first virial coefficients.

EOS	ΔB_3	ΔB_4	ΔB_5
<i>n</i> -butane			
ISPT ^a	-1.7	-5.2	-2.9
Nezbeda ^b	-2.4	-10.3	-12.0
Boublik ^c	-1.7	-10.3	-12.6
MW ^d	1.30	-2.2	-0.2
<i>n</i> -hexane			
ISPT ^a	-2.3	-5.7	-0.4
Nezbeda ^b	-3.9	-14.6	-16.4
Boublik ^c	-2.3	-13.7	-16.3
MW ^d	1.1	-2.8	1.7
<i>n</i> -octane			
ISPT ^a	-3.0	-6.5	1.3
Nezbeda ^b	-5.8	-19.4	-21.8
Boublik ^c	-3.0	-17.2	-20.3
MW ^d	-0.1	-4.7	1.7
Global from <i>n</i> -butane to <i>n</i> -octane (including <i>n</i> -pentane and <i>n</i> -heptane)			
ISPT ^a	-2.4	-6.0	-1.3
Nezbeda ^b	-4.1	-14.8	-17.7
Boublik ^c	-2.4	-13.8	-16.8
MW ^d	0.7	-3.4	0.5

^aReference 30.

^bReference 32.

^cReference 33.

^dThis work.

cause of Eq. (1) that means that B_3^*, B_4^*, B_5^* according to EOS are linear functions of B_2^* . We should mention that Eq. (8) was first proposed by Boublik,²³ although Boublik used Eq. (3) as the definition of α instead of our choice given by Eq. (1).

In addition to Eq. (2) and Eq. (8), we shall analyze the results of two other EOS which are the most reliable ones in the case of hard convex bodies. These are the EOS proposed by Nezbeda³² and by Boublik.³³

We shall define ΔB_k as

$$\Delta B_k = \frac{100}{n_{\text{conf}}} \sum_{i=1}^{n_{\text{conf}}} \frac{(B_{k,i}^{\text{EOS}} - B_{k,i}^{\text{MC}})}{B_{k,i}^{\text{MC}}}, \quad (9)$$

where n_{conf} stands for the number of conformers of the alkane. Usually, the sign of the deviations in Eq. (9) is the same for all the conformers of a given *n*-alkane so that the sign of ΔB_k is meaningful. Therefore, we do not take absolute values in Eq. (9).

In Table III we summarize the deviations for *n*-butane, *n*-hexane, *n*-octane, and the average of the *n*-alkanes from butane up to octane. The virial coefficients of Boublik EOS and Nezbeda EOS are usually too low and the errors are important. The MW yields the best predictions of the virial coefficients, making the results of the ISPT somewhat worse. The small error in B_2^* is due to a cancellation of terms of different sign in Eq. (9). Overall, the MW gives very good results for the virial coefficients. This is further illustrated in Fig. 2.

In Tables I and II we have shown the values of α for all the conformers of each alkane. However, one would gen-

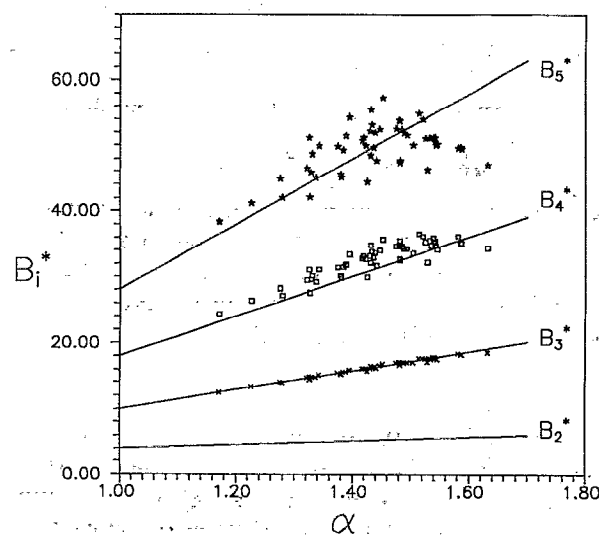


FIG. 2. Reduced virial coefficients $B_i^* = B_i/V^{i-1}$ as a function of α . The solid lines are the results from Eq. (8) and the symbols are the numerical results of Table I and II for the *n*-alkanes up to octane.

erally be more interested in determining for a given alkane an averaged value of α which will be denoted as $\bar{\alpha}$. Since the alkane is within our model, a mixture of conformers this is equivalent to find a mixing rule so that $\bar{\alpha}$ can be determined from the α_i of the different conformers. We shall use the simple prescription

$$\bar{\alpha} = \sum_{\text{conformers}} x_i(T) \alpha_i, \quad (10)$$

where the summation runs over all the conformers of the given *n*-alkane given in Tables I and II. The mixing rule given by Eq. (10) can be obtained from other proposed mixing rules³⁴ by neglecting differences in volume and surface area of the conformers since they are almost identical. The problem to obtain $\bar{\alpha}$ is to find the set of x_i . By now, we shall identify x_i with the ideal gas population of conformer *i*. We shall assume that the intramolecular Hamiltonian of a molecule with fixed bond angles and lengths may be written as

$$H^{\text{intra}} = \sum_{j=i>5} u_{ij}^{\text{HS}}(r_{ij}) + \sum_{\text{bonds}} u_{\text{tor}}(\phi_i), \quad (11)$$

where the first sum is over sites of the molecules being u^{HS} a hard sphere potential, the second sum is over bonds (excepting the last and the first), ϕ_i denotes the torsional angle of bond *i*, and u_{tor} is the torsional potential. First let us transform the continuous torsional potential u_{tor} into the RIS approximation. For that purpose we shall set the molar fraction of the *trans* conformer x_t of *n*-butane given by

$$x_t = \frac{\int_{-\pi/3}^{\pi/3} \exp[-u_{\text{tor}}(\phi)/kT] d\phi}{\int_{-\pi}^{\pi} \exp[-u_{\text{tor}}(\phi)/kT] d\phi} \quad (12)$$

to that obtained from the RIS approximation x_t' which is given by

$$x_i' = \frac{1}{1 + 2 \exp(-D/kT)} \quad (13)$$

By imposing the condition that $x_i = x_i'$ we find that

$$D(T; [u_{\text{tor}}]) = -kT \ln[0.5(1 - x_i)/x_i], \quad (14)$$

where the notation $D(T; [u_{\text{tor}}])$ indicates that D is a function of T and a functional of u_{tor} . Equation (14) transforms the problem into the RIS approximation. The energy of a conformer E_i with the Hamiltonian of Eq. (11) is now given within the RIS approximation by

$$E_i = c_i D(T; [u_{\text{tor}}]) \quad (15)$$

where c_i stands for the number of *gauche* bonds of conformer i . In Eq. (15) we have suppressed the first term on the right-hand side of Eq. (11) since once the pentane effect has been taken into account by dropping the gg' sequences for short chains (up to octane) no other overlap between sites separated by four or more bonds²⁵ occurs. For longer chains that will not, in general, be true so that this term introduces the so-called excluded volume. The molar fraction of conformer i is then obtained as

$$Z = \sum \Omega_i \exp(-E_i/kT), \quad (16)$$

$$x_i = \frac{\Omega_i \exp(-E_i/kT)}{Z}, \quad (17)$$

where the summation in Eq. (16) is over all the allowed conformers and where Ω_i stands for the degeneracy of conformer i . For instance for pentane $\Omega_{ig}=4$ since we have four equivalent conformers, namely, the tg^+ , tg^- , g^+t , g^-t . Equations (12)–(17) allow us to compute the molar fraction of conformer i in the ideal gas and constitute a way of passing from the continuous potential to the RIS approximation. Proceeding in this way we have computed $\bar{\alpha}$ for the n -alkanes by using the torsional potential proposed by Rickaert and Bellemans.³⁵ For isopentane we used the torsional potential proposed by Jorgensen.⁹ In Fig. 3 we show $\bar{\alpha}$ as a function of T for all the alkanes of Table I and II. For each alkane $\bar{\alpha}$ decreases as T increases. This is due to an increase in the population of conformers with one or several *gauche* bonds (which are more spherical than the all-*trans* conformer). $\bar{\alpha}$ increases with the length of the chain and the jump in $\bar{\alpha}$ from an n -alkane to the next is of about 0.08. For neopentane $\bar{\alpha}$ is very similar to that of n -butane, smaller than that of iso-pentane and much smaller than that of n -pentane.

The parameter $\bar{\alpha}$ as defined in this section defines the nonsphericity of the molecule as related to the averaged ratio of the excluded volume to that of the molecular volume. In that sense $\bar{\alpha}$ is a measure of the nonsphericity of the molecular shape and therefore of the short range repulsive forces. Another parameter of the nonsphericity of the molecule widely used in chemical engineering is the acentric factor ω . The acentric factor³⁶ is a measure of the noncentral character of the intermolecular forces including short range and long range interactions. For a family of substances such as the alkanes with similar type of long

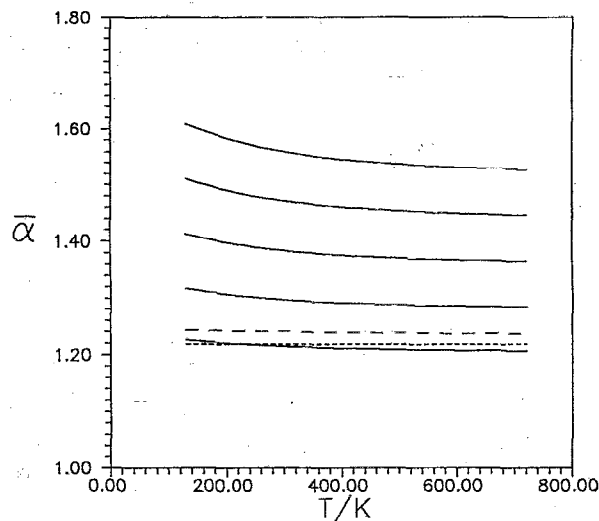


FIG. 3. Average value of the nonsphericity parameter $\bar{\alpha}$ [see Eq. (10) of the text] as a function of temperature for different alkanes. Torsional potential from Ref. 35 for n -alkanes and from Ref. 9 for isopentane were used. Solid lines from top to bottom are for n -octane, n -heptane, n -hexane, n -pentane, and n -butane. The long dashed line stands for isopentane and the short dashed for neopentane.

range dispersion forces, one may suspect that these two parameters are mutually related. This is illustrated in Fig. 4 where we see that $\bar{\alpha}$ and ω are indeed related within the family of the alkanes (n -alkanes and branched alkanes). Note the almost identical value of ω for n -butane and neopentane in agreement with the similarity found in Fig. 3 for $\bar{\alpha}$.

This section shows how the MW EOS provides reliable predictions of the virial coefficients of hard n -alkane models. We also illustrate how to transform from a continuous

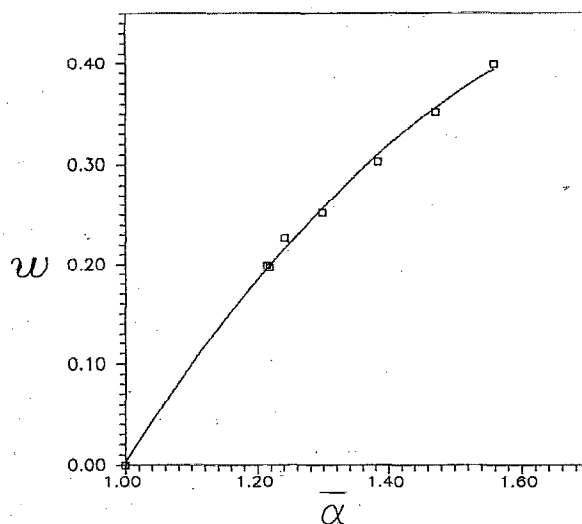


FIG. 4. Acentric factor ω of alkanes vs $\bar{\alpha}$. The experimental values of ω were obtained from Ref. 37. $\bar{\alpha}$ was evaluated at $T=298.15$ K using the torsional potential of Ryckaert and Bellemans (Ref. 35) for n -alkanes and that of Ref. 9 for isopentane. The solid line is a least squares fit to the data and is given by $\omega = -1.61089 + 2.19973\bar{\alpha} - 0.586238\bar{\alpha}^2$.

torsional potential to the RIS model and how to obtain averages over conformation population. In the next section we shall explore the possibilities of the MW EOS for predicting the fluid behavior of hard models of *n*-alkanes.

III. EQUATION OF STATE OF HARD *n*-ALKANES

In this section we are interested in studying the fluid behavior of a model whose Hamiltonian is given by

$$H = H^{\text{intra}} + H^{\text{inter}} \quad (18)$$

with H^{intra} given by Eq. (11) and H^{inter} which is the intermolecular pair potential is a site-site hard sphere potential between sites of different molecules. We again transform the problem into the RIS approximation by using Eqs. (12)–(17). Then the average value of α , namely, $\bar{\alpha}$ is obtained from Eq. (10). Analogously the packing fraction \bar{y} will be obtained as

$$\bar{y} = \rho \sum x_i V_i. \quad (19)$$

Then Eqs. (10)–(19) along with Eq. (8) constitute our theoretical approach to the EOS of the hard *n*-alkane model. All the needed quantities as α_i and V_i are given in Tables I and II. It would be desirable to compare the predictions of this EOS with some simulation results. Unfortunately, to our knowledge there is no reported simulation of hard *n*-alkane molecules. However, for butane, pentane, and octane there are some computer simulations results^{7,13,14,38} of the purely repulsive WCA potential. In those simulations $l = 1.53$ Å, $\theta = 109.5^\circ$, the torsional potential was that proposed by Ryckaert and Bellemans³⁵ and the site-site interaction was a WCA repulsive with $\sigma = 3.923$ Å and $\epsilon/k = 72$ K. In order to relate the WCA repulsive model with a hard model we shall keep the bond length and angles. We shall obtain the diameter of the corresponding hard sphere site d by using Barker-Henderson prescription³⁹ so that

$$d = \int_0^{2^{1/6}\sigma} \{\exp[-u_{\text{WCA}}(r)/kT] - 1\} dr. \quad (20)$$

Typical values for $L^* = l/d$ obtained in this way range in the interval (0.39, 0.4123) depending on the temperature. That generates a new problem since in Tables I and II we report values of α only for the case $L^* = 0.4123$. To overcome this problem we have calculated B_i^* ($i = 2, 3, 4, 5$) for the model of Fig. 1 with $L^* = 0.3900$ instead of $L^* = 0.4123$. The obtained results for *n*-butane, *n*-pentane, and *n*-hexane are shown in Table IV. We see how α is slightly modified by a change in L^* . Since the changes are small we may expect that a linear interpolation of α for each conformer should provide a fairly good estimation of α for intermediate values of L^* .

The computation of the molecular volume for any value of L^* can be easily done numerically. Afterward, we received a FORTRAN program to calculate this volume analytically. We checked our numerical results with the analytical procedure proposed in Ref. 40 and found perfect agreement. Equation (20) converts the WCA conformer into a hard *n*-alkane with a known value of α_i and V_i .

TABLE IV. Virial coefficients of hard *n*-alkanes (*n*-butane to *n*-hexane) conformers with $L^* = 0.3900$. We used 10^6 independent configurations to determine the virial coefficients.

Conformer	V/d^3	B_2^*	B_3^*	B_4^*	B_5^*	α
<i>n</i> -butane						
<i>t</i>	1.3845	4.6257	12.769	24.45	38.20	1.2086
<i>g</i>	1.3767	4.4946	12.285	23.67	36.72	1.1649
<i>n</i> -pentane						
<i>tt</i>	1.6692	4.8941	13.970	26.82	41.31	1.2980
<i>tg</i>	1.6614	4.7618	13.482	26.11	40.43	1.2539
<i>gg</i>	1.6536	4.6055	12.889	25.41	39.55	1.2018
<i>gg'</i>	1.6099	4.4592	12.173	23.71	37.17	1.1531
<i>n</i> -hexane						
<i>ttt</i>	1.9544	5.1679	15.165	28.70	39.86	1.3893
<i>ttg</i>	1.9466	5.0360	14.781	28.92	43.98	1.3453
<i>tgt</i>	1.9463	5.0408	14.737	28.60	44.33	1.3469
<i>tgg</i>	1.9394	4.8703	14.143	28.17	44.37	1.2901
<i>gtg</i>	1.9392	4.8882	14.216	28.28	43.14	1.2960
<i>gtg'</i>	1.9391	4.9183	14.250	27.96	42.83	1.3061
<i>ggg</i>	1.9313	4.7405	13.545	26.95	42.50	1.2468

Applying Eqs. (10)–(19) allowed us to compute $\bar{\alpha}$ and \bar{y} which can be readily substituted into Eq. (8) to obtain the pressure through the isotherm. The results obtained in this way are illustrated in Fig. 5 and in Table V. The agreement between the simulation and the theoretical results is fairly good. Similar agreement between Wertheim equation and Monte Carlo simulation has also been obtained for neopentane,⁴¹ but these authors preferred to use a different type of equation. Simulation of longer hard *n*-alkane models would be desirable to check the predictions of the proposed MW EOS for longer chains.

One important point of our treatment is to assume that the population of each conformer can be taken from the ideal gas distribution as given by Eqs. (12)–(17). We therefore neglect condensed phase effects on the conformer population. One may argue that the error introduced by that approximation into the equation of state would be large. We analyze this point and the conformational equilibria of the fluid phase in the next section.

IV. CONFORMATIONAL EQUILIBRIA OF HARD *n*-ALKANES IN FLUID PHASE

We already mentioned that according to the RIS approximation, an *n*-alkane can be regarded as a multicomponent mixture in chemical equilibrium. For a given density and temperature we can write the Helmholtz free energy as

$$A/NkT = \sum x_i \ln(x_i/\Omega_i) + \sum x_i c_i D/(kT) + A^{\text{res}}(\mathbf{x})/NkT, \quad (21)$$

$$A^{\text{res}}(\mathbf{x})/NkT = \int_0^\rho [Z(\mathbf{x}, \rho') - 1]/\rho' d\rho', \quad (22)$$

$$\sum x_i = 1. \quad (23)$$

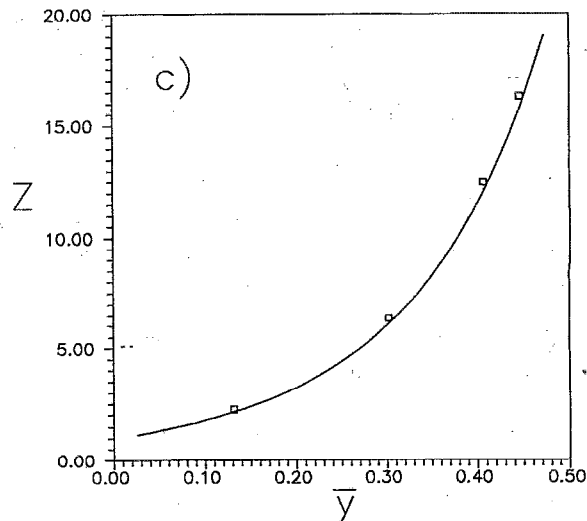
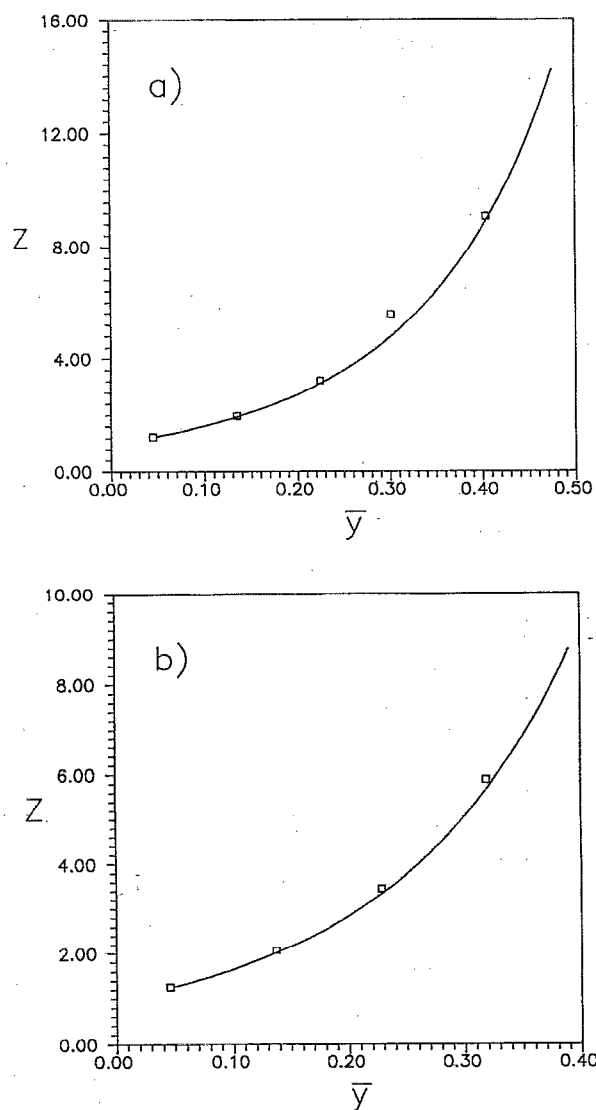


FIG. 5. Compressibility factor Z for a WCA purely repulsive model. The squares are simulation results from Ref. 13 for n -butane and n -pentane and from Ref. 38 for n -octane. The solid line stands for the MW EOS [Eq. (8) of the text]. (a) Results for n -butane. (b) Results for n -pentane. (c) Results for n -octane.

It is implicit in this equation that we are dealing with short chains (i.e., up to n -octane) so that the only effect of the excluded volume is to prevent the gg' sequence. The summation in Eq. (21) is therefore over all the conformers presented in Tables I and II. The vector \mathbf{x} denotes the set

TABLE V. Conformational equilibria of n -butane as obtained from free energy minimization. The states A, B, C corresponds to the notation of Ref. 7. The MC results are also from Ref. 7. x_i^{theo} corresponds to the molar fractions of *trans* conformer obtained from Eq. (24) of the main text and x_i^{ideal} corresponds to the ideal gas population of the *trans* conformer. Numbers in brackets are the figures where some uncertainty exists.

	A	B	C
x_i^{ideal}	0.770 680 1	0.657 604 0	0.564 648 3
x_i^{MC}	0.729(6)	0.611(6)	0.528(5)
x_i^{theo}	0.710	0.592	0.504
$Z(x_i^{\text{ideal}})$	14.07	12.31	10.72
$Z(x_i^{\text{theo}})$	14.02	12.26	10.68
Z^{MC}	13.9(1)	12.3(1)	10.7(1)
$A(x_i^{\text{ideal}})/NkT$	5.303	4.627	3.983
$A(x_i^{\text{theo}})/NkT$	5.294	4.618	3.976

of x_i . The first two terms on the right-hand side of Eq. (21) represent the ideal contribution to the free energy whereas the last one is the residual part. For T and ρ constant the condition of thermodynamic equilibrium is that A be a minimum with respect to all the independent x_i [which is the number of conformers minus one due to the constraint given by Eq. (23)]. In fact, it is easy to show that when A^{res}/NkT is zero then the minimum of Eq. (21) is obtained when the x_i satisfy Eq. (17). Moreover, minimizing Eq. (21) with respect to the independent x_i is equivalent to imposing the condition of equal chemical potential for all the conformers. Equation (8) is our expression for the compressibility factor of the n -alkane. The dependence of Z with \mathbf{x} represented by $Z(\mathbf{x})$ is established through Eqs. (10) and Eq. (19). Now, and that is the difference with the previous section, we allow the x_i to be independent variables so that we shall not impose the x_i obtained from the ideal gas population. We shall obtain the x_i by solving

$$\left(\frac{\partial A/NkT}{\partial x_i} \right) = 0 \quad i=1, \dots, n_{\text{conf}}-1 \quad (24)$$

along with Eqs. (21)–(23) and Eq. (8). The idea of minimizing A for determining conformational equilibria was first proposed by Enciso *et al.*⁴² in their study of butane.

When $Z(x)$ is obtained from Eq. (8) then the integral of Eq. (22) can be performed analytically to yield

$$\frac{A^{\text{res}}}{NkT} = 2(\alpha - 1) \ln \left[\frac{2(1-y)^3}{(2-y)} \right] - \frac{(2\alpha - 1)(2y - 3)}{(1-y)^2} - 3(2\alpha - 1). \quad (25)$$

We have solved Eq. (24) for the n -alkanes from butane up to n -octane for several densities. We present in Table V the results for n -butane. In the previous section we compared our theoretical predictions with the MC results of Almaraz *et al.*⁷ for the WCA repulsive model by using the ideal gas population of conformers. Now after performing the free energy minimization we observed a decrease of the *trans* populations in the fluid phase. Our predictions for this decrease are in fair agreement with the shift observed in the MC simulations of this system. The origin of this shift is as follows. The *trans* and *gauche* conformers have very similar volume and therefore \bar{y} is very slightly affected by a decreases of x_i . However, the differences between α_i and α_g are important. A decreases of x_i provokes a significant decrease of $\bar{\alpha}$ and that provokes a decrease of A^{res}/NkT as can be shown from Eq. (25).

In Table VI we show the results of the conformational equilibria for n -hexane and n -heptane. In the case of hexane at $y=0.50$, there is a significant decrease in the population of the *ttt* conformer and a small decrease in the population of the *ttg* and *tgt* conformers. The population of the rest of the conformers increases. Again, we observe that the population of the more anisotropic conformers decreases in agreement with what we found for butane. Moreover, some conformers as *gtg* and *gtg'* which have identical population at zero density present now slightly different population in the fluid phase. The slightly more spherical *gtg* is favored over the *gtg'*. As a general rule those conformers with $\alpha_i > \bar{\alpha}$ will undergo a decrease in their population when going from the gas to the fluid phase and the opposite behavior is found when $\alpha_i < \bar{\alpha}$. Moreover, the magnitude of the change (and the sign) in conformer population is roughly proportional to the magnitude of $(\bar{\alpha} - \alpha_i)$. For instance, in n -hexane the all-*trans* conformer undergoes a bigger decrease than conformers having a *gauche* bond. The results for n -heptane show the same trends that those found for n -hexane.

Another important point is that the differences between Z and A obtained from the free energy minimization and obtained by imposing ideal gas population are small. This is true for butane and for longer n -alkanes. The differences are probably smaller than the error due to the use of an approximate EOS. This suggests that if only the thermodynamic description of the n -alkane is important, then taking x from the ideal gas distribution will introduce minor errors whereas it constitutes a very simple procedure. The free energy minimization constitute a more rigorous route, but it yields only a small correction to A and Z and

TABLE VI. Conformer population of hard models of n -hexane and n -heptane as obtained from the solution of Eq. (24) of the text. The reduced density ρ^* is defined as $\rho^* = \rho d^3$, where d is the diameter of the hard sphere site. The results for $\rho^*=0$ corresponds to the ideal gas population. The intermediate density corresponds approximately to $\bar{y}=0.20$ whereas the last one corresponds to about $\bar{y}=0.50$. The last two columns show the values of Z and A/NkT . Numbers in brackets were calculated using ideal gas population.

n -hexane	$\rho^*=0$	$\rho^*=0.10$	$\rho^*=0.25$
<i>ttt</i>	0.3110	0.297 613 6	0.220 697 3
<i>ttg</i>	0.3327	0.332 497 3	0.329 210 6
<i>tgt</i>	0.1664	0.166 396 5	0.163 071 2
<i>tgg</i>	8.8982E-02	9.601 064 8E-02	0.134 052 1
<i>gtg</i>	4.4491E-02	4.699 229 4E-02	6.517 241 9E-02
<i>gtg'</i>	4.4491E-02	4.707 756 3E-02	6.127 920 7E-02
<i>ggg</i>	1.1898E-02	1.341 217 8E-02	2.651 709 3E-02
Z	1.000	3.039 0 (3.041 6)	20.93 (21.18)
A/NkT	-1.1678	0.303 10 (0.303 91)	6.5153 (6.5557)
n -heptane	$\rho^*=0$	$\rho^*=0.085$	$\rho^*=0.215$
<i>tttt</i>	0.2143	0.2010	0.1325
<i>tttg</i>	0.2292	0.2267	0.1998
<i>ttgt</i>	0.2292	0.2269	0.2014
<i>ttgg</i>	6.1304E-02	6.4383E-02	8.3241E-02
<i>gttg</i>	6.1304E-02	6.3839E-02	7.8357E-02
<i>gtgt'</i>	6.1304E-02	6.3255E-02	7.3698E-02
<i>gtgt</i>	3.0652E-02	3.2378E-02	4.2882E-02
<i>gttg'</i>	3.0652E-02	3.1822E-02	3.8411E-02
<i>gttg'</i>	3.0652E-02	3.2346E-02	4.2822E-02
<i>tggg</i>	1.6395E-02	1.8169E-02	3.1770E-02
<i>gtgg</i>	1.6395E-02	1.8747E-02	3.9307E-02
<i>gtg'g'</i>	1.6395E-02	1.8006E-02	2.9955E-02
<i>gggg</i>	2.1922E-03	2.5471E-03	5.8149E-03
Z	1.000	3.0839 (3.0873)	21.47 (21.81)
A/NkT	-1.5404	-0.0335 (0.0324)	6.433 (6.487)

it becomes more and more involved as the length of the chain increases.

We would like to finish this work by stressing that our study of conformer population of this section only refers to hard n -alkane models. Caution should be taken when extrapolating the conclusions of this section to either models of n -alkanes incorporating attractive forces or real n -alkanes. For instance, in the case of butane there is strong evidence arising from computer simulation^{7-9,11} that a repulsive WCA model undergoes an appreciable population change when going from the gas to the liquid whereas at the same conditions a site-site Lennard-Jones model does not present any significant change. That should be a reminder of the fact that the equilibrium population in fluid phase would, in general, be different for a hard model and for a model incorporating attractive forces as well. For longer n -alkanes^{8,9,43} it seems that the conformational change is also very modest for models with both repulsive and attractive forces. In this section we showed how in hard models there is a significant decrease in the population of the less spherical conformers. That suggests to us that attractive forces favor the less spherical conformers so that the ideal gas population is restored. Repulsive and attractive force would probably favor different conformers and the net balance would be an almost complete cancellation for liquids at low pressures. Clearly, at very high

liquid densities or pressures the repulsive forces would dominate the conformational equilibria and the trends observed in this section illustrate the type of changes that may be expected most likely.

V. CONCLUSIONS

The virial coefficients up to the fifth of hard models of n -alkanes have been calculated. We define the nonsphericity parameter α through the excluded volume (i.e., B_2) of the hard model. For a given n -alkane the anisotropy of the conformers decreases as the number of *gauche* bonds increases. The average value of α , namely, $\bar{\alpha}$ increases with the length of the n -alkane and decreases with branching. As expected, the acentric factor ω and $\bar{\alpha}$ are related for alkanes so that they are nonindependent and we have found how to correlate them.

We propose a modified version of Wertheim EOS (MW) which allows the study of chains of n -alkanes made up of overlapping molecules. The MW predictions of the virial coefficients are in very good agreement with the numerical results. Also, the proposed MW agrees very well with computer simulation results of the WCA repulsive models at high densities. The MW EOS constitutes then a reliable tool for the prediction of virial coefficients and EOS of n -alkane models up to octane.

We have also analyzed condensed phase effects on conformational equilibria. The population of the less spherical conformers decreases at liquid densities in favor of the more spherical ones. However, this change in population affects only slightly the EOS and free energy of the fluid. Therefore, to take the ideal gas population to determine Z and A of the fluid will introduce only a small error in the determination of the properties of the liquid. That constitutes a reasonable approximation when only thermodynamic properties of the fluid are required.

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