

Potential parameters of methyl and methylene obtained from second virial coefficients of n-alkanes

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The second virial coefficients of a number of n-alkanes (from butane to hexadecane) have been evaluated by using the Rotational Isomeric State model. Methyl and methylene groups have been modelled as Lennard-Jones (12 - 6) interaction sites centered on the position of the carbon atoms. Equal size has been assigned to the methyl and methylene groups but differences in the well-depth of the potential were considered. We have chosen the values of the potential well-depths of methyl and methylene group to fit the second virial coefficient of several n-alkanes in a range of about 300 K. The agreement with experimental results is good. Then, it is shown that a simple site-site potential model is able to reproduce the second virial coefficient of several n-alkanes in a wide range of temperatures.

1. Introduction

n-alkanes are molecules with a high theoretical and industrial interest. They are made up by two methyl groups $-\text{CH}_3$ in the first and last position of the chain connected by several methylene groups $-\text{CH}_2$. In order to describe the thermodynamic properties of n-alkanes, a model potential for the intramolecular and intermolecular interactions is required. A common idea to describe interactions between molecules is to model them as pairwise additive interactions between atoms. This idea, successfully used for small molecules [1] becomes unmanageable for molecules with many atoms like long n-alkanes. A method to simplify the calculations is to consider a group of atoms as an interaction site. A natural choice for n-alkanes consists in taking the $-\text{CH}_3$ and $-\text{CH}_2$ groups as interaction sites. Typical choices for the pair site interaction are the square-well or the Lennard-Jones (LJ) potentials.

This kind of potential model has been used in the study of small hydrocarbons and their derivatives in the liquid state by using Monte Carlo [2] (MC) and Molecular Dynamics [3-9] (MD) techniques. Little work has, however, been addressed to the search of effective potential parameters for $-\text{CH}_3$ and $-\text{CH}_2$ able to describe the thermodynamic behaviour of n-alkanes in the liquid state. In the gaseous state this potential model was used with success in long n-alkanes to obtain the second virial coefficient, $B(T)$ [10], and transport properties [11]. Even in this case the situation is not, however, completely satisfactory.

Recently López Rodríguez and Freire [10] have shown that if $-\text{CH}_3$ and $-\text{CH}_2$ are modelled as LJ centres with the same size, σ , and the same energetic parameter, ϵ , then this parameter should change from one n-alkane to another to obtain a good agreement with experimental values of $B(T)$. Though the procedure is able to reproduce simultaneously experimental results for the viscosity [11], with only small changes in

the parameters, this change of ε with n is not consistent with the intuitive idea that the nature of $-\text{CH}_3$ and $-\text{CH}_2$ groups is not too much affected by the length or position in the chain. The question is then whether it is possible to describe the experimental values of $B(T)$ of a number of n -alkanes in a broad range of temperatures modelling $-\text{CH}_3$ and $-\text{CH}_2$ as LJ interaction sites with constant potential parameters.

In this work we have tried to achieve a good description of $B(T)$ of several n -alkanes in a broad range of temperatures with a simple intermolecular potential model in which $-\text{CH}_3$ and $-\text{CH}_2$ have the same size but differ in their energetic interaction, and with a simple intramolecular potential to describe the conformational equilibria in gas phase. If this description is good enough with such a simple model it is obvious that more elaborated models, including for example differences in the size of $-\text{CH}_3$ and $-\text{CH}_2$, would lead to a further improvement of the agreement with the experimental results.

The scheme of the work is as follows. In section 2 we describe the molecular model and the details of the evaluation of $B(T)$ as well as the method of determination of the potential parameters. In section 3 we show the results obtained and in section 4 we give the conclusions of the work.

2. Model and numerical procedure

The n -alkane chain is modelled by using the approximation of Rotational Isomeric State [12] (RIS). This model considers a discrete number of conformers (each one with a given statistical weight) associated with the internal rotation of each bond along the chain. It has also been applied in previous conformational studies of n -alkanes [13, 14]. The great advantage of RIS is that the number of possible conformers of an n -alkane is discrete, avoiding spurious sampling over unrealistic values of the rotational (torsional) angles.

We place the position of the sites ($-\text{CH}_3$ or $-\text{CH}_2$) on the equilibrium positions of the carbons (C) of the chain. Therefore the bond distance l and the bond angle θ (see figure 1) are fixed. We shall choose $l = 1.53 \text{ \AA}$ and $\theta = 112^\circ$ for all the n -alkanes studied [12]. The torsional angles ϕ (defined in the C-C bond) can take only the values (RIS approximation) of 0° (trans isomer) 120° (gauche⁺ isomer) and 240° (gauche⁻ isomer).

Let us now specify the functional form used for the potential. In the following formulae we shall give numbers to the sites of the chain starting by a $-\text{CH}_3$ group, numbering successively the $-\text{CH}_2$ groups and finishing with the terminal $-\text{CH}_3$ group. With this criterion the intermolecular potential is given by

$$U_{\text{inter}} = \sum_{i=1}^{n_s} \sum_{j=1}^{n_s} 4\varepsilon_{ij}[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6], \quad (1)$$

where n_s is the number of sites of the chain, r_{ij} is the distance between the interaction site i of molecule 1 and the interaction site j of molecule 2, σ and ε_{ij} are characteristic interaction parameters that have to be determined. The values of ε_{ij} are given by

$$\begin{aligned} \varepsilon_{ij} &= \varepsilon_{\text{CH}_3-\text{CH}_3} = \varepsilon_1 && \text{if } i = 1 \text{ or } i = n_s \text{ and } j = 1 \text{ or } j = n_s, \\ \varepsilon_{ij} &= \varepsilon_{\text{CH}_3-\text{CH}_2} = \varepsilon_2 && \left\{ \begin{array}{l} \text{if } i = 1 \text{ or } i = n_s \text{ and } j \neq 1 \text{ and } j \neq n_s, \\ \text{if } j = 1 \text{ or } j = n_s \text{ and } i \neq 1 \text{ and } i \neq n_s, \end{array} \right. \\ \varepsilon_{ij} &= \varepsilon_{\text{CH}_2-\text{CH}_2} = \varepsilon_3 && \text{if } i \neq 1 \text{ and } i \neq n_s \text{ and } j \neq 1 \text{ and } j \neq n_s. \end{aligned} \quad (2)$$

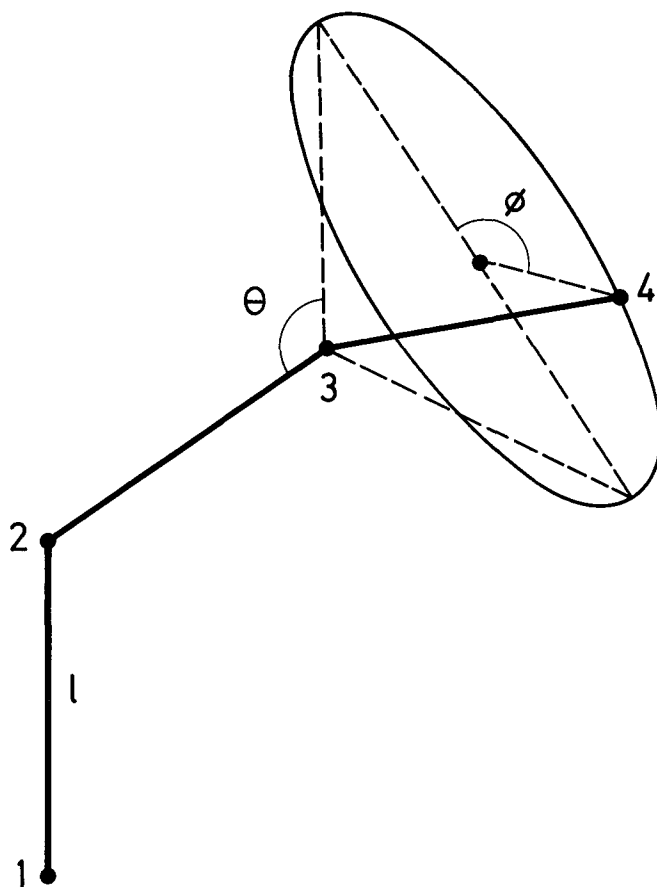


Figure 1. Geometry of the chain, where l is the bond length, θ the internal angle between bonds and ϕ the torsional angle.

For $\varepsilon_{\text{CH}_3\text{-CH}_2}$ the energetic Lorentz–Berthelot rule will be used

$$\varepsilon_{\text{CH}_3\text{-CH}_2} = \varepsilon_2 = (\varepsilon_1 \varepsilon_3)^{1/2}. \quad (3)$$

The short-range intramolecular potential is given by [12]

$$U_{\text{intra}}^{\text{short}} = E_c + \sum_{i=4}^{n_b} E_{\text{ab},i}, \quad (4)$$

where a, b, c = trans (t), gauche⁺ (g⁺), gauche⁻ (g⁻), respectively. The index i runs over bonds and n_b is the number of bonds of the chain. a denotes the state of bond $i - 1$ and b that of bond i . The first term of the sum E_c is a function of only one angle (the first torsional angle) and hence indexed by c alone. The energy $E_{\text{ab},i}$ is appropriately regarded as the contribution to U_{intra} associated with the assignment of bond i to state b, bond $i - 1$ in state a. This way we consider the energy associated to the interactions between units separated by less than five bonds along the chain. We shall use the following values [12]

$$\begin{aligned} E_{\text{at}} &= 0 && \text{for } a = \text{t, g}^+, \text{g}^-, \\ E_{\text{tg}^+} &= E_{\text{tg}^-} = E_{\text{g}^+\text{g}^+} = E_1 = 2.93 \text{ kJ mol}^{-1}, \end{aligned} \quad (5)$$

$$E_{g\pm g\mp} = E_2 = 11.29 \text{ kJ mol}^{-1}.$$

The long range intramolecular potential is given by

$$U_{\text{intra}}^{\text{long}} = \sum_{i=1}^{n_s-5} \sum_{j=i+5}^{n_s} 4\epsilon_{ij}[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6], \quad (6)$$

where r_{ij} is the distance between the site i of a molecule and site j or the same molecule.

The second virial coefficient of a pure non-flexible molecule is given by [15]

$$B(T) = -\frac{1}{2} \int [\langle \exp(-\beta U_{\text{inter}}) \rangle_{\omega} - 1] 4\pi r^2 dr, \quad (7)$$

where $\beta = (kT)^{-1}$, k is the Boltzmann constant, U_{inter} holds for the intermolecular potential, r for the distance between the molecular centres of masses and the bracket with the subscript ω stands for geometrical average over the relative orientations.

The RIS model describes the n-alkane as a mixture of isomers. The second virial coefficient of the n-alkane can be regarded as the second virial coefficient of the mixture of conformers and is given by

$$B(T) = -\frac{1}{2} \sum_{\alpha=1}^{n_{\text{iso}}} \sum_{\eta=1}^{n_{\text{iso}}} x_{\alpha} x_{\eta} \int [\langle \exp(-\beta U_{\text{inter}_{\alpha\eta}}) \rangle_{\omega_{\alpha}\omega_{\eta}} - 1] 4\pi r^2 dr, \quad (8)$$

where x_{α} is the molar fraction of the α isomer and the expression $\langle \exp(-\beta U_{\text{inter}_{\alpha\eta}}) \rangle_{\omega_{\alpha}\omega_{\eta}}$ is the orientational average of the Boltzmann factor of the intermolecular potential between the isomers α and η at a distance r between the centre of mass. n_{iso} is the number of isomers of the n-alkane. The equilibrium molar fraction of the isomer μ , x_{μ} , which can also be regarded as the probability of finding this isomer in the gas state is given by

$$x_{\mu} = \frac{\exp(-\beta U_{\text{intra}_{\mu}})}{\sum_{\alpha=1}^{n_{\text{iso}}} \exp(-\beta U_{\text{intra}_{\alpha}})} = \frac{\exp(-\beta U_{\text{intra}_{\mu}})}{Z_{\text{intra}}}. \quad (9)$$

If we assume that

$$U_{\text{intra}} = U_{\text{intra}}^{\text{short}} + U_{\text{intra}}^{\text{long}}, \quad (10)$$

where $U_{\text{intra}}^{\text{short}}$ is the intramolecular energy due to all the interactions between units i and j of the chain, such that $i - j < 5$ and $U_{\text{intra}}^{\text{long}}$ considers all the interactions with $i - j \geq 5$; then

$$Z_{\text{intra}} = Z_{\text{intra}}^{\text{short}} Z_{\text{intra}}^{\text{long}}. \quad (11)$$

If we substitute (9)–(11) into (8) we obtain

$$B(T) = -2\pi \int \left(\frac{\sum_{\alpha} \sum_{\eta} \exp(-\beta[U_{\text{intra}_{\alpha}}^{\text{short}} + U_{\text{intra}_{\eta}}^{\text{short}}])}{Z_{\text{intra}_{\alpha}}^{\text{short}} Z_{\text{intra}_{\eta}}^{\text{short}}} \times \frac{\exp(-\beta[U_{\text{intra}_{\alpha}}^{\text{long}} + U_{\text{intra}_{\eta}}^{\text{long}}])}{Z_{\text{intra}_{\alpha}}^{\text{long}} Z_{\text{intra}_{\eta}}^{\text{long}}} \langle \exp(-\beta U_{\text{inter}_{\alpha\eta}}) \rangle_{\omega_{\alpha}\omega_{\eta}} - 1 \right) r^2 dr. \quad (12)$$

Let us now define

$$P_{\text{intra}\mu}^{\text{short}} = \frac{\exp(-\beta U_{\text{intra}\mu}^{\text{short}})}{\sum_{\alpha} \exp(-\beta U_{\text{intra}\alpha}^{\text{short}})}, \tag{13}$$

which represents the probability of finding the isomer μ in the gas phase for the studied n-alkane assuming that all the intramolecular potential can be described by the short-range term. Defining $P_{\text{intra}\mu}^{\text{long}}$ in an analogous way to (13), then (12) can be written as

$$B(T) = -2\pi \int \left(\sum_{\alpha} \sum_{\eta}^{n_{\text{iso}}} P_{\text{intra}\alpha}^{\text{short}} P_{\text{intra}\alpha}^{\text{long}} P_{\text{intra}\eta}^{\text{short}} P_{\text{intra}\eta}^{\text{long}} \langle \exp(-\beta U_{\text{inter}\alpha\eta}) \rangle_{\omega_{\alpha}\omega_{\eta}} - 1 \right) r^2 dr. \tag{14}$$

Rearranging terms in (14)

$$B(T) = -2\pi \int [\langle \exp(-\beta U_{\text{inter}\alpha\eta}) \exp(-\beta U_{\text{intra}\alpha}^{\text{long}}) \times \exp(-\beta U_{\text{intra}\eta}^{\text{long}}) \rangle_{\omega_{\alpha}\omega_{\eta}} P_{\text{intra}\alpha}^{\text{short}} P_{\text{intra}\eta}^{\text{short}} (Z_{\text{intra}\alpha}^{\text{long}} Z_{\text{intra}\eta}^{\text{long}})^{-1} - 1] r^2 dr. \tag{15}$$

Equation (15) is the basic formula used in this work for evaluating $B(T)$. The average over $\langle \rangle_{\omega_{\alpha}\omega_{\eta}} P_{\text{intra}\alpha}^{\text{short}} P_{\text{intra}\eta}^{\text{short}}$ is carried out using a Monte Carlo method.

Having explained the RIS model, the intermolecular and intramolecular potential and the formulae for evaluating $B(T)$, let us briefly explain the algorithm to evaluate $B(T)$ which was already used in [10]

- (1) A distance r between the centre of mass is chosen.
- (2) We generate the conformation of the chain 1 (i.e. α) according to the distribution probability given by $U_{\text{intra}\alpha}^{\text{short}}$. (Adequate formulae [16] for the conditional probability of each rotational angle are employed in the sampling procedure.)
- (3) We repeat step (2) and generate the conformation of the chain 2 (i.e. η).
- (4) We put the centre of mass of molecule 2 on a random point of the sphere (centred in the centre of mas of molecule 1) with radius r and two randomly selected angular polar coordinates.
- (5) We rotate molecule 2 randomly by choosing three Euler angles to define the orientation of its internal frame with respect to that of molecule 1.
- (6) We calculate the functions $\exp(-\beta U_{\text{inter}\alpha\eta})$, $\exp(-\beta U_{\text{intra}\alpha}^{\text{long}})$ and $\exp(-\beta U_{\text{intra}\eta}^{\text{long}})$.
- (7) We repeat again steps (2) to (6) n_f times.
- (8) We evaluate then the function

$$\frac{\langle \exp(-\beta U_{\text{inter}\alpha\eta}) \exp(-\beta U_{\text{intra}\alpha}^{\text{long}}) \exp(-\beta U_{\text{intra}\eta}^{\text{long}}) \rangle_{\omega_{\alpha}\omega_{\eta}} P_{\text{intra}\alpha}^{\text{short}} P_{\text{intra}\eta}^{\text{short}} (Z_{\text{intra}\alpha}^{\text{long}} Z_{\text{intra}\eta}^{\text{long}})^{-1}}{\sum_{i=1}^{n_f} \exp(-\beta U_{\text{inter}\alpha_i\eta_i}) \exp(-\beta U_{\text{intra}\alpha_i}^{\text{long}}) \exp(-\beta U_{\text{intra}\eta_i}^{\text{long}})} = 1 + f_M(r). \tag{16}$$

- (9) We repeat steps (1) to (8) for several values of r (typically 20 to 30 values of r were sampled).

Table 1. Number of $\text{CH}_3\text{-CH}_3$ interactions, $n_{\text{CH}_3\text{-CH}_3}$, $\text{CH}_3\text{-CH}_2$ interactions, $n_{\text{CH}_3\text{-CH}_2}$, and $\text{CH}_2\text{-CH}_2$ interactions, $n_{\text{CH}_2\text{-CH}_2}$, for n-alkanes as a function of the length of the chain n .

n	$n_{\text{CH}_3\text{-CH}_3}$	$n_{\text{CH}_3\text{-CH}_2}$	$n_{\text{CH}_2\text{-CH}_2}$
4	4	8	4
5	4	12	9
6	4	16	16
7	4	20	25
8	4	24	36
16	4	56	196

(10) We evaluate numerically the integral

$$B(T) = -2\pi \int_0^\infty f_M(r)r^2 dr. \quad (17)$$

We have established the following numerical procedure to find a set of potential parameters (ε_1 , ε_2 , ε_3) able to fit the experimental values of $B(T)$ of n-butane, n-pentane, n-hexane, n-heptane, n-octane and n-hexadecane in a range of about 300 K for a given value of σ . As ε_2 is given by (3) only ε_1 and ε_3 have to be determined. An initial guess of the value of ε_3 is needed. In table 1 we see that the number of interactions $\text{CH}_2\text{-CH}_2$ increases with the length of the chain and become dominant for long chains. An upper limit of ε_3 can, therefore, be obtained by fitting $B(T)$ of n-hexadecane using a model in which all the interaction sites are equivalent (i.e. same value of σ and ε). In table 2 the parameters obtained in [10] for different n-alkanes by fitting to the experimental values of $B(T)$ in a model with $\varepsilon_1 = \varepsilon_2 = \varepsilon_3$ are shown. From table 2 it is clear that ε decreases as the length of the chain increases.

Once this estimation of ε_3 has been achieved, we choose three values of ε_3 close to the estimated value, which are denoted as ε_3^a , ε_3^b and ε_3^c . Typically the difference between ε_3^c/k and ε_3^a/k is 10 K. Then, we fix a value of ε_3 , for instance ε_3^a and look for a value of ε_1 able to fit $B(T)$ of n-butane in a range of 300 K, which we label as ε_{1B}^a . In the same way we look for a value of ε_1 able to fit $B(T)$ of n-hexane, ε_{1H}^a , and a value of ε_1 able to fit $B(T)$ of n-octane, ε_{1O}^a . We have, therefore, obtained for ε_3^a three values of ε_1 , namely ε_{1B}^a , ε_{1H}^a and ε_{1O}^a .

We repeat again the procedure for the other two values of ε_3 (ε_3^b , ε_3^c) and obtain for every value of ε_3 three values of ε_1 corresponding to n-butane, n-hexane and n-octane. Finally the nine pairs of values (ε_3 , ε_1) are plotted and the values of ε_1 for a given n-alkane are connected by a straight line. In figure 2 we show the resulting plot for $\sigma = 3.923 \text{ \AA}$. We see in figure 2 that there is a region of the plot in which the three curves intersect each other determining the coordinates of a point. The coordinates

Table 2. Potential parameters from [10] for n-alkanes, considering the CH_3 and CH_2 as identical groups with $\sigma = 3.923 \text{ \AA}$.

n	$(\varepsilon/k)/\text{K}$
4	78
5	69
6	67
7	63
8	61.5
16	54

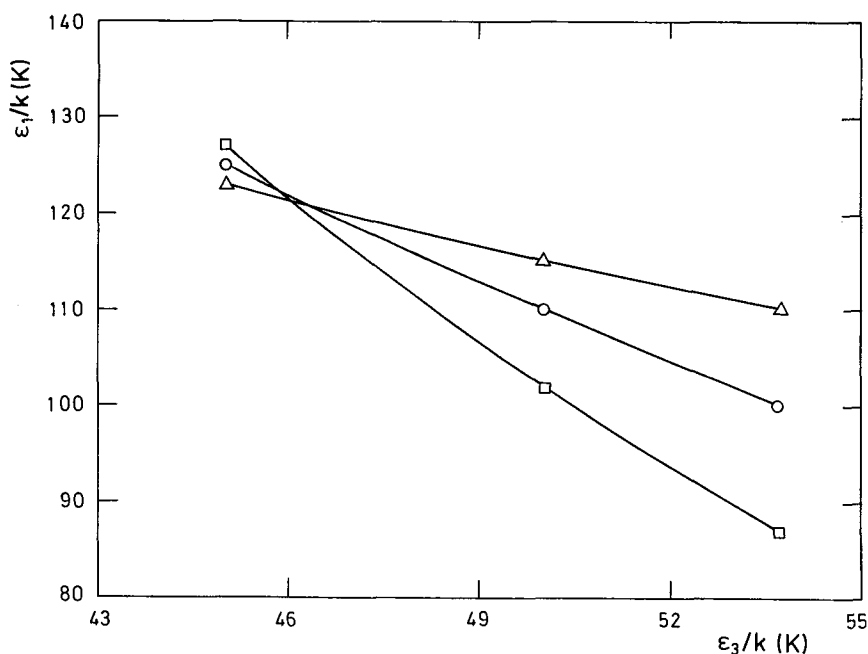


Figure 2. ϵ_1 as a function of ϵ_3 for n-butane (Δ) n-hexane (\circ) and n-octane (\square). The obtained points were connected by a smooth line. The value of σ was taken to be $\sigma = 3.923 \text{ \AA}$. The coordinates of the point where the three lines become very close are $\epsilon_1/k = 121.6 \text{ K}$ and $\epsilon_3/k = 46.1 \text{ K}$.

of this point define a pair of values ϵ_3 , ϵ_1 for the value of σ studied able to reproduce $B(T)$ for n-butane, n-hexane and n-octane in a range of 300 K. These values of ϵ_1 and ϵ_3 constitute our estimation of ϵ for the interactions $\text{CH}_2\text{-CH}_2$ and $\text{CH}_3\text{-CH}_3$, respectively.

In the next section we show the results obtained using this procedure.

3. Results and discussion

Two values of σ have been chosen for this study. For every value of σ the procedure of the preceding section has been applied to determine ϵ_1 , ϵ_2 and ϵ_3 . The chosen values were $\sigma = 3.70 \text{ \AA}$ and $\sigma = 3.923 \text{ \AA}$. The second value corresponds to the value of σ used by Rickaert and Bellemans in their study of n-alkanes in liquid state and has been often used in the literature [3, 4]. The search for the parameters ϵ_1 and ϵ_3 is very time consuming. For this reason the number of conformations, n_r , used for every value of r in the determination of ϵ_1 and ϵ_3 has been restricted to 500. The parameters obtained in this way are shown in table 3.

Once the parameters ϵ_1 and ϵ_3 have been obtained for the two values of σ studied, we evaluate the second virial coefficient of all the series of n-alkanes from n-butane to n-octane and also for n-hexadecane using a large number of conformations for every value of r , $n_r = 10\,000$. Table 4 shows the results obtained with the potential parameters of this work. As we can see a correct description of $B(T)$ for all the studied n-alkanes is achieved. This is important because the potential parameters σ , ϵ_1 , ϵ_2 , ϵ_3 were the same in all the n-alkanes studied. The results are only slightly worse than those previously obtained by López Rodríguez and Freire [10] with a model in which

Table 3. Potential parameters of methyl and methylene groups of this work obtained from second virial coefficient of n-alkanes. The methyl and methylene groups interact through a LJ (12-6) with the same σ but differing in the energy parameter ϵ . For the meaning of ϵ_1 , ϵ_2 and ϵ_3 see the text.

Set	$\sigma/\text{\AA}$	$(\epsilon_1/k)/\text{K}$	$(\epsilon_2/k)/\text{K}$	$(\epsilon_3/k)/\text{K}$
I	3.70	135.0	83.9	52.1
II	3.923	121.6	74.8	46.1

$-\text{CH}_3$ and $-\text{CH}_2$ were treated as equivalent groups but the value of ϵ was changed from n-alkane to n-alkane to get agreement with the experimental results of $B(T)$. From the results of table 4 it seems that the variation of ϵ with the n-alkane found in [10] can be explained by the energetic difference existing between a $-\text{CH}_3$ and a $-\text{CH}_2$ group. To gain further evidence on this point we tried to relate the parameters ϵ_1 and ϵ_3 obtained in this work for $\sigma = 3.923 \text{\AA}$ (set II of table 3) with the previously obtained values [10] of ϵ of several n-alkanes (table 2). The simplest idea is to consider the values of ϵ of table 2 as weighted averaged of ϵ_1 , ϵ_2 and ϵ_3 according to the formula

$$\epsilon = (n_{\text{CH}_3-\text{CH}_3}\epsilon_1 + n_{\text{CH}_3-\text{CH}_2}\epsilon_2 + n_{\text{CH}_2-\text{CH}_2}\epsilon_3)n^{-2}. \quad (18)$$

Table 4. Second virial coefficient in cc/mol of n-alkanes, from experimental results $B(T)^{\text{exp}}$ [17] and from theoretical calculations. $B(T)^{\text{exp}}$ for hexadecane were estimated with the method of corresponding states (see table 5 of [17]).

n	T/K	$B(T)^{\text{exp}}$	$B(T)^{\text{a}}$	$B(T)^{\text{b}}$	$B(T)^{\text{c}}$
4	250	-1170 ± 30	-1105	-1144	-1138
4	280	-862 ± 20	-862	-885	-888
4	340	-535 ± 20	-574	-586	-592
4	400	-370 ± 20	-411	-419	-425
4	560	-164 ± 10	-196	-203	-202
5	300	-1180 ± 60	-1087	-1188	-1183
5	400	-575 ± 15	-575	-622	-627
5	500	-339 ± 15	-349	-380	-384
5	600	-211 ± 15	-226	-250	-252
6	320	-1640 ± 60	-1520	-1516	-1488
6	360	-1180 ± 40	-1143	-1136	-1130
6	400	-900 ± 30	-890	-887	-888
6	500	-510 ± 20	-530	-529	-531
6	600	-318 ± 15	-343	-345	-345
7	350	-1800 ± 80	-1690	-1710	-1703
7	400	-1230 ± 50	-1205	-1218	-1214
7	500	-680 ± 40	-698	-710	-722
7	600	-430 ± 30	-445	-455	-465
8	380	-1990 ± 140	-1897	-1857	-1839
8	440	-1310 ± 100	-1290	-1267	-1270
8	520	-834 ± 40	-854	-845	-851
8	580	-638 ± 40	-653	-649	-653
16	435.09	-8234	-7550	-6785	-6761
16	580.12	-3063	-2955	-2722	-2808
16	725.15	-1528	-1493	-1381	-1449
16	870.18	-836	-865	-805	-846

^aFrom [10] with the parameters given in table 2.

^bFrom the parameter set I of table 3 of this work.

^cFrom the parameter set II of table 3 of this work.

Table 5. Values of ε as estimated from (18) using ε_1 , ε_2 and ε_3 from the set II of table 3, and as given from [10].

n	(18) (ε/k)/K	[10] (ε/k)/K
4	79.3	78
5	71.9	69
6	67.2	67
7	63.9	63
8	61.6	61.5
16	53.5	54

In table 5 we show the estimate of ε according to (18), using the values of ε_1 , ε_2 and ε_3 from this work (set II of table 3), and the values of ε obtained previously in [10]. The agreement is very good, again confirming the idea that the decrease (table 2) found in ε with the length of the chain arises from neglecting the energetic differences in the methyl and methylene groups.

Table 6 shows the relative deviations of the calculated values of $B(T)$ (see table 4) from the experimental results. The proposed parameters of table 3 give an average relative error of 8% while the average error of the previous treatment of [10] was about 6%. To use a constant parameter set for all the n-alkanes instead of using a parameter set for every n-alkane only degrades the average accuracy by about 2%. The average error in $B(T)$ from the parameter set I of table 3 is slightly smaller than that of set II. Nevertheless, the differences are small and other properties (i.e. viscosity) should be evaluated to decide which of the two proposed sets describes better the pair interaction.

We should remind the reader that the parameters of table 3 have been derived through the use of the approximate RIS model and a particular choice for the values E_1 and E_2 given in (5). To evaluate the effect on $B(T)$ due to a change in E_1 and E_2 with the proposed potential parameters we have calculated $B(T)$ for n-octane with $E_1 = 2.09 \text{ kJ mol}^{-1}$ and $E_2 = 12.54 \text{ kJ mol}^{-1}$ (values which seem to be adequate for liquid phase simulations [12]). The results are shown in table 7. The results of table 7 for the second virial coefficient of n-octane are very similar to the ones obtained with our initial choice of E_1 and E_2 (see last column of table 4). Although the optimum values of ε_1 and ε_3 depend on the choice of E_1 and E_2 , this dependence is weak as far as a reasonable choice of E_1 and E_2 is performed.

Table 6. Average relative deviation Δ (in %) between the calculated and the experimental values of $B(T)$ for n-alkanes. The calculated and experimental values were given in table 4.

n	Δ^a	Δ^b	Δ^c
4	10.8	13.0	13.3
5	5.5	11.8	12.6
6	5.3	5.7	6.2
7	3.9	4.5	5.8
8	3.0	3.9	4.4
Average deviation	5.7	7.8	8.5

^aFrom [10] with the parameters given in table 2.

^bFrom the parameter set I of table 3 of this work.

^cFrom the parameter of set II of table 3 of this work.

Table 7. $B(T)$ of n-octane evaluated with the parameter set II of table 3 and the values of $E_1 = 2.09 \text{ kJ mol}^{-1}$ and $E_2 = 12.54 \text{ kJ mol}^{-1}$.

T/K	$B(T)^{\text{exp}}$	$B(T)$
380	-1990 ± 140	-1814
440	-1310 ± 100	-1264
520	-834 ± 40	-842
580	-638 ± 40	-650

A good description of $B(T)$ of n-alkanes has been achieved with the potential parameters of table 3. The situation is not, however, completely satisfactory. The values of ϵ_1 are very large compared with the values of ϵ_3 . Although the well depth should be larger in the methyl than in the methylene group due to the presence of an additional hydrogen atom, the differences are too large. The ratio ϵ_1 to ϵ_3 found in the parameter sets of table 3 is about 2.5. Atom-atom potentials suggest that a more reasonable ratio of ϵ_1 to ϵ_3 would be in the range 1.5–2. We think that the high ϵ_1 to ϵ_3 ratio found in this work arises from neglecting the differences in volume of methyl and methylene groups. Methyl has not only a deeper well but also a larger volume than the methylene group. To prove that the ratio ϵ_1 to ϵ_3 decreases when a larger value of σ is given to the methyl than to the methylene group we have repeated the fitting procedure of section 2 with two values of σ , σ_1 for the methyl and σ_3 for the methylene group. The Lorentz–Berthelot rule was also used for σ in the crossed methyl–methylene interactions. The values of σ_1 and σ_3 were chosen so that their mean is equal to 3.923 \AA . We show in table 8 the values obtained for ϵ_1 , ϵ_2 and ϵ_3 . ϵ_1 decreases as σ_1 increases. ϵ_3 increases as σ_3 decreases. The ratio ϵ_1 to ϵ_3 then takes more reasonable values once the differences in volume of methyl and methylene groups are considered.

Table 8. Potential parameters of methyl and methylene groups. ϵ_1 and ϵ_3 were obtained using the procedure of section 2 with σ_1 and σ_3 fixed. We choose values of σ_1 and σ_3 so that their mean is 3.923 \AA . We also show the values of ϵ_2 obtained from the Lorentz–Berthelot rule.

$\sigma_1/\text{\AA}$	$\sigma_3/\text{\AA}$	$(\epsilon_1/k)/\text{K}$	$(\epsilon_2/k)/\text{K}$	$(\epsilon_3/k)/\text{K}$	ϵ_1/ϵ_3
3.923	3.923	121.6	74.8	46.1	2.64
3.983	3.863	119.0	75.4	47.8	2.49
4.123	3.723	112.9	76.8	52.3	2.16
4.323	3.523	106.3	78.8	58.5	1.82

On the other hand, one can expect that the agreement with experimental results of $B(T)$ would improve if two different values of σ for the $-\text{CH}_3$ and the $-\text{CH}_2$ were used along with the two different values of ϵ . Although that would be desirable, it is clear that the search for a potential parameter set would now become very complicated since it would be necessary to determine σ_1 , σ_3 , ϵ_1 , ϵ_3 . That would be much more difficult than the determination of ϵ_1 and ϵ_3 with σ_1 and σ_3 fixed that we have carried out in this work.

Finally, the potential parameters given in table 3 should be regarded as pair potentials for describing the behaviour of n-alkanes in gaseous phase. They should not necessarily describe the liquid behaviour of n-alkanes.

4. Conclusions

A simple model, which considers the $-\text{CH}_3$ and $-\text{CH}_2$ as sites interacting through a LJ (12-6) with the same σ and different ϵ , is able to reproduce $B(T)$ of n-alkanes in a broad range of temperatures. A procedure to find the potential parameters has been proposed. The variation found previously of ϵ with the length of the n-alkane can now be explained in terms of the differences of the energetic interaction of $-\text{CH}_3$ and $-\text{CH}_2$ groups. We have found two good parameter sets to describe $B(T)$ of n-alkanes. The first is $\sigma = 3.70 \text{ \AA}$, $\epsilon_1/k = 135.0 \text{ K}$, $\epsilon_2/k = 83.9 \text{ K}$, $\epsilon_3/k = 52.1 \text{ K}$. The second is $\sigma = 3.923 \text{ \AA}$, $\epsilon_1/k = 121.6 \text{ K}$, $\epsilon_2/k = 74.8 \text{ K}$, $\epsilon_3/k = 46.1 \text{ K}$. We believe that these potential parameter sets describe reasonably well the behaviour of n-alkanes in the gas phase, though more reasonable differences between ϵ_1 and ϵ_3 are found when different values of σ are assigned to the different groups.

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References

- [1] LAL, M., and SPENCER, D., 1973, *J. Chem. Soc. Faraday Trans. II*, **69**, 1502.
- [2] ALMARZA, N. G., ENCISO, E., ALONSO, J., BERMEJO, F. J., and ALVAREZ, M., 1990, *Molec. Phys.*, **70**, 3.
- [3] RICKAERT, J. P., and BELLEMANS, A., 1975, *Chem. Phys. Lett.*, **30**, 123.
- [4] RICKAERT, J. P., and BELLEMANS, A., 1978, *Faraday Discuss. Chem. Soc.*, **66**, 95.
- [5] WOJCIK, M., GUBBINS, K. E., and POWLES, J. G., 1982, *Molec. Phys.*, **45**, 1209.
- [6] VEGA, C., SAAGER, B., and FISCHER, J., 1989, *Molec. Phys.*, **68**, 1079.
- [7] JORGENSEN, W. L., MADURA, J. D., and SWENSON, C. J., 1984, *J. Am. Chem. Soc.*, **106**, 6638.
- [8] TOXVAERD, S., 1988, *J. chem. Phys.*, **89**, 3808.
- [9] GUPTA, S., YANG, J., and KESTNER, N. R., 1988, *J. chem. Phys.*, **89**, 3733.
- [10] LÓPEZ RODRÍGUEZ, A., and FREIRE, J. J., 1988, *Molec. Phys.*, **63**, 591.
- [11] FREIRE, J. J., and LÓPEZ RODRÍGUEZ, A., 1988, *Molec. Phys.*, **63**, 601.
- [12] FLORY, P. J., 1969, *Statistical Mechanics of Chain Molecules* (Wiley).
- [13] YOON, D. Y., and FLORY, P. J., 1978, *J. chem. Phys.*, **69**, 2536.
- [14] FREIRE, J. J., and FIXMAN, M., 1978, *J. chem. Phys.*, **69**, 634.
- [15] GRAY, C. G., and GUBBINS, K. E., 1984, *Theory of Molecular Liquids* Vol. 1 (Clarendon Press).
- [16] RUBIO, A. M., and FREIRE, J. J., 1982, *Macromolecules*, **15**, 1441.
- [17] DYMOND, J. H., CHOLINSKI, J. A., SZAFRANSKI, A., and WYRZYKOWSKA-STANKIEWICZ, D., 1986, *Fluid Phase Equilib.*, **27**, 1.