SECOND VIRIAL COEFFICIENT OF THE 2cLJ, 3cLJ AND 4cLJ MOLECULES

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The second virial coefficient was evaluated for the two-centre, three-centre and four-centre Lennard–Jones molecules with the site–site distance $l \in (0,1)$ at the reduced temperatures $T_r = 0.6 - 3.0$. The obtained data are correlated by an expression derived originally for the Kihara non-spherical molecules; the same value of the σ-parameter is considered for the both pair potentials whereas $\varepsilon_{\text{Kihara}}/\varepsilon_{\text{ncLJ}}$ and $l_{\text{Kihara}}/l_{\text{ncLJ}}$ vary with the increasing values of l_{ncLJ}. Values of the virial coefficient of the individual ncLJ molecules agree within error bars with experimental values in the whole temperature range studied; with only slightly higher deviations also data for the single 2cLJ, 3cLJ and 4cLJ molecules for all the l_{ncLJ} values can be correlated.

The second virial coefficient represents itself an important thermodynamic quantity which enables to determine the phase behaviour of mildly dense gases. Whereas exact (analytic) expressions are available for many pair potentials of the central type (which depend only on the centre-to-centre distance, r, and are typical for the so-called simple fluids) and potentials used to characterize interactions of polar spherical molecules, the situation is less favorable in the case of non-spherical molecules. For non-spherical molecules essentially two different types of potentials have been used, namely the multicentre pair potential and the generalized Kihara potential[1 – 3]. In the former case, several interaction sites are ascribed to the studied molecule and the total interaction potential is given by a sum of all the site–site contributions (with exception of those of sites on the same molecule). In the case of the Kihara potential, convex cores are ascribed[3] to the given molecule and the interaction pair potential is assumed to be the function of the shortest surface-to-surface distance only. Due to the fact that the Kihara pair potential depends only on the surface-to-surface distance, it is possible to write for such

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molecules exact expressions for the second virial coefficient, too. They are simple extensions of those for the corresponding pair potentials of simple fluids[3] (e.g. the 12-6 function). In the case of systems where molecules interact via the multicentre pair potential, e.g. the two-centre Lennard–Jones (2cLJ) potential, the interaction energy is given by four contributions of the 12-6 functions for four different site–site distances $r_{12}^{\alpha\beta}$ which are related[4] to the centre-to-centre distance r_{12} and orientation angles $\omega_i \equiv \theta_i\ \phi_i$. Because of this complexity of the pair potential, an exact formula for the 2cLJ and other multicentre Lennard–Jones (ncLJ) molecule fluids is not available.

Contrary to this situation, simulations in the multicentre molecule systems are simpler than those in the Kihara fluids and numerous simulation data have been published for dense 2cLJ systems. In order to be able to describe in a simple way the behaviour of these systems at densities tending to zero, approximate methods to correlate and predict values of the second virial coefficient of the ncLJ systems have been sought. Kohler and Quirke[5] assumed that the Boyle temperature, T_B, was a suitable quantity to reduce the temperature scale. However, values of T_B result from the fitting procedure; moreover, data in a broad temperature range were necessary. In our previous attempt[6] we considered the expression for the second virial coefficient of the Kihara rod-like molecules with three Padé (3,2)-approximants and assumed that the expression for the 2cLJ potential had the same form as that for the Kihara rod-like potential with the same value of σ and $\varepsilon/\boldsymbol{k}$ and the rod length equal to the site–site distance. Values of the coefficients in the above-mentioned approximants were determined on the basis of the computer data of the 2cLJ systems. The method was limited to the 2cLJ molecules with the reduced site–site distance $l < 0.6$; reasonable agreement between the calculated and experimental data was obtained.

Recently, we studied systems of non-spherical rod-like molecules assuming the Kihara pair potential[7,8]. We applied the perturbation theory to describe the equilibrium behaviour of fluids along the coexistence curve. Comparison of the obtained Kihara potential parameters with results of a similar approach, used by Fischer and Kohler[9,10] for the 2cLJ systems, revealed considerable interrelations between potential parameters of both the potentials[7,8]. This finding has motivated our present attempt to correlate the ncLJ virial coefficients by expressions derived for the Kihara rod-like molecules in which modified values of parameters $\varepsilon/\boldsymbol{k}$, σ and l are used instead of those of the ncLJ systems.

This paper is divided into two parts: In the first part we give a brief survey of expressions for the second virial coefficient for the mentioned pair potentials followed by the results of our machine evaluation of B_{2cLJ}, B_{3cLJ} and B_{4cLJ} in the temperature range (0.6,3). The second part is devoted to the correlation of the experimental data. This correlation is performed on three levels, namely (i) for the individual molecules in the given temperature range (ii) for all the 2cLJ molecules, 3cLJ molecules and 4cLJ molecules (iii) for all the molecules studied in the whole temperature range.

THEORETICAL

A general expression for the second virial coefficient, B, follows from the theory of moderately dense fluids[2,4,6,11]

$$B = \frac{1}{2!V} \int [\exp^{-u(\boldsymbol{12})/kT} - 1]\, \mathrm{d}\boldsymbol{1}\, \mathrm{d}\boldsymbol{2}\,, \tag{1}$$

where $\mathrm{d}\boldsymbol{i} = \mathrm{d}\boldsymbol{r}\, \mathrm{d}\omega$ stands for the differential of the generalized coordinate of molecule i and $\omega \equiv \theta,\phi$ for the normalized angular coordinates, T and V denote temperature and volume and k is the Boltzmann constant. For the both pair potentials it is possible to transform the variables $[\boldsymbol{r_1},\boldsymbol{r_2}] \rightarrow [\boldsymbol{r_1},\boldsymbol{r_{12}}]$ and to perform integration with respect to $\boldsymbol{r_1}$. One obtains

$$B = \frac{1}{2} \int\!\!\int\!\!\int [\exp^{-u(r_{12},\omega_1,\omega_2)/kT} - 1]\, \mathrm{d}\boldsymbol{r_{12}}\, \mathrm{d}\omega_1\, \mathrm{d}\omega_2\,. \tag{2}$$

This expression represents the basic formula used in the computer evaluation of the second virial coefficient of the 2cLJ, 3cLJ and 4cLJ molecules whose pair potential is

$$u(\boldsymbol{r},\omega_1,\omega_2) = \sum_{1}^{n^2} u^{\alpha\beta}\,(r_{12}^{\alpha\beta})\,. \tag{3}$$

For the Kihara pair potential

$$u(r_{12},\omega_1,\omega_2) = u(s) = 4\,\varepsilon\,[(\sigma/s)^{12} - (\sigma/s)^{6}] \tag{4}$$

Eq. (*2*) can be rewritten into the form

$$B = \frac{1}{2} \int_0^\infty [\exp^{-u(s)/kT} - 1]\, S_{1+s+2}\, \mathrm{d}s\,, \tag{5}$$

where S_{1+s+2} stands for the mean surface area of two convex cores 1 and 2 with the surface-to-surface distance s.

For two identical rod-like molecules S_{1+s+2} can be expressed in terms of the surface area of the single core (a rod of a length $\sigma\, l_{\mathrm{Kihara}}$), S_i and the mean curvature integral divided by $4\,\pi$, $R_i\,(= l\,\sigma/4)$. After substitution into Eq. (*5*) one obtains

$$B/\sigma^3 = \frac{2\pi}{3}\int_0^\infty f\,\mathrm{d}(s^3) + 4\pi\,(R_i/\sigma)\int_0^\infty f\,\mathrm{d}(s^2) + 4\pi\,(R_i/\sigma)^2\int_0^\infty f\,\mathrm{d}s\,, \tag{6}$$

where f stands for the Mayer function $f = (\exp[-u/\boldsymbol{k}T] - 1)$. Integral in the first term of the last equation is just equal to that of the expression for the Lennard–Jones molecules; exact solution can be obtained after expansion of a part of the exponential function[11,12]. A similar method was used also for the determination of the remaining two integrals[3]. All three integrals are functions of the reduced temperature, $T_\mathrm{r} = \boldsymbol{k}T/\varepsilon_\mathrm{Kihara}$. The expansions for the above integrals, b_3^*, b_2^*, b_1^*, can be expressed[13] in the form of the Padé (3,2)-approximants

$$b_i^* = (2\,T_\mathrm{r}^{-1/2})^{i/6}\,\frac{a_i + b_i\,T_\mathrm{r}^{-1/2} + c_i\,T_\mathrm{r}^{-1/2}}{1 + d_i\,T_\mathrm{r}^{-1/2}}\,, \tag{7}$$

where a_i, b_i, c_i, and d_i are

$a_3 = 1.18163$ $b_3 = -2.23086$ $c_3 = 0.08095$ $d_3 = -0.46061$
$a_2 = 1.09948$ $b_2 = -1.32389$ $c_2 = 0.06148$ $d_2 = -0.47330$
$a_1 = 1.03825$ $b_1 = -0.80242$ $c_1 = -0.07053$ $d_1 = -0.48277$.

In our previous approximative method to correlate the 2cLJ virial coefficient we modified coefficients $a_3 - d_1$. Here we assume that Eqs (*6*) and (*7*) can be used even for ncLJ molecules once we modify values of the pair potential parameters.

The Second Virial Coefficient of the 2cLJ, 3cLJ and 4cLJ Molecules

In the course of the numerical determination of the second virial coefficient of the 2cLJ molecules with parameters $\varepsilon^{\alpha\beta}/\boldsymbol{k}$, $\sigma^{\alpha\beta} = \sigma$ and l_2clj we employed Eq. (*2*), where we expressed $r_{12}^{\alpha\beta}$ in terms of r_{12} and three angles, θ_1, θ_2 and ϕ_{12}. In order to avoid integration over a large interval of distances where the Mayer function practically vanished we performed the coordinate transformation $r \rightarrow 1/\zeta$. We define $\varepsilon_\mathrm{2cLJ} = 4\varepsilon^{\alpha\beta}$ so that $T_\mathrm{r} = T/\varepsilon_\mathrm{2cLJ} = T/4\varepsilon^{\alpha\beta}$. Values of the second virial coefficient were determined by the Monte Carlo integration in which $2\,.\,10^6$ configurations were generated.

In the beginning of the work the method was tested by a comparison of the calculated second virial coefficient of hard dumbells and of the 2cLJ molecules (with the reduced site–site distance $l_\mathrm{2clj} = 0.5$) with data from the literature[2,4]. Agreement within the combined error estimates was obtained. Data of Maitland et al.[2] for the 2cLJ system covers the range of l_2cLJ (0.06) only. We thus determined B for the reduced site–site distance $l_\mathrm{2cLJ} = 0.7$, 0.8, 0.9 and 1.0. The obtained values of B together with the data of Maitland et al.[2] are listed in the first part of Table I. We estimate the error of our $B_\mathrm{2cLJ}/(\pi\sigma^3/6)$ values to be 0.002.

TABLE I
The second virial coefficient of the 2-centre, 3-centre and 4-centre Lennard–Jones molecules

	T_r					
	0.6	0.8	1.0	1.4	2.0	3.0
			2cLJ			
0.1	–5.846	–3.527	–2.389	–1.276	–0.555	–0.059
0.2	–5.120	–3.081	–2.060	–1.046	–0.383	0.075
0.3	–4.400	–2.613	–1.701	–0.784	–0.178	0.241
0.4	–3.790	–2.195	–1.369	–0.530	0.028	0.413
0.5	–3.287	–1.834	–1.072	–0.293	0.227	0.585
0.6	–2.871	–1.521	–0.808	–0.074	0.416	0.752
0.7	–2.514	–1.241	–0.563	0.134	0.600	0.918
0.8	–2.213	–0.999	–0.349	0.322	0.769	1.072
0.9	–1.979	–0.800	–0.167	0.488	0.924	1.217
1.0	–1.755	–0.605	0.014	0.655	1.081	1.364
			3cLJ			
0.1	–5.380	–3.243	–2.180	–1.131	–0.447	0.024
0.2	–4.110	–2.417	–1.547	–0.668	–0.086	0.316
0.3	–3.080	–1.683	–0.949	–0.198	0.302	0.648
0.4	–2.286	–1.074	–0.429	0.237	0.680	0.981
0.5	–1.620	–0.532	0.051	0.655	1.056	1.322
0.6	–1.021	–0.026	0.512	1.069	1.434	1.671
0.7	–0.467	0.458	0.961	1.479	1.816	2.028
0.8	0.059	0.930	1.404	1.891	2.203	2.391
0.9	0.525	1.362	1.819	2.284	2.577	2.746
1.0	0.981	1.787	2.225	2.668	2.941	3.088
			4cLJ			
0.1	–4.891	–2.936	–1.950	–0.968	–0.323	0.123
0.2	–3.281	–1.829	–1.069	–0.294	0.222	0.578
0.3	–2.088	–0.915	–0.290	0.354	0.782	1.071
0.4	–1.098	–0.098	0.441	0.998	1.364	1.602
0.5	–0.237	0.648	1.127	1.621	1.939	2.136
0.6	0.569	1.376	1.813	2.259	2.539	2.700
0.7	1.368	2.109	2.510	2.915	3.160	3.287
0.8	2.188	2.880	3.252	3.619	3.831	3.924
0.9	3.003	3.648	3.990	4.319	4.495	4.549
1.0	3.677	4.302	4.631	4.940	5.094	5.124

Next, we evaluated the second virial of the linear 3cLJ molecules where both the site–site distances were the same; thus, the inner site coincided with the centre of the molecule. In the case of the 3cLJ molecule, $T_r = T/\varepsilon_{3cLJ} = T/9\varepsilon^{\alpha\beta}$. Data of the second virial coefficient, $B_{3cLJ}/(\pi\sigma^3/6)$, for $l_{3cLJ} \in (0,1)$ are given in the second part of Table I; their error estimate amounts 0.004.

Finally, we evaluated B_{4cLJ} of the linear 4cLJ fluid by the same procedure from $2 - 3 \,.\, 10^6$ configurations. The neighbour sites on the rod were all situated a distance l_{4cLJ} apart, so that the reduced end-to-end distance was $3\, l_{4cLJ}$. The obtained data (with the error estimate 0.008) are listed in the last part of Table I.

Correlation of the ncLJ Virial Coefficients

Our correlation method is based on the idea of a close resemblance of the n-centre Lennard–Jones and Kihara potentials. Our previous work has indicated[7,8] that for the given 2cLJ molecule with parameters ε_{2cLJ}, σ_{2cLJ} and l_{2cLJ} the Kihara model exists (with parameters $\varepsilon_{Kihara} = E\varepsilon_{2cLJ}$, $\sigma_{Kihara} = S\sigma_{2cLJ}$ and $l_{Kihara} = Ll_{2cLJ}$) such that the orthobaric data along the coexistence curve can be fairly well described when general dependences of L, S, and E on l were used. The question then arose whether the mentioned idea could be applied also to the case of virial coefficients. Thus, in the first step of our work, we employed the above mentioned expression for the Kihara rod-like model to correlate “experimental” data of the individual 2cLJ molecules in the studied temperature range, $T_r \in (0.6, 3.0)$. It was found that for three adjustable parameters, E, S, L, perfect agreement of the calculated and experimental data was obtained. In our study of dense fluids[7] we considered only two adjustable parameters keeping $L = 1$. When we introduced the same approximation for the correlation of the virial coefficient, the agreement of the calculated and experimental data was less good. However, taking $S = 1$ and varying E and L we obtained agreement almost within error estimates. This is obvious from Table II where the comparison of the calculated and experimental second virial coefficient of the 2cLJ, 3cLJ, 4cLJ molecule fluid with $l_{ncLJ} = 0.5$ is given. When the resulting values of E and L were plotted as functions of the site–site distance, l_{ncLJ}, smooth, almost linear dependences result, see Figs 1*a* and 1*b*. We therefore attempted to correlate B_{2cLJ} in the whole range of temperatures and site–site lengths. The following dependences for L and E were assumed:

$$L = (a + b\,l + cl^2) \tag{8}$$

and

$$(1/E) = 1 + d\,l + f\,l^2 + g\,l^3 + h\,l^4\,, \tag{9}$$

where the subscript 2cLJ of the variable l_{2cLJ} was omitted for simplicity. From the optimization procedure applied to a set of 60 state points of the 2cLJ fluid we found

$$a = 0.25793 \quad b = 1.33519 \quad c = -0.77092$$
$$d = 0.13343 \quad f = 3.76442 \quad g = -4.34838 \quad h = 1.60747 \; .$$

Comparison of the correlated and experimental data, given in Table III reveals the fact that the method yields a good prediction of the second virial coefficient of the studied molecules; the standard deviation in *B* amounts 0.009. Actually, the agreement

TABLE II
Results of the data fitting of the second virial coefficients of the 2cLJ, 3cLJ and 4cLJ molecules, all with the reduced site–site distance l = 0.5

T_r	2cLJ		3cLJ		4cLJ	
0.6	–3.287	–0.003	–1.620	0.002	–0.237	0.001
0.8	–1.834	0.000	–0.532	–0.000	0.648	–0.002
1.0	–1.072	0.003	0.051	0.003	1.127	–0.001
1.4	–0.293	0.004	0.655	0.004	1.621	–0.000
2.0	0.227	0.002	1.056	0.004	1.939	0.001
3.0	0.585	–0.002	1.322	0.004	2.136	0.001

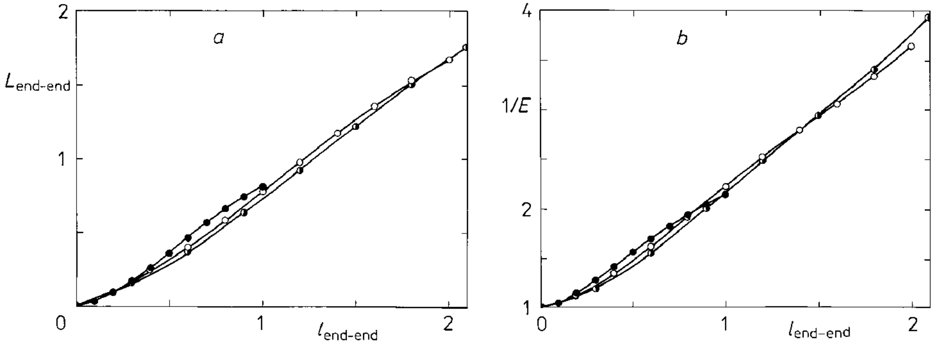

FIG. 1
The comparison of the calculated dependences of: *a* the *L*-ratios and *b* the *E*-ratios on the end-to-end distance l with the “experimental” results for the 2cLJ (●), 3cLJ (❍) and 4cLJ (❍) molecules

TABLE III
Deviations of the calculated and experimental second virial coefficients the individual sets of 2cLJ, 3cLJ and 4cLJ molecules

l	T_r					
	0.6	0.8	1.0	1.4	2.0	3.0
			2cLJ			
0.1	0.010	0.011	0.012	0.015	0.016	0.013
0.2	–0.019	–0.006	0.001	0.006	0.007	0.005
0.3	–0.014	–0.007	–0.003	–0.001	–0.003	–0.007
0.4	0.005	0.001	0.000	–0.002	–0.007	–0.012
0.5	0.015	0.007	0.004	0.000	–0.006	–0.012
0.6	0.013	0.008	0.007	0.004	–0.001	–0.006
0.7	–0.005	–0.003	–0.001	0.002	0.001	–0.003
0.8	–0.022	–0.010	–0.003	0.003	0.006	0.005
0.9	–0.005	0.002	0.006	0.009	0.009	0.008
1.0	0.007	0.002	–0.000	–0.004	–0.008	–0.011
			3cLJ			
0.1	0.007	0.018	0.025	0.034	0.038	0.038
0.2	–0.039	–0.016	–0.003	0.009	0.014	0.015
0.3	–0.014	–0.014	–0.012	–0.009	–0.009	–0.013
0.4	0.025	0.005	–0.002	–0.009	–0.015	–0.021
0.5	0.035	0.012	0.004	–0.005	–0.012	–0.018
0.6	0.018	0.007	0.004	–0.001	–0.003	–0.006
0.7	–0.008	–0.002	0.001	0.005	0.008	0.008
0.8	–0.033	–0.015	–0.006	0.004	0.010	0.015
0.9	–0.009	–0.001	0.001	0.006	0.010	0.014
1.0	0.021	0.006	–0.003	–0.010	–0.013	–0.010
			4cLJ			
0.1	–0.025	0.003	0.017	0.031	0.038	0.123
0.2	–0.009	–0.006	–0.002	0.003	0.005	0.028
0.3	0.028	0.006	–0.001	–0.007	–0.011	–0.015
0.4	0.004	–0.010	–0.015	–0.018	–0.021	–0.023
0.5	–0.006	–0.004	0.000	0.003	0.006	0.007
0.6	0.000	0.006	0.011	0.016	0.020	0.024
0.7	0.002	–0.003	–0.006	–0.009	–0.010	0.009

is considerably better than that obtained in our previous treatment[6] for 2cLJ systems of $l_{2cLJ} \in$ (0.1 – 0.6).

Similar accordance was found for the 3cLJ fluids, too. For the coefficients a – h it holds

a = 0.82460 b = 2.07212 c = –1.22240
d = 0.48739 f = 7.88557 g = –10.00001 h = 4.28459 .

The standard deviation is 0.016.

For the 4cLJ systems with l_{4cLJ} = 0.1 – 0.7 (for the higher site–site distances and considered reduced temperatures, great positive values of the virial coefficient result, out of practical importance) we found

a = 1.16480 b = 4015103 c = –3.17804
d = 0.64362 f = 15.20336 g = –24.73544 h = 14.70230

with the standard deviation 0.017. It appears that the standard deviations of the considered sets amount 2 – 3 times the error estimates of the pseudoexperimental data. Comparison of values of the E and L parameters determined for the individual molecules, with the predicted dependences is depicted in Fig 1*a* and 1*b*. It is evident that curves in the both figures lie quite close together once we consider end-to-end distance instead of l_{ncLJ} as the independent variable. It is thus desirable to look for the coefficients enabling the determination of the second virial coefficient of all the linear ncLJ fluids. From the optimization procedure, where we used the sum of squares of deviations in the virial coefficients as the objective function, the following coefficient resulted:

a = 0.51780 b = 0.37648 c = –0.10807
d = 0.38685 f = 1.79619 g = –1.27312 h = 0.310729 .

The standard deviation in this case is relatively high, i.e. 0.090, see Table IV.

DISCUSSION

In this paper we present results of our evaluation of the second virial coefficient of the two-centre Lennard–Jones molecules [with reduced site–site distance $l \in$ (0.7,1)], three-centre Lennard–Jones and four-centre Lennard–Jones model molecules with $l \in$ (0,1). The Monte Carlo integration method was used where usually 2 . 10^6 configurations were generated; the reduced temperatures $T_r \in$ (0.6 – 3.0) were considered. It appears that the second virial coefficient of the consequent ncLJ models increases rapidly towards high possitive values with the increasing values of the reduced site–site distance.

In order to correlate the obtained data of the virial coefficient, we propose a method in which the (exact) expressions derived for the Kihara molecules with rod-like cores

TABLE IV
Deviations of the calculated and experimental second 2cLJ, 3cLJ and 4cLJ molecules from the unique fitting procedure

l	T_r					
	0.6	0.8	1.0	1.4	2.0	3.0
			2cLJ			
0.1	0.038	0.032	0.032	0.035	0.036	0.033
0.2	–0.117	–0.057	–0.029	–0.004	0.010	0.016
0.3	–0.219	–0.129	–0.086	–0.048	–0.027	–0.015
0.4	–0.241	–0.155	–0.0114	–0.077	–0.056	–0.044
0.5	–0.212	–0.149	–0.118	–0.091	–0.076	–0.068
0.6	–0.158	–0.124	–0.107	–0.093	–0.085	–0.082
0.7	–0.101	–0.095	–0.093	–0.090	–0.090	–0.093
0.8	–0.034	–0.052	–0.062	–0.072	–0.080	–0.087
0.9	0.065	0.016	–0.009	–0.036	–0.055	–0.069
1.0	0.145	0.073	0.036	–0.003	–0.030	–0.049
			3cLJ			
0.1	0.143	0.105	0.091	0.081	0.074	0.067
0.2	0.079	0.067	0.064	0.061	0.058	0.053
0.3	0.051	0.038	0.034	0.031	0.029	0.022
0.4	0.039	0.023	0.018	0.013	0.009	0.004
0.5	0.010	0.000	–0.001	–0.002	–0.005	–0.007
0.6	–0.035	–0.028	–0.022	–0.017	–0.013	–0.011
0.7	–0.072	–0.049	–0.037	–0.024	–0.015	–0.009
0.8	–0.083	–0.056	–0.041	–0.026	–0.016	–0.007
0.9	–0.012	–0.008	–0.008	–0.006	–0.004	–0.001
1.0	0.102	0.063	0.040	0.018	0.005	0.000
			4cLJ			
0.1	0.272	0.194	0.163	0.136	0.118	0.103
0.2	0.252	0.184	0.154	0.127	0.109	0.092
0.3	0.174	0.131	0.114	0.098	0.087	0.077
0.4	0.042	0.044	0.049	0.054	0.057	0.058
0.5	–0.046	–0.008	0.015	0.038	0.055	0.065
0.6	–0.056	–0.022	–0.002	0.019	0.034	0.045
0.7	0.011	–0.009	–0.019	–0.031	–0.037	–0.039

are used considering modified (effective) pair potential parameters. It is assumed that the thickness of the effective Kihara potential equals to the σ-parameter of the ncLJ model. Because we substitute for the site–site interactions, acting at the ends of bonds (of the two-centre model) interactions along the whole rod, one can expect shortening of this effective rod length in comparison with the original site–site distance. From similar reasons, a decrease in the effective $\varepsilon/\boldsymbol{k}$ value (with respect of the value of the ncLJ model) with the increasing value of l can be expected. Actually in the more elaborate method one can consider the effect of the decrease of the ratio E with the increasing value of l in the effective thickness (an increase) and the effect of both these changes on the ratio L.

In the simpler method considered in this paper (i.e. under assumption of the equivalence of thickness and σ) for all the site–site distances a set of $\varepsilon_{\text{Kihara}}$ and l_{Kihara} can be found which yield a perfect correlation of the second virial coefficients in the considered temperature range for the given ncLJ model. The ratios L and E were almost linear functions of the site–site distance; unfortunately, assumption of the linear dependence leads to a rather crude correlation. We thus have considered polynomials in l (it appears that the E-ration is a linear function of L) taking into account the limitating values of both the ratios for l tending to zero.

Whereas the optimization procedure in which all the values of the second virial coefficient of the models with the same number of sites in molecules leads to a fair correlation of the data of the individual models, a similar approach for all the B-values irrespective the number of sites in molecules (where the end-to-end distance is considered) yields too harsch description.

In our previous work on the statistical thermodynamic description of the dense fluids composed of linear molecules we have empirically found interrelations between the Kihara and the 2cLJ potential parameters. In the mentioned study[7] we assumed equal values of the reduced length parameters. It is, however, interesting to find out how our new rules, expressed by Eqs (*8*) and (*9*) predict the effective Kihara parameters in cases when all three parameters were adjusted and σ_{2cLJ} and σ_{Kihara} were approximately the same. This is the case of Cl_2 where $\sigma_{\text{2cLJ}} = 0.3262$ and $\sigma_{\text{Kihara}} = 0.3234$ nm. According to Eqs (*8*) and (*9*) $l_{\text{Kihara}} = 0.600$ and $\varepsilon_{\text{Kihara}} = 431$ K compared with the values adjusted to the orthobaric data[7] 0.621 and 424 K. A fair accordance is obvious.

It can be concluded that the proposed method which employs the modified potential parameters to correlate equilibrium data of fluids interactive through the multicentre pair potential via the thermodynamic functions of the Kihara fluid – with the interaction parameters interrelated by simple formulas – is practical and fairly general.

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