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The second virial coefficient of quadrupolar two center Lennard-Jones models†

Carlos Menduiña, Carl McBride and Carlos Vega

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

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The second virial coefficient of 2-center Lennard-Jones molecules which have an embedded point quadrupole has been determined *via* numerical integration. A number of models with different reduced bond lengths and quadrupole moments have been considered. For each model the second virial coefficient has been determined for a range of temperatures. It is shown that the presence of the quadrupole moment significantly raises the Boyle temperature and, for a certain temperature, reduces the value of the second virial coefficient with respect to the non-polar model. Empirical fits for B_2 are given which reproduce the generated data. It is also shown that the inclusion of the quadrupole considerably improves the description of B_2 for real substances which have a significant quadrupole moment, as is the case for CO_2. The inclusion of the quadrupole is also required for understanding the cross virial coefficient between a spherical and a quadrupolar molecule, for example the interaction between Xe and CO_2.

1 Introduction

At low densities the equation of state of a gas can be described by the virial expansion. In this expansion the compressibility factor is given in powers of the density, and the coefficients of the expansion are known as the virial coefficients. These virial coefficients are temperature dependent (except for 'hard body' fluids). Virial coefficients of real systems can be measured experimentally by a number of different techniques.[1,2] In the early nineteen-thirties it was shown that the virial coefficients can be determined if the intermolecular forces between the molecules are known.[3–5] Second, third, and fourth virial coefficients can be computed by evaluating certain integrals involving two, three and four molecules, respectively. The expression for the second virial coefficient, B_2, is especially simple since it is given by minus one half of the integral of the angle-averaged Mayer function over all possible values of the distance between the center of mass (*i.e.* reference points) of the two molecules. The second virial coefficient can be obtained quite easily for molecules interacting through a pair potential of spherical symmetry. B_2 can be numerically evaluated in just a few seconds with currently available computers, or, for hard spheres, square well (SW) potentials and for Lennard-Jones (LJ) particles analytical expressions are available.[4] For hard convex bodies, B_2 can be determined analytically.[6] This is also the case for molecules which interact *via* the Kihara potential.[7,8] However, in general, the only way of determining B_2 is by numerically evaluating the integrals.

In the modeling of real fluids the interaction site model (ISM) is probably the most popular. In this model atoms or groups of atoms in the molecule are replaced by Lennard-Jones interaction sites. For instance, N_2 is described by two LJ sites located at, or near to, the two nitrogen atoms of the molecule.[9,10] Another example is the modeling of hydrocarbons in computer simulations, which is usually performed by replacing the CH_3 and CH_2 groups by LJ interaction sites.[11–13] The only way to determine B_2 for these non-spherical models is to evaluate the integral numerically. Probably one of the simplest ISM is the two center Lennard-Jones model (hereinafter denoted as 2CLJ). In this model the molecule is described by two LJ sites located at a distance of L apart. This model can be very useful in describing diatomic molecules such as N_2, O_2, F_2, Cl_2, or even polyatomic molecules such as ethane, ethene, acetylene or carbon dioxide.[9,10,14] Determination of B_2 for 2CLJ models was performed by Maitland *et al.* twenty years ago.[15] In the appendix of their book, they provide tabular results for B_2 for the 2CLJ model as a function of the temperature and of the reduced bond length $L^* = L/\sigma$. These are the parameters that are required to define the geometry of the model, σ being the characteristic parameter of the LJ interaction. Later, Boublik[16] evaluated B_2 for the 2CLJ model for other elongations and temperatures (and also considered the linear 3CLJ and 4CLJ models). However, the 2CLJ should be considered as a first approximation to the pair interaction between molecules such as those mentioned before. In fact, it is well known that in N_2, O_2, F_2, ethane and especially for Cl_2, ethene, acetylene, and CO_2 the charge distribution of the molecule is not symmetric and therefore the molecule has a non-zero quadrupole moment.[17] The quadrupole moment plays a fundamental role in understanding many of the properties of these substances.

Somewhat surprisingly the study of the second virial coefficient of 2CLJ molecules which have an embedded quadrupole moment (we shall call this the 2CLJQ model) has received very little attention. One cannot provide an explanation for the lack of data for this model since determination of B_2 for these kinds of molecules can be readily performed nowadays even with personal computers. Moreover, data of B_2 for 2CLJQ models can be useful in two different and complementary ways. First, the inclusion of the quadrupole will certainly improve the description of B_2 for real substances. Secondly, the data would clarify the effect that the quadrupole moment

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† Electronic Supplementary Information available. See http://www.rsc.org/suppdata/cp/b0/b009509p/

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has on B_2 and other properties, such as the Boyle temperature T_B. The lack of data for B_2 is even more surprising taking into account that the effect of the quadrupole moment on the vapor–liquid equilibria[18] or even in the fluid–solid equilibria[19,20] has been studied previously.

In this work it is our intention to fill this gap in the literature. In this paper we shall determine the second virial coefficient for a number of 2CLJQ models for a range of temperatures. In each of the cases the quadrupole moment will be described by an ideal quadrupole located at the center of mass of the molecule. Our aim is twofold. Firstly it will be shown that the inclusion of the quadrupole considerably improves the description of B_2 of real substances. Secondly, our aim is to gain a basic understanding of the effect that the quadrupole has on B_2 and other quantities, such as T_B. For 2CLJQ molecules B_2 is a function of $B_2(T, L^*, Q)$ hence the quantity of generated data exceeds that which can be presented in a tabular way. For this reason, empirical fits are provided for B_2.

The layout of the paper is as follows. In Section 2 we present details of the model and the calculation of B_2. In Section 3 we calculate, and provide empirical fits for, B_2 and T_B for a number of 2CLJQ models. Also in this section the 2CLJQ model is used to describe the second virial coefficient of real susbstances and mixtures.

2 Model and calculation details

In this work molecules are described by a two center Lennard-Jones model (2CLJ). The two sites are located at a distance of L apart and are identical, thus describing homonuclear diatomic molecules. The parameters controlling the Lennard-Jones interaction (LJ) are σ and ε. At the center of mass of the molecule we locate a point quadrupole. We shall denote this model as the two center Lennard Jones quadrupolar model (2CLJQ). The model is described by two reduced quantities, namely, the reduced bond length $L^* = L/\sigma$ and the reduced quadrupole moment $(Q^*)^2$ which is obtained by:

$$(Q^*)^2 = \frac{Q^2}{\varepsilon\sigma^5} \tag{1}$$

The pair interaction between a pair of molecules is given by:

$$u(1, 2) = \sum_{i=1}^{2} \sum_{j=1}^{2} u_{ij}^{\mathrm{LJ}} + u_{QQ} \tag{2}$$

where u_{ij} and u_{QQ} are given by:

$$u_{ij}^{\mathrm{LJ}} = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{3}$$

$$u_{QQ}/\varepsilon = \frac{3(Q^*)^2}{4(r^*)^5}\left(1 - 5(c_1^2 + c_2^2 + 3c_1^2c_2^2) + (s_1s_2c_{12} - 4c_1c_2)^2\right) \tag{4}$$

where r_{ij} is the distance between site i of molecule 1 and site j of molecule 2, $r^* = r/\sigma$ is the reduced distance between the centers of mass of the molecule and the meaning of $c_i = \cos(\theta_i)$, $s_i = \sin(\theta_i)$ and $c_{12} = \cos(\phi_2 - \phi_1)$ is illustrated in Fig. 1.

The reduced second virial coefficient $B_2^* = B_2/\sigma^3$ has been computed as a function of the reduced temperature $T^* = T/(\varepsilon/k)$ for a number of linear models. We have considered models with $L^* = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1$ and with $(Q^*)^2 = 0, 0.5, 1, 1.5, 2, 3, 4$. In total, we consider 77 models in this study.

The value of the second virial coefficient of a molecule can be obtained by evaluating the following expression:

$$B_2 = -\frac{1}{2}\int (\langle \exp(-\beta u)\rangle - 1) 4\pi r^2\, \mathrm{d}r \tag{5}$$

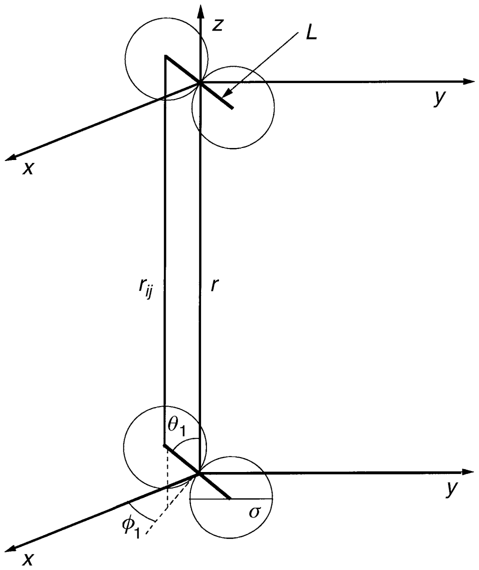

Fig. 1 Model used in this work.

where $\beta = 1/(kT)$, r is the distance between the center of mass of two molecules and $\langle \exp(-\beta u)\rangle$ is the orientational average of the Boltzmann factor between two molecules for a fixed value of r. Obviously, the complexity of the calculation of B_2 for a non-spherical molecule arises in the determination of $\langle \exp(-\beta u)\rangle$. In this work $\langle \exp(-\beta u)\rangle$ was evaluated for each value of r using Conroy's integration method[21] as implemented by Nezbeda *et al.*[22] We used 76 079 relative orientations for each value of r (which corresponds to $M = 152\,158$ and $d = 6$ in the Nezbeda *et al.* paper). The average $\langle \exp(-\beta u)\rangle$ is evaluated for 451 different values of r (from $r = 0$ up to $r = 20\sigma$). Finally the integral of eqn. (5) is obtained by using Simpson's integration rule. For each model B_2 has been evaluated for about 200 different temperatures. The calculation of B_2 for a certain model requires *ca.* 1 h of CPU time on a PentiumIII 400 MHz personal computer. Therefore the total CPU time used in this work constitutes around three days of CPU time. That clearly illustrates how the determination of B_2 for 2CLJQ falls within the range of affordable problems with current computers.

3 Results

Let us start by analyzing the effect of the quadrupole moment on B_2. For this purpose we shall compare B_2 for two models which have the same elongation but having different quadrupole moments. In Fig. 2a results are shown for two models with the same anisotropy (*i.e.* $L^* = 1$) but with different quadrupole moments (*i.e.* $(Q^*)^2 = 0, 4$). Results are presented as a function of the reduced temperature, defined as $T^* = T/(\varepsilon/k)$. As expected, for a given temperature the second virial coefficient becomes lower for the quadrupolar model. Notice that although the un-weighted orientational average of the quadrupolar potential is zero, $\langle u_{QQ}\rangle = 0$, this is not the case for the average of the Boltzmann factor.[17] Therefore the presence of the quadrupole increases the strength of the attractive forces in the system, which explains the decrease in B_2 for a certain temperature. Notice that the effect of the quadrupole on B_2^* is very small at high temperatures. In Fig. 2b results are presented for two models with $L^* = 0.3$ and different quadrupole moments. Similar conclusions are obtained in this case.

In Fig. 3a the second virial coefficient for $(Q^*)^2 = 0$ is plotted for two values of L^*, namely $L^* = 0.3$ and $L^* = 1$. In Fig. 3b similar results are presented for $(Q^*)^2 = 4$. As can be seen, for a certain value of the quadrupole the shorter molecule yields a lower value of B_2^*. Notice that differences in B_2 for two different elongation do not disappear at high temperatures.

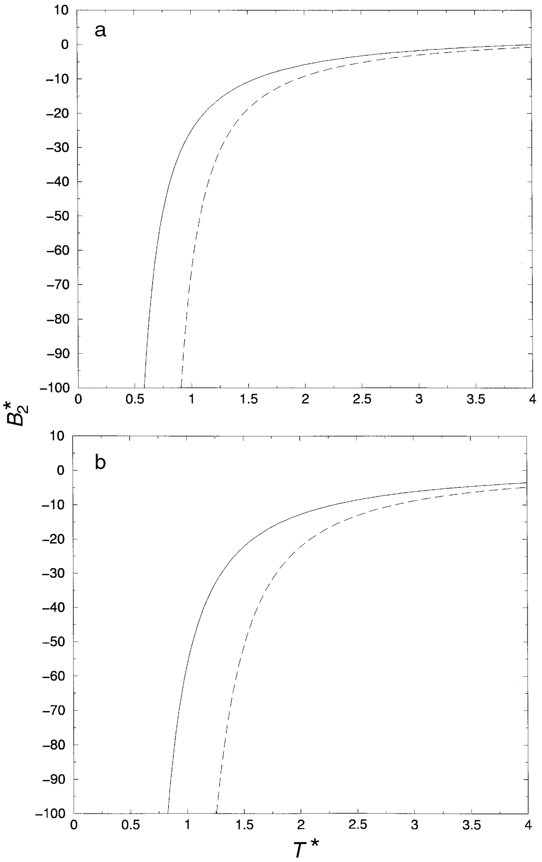

Fig. 2 Reduced second virial coefficient $B_2^* = B_2/\sigma^3$ as a function of the reduced temperature $T^* = T/(\varepsilon/k)$ for molecules with $(Q^*)^2 = 0$ (solid line) and $(Q^*)^2 = 4$ (dashed line). (a) Results for $L^* = 1$; (b) results for $L^* = 0.3$.

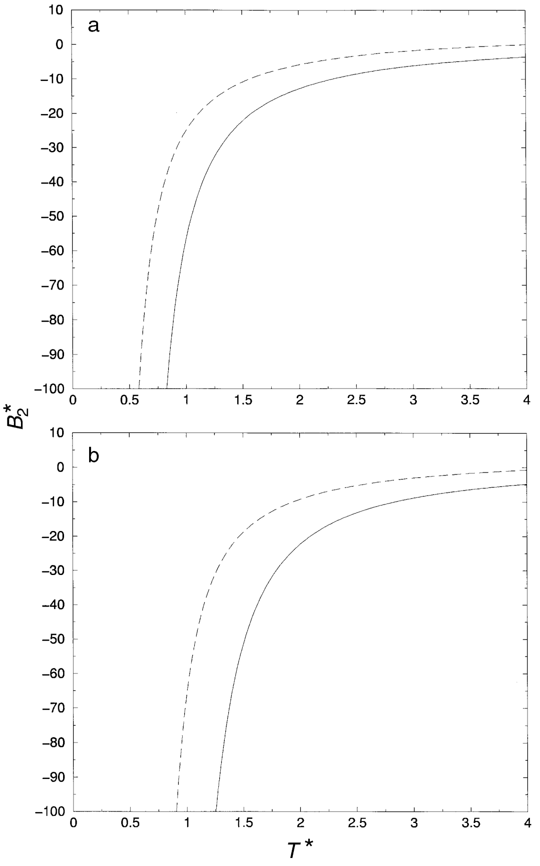

Fig. 3 Reduced second virial coefficient for models of different elongation $L^* = 0.3$ (solid line) and $L^* = 1$ (dashed line). (a) When the reduced quadrupole moment is zero; (b) when the reduced quadrupole moment is $(Q^*)^2 = 4$.

In addition to the second virial coefficient calculations we have also determined the Boyle temperature, T_B, of each model. The Boyle temperature is defined as the temperature where:

$$B_2(T = T_B) = 0 \tag{6}$$

In Fig. 4 the Boyle temperature is plotted as a function of L^* for two values of $(Q^*)^2$, namely $(Q^*)^2 = 0, 4$. We can see that T_B decreases with L^* and increases with $(Q^*)^2$. We should mention that for $L^* = 0$ and $(Q^*)^2 = 0$ we recover the Boyle temperature of the spherical LJ system. Notice however, that when $L^* = 0$ the 2CLJ model becomes a LJ system with four identical interactions instead of the usual one with just one interaction. This explains why our curves of T_B^* tends to four times the Boyle temperature of the LJ fluid when L^* tends to zero. Results of the Boyle temperature for the models considered in this work are presented in Table 1.

The number of generated data for B_2 for the 2CLJQ is of the order of 20000 points. Therefore, tabular presentation is out of question. The original data can be obtained from the authors upon request or directly from the electronic supplementary information (ESI) system of this journal.†

We have fitted our values to an empirical expression. The proposed expression is as follows:

$$\begin{aligned}
B_2^* = {} & ((d_1 + d_2 L^* + d_3 L^{*2} + d_4 L^{*3}) \\
& + Q^{*2}(c_1 + c_2 L^* + c_3 L^{*2}) \\
& + Q^{*4}(c_4 + c_5 L^* + c_6 L^{*2})) \\
& + ((d_5 + d_6 L^* + d_7 L^{*2} + d_8 L^{*3}) \\
& + Q^{*2}(c_7 + c_8 L^* + c_9 L^{*2}) \\
& + Q^{*4}(c_{10} + c_{11} L^* + c_{12} L^{*2}))/T^* \\
& + ((d_9 + d_{10} L^* + d_{11} L^{*2}) \\
& + Q^{2*}(c_{13} + c_{14} L^* + c_{15} L^{*2}) \\
& + Q^{*4}(c_{16} + c_{17} L^* + c_{18} L^{*2}))/T^{*2} \\
& + ((d_{12} + d_{13} L^* + d_{14} L^{*2}) \\
& + Q^{*2}(c_{19} + c_{20} L^* + c_{21} L^{*2}) \\
& + Q^{*4}(c_{22} + c_{23} L^* + c_{24} L^{*2}))/T^{*3} \\
& + ((d_{15} + d_{16} L^* + d_{17} L^{*2}) \\
& + Q^{*2}(c_{25} + c_{26} L^* + c_{27} L^{*2}) \\
& + Q^{*4}(c_{28} + c_{29} L^* + c_{30} L^{*2}))/T^{*4} \\
& + ((d_{18} + d_{19} L^* + d_{20} L^{*2}) \\
& + \mathrm{Q}^{*2}(c_{31} + c_{32} L^* + c_{33} L^{*2}) \\
& + Q^{*4}(c_{34} + c_{35} L^* + c_{36} L^{*2}))/T^{*5} \\
& + ((d_{21} + d_{22} L^* + d_{23} L^{*2}) \\
& + Q^{*2}(c_{37} + c_{38} L^* + c_{39} L^{*2}) \\
& + Q^{*4}(c_{40} + c_{41} L^* + c_{42} L^{*2}))/T^{*6}
\end{aligned} \tag{7}$$

As can be seen in our trial equation for the fit, the reduced second virial coefficient is fitted as a polynomial of the reduced inverse temperature[23,24] $1/T^*$. We also tried a polynomial[25] of $1/\sqrt{(T^*)}$ but the results were not significantly better. The coefficients of the expansion are fitted to a quadratic polynomial in $(Q^*)^2$. The coefficients labeled as d_i were first obtained by fitting the results for the non-polar models. Once obtained, the coefficients c_i were obtained by including the data for the quadrupolar models. For each model, the range of reduced temperatures considered is chosen as follows. The minimum temperature $T^*_{\min}$ corresponds to the temperature for which $B_2^* \simeq -55$ and the maximum temperature $T^*_{\max}$ corresponds to T_B^*. The parameters obtained from the fit are presented in Table 2. The fit of eqn. (7) should not be used

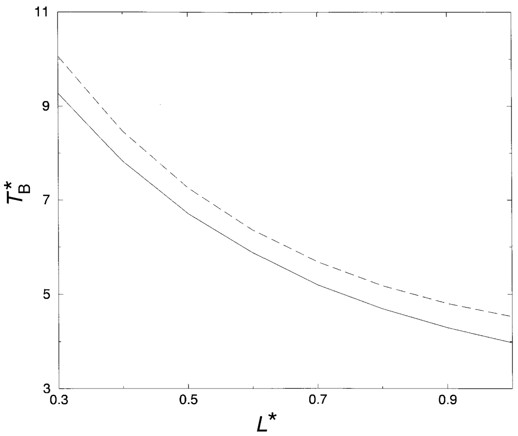

Fig. 4 Reduced Boyle temperature T_B^* as a function of the bond length for $(Q^*)^2 = 0$ (solid line) and $(Q^*)^2 = 4$ (dashed line).

outside of the range for which it was designed, which corresponds to $L^* = (0.2, 1)$ (that covers the typical range of lengths for real diatomic molecules), $(Q^*)^2 = (0, 4)$, and $T = (T_{\min}, T_{\max})$. The error of the fit is:

$$\frac{\sum_1^{12637} |B_2^* - B_{2(\text{fitted})}^*|}{N_{\text{points}}} = 0.08 \qquad (8)$$

We have also separately fitted the results for $L^* = 0$ (*i.e.* for quadrupolar spherical molecules) after having found that a direct fit of the lengths $L^* = (0, 1)$ substantially increases the error in the fitted points. We have fitted B_2^* of the spherical molecule to the following expression:

$$\begin{aligned} B_2^* = {} & \\ & (d_1 + c_1 Q^{*2} + c_2 Q^{*4} + c_3 Q^{*6} + c_4 Q^{*8}) \\ & + (d_2 + c_5 Q^{*2} + c_6 Q^{*4} + c_7 Q^{*6} + c_8 Q^{*8})/T^* \\ & + (d_3 + c_9 Q^{*2} + c_{10} Q^{*4} + c_{11} Q^{*6} + c_{12} Q^{*8})/T^{*2} \\ & + (d_4 + c_{13} Q^{*2} + c_{14} Q^{*4} + c_{15} Q^{*6} + c_{16} Q^{*8})/T^{*3} \\ & + (d_5 + c_{17} Q^{*2} + c_{18} Q^{*4} + c_{19} Q^{*6} + c_{20} Q^{*8})/T^{*4} \\ & + (d_6 + c_{21} Q^{*2} + c_{22} Q^{*4} + c_{23} Q^{*6} + c_{24} Q^{*8})/T^{*5} \\ & + (d_7 + c_{25} Q^{*2} + c_{26} Q^{*4} + c_{27} Q^{*6} + c_{28} Q^{*8})/T^{*6} \qquad (9) \end{aligned}$$

The parameters of the fit of B_2^* for spherical quadrupolar models are presented in Table 3. The error of the fit for the spherical quadrupolar molecule is:

$$\frac{\sum_1^{846} |B_2^* - B_{2(\text{fitted})}^*|}{N_{\text{points}}} = 0.02 \qquad (10)$$

Table 1 Reduced Boyle temperature $T_B^* = T_B/(\varepsilon/k)$ of 2CLJQ models for several reduced bond lengths and quadrupoles

	Q^{*2}						
L^*	0	0.5	1.0	1.5	2	3	4
0.0	3.418	3.513	3.780	4.187	4.705	5.999	7.563
0.1	12.827	12.849	12.913	13.019	13.165	13.570	14.114
0.2	11.044	11.060	11.110	11.191	11.304	11.618	12.042
0.3	9.269	9.283	9.321	9.384	9.471	9.713	10.039
0.4	7.822	7.835	7.867	7.919	7.989	8.184	8.445
0.5	6.705	6.719	6.749	6.795	6.856	7.022	7.242
0.6	5.852	5.868	5.898	5.942	5.999	6.148	6.344
0.7	5.196	5.216	5.248	5.292	5.347	5.490	5.672
0.8	4.688	4.712	4.747	4.793	4.849	4.991	5.168
0.9	4.290	4.319	4.358	4.407	4.467	4.612	4.792
1.0	3.976	4.009	4.053	4.108	4.172	4.328	4.518

Table 2 Parameters of the fit for the second virial virial coefficient of 2CLJQ models (see eqn. (7) of the main text.) The range where this fit is valid corresponds to $L^* = (0.2\text{–}1)$, $(Q^*)^2 = (0\text{–}4)$, $B_2^* > -55$ and $T < T_B$

$d_1 = 1.898\,752\,869\,394\,235$
$d_2 = -2.466\,373\,474\,333\,950\,7$
$d_3 = 12.293\,229\,090\,338\,604$
$d_4 = -9.673\,895\,464\,383\,694\,1$
$d_5 = -21.149\,276\,727\,890\,463$
$d_6 = 28.904\,989\,450\,954\,062$
$d_7 = -46.051\,630\,659\,710\,924$
$d_8 = 41.087\,573\,327\,607\,871$
$d_9 = -43.988\,684\,129\,240\,617$
$d_{10} = 70.285\,714\,711\,082\,861$
$d_{11} = -82.536\,277\,918\,044\,888$
$d_{12} = 13.144\,173\,894\,436\,049$
$d_{13} = 29.103\,500\,294\,603\,936$
$d_{14} = 11.617\,216\,129\,160\,731$
$d_{15} = -40.670\,962\,084\,910\,947$
$d_{16} = 6.824\,581\,677\,365\,086\,9$
$d_{17} = 0.894\,477\,026\,440\,632\,87$
$d_{18} = -15.292\,445\,640\,454\,407$
$d_{19} = 56.283\,981\,168\,719\,741$
$d_{20} = -35.166\,226\,201\,495\,178$
$d_{21} = 16.766\,523\,131\,527\,563$
$d_{22} = -40.554\,245\,351\,098\,778$
$d_{23} = 23.345\,122\,678\,621\,983$
$c_1 = 0.245\,883\,198\,304\,388\,01$
$c_2 = -0.966\,492\,720\,502\,574\,95$
$c_3 = 0.910\,518\,182\,022\,073\,46$
$c_4 = -0.132\,645\,233\,265\,985\,01$
$c_5 = 0.561\,523\,591\,326\,491\,77$
$c_6 = -0.747\,773\,848\,267\,097\,36$
$c_7 = -2.528\,884\,568\,905\,822\,6$
$c_8 = 8.266\,395\,658\,068\,102\,4$
$c_9 = -7.162\,937\,621\,580\,757\,9$
$c_{10} = 1.321\,190\,472\,763\,870\,4$
$c_{11} = -4.177\,144\,662\,831\,516\,1$
$c_{12} = 6.271\,011\,798\,369\,444$
$c_{13} = 8.785\,276\,382\,966\,827\,7$
$c_{14} = -19.487\,038\,352\,378\,768$
$c_{15} = 12.079\,315\,006\,562\,526$
$c_{16} = -7.033\,983\,804\,895\,499\,7$
$c_{17} = 9.665\,192\,819\,141\,443\,8$
$c_{18} = -16.541\,412\,215\,774\,777$
$c_{19} = -11.244\,081\,313\,925\,605$
$c_{20} = 9.450\,825\,035\,927\,826\,1$
$c_{21} = 2.192\,515\,765\,405\,800\,7$
$c_{22} = 12.643\,160\,083\,087\,501$
$c_{23} = 7.145\,011\,135\,708\,631\,2$
$c_{24} = 5.605\,752\,402\,850\,320\,9$
$c_{25} = 5.552\,709\,239\,457\,886\,5$
$c_{26} = 3.267\,348\,045\,863\,379$
$c_{27} = -10.397\,634\,077\,097\,413$
$c_{28} = -29.325\,145\,207\,901\,176$
$c_{29} = 9.826\,219\,509\,798\,299\,6$
$c_{30} = -4.762\,111\,811\,460\,831$
$c_{31} = 7.260\,212\,703\,708\,435\,6$
$c_{32} = 3.670\,369\,021\,231\,411\,3$
$c_{33} = -8.365\,525\,722\,288\,987\,6$
$c_{34} = 5.302\,898\,011\,918\,515\,8$
$c_{35} = 14.048\,340\,476\,474\,802$
$c_{36} = -11.825\,790\,877\,347\,865$
$c_{37} = -7.377\,225\,658\,874\,543\,5$
$c_{38} = -0.637\,429\,271\,929\,039\,64$
$c_{39} = 6.493\,822\,759\,856\,182\,2$
$c_{40} = 9.270\,272\,567\,768\,373\,1$
$c_{41} = -23.536\,291\,394\,452\,547$
$c_{42} = 14.402\,791\,576\,965\,646$

We shall now illustrate how the results for B_2 of 2CLJQ molecules can be applied to real models. Let us take CO_2 as an example. The second virial coefficient of CO_2 has been measured experimentally for a number of temperatures.[26] Let us now try to describe the experimental data with the 2CLJQ model. One possibility is to find the values of L^*, $(Q^*)^2$, σ, and ε that provide the best agreement with the experimental results. One drawback of this method is that the parameters obtained in this way lack any physical meaning. It seems more

Table 3 Parameters of the fit (see eqn. (9) of the main text) for the second virial virial coefficient of the spherical LJ quadrupolar model. The range where this fit is valid corresponds to $L^* = 0$, $(Q^*)^2 = (0\text{–}3)$, $B_2^* > -40$ and $T < T_B$

$d_1 = 1.533\,868\,683\,339\,934\,9$
$d_2 = -4.568\,695\,590\,217\,973\,1$
$d_3 = -2.317\,775\,851\,010\,862\,4$
$d_4 = 0.192\,414\,321\,560\,942\,35$
$d_5 = -0.123\,543\,159\,175\,493\,81$
$d_6 = -3.639\,064\,757\,846\,546\,12 \times 10^{-2}$
$d_7 = 3.371\,662\,535\,483\,408\,15 \times 10^{-3}$
$c_1 = 0.225\,541\,268\,987\,440\,87$
$c_2 = -0.162\,585\,189\,859\,545\,54$
$c_3 = -0.105\,490\,411\,759\,388\,86$
$c_4 = 2.665\,934\,668\,495\,285\,53 \times 10^{-2}$
$c_5 = -0.686\,220\,139\,455\,147\,37$
$c_6 = -2.184\,890\,959\,443\,585\,2$
$c_7 = 2.711\,569\,034\,953\,109\,6$
$c_8 = -0.396\,591\,794\,574\,943\,04$
$c_9 = -1.821\,823\,061\,439\,928\,4$
$c_{10} = 14.246\,453\,361\,099\,661$
$c_{11} = -10.933\,746\,864\,066\,601$
$c_{12} = 0.685\,138\,705\,436\,027\,4$
$c_{13} = 5.512\,334\,219\,305\,183$
$c_{14} = -24.945\,763\,515\,067\,306$
$c_{15} = 5.423\,975\,677\,573\,869\,4$
$c_{16} = 3.021\,153\,165\,417\,908\,2$
$c_{17} = -0.366\,181\,500\,998\,445\,6$
$c_{18} = -0.462\,721\,898\,042\,653\,73$
$c_{19} = 18.796\,536\,774\,318\,561$
$c_{20} = -6.583\,773\,646\,109\,092\,3$
$c_{21} = 2.605\,438\,882\,170\,298\,5$
$c_{22} = -9.704\,249\,155\,834\,423\,5$
$c_{23} = 7.255\,901\,241\,057\,437\,7$
$c_{24} = -6.283\,868\,083\,142\,980\,5$
$c_{25} = -3.278\,343\,494\,705\,186\,2$
$c_{26} = 12.335\,695\,801\,686\,716$
$c_{27} = -14.002\,835\,402\,583\,143$
$c_{28} = 5.789\,219\,550\,064\,681\,9$

appropriate to derive the value of some of the parameters from physical considerations. For instance, the bond length and molecular volume of many real molecules are well known. Therefore, our suggestion is to obtain L^* and σ from the molecular volume and the bond length (in the case of a diatomic molecule). Thus, once the bond length and molecular volume are known, this will determine L^* and σ by noting that the bond length L and molecular volume V_m of a diatomic molecule are given by:

$$L = L^*\sigma \tag{11}$$

$$V_m = \frac{\pi}{6}\sigma^3(1 + 1.5L^* - 1/2(L^*)^3) \tag{12}$$

In the case of a triatomic molecule as CO_2 it is not so obvious how to map the molecule into a 2CLJQ model. We should mention that CO_2 has been described by a 2CLJQ model previously in a number of papers.[9,10,14] Also, CO_2 has been described succesfully by using the Kihara quadrupolar model.[27] The reduced bond length used commonly for CO_2 in a number of models is close to $L^* = 0.80$, the typical width of the molecule[28,29] being about $\sigma = 2.95$ Å. These values provide a good description of the liquid phase properties, and as such they can be taken as being reasonable. How do we determine the other two parameters, namely, ε and $(Q^*)^2$? For a number of substances the quadrupole moment has been determined experimentally. See for instance the excellent review by Gray and Gubbins for extensive tables of quadrupole moments.[17] It should be mentioned however, that the typical uncertainty of experimental values is quite large and can be of up to 40%. Once the experimental value of the quadrupole moment, Q_{exp}, is known, the reduced quadrupole is obtained from the formula:

$$(Q^*) = \frac{85.11025 Q_{exp}}{\sqrt{(\varepsilon/k)(\sigma/A)^5}} \tag{13}$$

where Q_{exp} is given in units of 10^{-26} esu (which is the standard way of reporting the experimental values). For CO_2 the experimental[17,30] value of the quadrupole moment is $Q_{exp} = -4.5$ (in 10^{-26} esu units) although some recent measurements suggest the somewhat lower value $Q_{exp} = -4.0$.[31] Once L^*, σ and Q_{exp} are derived we proceed as follows. A value for ε is chosen. By using this value of ε the reduced quadrupole moment is obtained from eqn. (13). The value of B_2 is then computed for this model at $T = 273.15$ K and is compared with the experimental value. If they do not match then another value of ε is chosen and B_2 is recalculated. This is repeated until for a certain choice of ε the calculated and the experimental value of B_2 at $T = 273.15$ K match. In Table 4 the parameters used to describe CO_2 are shown. In Fig. 5 B_2 for CO_2 is shown. Symbols correspond to experimental results and the solid line represents the results obtained in this work using the model described in Table 4. As can be seen, the agreement between experimental and theoretical predictions is rather good. Let us now illustrate how the inclusion of the quadrupole moment is essential to the description B_2 for CO_2. For that purpose we shall use a second model which has the same value of L^* and σ but with $(Q^*)^2 = 0$. The value of ε for this non-polar model is again obtained by fitting B_2 at $T = 273.15$ K. The value of ε for this non-polar model is given in Table 4. Notice that when the quadrupole is not included a larger value of ε is needed to reproduce the second virial coefficient at $T = 273.15$ K. Therefore we forced both models, the quadrupolar and the non-polar models to reproduce B_2 of CO_2 at $T = 273.15$ K. In Fig. 5 the theoretical predictions for the non-polar model are shown as a dashed line. As can be seen, the non-polar model does not provide such a good

Table 4 Parameters used to describe real molecules with the 2CLJQ model

Substance	L/A	σ/A	(ε/k)/K	$Q/(10^{-26}$ esu)
Xe	0	4.099	224.5	0
CO_2	2.3572	2.946	123.0	−4.5
CO_2	2.3572	2.946	161.10	0
Ethane	1.54	3.825	103.31	0
Ethylene	1.34	3.79	83.85	4.0

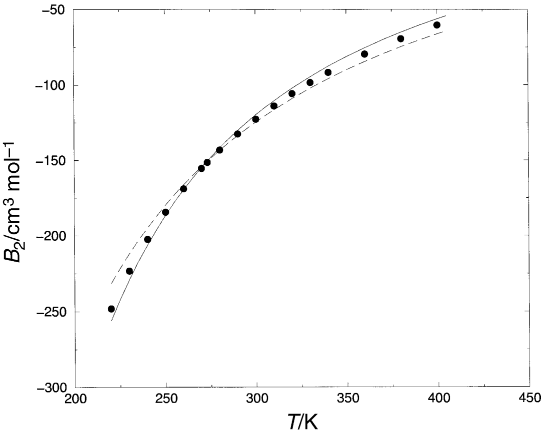

Fig. 5 Second virial coefficient of CO_2 as obtained from experiment (symbols) and from the calculations of this work for the 2CLJQ model. The parameters used for the 2CLJQ are those given in Table 4. Results for $(Q^*)^2 = 0$ (dashed line), results for the quadrupolar model of CO_2 described in Table 4 (*i.e.* $(Q^*)^2 = 5.47$) (solid line).

description of the experimental results. The conclusion that we come to by looking at Fig. 5 is that the inclusion of the quadrupole moment significantly improves the description of the second virial coefficient of a molecule such as carbon dioxide. When attractive dispersion forces from the 2CLJQ are replaced by a more sophisticated version obtained from quantum mechanical calculations the agreement between experiment and calculations can even be quantitative.[32] This is not only true for gas phase properties. It is well known that the inclusion of the quadrupole greatly improves the description of liquid phase properties, and it is absolutely essential[19] for the description of the solid phase of CO_2 (without the quadrupole it is impossible to stabilize the experimental solid phases of CO_2).

Although we have presented results for CO_2 the same procedure can be applied to other substances. We hope the results provided in this work (along with the fits) encourage further application of the 2CLJQ model to the description of B_2 to real substances.

All the results presented so far correspond to pure fluids. However, the inclusion of the quadrupole can be important in order to understand some properties of mixtures. The second virial coefficient of a binary mixture is given by the following expression:

$$B_2 = x_1^2 B_2^{11} + 2x_1 x_2 B_2^{12} + x_2^2 B_2^{22} \tag{14}$$

where B_2^{ii} is the second virial coefficient of component i, and B_2^{ij} is the crossed second virial coefficient between component i and component j. The crossed second virial coefficient between Xe and several molecules (*i.e.* CO_2, ethane and ethylene) have recently been measured experimentally.[33,34] We shall try to describe the experimental values. For that purpose the parameters of the 2CLJQ model were obtained for the pure substances by imposing values for L^*, σ and Q_{exp} and choosing ε to reproduce the experimental value of B_2 at $T = 273.15$ K. The values of σ and L^* for Xe, ethane and ethylene were taken from parameters that correctly describe the liquid phase[4,35–37] and the reduced quadrupole is obtained by using the experimental value of the quadrupole moment.[17]

The parameters obtained are presented in Table 4. In Table 5 the second virial coefficient at $T = 273.15$ K as obtained from experiment and from our fit are shown. Obviously the agreement is excellent since we forced ε to reproduce the experimental results. Once the parameters for the pure substances have been determined we shall assume that the parameters for the cross interaction in the mixture are given by the Lorenz–Berthelot combination rules:

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \tag{15}$$

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \tag{16}$$

Sometimes additional parameters are included to account for possible deviations from the Lorentz–Berthelot rules but here we shall assume that they are valid. In eqn. (1) we replace $(Q^*)^2$ by $Q_1^* Q_2^*$ where $(Q_1)^*$ and $(Q_2)^*$ are the reduced quadrupole moments of molecules 1 and 2, respectively. In Table 6 the crossed virial coefficients obtained from experiment and from the calculations are presented. The agreement between experiment and our calculations is quite good. Notice that although we have fitted the results for the pure components it is not obvious that the calculations should be able to accurately reproduce the crossed virial coefficient.

Table 5 Second virial coefficient at $T = 273.15$ K in $cm^3\ mol^{-1}$ as obtained from experiment and from the calculations of this work for the 2CLJQ model with the parameters of Table 4. The value of ε presented in Table 4 was chosen to reproduce the experimental value at this temperature

Substance	Experimental	Calculated
Xe	−155.7	−155.6
CO_2	−150.7	−150.6
Ethane	−222.9	−222.7
Ethylene	−168.8	−168.6

Table 6 Crossed second virial coefficient B_{12} at $T = 273.15$ K in $cm^3\ mol^{-1}$ as obtained from experiment and from the calculations of this work for the 2CLJQ model with the parameters of Table 3 and the Lorentz–Berthelot rules for the crossed interaction

Mixture	Experimental	Calculated
Xe–CO_2	−126.4	−129.4
Xe–Ethane	−187.2	−187.6
Xe–Ethylene	−158.4	−158.8

Let us analyze in more detail the results for the Xe + CO_2 mixture. As can be seen in Table 5, for $T = 273.15$ K the values of B_2 for Xe and CO_2 are $-156\ cm^3\ mol^{-1}$ and $-151\ cm^3\ mol^{-1}$, respectively. One would naïvely expect that the crossed virial coefficient will fall between those two values (this is quite often found experimentally for many other systems). However, the experimental value of B_{12} for this mixture is $B_{12} = -126\ cm^3\ mol^{-1}$. How does one explain such a large deviation? The calculations reproduce this trend since they yield $B_{12} = -129\ cm^3\ mol^{-1}$, which is in fair agreement with the experimental result. The calculations provide the answer to this puzzling feature. The value of B_{12} for this mixture arises from the fact that there is no quadrupole–quadrupole interaction between Xe and CO_2 since the quadrupole moment of a spherical molecule, such as Xe, is zero. Since the quadrupolar interaction is missing the interaction between these two molecules is less attractive and that explains the high value of B_{12}. Basically the value of B_{12} is given by the dispersion interactions between Xe and CO_2. Therefore the presence or absence of quadrupole moment in one or both of the two molecules of a mixture can be very important in correctly describing the crossed virial coefficient.[38] The high value of B_{12} also suggests low miscibility for Xe and CO_2 in the liquid phase. We should mention that in this study we have not included polarizability within the model. The fact that spherical molecules can be polarized by a polar molecule has not been considered here although, as shown in a recent work, the effect may be important especially for the case of a spherical particle interacting with a dipolar one.[39]

The results given in Table 6 show that the second virial coefficient between a spherical molecule and a molecule with a strong quadrupole moment is significantly higher than one should expect. The reason for this is that the polar interaction does not appear in the crossed interaction.

We shall finish by evaluating some other properties of interest for the ethylene + CO_2 mixture. The Joule–Thomson coefficient of a pure fluid is usually obtained from the following relationship:

$$^0\phi = B_2 - T\frac{\mathrm{d}B_2}{\mathrm{d}T} \tag{17}$$

The coefficient $^0\phi_{\mathrm{mixture}}$ for the mixture is then obtained from:

$$^0\phi_{\mathrm{mixture}} = x_1^2\,{}^0\phi_1 + x_2^2\,{}^0\phi_2 + 2x_1x_2\,{}^0\phi_{12} \tag{18}$$

where $^0\phi_1$, $^0\phi_2$ are the values of the Joule–Thomson coefficient for components one and two, respectively, and $^0\phi_{12}$ is the value of the Joule–Thomson coefficient for the cross interaction. In Fig. 6 results are presented for the Joule–Thomson coefficient for ethylene + CO_2.[40] Symbols correspond to experimental results whereas the solid line corresponds to the

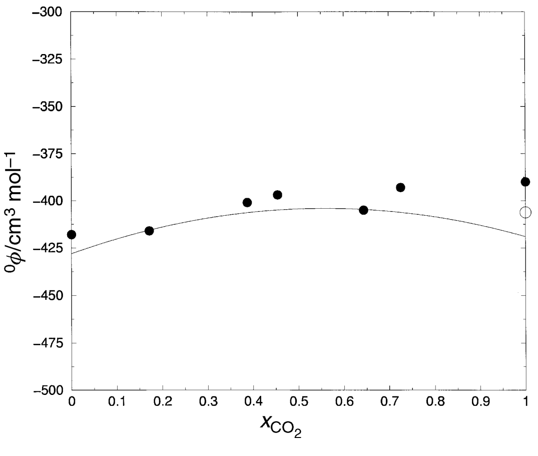

Fig. 6 Joule–Thomson coefficient for the ethylene–CO_2 mixture at $T = 298.15$ K as obtained from experiment[40] (filled symbols) and for the 2CLJQ model with the parameters presented in Table 4. The open symbol for pure CO_2 has been evaluated by using eqn. (17) and the most recent experimental data available for B_2 of CO_2.

calculations of this work. As can be seen the calculations show fair agreement with experiment. It should be noted that for pure CO_2 the experimental value of $^0\phi_2$ is probably too high. In fact, re-evaluating $^0\phi_2$ with the best data currently available for the second virial coefficient of CO_2 yields the point denoted by the open circle of Fig. 6. This example illustrates that not only virial coefficients but also other related properties, such as the Joule–Thomson coefficient, can be obtained from the calculations.

4 Conclusions

In this paper the second virial coefficient has been calculated for a number of two-center LJ models which have a point quadrupole. Elongations in the range $L^* = (0–1)$, and quadrupole moments in the range $(Q^*)^2 = (0–4)$ were considered. In total, 77 different models have been analyzed. For each model B_2 has been computed for around 200 different temperatures. The experimental results of B_2 were fitted to an empirical expression. The Boyle temperature was also computed for those 77 different models. The source data as well as the programs of the fit are available upon request (cvega@eucmos.sim.ucm.es) or can be obtained directly from the electronic supplementary information (ESI) system of this journal.†

The presence of the quadrupole moment is seen to reduce the second virial coefficient with respect to that of the non-polar model. The inclusion of a quadrupole serves to increase the value of the Boyle temperature.

It has also been shown how the introduction of the quadrupole significantly improves the description of the second virial coefficient for molecules which have a large quadrupole moment, as is the case for carbon dioxide. We hope the data obtained in this work can be useful for workers trying to describe experimental results of B_2 of real substances with the 2CLJQ model. Even those workers looking for potential parameters to describe liquid properties can benefit from these kinds of studies. In fact, they could proceed in a two step approach in the search of the potential parameters set. They can first determine a set of potential parameters describing the gas phase (*i.e.* the second virial coefficient) and then proceed to a refinement of the parameters by using computer simulations in the liquid phase. It should be stated that parameters describing gas phase properties do not describe particularly well the liquid phase properties and *vice versa.* One should bear in mind that three body forces play an important role in determining liquid phase properties whereas they do not appear in the gas phase. Therefore, potential parameters determined for the liquid phase can be considered as effective potential parameters rather than the true pair potential parameters.

We have also shown that the quadrupolar interactions play an important role in understanding the crossed second virial coefficient B_{12} between spherical and polar molecules. In particular, we have shown that the anomalous low value of B_{12} for mixtures as Xe and CO_2 is due to the absence of quadrupolar energy in the pair interaction.

Work on the determination of the third virial coefficient for 2CLJQ is in progress. Also, to the best of our knowledge there has been no calculation of the third virial coefficient for the non-polar 2CLJ model. Furthermore, a study of the effect of a dipole moment on the second virial coefficient would be of much interest.[41]

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References

1 A. A. Fredenslund, J. Mollerup and L. J. Christiansen, *Cryogenics*, 1973, **13**, 414.
2 F. Fontalba, K. N. Marsh, J. C. Holste and K. R. Hall, *Fluid Phase Equilib.*, 1988, **41**, 141.
3 J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley and Sons Inc., New York, 1940.
4 D. A. McQuarrie, *Statistical Mechanics*, Harper and Row, New York, 1976.
5 J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, Academic Press, New York, 1986.
6 T. Boublik and I. Nezbeda, *Collect. Czech. Chem. Commun.*, 1986, **51**, 2301.
7 T. Kihara, *Intermolecular Forces*, John Wiley and Sons, Bath, 1978.
8 C. Vega and D. Frenkel, *Mol. Phys.*, 1989, **67**, 633.
9 K. Singer, A. J. Taylor and J. V. L. Singer, *Mol. Phys.*, 1979, **37**, 1239.
10 C. S. Murthy, K. Singer and I. R. McDonald, *Mol. Phys.*, 1981, **44**, 135.
11 J. P. Ryckaert and A. Bellemans, *Faraday Discuss. Chem. Soc.*, 1978, **66**, 95.
12 B. Smit, S. Karaborni and J. I. Siepmann, *J. Chem. Phys.*, 1995, **102**, 2126.
13 C. Vega and A. Lopez Rodriguez, *J. Chem. Phys.*, 1996, **105**, 4223.
14 D. Moller and J. Fischer, *Fluid Phase Equilib.*, 1994, **100**, 35.
15 G. C. Maitland, W. Rigby, E. B. Smith and W. A. Wakeham, *Intermolecular Forces, Their origin and determination*, Clarendon Press, Oxford, 1981.
16 T. Boublik, *Collect. Czech Chem. Commun.*, 1994, **59**, 756.
17 K. E. Gubbins and C. G. Gray, *Theory of Molecular Liquids*, Oxford University Press, Oxford, 1984.
18 B. Garzon, S. Lago, C. Vega, E. de Miguel and L. F. Rull, *J. Chem. Phys.*, 1994, **101**, 4166.
19 C. Vega and P. A. Monson, *J. Chem. Phys.*, 1995, **102**, 1361.
20 C. Vega, B. Garzon, S. Lago and P. A. Monson, *J. Mol. Liq.*, 1998, **76**, 157.
21 H. Conroy, *J. Chem. Phys.*, 1967, **47**, 5307.
22 I. Nezbeda, J. Kolafa and S. Labik, *Czech. J. Phys. B*, 1989, **39**, 65.
23 J. H. Dymond, J. A. Cholinski, A. Szafranski and D. Wyrzykowska Stankewicz, *Fluid Phase Equilib.*, 1986, **27**, 1.
24 C. Tsonopoulos and J. H. Dymond, *Fluid Phase Equilib.*, 1997, **133**, 11.
25 J. Pavlicek, K. Aim and T. Boublik, *Collect. Czech. Chem. Commun.*, 1993, **58**, 2489.
26 J. H. Dymond and E. B. Smith, *The virial coefficient of pure gases and mixtures*, Clarendon Press, Oxford, 1980.
27 T. Boublik, *Mol. Phys.*, 1991, **73**, 417.
28 T. Boublik, *J. Chem. Phys.*, 1987, **87**, 1751.

29 C. Vega and K. E. Gubbins, *Mol. Phys.*, 1992, **75**, 881.

30 D. Stogryn and A. P. Stogryn, *Mol. Phys.*, 1966, **11**, 371.

31 C. Graham, J. Pierrus and R. E. Raab, *Mol. Phys.*, 1989, **67**, 939.

32 M. Luckcas and K. Lucas, *Fluid Phase Equilib.*, 1989, **45**, 7.

33 A. Aguiar Ricardo and M. Nunes da Ponte, *J. Phys. Chem.*, 1996, **100**, 18839.

34 A. Aguiar Ricardo, M. Nunes da Ponte and J. Fischer, *J. Phys. Chem.*, 1996, **100**, 18844.

35 A. E. Sherwood and J. M. Prausnitz, *J. Chem. Phys.*, 1964, **41**, 429.

36 T. M. Reed and K. E. Gubbins, *Applied Statistical Mechanics*, McGraw-Hill, New York, 1973.

37 S. K. Nath, F. A. Escobedo, J. J. de Pablo and I. Patramai, *Ind. Eng. Chem. Res.*, 1998, **37**, 3195.

38 C. J. Wormald and P. W. Johnson, *J. Chem. Thermodyn.*, 1999, **31**, 1085.

39 T. Boublik and J. Winkelmann, *Mol. Phys.*, 1999, **96**, 435.

40 A. Charnley, J. S. Rowlinson, J. R. Sutton and J. R. Townley, *Proc. R. Soc. London, Ser. A*, 1955, **230**, 354.

41 C. Vega, B. Saager and J. Fischer, *Mol. Phys.*, 1989, **68**, 1079.