

# Critical properties of molecular fluids from the virial series

L. G. MacDowell, C. Menduiña, and C. Vega

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

E. de Miguel

*Departamento de Física Aplicada, Facultad de Ciencias Experimentales, Universidad de Huelva, 21071, Huelva, Spain*

(Received 18 June 2003; accepted 4 September 2003)

We present results for the fourth virial coefficient of quadrupolar Lennard-Jones diatomics for several quadrupole moments and elongations. The coefficients are employed to predict the critical properties from two different truncated virial series. The first one employs the exact second and third virial coefficients, calculated in our previous work. The second includes also the exact fourth virial coefficient as obtained in this work. It is found that the first method yields already fairly good predictions. The second method significantly improves on the first one, however, yielding good results for both the critical temperature and pressure. Particularly, when compared with predictions from perturbation theories available in the literature, the virial series to fourth order compares favorably for the critical temperature. The results suggest that the failure of perturbation theories to predict the critical temperature and pressure is not only related to the neglect of density fluctuations, but also to poor prediction of the virial coefficients. © 2003 American Institute of Physics.  
[DOI: 10.1063/1.1622373]

## I. INTRODUCTION

The virial series is a simple and physically based equation of state which allows to describe the  $pVT$  behavior over a wide range of conditions, as well as to explore the nature of molecular interactions.<sup>1</sup> Despite of its formal simplicity, the use of this equation of state has been limited, since both experimental and theoretical calculations beyond the second virial coefficient have proven to be rather difficult.<sup>2</sup> Nevertheless, the study of virial coefficients has been extremely fruitful in the development of widely employed equations of state for hard fluids, such as hard spheres,<sup>3</sup> hard convex bodies,<sup>4</sup> or even hard sphere chain fluids.<sup>5</sup> The information on virial coefficients of more realistic fluids incorporating attractive interactions is much more limited, however. Comprehensive data of the higher virial coefficients over a wide range of temperatures is available only for simple atomic fluids, such as the square well,<sup>6</sup> and the Lennard-Jones.<sup>7-9</sup> For molecular fluids, however, only a few calculations of the third virial coefficients have been reported,<sup>10-13</sup> and very few less, if any, for higher order coefficients. Despite this lack of knowledge, the virial series of simple molecular fluids has attracted much attention recently. First, it has been recognized that the knowledge of just a few virial coefficients may provide a simple and accurate equation of state for use in the field of supercritical extraction.<sup>13-15</sup> Second, it has been also observed that the series performs rather well very close to the critical point, providing accurate estimates of the critical properties.<sup>12,16,17</sup> Actually, this idea had been exploited long time ago. By using numerical results for the second, third, and fourth virial coefficients of the Lennard-Jones fluid, Barker and Monaghan estimated the critical temperature to be  $k_B T_c / \epsilon = 1.300$ .<sup>6</sup> This prediction is not only in very good

agreement with presently available results, i.e.,  $k_B T_c / \epsilon = 1.309$ ;<sup>18</sup> it is also more accurate than the extrapolation obtained some years later from computer simulations ( $k_B T_c / \epsilon = 1.36$ ),<sup>19</sup> and accepted for about two decades (see, e.g., Ref. 20). Fortunately, the computational resources presently available allow us to calculate, for the first time, fourth virial coefficients of molecular models with attractive forces, thus allowing to test the generality of this idea for a great variety of models.

The remaining of this paper is organized as follows. In the next section we introduce the model and describe the numerical method employed to calculate fourth virial coefficients. In Sec. III we present and discuss the results. Finally, in Sec. IV we present our conclusions.

## II. MODEL AND CALCULATION DETAILS

We will henceforth consider Lennard-Jones diatomic molecules with bond length  $L$  and an embedded point quadrupole. The full interaction potential may be expressed as

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

where  $u_{ij}$  are site-site Lennard-Jones potentials which only depend on the distance,  $d_{ij}$  between the sites,

$$u_{ij}^{\text{LJ}} = 4\epsilon \left\{ \left( \frac{\sigma}{d_{ij}} \right)^{12} - \left( \frac{\sigma}{d_{ij}} \right)^6 \right\} \quad (2)$$

while  $u_{QQ}$  is a quadrupole potential which depends on the total quadrupole moment,  $Q$ , the distance between the center of the molecules,  $r_{12}$ , and their relative orientation:<sup>21</sup>

$$u_{QQ} = \frac{3Q^2}{4r_{12}^5} (1 - 5(c_1^2 + c_2^2 + 3c_1^2c_2^2) + 2(s_1s_2c_{12} - 4c_1c_2)^2), \quad (3)$$

where  $c_i = \cos \theta_i$ ,  $s_i = \sin \theta_i$ , and  $c_{12} = \cos(\phi_2 - \phi_1)$ , while  $\theta_i$  and  $\phi_i$  are the polar and azimuthal angles required to specify the orientation of molecule  $i$ . Since the quadrupole potential shows a divergence for molecules whose center of mass coincides, the Lennard-Jones interaction sites are embedded by hard spheres of diameter  $\sigma/\sqrt{2}$ . Such a diameter is the smallest choice one can make in order to avoid overflow of the Boltzmann factor for overlapping molecules with bond length  $L = 1.0$ ,

The fourth virial coefficient,  $B_4$ , is calculated as a sum of three different contributions,<sup>1,21</sup>

$$B_4 = 3D_4 + 6D_5 + D_6. \quad (4)$$

Each of the terms in the sum is obtained as a multidimensional integral of the form<sup>1,21</sup>

$$D_k = -\frac{1}{8V} \int \int \int \langle G_k \rangle_{\omega_1, \omega_2, \omega_3, \omega_4} \mathbf{dr}_1 \mathbf{dr}_2 \mathbf{dr}_3 \mathbf{dr}_4, \quad (5)$$

where  $\langle \dots \rangle_{\omega_1, \omega_2, \omega_3, \omega_4}$  denotes an unweighted average over molecular orientations, and  $G_k$  are products of Mayer functions,  $f_{ij} = \exp(-u(i,j)/k_B T) - 1$ ,

$$G_4 = f_{12}f_{23}f_{34}f_{41}, \quad (6)$$

$$G_5 = f_{12}f_{23}f_{34}f_{41}f_{13}, \quad (7)$$

$$G_6 = f_{12}f_{23}f_{34}f_{41}f_{13}f_{24}. \quad (8)$$

For linear molecules as the ones considered in this work, it is seen that the calculation of the fourth virial coefficient involves a 20-dimensional integral. Taking into account translational and rotational invariance, the integral is reduced to a 14-dimensional quadrature. Owing to the high dimensionality of the integral, the evaluation of fourth virial coefficients has become feasible only recently. In practice, the integral must be solved using a Monte Carlo method. The procedure is essentially that described previously for the calculation of  $B_3$ ,<sup>22</sup> with the difference that one must further sample the five degrees of freedom specifying the position and orientation of the fourth molecule. Sampling of the fourth molecule is performed in the same way as for the third molecule in calculations of  $B_3$ . A detailed account of the methodology may be found elsewhere.<sup>22</sup> By randomly sampling the configurations as specified, the  $D_k$  coefficients involved in the calculation of  $B_3$  are given by

$$D_k = -2^3 \pi^3 R_{\max}^3 \frac{1}{N_t} \sum_{N_t} G_k r_{12}^2 r_{13}^2 r_{14}^2. \quad (9)$$

TABLE I. Cluster integrals required in the calculation of  $B_4$ . Results are shown for  $L/\sigma = 1$  and two quadrupole moments. The numbers in parentheses are the estimated error bars (not available for  $Q^2/\epsilon\sigma^5 = 1$ ). Note that the integrals are multiplied by the appropriate weights [cf. Eq. (4)].

$Q^2/\epsilon\sigma^5$	$k_B T/\epsilon$	$3 \times D_4/\sigma^9$	$6 \times D_5/\sigma^9$	$1 \times D_6/\sigma^9$
0.0	1.569 91	-372(2)	384(2)	7.4(0.7)
0.0	1.708 43	-219(1)	246(1)	0.13(0.4)
0.0	1.846 95	-143(1)	169(1)	-4.0(0.2)
0.0	1.985 47	-104(5)	125(1)	-5.2(0.2)
0.0	2.123 99	-81.7(0.4)	99.4(0.4)	-5.9(0.1)
1.0	1.591 97	-396	402	10.7
1.0	1.732 44	-227	256	0.35
1.0	1.872 91	-146	174	-3.2
1.0	2.013 38	-105	126	-5.0
1.0	2.153 84	-80	100	-5.7

In the above equation,  $N_t$  is the total number of configurations considered, while  $R_{\max}$  is the largest distance away from the origin where the centers of molecules were sampled. If we assume that the Mayer function vanishes for center to center distances larger than  $r_c$ , then, geometrical considerations allow us to set  $R_{\max} = 2r_c$ .

In our previous calculations for  $B_3$  we have shown that increasing  $r_c$  beyond  $r_c/\sigma = 5$  does not result in a significant improvement. The reason is that the statistical error bars very much increase with increasing  $r_c$ , so that whichever gain in accuracy due to better convergence is disguised by the increased error bars. As expected, similar difficulties were found for  $B_4$ , so that we keep this value here for consistency. A single  $B_4$  calculation involved averaging 200 independent blocks, while each block was obtained as a Monte Carlo average over  $90 \times 10^6$  configurations. The calculations were performed in a dual 2000 MHz Athlon machine. A single processor could deal with  $200 \times 30 \times 10^6$  configurations in about 11 hours of cpu time. Despite the considerable computational effort, the error in the calculations is about 5% but may be much larger for the lowest temperatures considered.

### III. RESULTS AND DISCUSSION

Calculations were performed for five different elongations,  $L/\sigma = 0.2, 0.4, 0.6, 0.8,$  and  $1.0$ . For each elongation, five different reduced square quadrupoles were considered,  $Q^2/\epsilon\sigma^5 = 0, 1, 2, 3,$  and  $4$ . Calculations for  $L/\sigma = 0$  and two quadrupoles,  $Q^2/\epsilon\sigma^5 = 1, 2$  were also performed. Results were obtained for five different temperatures ranging between 0.85 and 1.15 times the critical temperature as obtained from computer simulations.<sup>18</sup> We have checked our code by comparing with bibliographic results for the Lennard-Jones fluid,<sup>7,9</sup> and for hard-dumbbells.<sup>4</sup> Good agreement was found in all cases.

In Table I we show the contributions to  $B_4$  which arise from the graphs  $G_4$ ,  $G_5$ , and  $G_6$ . Results are shown for  $L/\sigma=1$ ,  $Q^2/\epsilon\sigma^5=0, 1$  and several temperatures. Note that  $D_4$ ,  $D_5$ , and  $D_6$  have been multiplied by their corresponding weight factors (i.e., 3, 6, and 1, respectively), so that their relative contribution to  $B_4$  may be observed at once. The first five rows of the table show results for  $L/\sigma=1$ ,  $Q^2/\epsilon\sigma^5=0$  for five different temperatures ranging from 0.85 and 1.15 times the critical temperature. Inspection of the data explain the temperature dependence observed for  $B_4$ , as well as the large error bars which arise in the numerical calculation of  $B_4$ . Typically, it is found that the contributions arising from  $D_4$  and  $D_5$  are large, similar in absolute values, but of opposite sign. On the other hand,  $D_6$  is small, and of similar order of magnitude than the difference between  $D_4$  and  $D_5$ . For this reason, the final value for  $B_4$  is of much smaller magnitude than  $D_4$  and  $D_5$ . As a result, small relative errors in these coefficients result in a large relative error in  $B_4$ . It is also interesting to note the temperature dependence of  $D_4$ ,  $D_5$ , and  $D_6$ . As the temperature is increased above  $T_c$ , the absolute values of  $D_4$  and  $D_5$  become smaller, while that of  $D_6$  becomes larger. Accordingly, as temperature increases the relative contribution of  $D_6$  becomes more important. Note also that the contribution due to  $D_4$  decreases faster than that of  $D_5$ , so that their sum gradually becomes more positive. This effect is balanced by increasing negative values of  $D_6$ . The overall result of this competition is the appearance of a maximum in  $B_4$ , close to the critical temperature.

The results for the fourth virial coefficients calculated in this work are gathered in Table II. Despite the lengthy calculations, the error bars are found to be rather large, especially at low temperatures. Also note that the error bars increase systematically with increasing elongation. For all the models considered,  $B_4$  is found to be positive at the critical point. As an example, Fig. 1 shows a plot of  $B_4$  as a function of temperature for  $L/\sigma=0.2$  and  $L/\sigma=0.6$  and several quadrupoles, where it is seen that within the temperature range considered  $B_4$  remains positive. We find that when the temperature is expressed in units of the critical temperature, the results for a given elongation but different quadrupole roughly collapse into a single curve, so that in this scale the effect of the quadrupole may be neglected, particularly at high temperature. Note, however, that this behavior is less clearly observed for  $L=0.6$ , especially at the lower temperatures. Nevertheless, for the higher temperatures the results do seem to collapse within statistical accuracy, while the large error bars for the two lowest temperatures make this comparison somewhat difficult.

One useful application of the virial series is the prediction of critical properties. To this end, we consider two different truncated virial series. The first one (VSB3) is truncated to third order, so that the equation of state is

$$\frac{p(\rho, T)}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3, \quad (10)$$

where  $B_2$  and  $B_3$  are taken from work reported previously.<sup>23,22</sup> In a second approximation (VSB4), we attempt to improve on the previous equation by considering a virial series truncated to fourth order, using the results of this work for  $B_4$ ,

$$\frac{p(\rho, T)}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + B_4(T)\rho^4. \quad (11)$$

In order to obtain the critical properties from these series, we fit our numerical results for  $B_3$  and  $B_4$  to sixth and second order polynomials in  $\exp(\epsilon/k_B T)$ , respectively.

In Fig. 2 we show results for the critical temperature obtained from the two different series for models with  $L/\sigma=0.2, 0.4, 0.6$ , and  $0.8$ . The theoretical predictions are compared with computer simulation results obtained by Stoll *et al.*<sup>18</sup> It is found that VSB3 already yields reasonable results, especially for those models with larger bond distances. Using the exact value for  $B_4$ , however, improves the situation significantly, yielding predictions for the critical temperature which typically lie within 1% of the simulation results. Also note that VSB3 systematically over predicts  $T_c$ , while VSB4 always under predicts  $T_c$ , so that the two methods would seem to bracket the simulation results.

A similar plot for the critical pressure is shown in Fig. 3, with results for  $L/\sigma=0.2, 0.4$ , and  $0.8$ . As for the critical temperature, VSB3 systematically over predicts the simulation results, while VSB4 systematically under predicts the results, although the latter approximation is clearly in better agreement. Once more, the agreement seems to improve with those models with larger bond length.

Finally, predictions for the critical density are shown in Fig. 4. Only results for  $L/\sigma=0.2$  and  $0.8$  are shown, for the sake of clarity. In this case it is found that VSB3 and VSB4 still bracket the simulation results, but the agreement is overall not as good. Surprisingly, in this case VSB3 is everywhere in better agreement than VSB4.

The reason for the poor performance of VSB4 in predicting the critical density may be explained as follows. It has been shown that the critical compressibility factor of a virial series of order  $k$  is given, to a first approximation, by the following equation:<sup>24-26</sup>

$$Z_c = \frac{1}{3} + H(k-3) \sum_{i=4}^k B_i / |B_2|^{i-1}, \quad (12)$$

where  $H(l)$  is a Heaviside step function. For a series truncated at third order,  $Z_c$  is  $1/3$ . For  $k=4$ , one must add to this a term linear in  $B_4$ . Since  $B_4$  was shown to be positive at the critical point for all the models considered, it is clear that  $Z_c$  becomes even larger than  $1/3$ . Actually, experimental critical compressibility factors are usually smaller than  $1/3$ , so that adding  $B_4$  to the virial series results in a poorer agreement for the critical density.

TABLE II. Results for the fourth virial coefficient of quadrupolar Lennard-Jones diatomics for different bond length  $L$  and quadrupole,  $Q$ .  $\Delta B_4$  stands for the error bars obtained as  $1/\sqrt{N_f-1}$  times the standard deviation of the mean.

$L/\sigma$	$Q^2/\epsilon\sigma^5$	$k_B T/\epsilon$	$B_4/\sigma^9$	$\pm \Delta B_4/\sigma^9$	$L/\sigma$	$Q^2/\epsilon\sigma^5$	$k_B T/\epsilon$	$B_4/\sigma^9$	$\pm \Delta B_4/\sigma^9$
0.0	1.0	1.3600	0.69	0.39	0.6	1.0	2.6791	10.34	0.35
0.0	1.0	1.4800	2.35	0.21	0.6	1.0	2.8660	8.16	0.25
0.0	1.0	1.6000	2.17	0.12	0.6	2.0	2.1895	8.42	1.75
0.0	1.0	1.7200	1.90	0.08	0.6	2.0	2.3826	12.82	0.96
0.0	1.0	1.8400	1.50	0.06	0.6	2.0	2.5758	13.73	0.57
0.0	2.0	1.9125	1.83	1.72	0.6	2.0	2.7690	10.03	0.41
0.0	2.0	2.0812	2.24	0.73	0.6	2.0	2.9622	8.02	0.29
0.0	2.0	2.2500	1.43	0.38	0.6	3.0	2.2969	6.43	2.45
0.0	2.0	2.4188	1.13	0.24	0.6	3.0	2.4996	10.83	1.31
0.0	2.0	2.5875	0.69	0.13	0.6	3.0	2.7023	13.46	0.73
0.2	0.0	3.6473	3.24	0.16	0.6	3.0	2.9049	9.37	0.50
0.2	0.0	3.9691	4.54	0.11	0.6	3.0	3.1076	7.56	0.34
0.2	0.0	4.2909	4.29	0.07	0.6	4.0	2.4317	5.22	3.05
0.2	0.0	4.6128	3.70	0.05	0.6	4.0	2.6463	9.16	1.51
0.2	0.0	4.9346	3.14	0.04	0.6	4.0	2.8608	12.06	0.91
0.2	1.0	3.7053	3.23	0.18	0.6	4.0	3.0754	9.21	0.58
0.2	1.0	4.0322	4.47	0.12	0.6	4.0	3.2899	7.09	0.40
0.2	1.0	4.3592	4.29	0.08	0.8	0.0	1.7449	11.72	1.96
0.2	1.0	4.6861	3.64	0.05	0.8	0.0	1.8989	20.91	1.27
0.2	1.0	5.0130	3.09	0.04	0.8	0.0	2.0529	18.13	0.81
0.2	2.0	3.8628	2.27	0.33	0.8	0.0	2.2068	14.33	0.55
0.2	2.0	4.2036	4.39	0.20	0.8	0.0	2.3608	10.90	0.47
0.2	2.0	4.5445	4.31	0.12	0.8	1.0	1.7686	10.71	2.19
0.2	2.0	4.8853	3.39	0.09	0.8	1.0	1.9246	21.62	1.44
0.2	2.0	5.2261	2.85	0.07	0.8	1.0	2.0807	19.80	0.89
0.2	3.0	4.0952	1.63	0.51	0.8	1.0	2.2367	15.37	0.61
0.2	3.0	4.4565	4.19	0.28	0.8	1.0	2.3928	11.89	0.52
0.2	3.0	4.8178	4.24	0.18	0.8	2.0	1.8331	7.15	3.25
0.2	3.0	5.1792	3.10	0.12	0.8	2.0	1.9948	21.25	1.83
0.2	3.0	5.5405	2.63	0.09	0.8	2.0	2.1566	19.98	1.09
0.2	4.0	4.3777	1.08	0.79	0.8	2.0	2.3183	15.23	0.75
0.2	4.0	4.7640	3.94	0.41	0.8	2.0	2.4801	11.91	0.60
0.2	4.0	5.1503	4.18	0.26	0.8	3.0	1.9291	1.33	5.16
0.2	4.0	5.5365	2.77	0.17	0.8	3.0	2.0993	19.98	2.44
0.2	4.0	5.9228	2.39	0.11	0.8	3.0	2.2695	19.16	1.43
0.4	0.0	2.6856	5.57	0.37	0.8	3.0	2.4397	14.33	0.96
0.4	0.0	2.9225	8.54	0.25	0.8	3.0	2.6099	11.29	0.72
0.4	0.0	3.1595	7.77	0.17	0.8	4.0	2.0470	-7.19	7.95
0.4	0.0	3.3965	6.42	0.11	0.8	4.0	2.2276	17.91	3.37
0.4	0.0	3.6334	5.23	0.09	0.8	4.0	2.4083	17.75	1.93
0.4	1.0	2.7197	5.84	0.40	0.8	4.0	2.5889	13.13	1.24
0.4	1.0	2.9596	8.29	0.25	0.8	4.0	2.7695	10.33	0.88
0.4	1.0	3.1996	7.91	0.18	1.0	0.0	1.5699	21.61	2.91
0.4	1.0	3.4396	6.52	0.12	1.0	0.0	1.7084	24.80	1.82
0.4	1.0	3.6795	5.29	0.09	1.0	0.0	1.8470	20.02	1.14
0.4	2.0	2.8139	5.78	0.53	1.0	0.0	1.9855	15.73	0.79
0.4	2.0	3.0622	7.80	0.31	1.0	0.0	2.1240	12.36	0.54
0.4	2.0	3.3105	7.83	0.22	1.0	1.0	1.5920	16.67	3.20
0.4	2.0	3.5587	6.44	0.14	1.0	1.0	1.7324	29.33	1.73
0.4	2.0	3.8070	5.16	0.11	1.0	1.0	1.8729	23.99	1.12
0.4	3.0	2.9563	3.92	1.02	1.0	1.0	2.0134	16.03	0.68
0.4	3.0	3.2171	7.34	0.60	1.0	1.0	2.1538	14.23	0.47
0.4	3.0	3.4780	7.79	0.36	1.0	2.0	1.6520	9.86	6.04
0.4	3.0	3.7388	5.92	0.26	1.0	2.0	1.7977	23.55	3.26
0.4	3.0	3.9997	4.95	0.17	1.0	2.0	1.9435	22.55	1.98
0.4	4.0	3.1349	2.21	1.47	1.0	2.0	2.0892	18.58	1.23
0.4	4.0	3.4115	6.36	0.84	1.0	2.0	2.2350	13.53	0.87
0.4	4.0	3.6881	7.44	0.50	1.0	3.0	1.7405	-1.75	11.38
0.4	4.0	3.9647	5.54	0.34	1.0	3.0	1.8941	21.40	5.60
0.4	4.0	4.2413	4.67	0.21	1.0	3.0	2.0477	20.48	3.19
0.6	0.0	2.0926	9.59	1.23	1.0	3.0	2.2013	16.98	1.78
0.6	0.0	2.2773	13.63	0.69	1.0	3.0	2.3549	12.97	1.20
0.6	0.0	2.4619	13.06	0.48	1.0	4.0	1.8484	-13.40	23.09
0.6	0.0	2.6465	10.12	0.33	1.0	4.0	2.0115	20.68	10.66
0.6	0.0	2.8312	7.85	0.24	1.0	4.0	2.1746	18.31	5.72
0.6	1.0	2.1183	9.62	1.34	1.0	4.0	2.3377	14.58	2.78
0.6	1.0	2.3052	13.80	0.75	1.0	4.0	2.5008	12.33	1.75
0.6	1.0	2.4922	13.64	0.49	1.0	4.0			

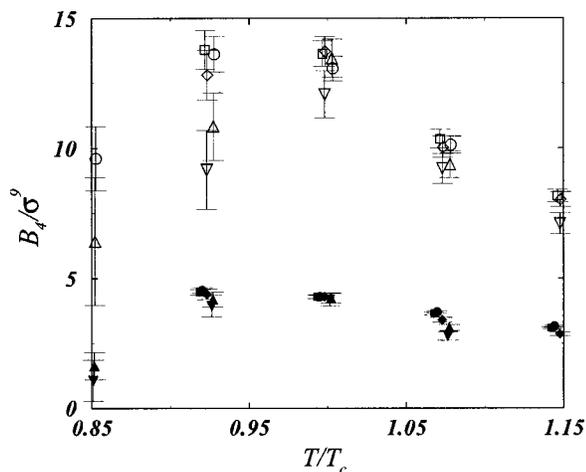


FIG. 1. Fourth virial coefficients as a function of temperature for  $L/\sigma=0.2$  (filled symbols) and  $L/\sigma=0.6$  (empty symbols); circles, squares, diamonds, triangle up, and triangle down correspond to  $Q^2/\epsilon\sigma^5=0, 1, 2, 3,$  and  $4,$  respectively.

It is also interesting to note that the critical density seems to be far less sensitive to changes in the quadrupole moment than the critical temperature and pressure. Such a behavior is probably the result of several factors, and a thorough explanation would be presumably rather involved. However, a simple explanation may be given in terms of a van der Waals mean field theory.<sup>27</sup> In such theories, one writes down the free energy in terms of two contributions. The first one is related to the short range repulsive interactions; the second one includes the effect of all attractive forces in a mean field approximation. For such a perturbation expansion, one can show that the critical density only depends on molecular parameters related to the harsh repulsive forces (i.e., molecular elongation and volume).<sup>28</sup> Hence, to a first approximation the critical density may be considered to depend only on the shape, but not on the quadrupolar interactions. According to this simple theoretical treatment, on the other hand, both critical temperature and pressure depend

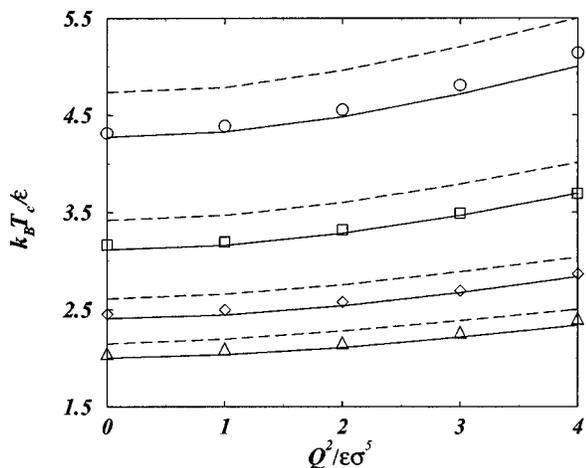


FIG. 2. Critical temperatures for different elongations as a function of the quadrupole moment. Symbols, simulation results from Ref. 18: circles,  $L/\sigma=0.2$ ; squares,  $L/\sigma=0.4$ ; diamonds,  $L/\sigma=0.6$ ; triangles,  $L/\sigma=0.8$ ; lines, theoretical estimates, VSB3 (dashed line), VSB4 (full line).

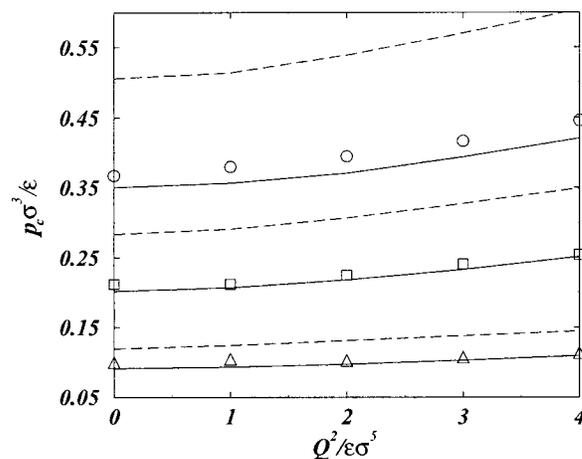


FIG. 3. As in Fig. 2 but for the critical pressure.

on the van der Waals constants, which accounts for the attractive interactions.<sup>28</sup> Therefore, to this low order approximation, the critical density should be less sensitive to changes in the quadrupole moment than the critical temperature and pressure.

An improvement of the predictions from the virial series with increasing anisotropy of the molecular core is observed. This trend could be expected, since the critical density of a molecule decreases with increasing anisotropy. Since our predictions are based on the virial series, one would then expect that they become the more accurate the smaller the critical density. However, the explanation may be somewhat more complicated. For example, in the case of the Lennard-Jones fluid, the critical temperature and pressure predicted from a virial series truncated to fourth order are  $k_B T_c/\epsilon=1.300$  and  $\sigma^3 \rho_c/\epsilon=0.122$ ,<sup>6</sup> in good agreement with computer simulation results,<sup>18</sup>  $k_B T_c/\epsilon=1.309$  and  $\sigma^3 \rho_c/\epsilon=0.118$ . (Note that the prediction for the critical temperature,  $k_B T_c/\epsilon=1.33$  made by Panagiotopoulos,<sup>29</sup> has been revised and lowered by several authors in later work.<sup>30,31,18</sup>) The agreement is far less satisfactory for the critical density, however. Indeed, the virial series predicts  $\sigma^3 \rho_c=0.268$ ,<sup>6</sup> while the simulation result is  $\sigma^3 \rho_c=0.31$ .<sup>29-31,18</sup> For the Lennard-Jones fluid and an embedded point quadrupole of  $Q^2/\epsilon\sigma^5$

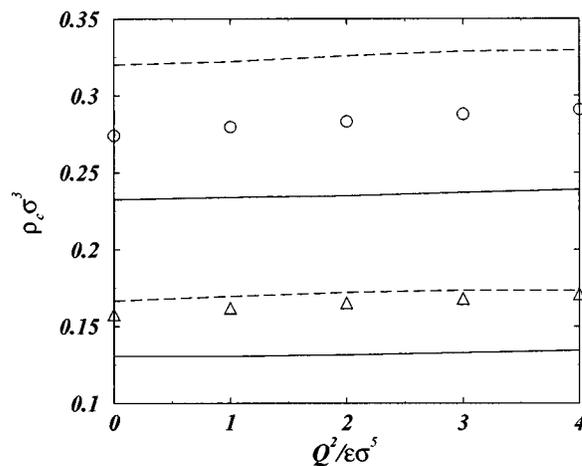


FIG. 4. As in Fig. 2 but for the critical density.

TABLE III. Critical properties for some selected molecular models with bond length  $L$  and quadrupole moment  $Q$ . The numbers on the left-hand side of the columns indicate simulation results from Ref. 18 (except second column, results from Refs. 32 and 30), while the numbers on the right-hand side indicate predictions as obtained from VSB4.

$L/\sigma$	$Q^2/\epsilon\sigma^5$	$k_B T_c/\epsilon$	$\sigma^3 \rho_c/\epsilon$	$\sigma^3 p_c/\epsilon$	$\sigma^3 \rho_c$	$\sigma^3 p_c$	$\sigma^3 \rho_c$
0.0	1.0	1.600	1.603	0.1486	0.1582	0.3395	0.2814
0.0	2.0	2.25	2.18	0.25	0.21	0.38	0.28
0.2	0.0	4.313	4.274	0.3670	0.3499	0.2740	0.2328
0.2	4.0	5.143	5.002	0.4460	0.4203	0.2908	0.2388
0.4	0.0	3.163	3.113	0.2116	0.2018	0.2251	0.1849
0.4	4.0	3.692	3.691	0.2540	0.2510	0.2358	0.1940
0.6	0.0	2.454	2.410	0.1353	0.1278	0.1850	0.1520
0.6	4.0	2.866	2.837	0.1665	0.1596	0.1960	0.1613
0.8	0.0	2.049	2.001	0.0995	0.0909	0.1577	0.1305
0.8	4.0	2.408	2.341	0.1140	0.1098	0.1710	0.1345

$=1$ , VSB4 predicts  $k_B T_c/\epsilon=1.60$ ,  $\sigma^3 p_c/\epsilon=0.16$ , and  $\sigma^3 \rho_c=0.28$ , to be compared with the simulation results  $k_B T_c/\epsilon=1.60$ ,  $\sigma^3 p_c/\epsilon=0.15$ , and  $\sigma^3 \rho_c=0.34$ . For  $Q^2/\epsilon\sigma^5=2$ , on the other hand, VSB4 predicts  $k_B T_c/\epsilon=2.18$  and  $\sigma^3 \rho_c=0.28$ , while according to simulation results,  $k_B T_c/\epsilon=2.25$  and  $\sigma^3 \rho_c=0.38$ .<sup>32,30</sup> Apparently, the decrease of accuracy with decreasing anisotropy affects the critical density much more than the critical temperature and pressure. We do note, however, that the predictions from VSB4 are subject to some statistical uncertainty, arising from the uncertainty in the virial coefficients themselves. In order to summarize these findings, Table III compares the critical properties obtained from simulation with those predicted by VSB4, for a number of models. From the table, it is seen that the performance of VSB4 increases with increasing elongation, although the results for  $L/\sigma=0$  are quite fair. The table also shows that the performance of VSB4 remains good for large quadrupole moments.

It would be interesting to compare the predictions obtained from VSB3 and VSB4 to predictions from thermodynamic perturbation theories. Unfortunately, these are usually numerically involved, and not that many results are available. In the literature we could only find predictions for critical properties of the Lennard-Jones plus quadrupole moment. Shing and Gubbins considered a perturbation theory to third order, cast on the form of a Padé approximant.<sup>33</sup> For a model with  $Q^2/\epsilon\sigma^5=2$ , they found  $k_B T_c/\epsilon=2.38$  and  $\sigma^3 \rho_c=0.40$ .<sup>34</sup> Similarly, using the linearized hypernetted chain or generalized mean field (LHNC-GMF),<sup>35,36</sup> they predict  $k_B T_c/\epsilon=2.43$  and  $\sigma^3 \rho_c=0.41$ .<sup>34</sup> A Padé approximant based on an approach by Twu *et al.*<sup>37</sup> was also employed by Stapleton *et al.*<sup>32</sup> for  $Q^2/\epsilon\sigma^5=1$ . Unfortunately, these authors do not give tabulated critical properties. From visual inspection, however, we estimate  $k_B T_c/\epsilon \approx 1.65$ . Comparing these results with those obtained from VSB4 and simulations (cf. preceding paragraph and Table III) it would seem that VSB4 performs better for the critical temperature, while both the Padé approximant and LHNC-GMF seem to yield better predictions for the critical density.

## IV. CONCLUSIONS

In summary, we have shown that a virial series truncated to fourth order yields good results for the critical temperature and pressure. The convergence of the series to this order is still, however, not fully satisfactory, because the agreement for the critical density is worse than that obtained for the series truncated to third order. The convergence is possibly very slow, and our experience on the calculation of  $B_4$  shows that the precise evaluation of  $B_5$  and higher order coefficients may be extremely time consuming. Nevertheless, the results suggest that the failure of classical theories to predict accurate critical temperatures and pressures is not only related to the neglect of fluctuations, but also, perhaps to a greater extent, to a poor prediction of the first few virial coefficients. An accurate prediction of the critical density from the virial series does seem unlikely, however.

## ACKNOWLEDGMENTS

Financial support is due to project No. BFM-2001-1420-C02-01 and BFM-2001-1420-C02-02 of the Spanish MCYT (Ministerio de Ciencia y Tecnología). L.G.M. would also like to thank the Universidad Complutense de Madrid and MCYT for the award of a Ramón y Cajal fellowship.

- J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
- J. H. Dymond and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures* (Clarendon, Oxford, 1980).
- N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**, 635 (1969).
- T. Boublik and I. Nezbeda, *Collect. Czech. Chem. Commun.* **51**, 2301 (1986).
- T. Boublik, C. Vega, and M. Diaz-Peña, *J. Chem. Phys.* **93**, 730 (1990).
- J. A. Barker and J. J. Monaghan, *J. Chem. Phys.* **36**, 2558 (1962).
- J. A. Barker and J. J. Monaghan, *J. Chem. Phys.* **36**, 2564 (1962).
- J. A. Barker, P. J. Leonard, and A. Pompe, *J. Chem. Phys.* **44**, 4206 (1966).
- T. Sun and A. S. Teja, *J. Phys. Chem.* **100**, 17365 (1996).
- E. de Miguel, L. F. Rull, and K. E. Gubbins, *Physica A* **177**, 174 (1991).
- A. Yethiraj and C. K. Hall, *Mol. Phys.* **72**, 619 (1991).
- P. G. Kusalik, F. Liden, and I. M. Svishchev, *J. Chem. Phys.* **103**, 10169 (1995).
- B. Tomberli, S. Goldman, and C. G. Gray, *Fluid Phase Equilib.* **187-188**, 111 (2001).
- C. G. Joslin, C. G. Gray, S. Goldman, B. Tomberli, and W. Li, *Mol. Phys.* **89**, 489 (1996).
- T. Boublik, *Fluid Phase Equilib.* **182**, 47 (2001).
- J. Janecek and T. Boublik, *Mol. Phys.* **98**, 93 (2000).
- J. Janecek and T. Boublik, *Mol. Phys.* **98**, 765 (2000).
- J. Stoll, J. Vrabec, H. Hasse, and J. Fischer, *Fluid Phase Equilib.* **179**, 339 (2001).
- D. Levesque and L. Verlet, *Phys. Rev.* **182**, 304 (1969).
- J. A. Barker and D. Henderson, *Rev. Mod. Phys.* **48**, 587 (1976).
- C. G. Gray and K. E. Gubbins, *Fundamentals of The International Series of Monographs on Chemistry* (Clarendon, Oxford, 1984), Vol. 1.
- L. G. MacDowell, C. Menduiña, C. Vega, and E. de Miguel, *Phys. Chem. Chem. Phys.* **5**, 2851 (2003).
- C. Menduiña, C. McBride, and C. Vega, *Phys. Chem. Chem. Phys.* **3**, 1289 (2001).
- L. G. MacDowell, M. Müller, C. Vega, and K. Binder, *J. Chem. Phys.* **113**, 419 (2000).
- C. Vega and L. G. MacDowell, *Mol. Phys.* **98**, 1295 (2000).
- L. Lue, D. G. Friend, and J. R. Elliott, Jr., *Mol. Phys.* **98**, 1473 (2000).
- D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976).
- L. G. MacDowell, C. Vega, and E. Sanz, *J. Chem. Phys.* **115**, 6220 (2001).
- A. Z. Panagiotopoulos, *Mol. Phys.* **61**, 813 (1987).
- B. Smit and C. P. Williams, *J. Phys.: Condens. Matter* **2**, 4281 (1990).
- A. Lotfi, J. Vrabec, and J. Fischer, *Mol. Phys.* **76**, 1319 (1992).

- <sup>32</sup>M. R. Stapleton, D. J. Tildesley, A. Z. Panagiotopoulos, and N. Quirke, *Mol. Simul.* **2**, 147 (1989).
- <sup>33</sup>G. Stell, J. C. Rasaiah, and H. Narang, *Mol. Phys.* **27**, 1393 (1974).
- <sup>34</sup>K. S. Shing and K. E. Gubbins, *Mol. Phys.* **45**, 129 (1982).

- <sup>35</sup>G. N. Patey, *Mol. Phys.* **34**, 427 (1977).
- <sup>36</sup>R. L. Henderson and C. G. Gray, *Can. J. Phys.* **56**, 571 (1978).
- <sup>37</sup>C. H. Twu, K. E. Gubbins, and C. G. Gray, *J. Chem. Phys.* **64**, 5186 (1976).