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Linear hard sphere models

Virial coefficients and equation of state

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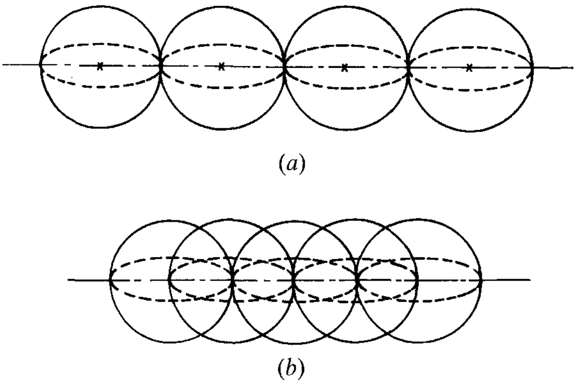
Virial coefficients of tangent hard spheres in a linear configuration have been determined numerically. Trends of the virial coefficients with the molecular anisotropy are similar to those of other linear models, such as hard spherocylinders or hard ellipsoids. Theoretical predictions of virial coefficients from different equations of state of hard body fluids are compared with the numerical results. None of them provides a completely satisfactory description of the lower virial coefficients when the anisotropy of the molecule is large. We propose a new method to build up an equation of state of hard linear models (prolate or oblate) from the knowledge of the first five virial coefficients. The equation of state obtained in this way provides a very good description of the equation of state of hard linear fluids at low, medium and high anisotropies.

1. Introduction

Hard body models of molecules have a great importance in liquid state theory since they may be used as reference systems in perturbation treatments of molecules with repulsive and attractive interactions [1, 2]. Hard linear molecules such as spherocylinders (HSPs) or hard ellipsoids (HEs) have been studied in a number of papers so that their equation of state (EOS) [3–5], virial coefficients [6–8] and phase diagram [4, 9] are relatively well known. Furthermore, Wertheim has recently proposed a theory of associated fluids [10–13]. The perturbation theory proposed by Wertheim may be used to predict the behaviour of chains of tangent hard spheres [14, 15]. This theory has been tested with respect to its ability to predict the virial coefficients and EOS of hard n-alkane models, and the results may be considered as very promising [16]. In this work we shall focus on the study of fluids of molecules made up by m tangent spheres in a linear configuration. We shall denote this model as the hard linear tangent spheres (HLTS) model. When $m = 1$ we get the hard sphere (HS) molecule and when $m = 2$ we get a particular case of the hard dumb-bell molecule. For these two cases, the virial coefficients [17, 18], phase diagram [19–21] and EOS [22] are now well known. More recently Amos and Jackson [23] and Boublik *et al.* [24] have obtained the EOS via computer simulation for trimers ($m = 3$) and tetramers ($m = 4$), respectively. Although analytical formulas exist for determining the second virial coefficient B_2 of HLTS with $m = 2$ and $m = 3$ [18, 25] and lower virial coefficients have been obtained for $m = 3$ (see reference [5] for details) no other virial coefficient has been reported for HLTS with larger values of m. In this work, we shall provide results for the lower virial coefficients of HLTS molecules with m ranging from 3 up to 7. Thus the ability of Wertheim and other EOSs to predict virial coefficients of HLTS models is analysed. We shall discuss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(*b*)

Figure 1. Hard models for this work. (*a*) Hard linear tangent spheres (HLTS). (*b*) Hard linear fused spheres with $L^* = 0{\cdot}5$. Dotted line shows the c_∞ axis in all cases.

differences and similarities in the behaviour of the lower virial coefficients of prolate linear convex models as HE or HSP, with respect to prolate linear non-convex molecules as HLTS. We analyse different procedures for building up an EOS from the knowledge of the lower virial coefficients. Moreover, we propose for prolate linear molecules a new method of building up an EOS from knowledge of the first virial coefficients, that yields better results than others previously proposed. The method is then extended to oblate molecules. The EOS built in that way allows us to predict reasonably well the behaviour of the fluid up to high densities of hard spheres and of highly anisotropic molecules as well. The new proposed EOS may prove to be useful in theoretical studies of liquid crystal formation of hard linear (prolate or oblate) models.

The scheme of the paper is as follows. Section 2 presents numerical results for the virial coefficients of HLTS. In section 3 we compare the numerical results with the predictions of different equations of state. Section 4 introduces a new method of building an equation of state from a knowledge of the lower virial coefficients. Section 5 contains the conclusions of this work.

2. Virial coefficients of hard linear tangent spheres

The model of HLTS consists of m hard spheres in contact in a linear rigid configuration, as illustrated in figure 1(*a*). We have evaluated the first five virial coefficients of HLTS with m ranging from $m = 3$ to $m = 7$ by the method of Ree and Hoover [17] as extended to hard molecular fluids by Rigby [26]. We have also evaluated the sixth virial coefficient. We have typically used ten million configurations for each reduced virial coefficient $B_i^* = B_i/V_m^{i-1}$ where B_i is the ith virial coefficient and V_m is the molecular volume. For some models two independent determinations were made. In the evaluation of B_6, we neglect a diagram corresponding to the one neglected by Ree and Hoover [17] in their determination of B_6 of hard spheres. For hard bodies, this diagram makes a positive although small contribution to B_6. Calculations of B_i^* for HLTS become increasingly time consuming as m increases and the computer time grows as m^2. The virial coefficients for HLTS are shown in table 1. Our numerical determination of B_2^* agrees very well with its analytical values

Table 1. Virial coefficients of linear tangent spheres. $B_i^* = B_i/V_m^{i-1}$. N stands for the number of independent configurations in the runs for the determination of B_i^*. α is defined through equation (1). The figures in parentheses represent the estimated error in the last quoted digits.

$N/10^6$	m	B_2^*	B_3^*	B_4^*	B_5^*	B_6^*	α
10	3	6·851	24·48	48·59	70	*	1·950
10	3	6·850 (2)	24·47 (1)	48·51 (17)	68 (3)	120 (52)	1·950
10	4	8·248	32·36	57·97	83	*	2·416
10	4	8·248 (4)	32·36 (2)	57·90 (13)	81 (5)	313 (85)	2·416
10	5	9·642	40·66	60·73	103	*	2·880
10	5	9·640 (3)	40·67 (3)	61·14 (31)	97 (8)	634 (141)	2·880
15	6	11·032	49·49	56·60	153	*	3·344
15	6	11·034 (2)	49·49 (3)	56·34 (35)	163 (10)	1460 (487)	3·345
20	7	12·421	58·47	42·57	298	*	3·807
20	7	12·423 (3)	58·49 (3)	42·53 (58)	295 (18)	1816 (865)	3·808

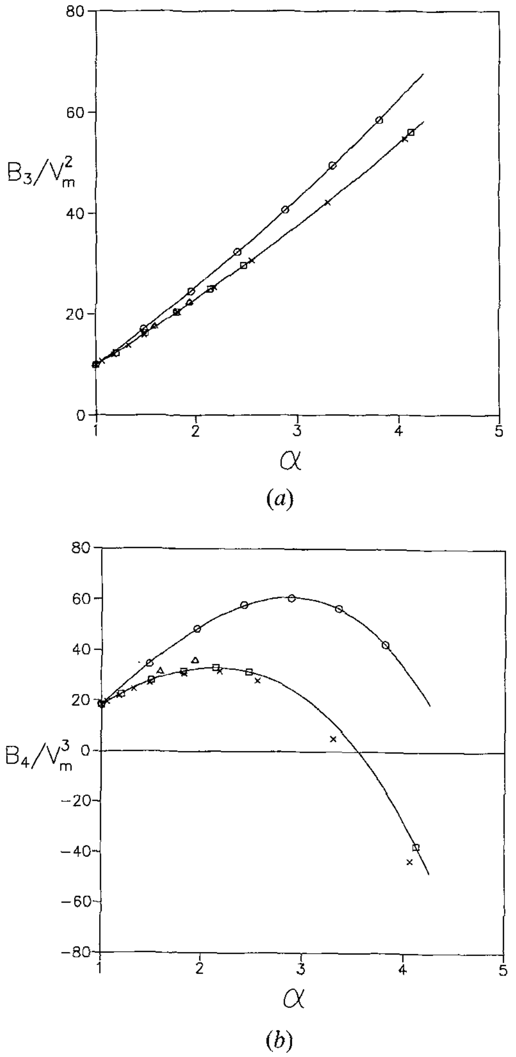
[18, 25] for $m = 2$ and $m = 3$, which constitutes a check of our algorithm. We have defined a nonsphericity parameter α^{R} according to the prescription first proposed by Rigby [27]:

$$B_2^* = 1 + 3\alpha^{\mathrm{R}}. \tag{1}$$

We see in table 1 that the nonsphericity α^{R} increases with the length of the molecules and the relation between α^{R} and m is roughly linear. In figure 2, we show the behaviour of B_3^*, B_4^* and B_5^* as a function of α^{R}. According to equation (1) two models with the same value of α^{R} have also the same B_2^*. For comparison we also present in figure 2 the results for B_i^* for HE and HSP molecules [5]. Trends are the same for all these prolate linear models. We see that B_3^* increases smoothly with α^{R}. However, B_4^* presents a completely different behaviour. It increases up to $\alpha^{\mathrm{R}} = 3$ ($m = 5$) and then it starts to decrease. The shape of the curve suggests that B_4 becomes negative for $m = 9$. The presence of negative B_4^* for prolate linear models was first found by Monson and Rigby [6] for HSP and more recently by Rigby [8, 28] for HE and the Gaussian overlap model. It is, therefore, a general feature of prolate linear models (convex and non-convex) at high elongations. The behaviour of B_5^* is shown in figure 2c. It increases slowly to $\alpha^{\mathrm{R}} = 3$ and then it increases rapidly. This again seems to hold for HE and HSP. In order to estimate virial coefficients at intermediate values of α^{R} we have fitted B_i^* to the empirical expression:

$$B_i^* = c_0^i + c_1^i\alpha + c_2^i\alpha^2 + c_3^i\alpha^3 + c_4^i\alpha^4. \tag{2}$$

The coefficients of equation (2) for HLTS, HE and HSP are shown in table 2. The results of this fitting are shown as the solid line in figure 2. We conclude from figure 2 that the virial coefficients of prolate linear models present similar features in their behaviour regardless of the details of their shape. These three models, HE, HSP and HLTS, reduce to the hard sphere case when $\alpha = 1$. As a consequence, the values of B_i^* for α close to one are very similar for these three geometries. This supports the idea of conformality [5], namely that the knowledge of B_2^* (or α since they are related through equation (1)) is enough for describing the EOS of the fluid regardless of the finer details of its shape. This idea seems to be justified for small α (i.e. $\alpha < 1{\cdot}4$). However, virial coefficients are sensitive to the details of the shape for



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(*b*)

Figure 2. Reduced virial coefficients $B_i^* = B_i/V_m^{i-1}$ of HE, HSP and HLTS as a function of α as defined in equation (1). Symbols stand for numerical results of this work for HLTS and from [6–8] for HE and HSP. Solid lines correspond to the least squares fit of equation (2). Open circles stand for HLTS, open squares correspond to HSP, crosses to HE and the open triangles are for hard linear fused spheres with $L^* = 0{\cdot}5$. (*a*) Results of $B_3^* = B_3/V_m^2$. (*b*) Results of $B_4^* = B_4/V_m^3$. (*continued*)

larger values of α. An interesting remark is that HE and HSP values of B_i^* are similar even for high α, whereas the values for HLTS differ significantly for the two convex models. This supports the idea that for prolate linear convex bodies of revolution ($D_{\infty h}$), the idea of conformality still holds for high values of α. However, B_i^* for HSP and HLTS differ significantly, showing that conformality does not extend to nonconvex bodies. The EOSs of HLTS must be different from that of HE or HSP for high values of α.

Moreover, the idea of spherical tangent atoms looks somewhat artificial from a

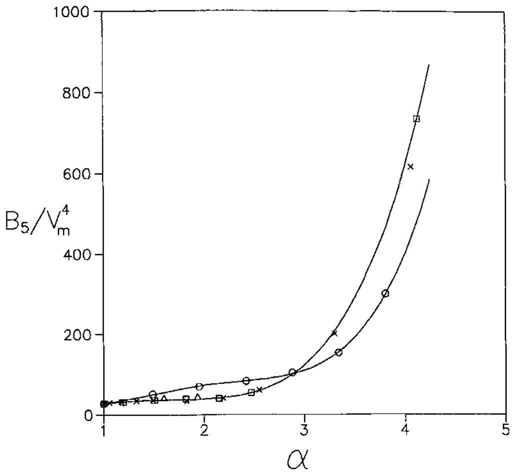

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Figure 2. (*continued*) (*c*) *Results of* $B_5^* = B_5/V_m^4$.

Table 2. Coefficients of the fitting of equation (2). The non-sphericity parameter α is defined by equation (1).

Model	i	c_0^i	c_1^i	c_2^i	c_3^i	c_4^i
HLTS	3	−3·171 44	12·087 06	1·084 37	0	0
	4	−15·212 28	28·734 04	7·837 45	−2·994 40	0
	5	131·047 76	−333·363 65	343·686 98	−130·563 92	17·417 35
HE	3	−0·926 66	10·020 82	0·905 84	0	0
	4	−8·056 88	28·462 51	0·276 61	−2·317 43	0
	5	−35·793 75	94·804 43	−19·555 44	−17·755 36	6·524 62
HSP	3	−1·227 19	10·375 90	0·851 29	0	0
	4	−9·295 60	30·074 28	−0·321 58	−2·092 30	0
	5	−9·489 04	23·409 32	48·156 36	−43·893 18	10·041 05

Table 3. Virial coefficients of hard linear fused spheres with $L^* = 0{\cdot}5$ (figure 1(*b*)). $B_i^* = B_i/V_m^{i-1}$. N stands for the number of independent configurations in the determination of B_i^*. The figures in parentheses represent the estimated error in the last quoted digits.

$N/10^6$	m	B_2^*	B_3^*	B_4^*	B_5^*	B_6^*	α
2	5	5·769 (4)	17·71 (2)	31·8 (2)	43 (3)	54 (56)	1·590
2	7	6·806 (4)	22·53 (3)	36·2 (2)	45 (4)	166 (94)	1·935
2	9	7·854 (6)	27·70 (4)	38·1 (4)	51 (11)	185 (130)	2·285

chemical point of view. We have therefore evaluated virial coefficients for hard linear spheres with a reduced atom–atom bond length $L^* = l/\sigma = 0{\cdot}5$ (see figure 1(*b*)). The results are shown in table 3 and in figure 2. We see how the virial coefficients of this model are much closer to those of the HSP model than to the HLTS model.

Table 4. Coefficients k_1, k_2 and k_3 of equation (3) for the EOS ISPT of [29], for the EOS proposed by Nezbeda [31] and the EOS proposed by Boublik [32].

	k_1	k_2	k_3
ISPT	$3\alpha - 2$	$3\alpha^2 - 3\alpha + 1$	$-\alpha^2$
Nezbeda	$3\alpha - 2$	$\alpha^2 + \alpha - 1$	$-\alpha(5\alpha - 4)$
Boublik	$3\alpha - 2$	$3\alpha^2 - 3\alpha + 1$	$-\alpha(6\alpha - 5)$

3. Theoretical predictions

Several EOSs have been proposed for HLTS. Boublik [29] modified the scaled particle theory of hard convex bodies of Gibbons [30] and proposed an improved version (ISPT). Later Nezbeda [31], by analyzing the virial coefficients of HSP models proposed a new EOS, which was slightly modified by Boublik [32]. These three EOSs are written in the form

$$Z = \frac{1 + k_1 y + k_2 y^2 + k_3 y^3}{(1 - y)^3} \tag{3}$$

where y is the packing fraction defined as $y = \rho V_m$, and ρ is the number density. The coefficients k_1, k_2 and k_3 are given in table 4 for the ISPT, Nezbeda and Boublik EOS. The virial coefficients obtained from equation (3) are given by

$$B_i^* = (k_2 + 3k_3) + 0{\cdot}5(1 - k_1 - 3k_2 - 5k_3)i + 0{\cdot}5(1 + k_1 + k_2 + k_3)i^2. \tag{4}$$

In fact, equation (3) can be recovered by resummation of the virial series with B_i^* given by equation (4). It can be shown that for a hard convex body, the non-sphericity parameter [5, 18] defined in equation (1) is given by

$$\alpha^{\mathrm{B}} = \frac{RS}{3V_m} \tag{5}$$

where R is $1/(4\pi)$ times the mean radius of curvature and S is the surface-area of the molecule. For convex bodies equation (1) and equation (5) provide the same value of α. For nonconvex bodies, for instance the HLTS model, R is ill defined. Boublik and Nezbeda [33] proposed for HLTS to take the mean radius of curvature from the corresponding HSP model with the same length to breadth ratio. For HLTS equation (1) and equation (5) yield different values of α, the difference being about 2% for $m = 3$ and 5% for $m = 7$.

Recently, another EOS has been proposed for HLTS by Wertheim [14] and independently by Chapman *et al.* [15]. This EOS, which will be denoted by W, reads

$$Z = m\frac{(1 + y + y^2 - y^3)}{(1 - y)^3} - (m - 1)\frac{(1 + y - y^2/2)}{(1 - y)(1 - y/2)}. \tag{6}$$

Following the work of Boublik [34], we have recently modified equation (6) to allow for overlapping of hard spheres. This modified version [16] of Wertheim's EOS (MW) read

$$Z = (2\alpha^{\mathrm{R}} - 1)\frac{(1 + y + y^2 - y^3)}{(1 - y)^3} - (2\alpha^{\mathrm{R}} - 2)\frac{(1 + y - y^2/2)}{(1 - y)(1 - y/2)} \tag{7}$$

Equation (7) differs from that proposed by Boublik only in the way of defining α (α^{R}

in equation (7) instead of α^{B} which is the choice of Boublik). Equation (6) does not yield exact results for B_2^* whereas equation (7) does. In what follows we shall use equation (1) as our definition of α. Equation (7) provides a very good description of virial coefficients and EOS of hard n-alkane models [16]. The virial coefficients obtained from equation (7) are

$$B_2^* = 1 + 3\alpha, \tag{8}$$

$$B_3^* = 14{\cdot}5\alpha - 4{\cdot}5, \tag{9}$$

$$B_4^* = 30{\cdot}25\alpha - 12{\cdot}25, \tag{10}$$

$$B_5^* = 50{\cdot}125\alpha - 22{\cdot}125. \tag{11}$$

None of the presented EOSs yields completely satisfactory results for virial coefficients of HLTS and this is specially true for the highest elongations. The ISPT, The Nezbeda and Boublik EOSs predict a linear variation in α for k_1 and a quadratic dependence for k_2 and k_3 (see table 4). According to these three EOSs, B_i^* (except B_2^*) is a quadratic function of α. All these three EOSs provide a fair prediction of B_3^*. For B_4^*, ISPT and Boublik EOSs fail because they give positive values of B_4^* when $\alpha \Rightarrow \infty$. Only the Nezbeda EOS predicts negative values for B_4^* when $\alpha \Rightarrow \infty$ although the quantitative agreement is not very good. For B_5^*, ISPT and Boublik EOSs capture the trends of the numerical results although they are not very precise. The Nezbeda EOS shows a maximum in B_5^* which is not observed in the numerical results. Equation (7) predicts that the virial coefficients are linearly increasing functions of α (see equations (8–11)). This EOS provides good virial coefficients for HLTS up to $\alpha = 2{\cdot}5$ ($m = 4$) but it fails for higher values of α. In particular, this EOS is unable to predict negative values of B_4^* for very elongated molecules.

To summarize, B_3^* is well represented by a linear function of α. B_4^* by a quadratic function of α (which shows a maximum) and B_5^* as an increasing function of α (linear for small α and of higher order for higher anisotropies). None of the presented EOSs is able to reproduce all these features simultaneously. Furthermore, we observe in figure 2 that all these features are common for HLTS, HE and HSP models.

We have focused so far on the variation of a given virial coefficient B_i^* with the anisotropy (i.e. α) for a given value of i. Now we shall analyse the variation of B_i^* with i for a given molecule (α fixed). In figure 3 we present results of the virial coefficients of HLTS for $m = 1$, 3, 5 and 7 as a function of i. We see that the virial coefficients of HS fit relatively well to a quadratic form in i. This fact justifies the success of the Carnahan–Starling [35] EOS since this equation predicts a quadratic variation of B_i^* with i. We see from figure 3 that to assume a quadratic form for B_i^* would still be a reasonable approximation when $m = 3$. However, the assumption of a quadratic variation of B_i^* with i would be a poor approximation for $m = 5$ or for $m = 7$. The quadratic form cannot describe the presence of a maximum and a minimum (at least) in B_i^* as a function of i. The ISPT, Nezbeda and Boublik EOSs predict a quadratic form (see equation (4)) for B_i^* as a function of i and this is a bad approximation for long molecules, as can be seen in figure 3.

Thus all the EOSs analysed fail either in the prediction of the variation of B_i^* with α for a given i or in the variation of B_i^* with i for a given α. Although the error is small for medium anisotropies (and that explains their success in describing hard models of common molecules) it becomes more important for large anisotropies.

In the next section we shall try to illustrate a different approach to the problem.

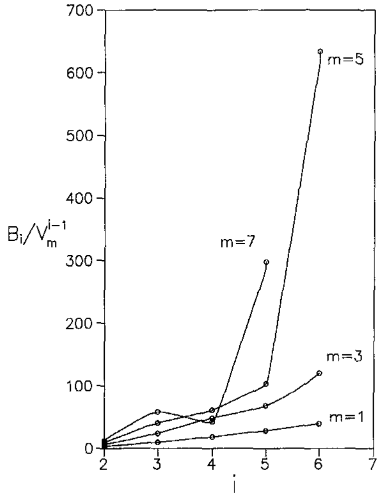

Figure 3. B_i^* of HLTS as a function of i for the cases $m = 1$, $m = 3$, $m = 5$ and $m = 7$. m is the number of tangent spheres. Solid lines are only a guide to the eye.

The idea is now to get an EOS from knowledge (through numerical determination) of the lower virial coefficients.

4. Building equations of state from virial coefficients

In this section, we shall briefly describe some previous attempts at building up an EOS from the knowledge of the first few virial coefficients. Finally we shall propose a new method which in general yields better results for the EOS of long molecules than others proposed so far.

4.1. *The PF2 approach*

The first possibility is to use an EOS of the form of equation (3) but choose k_1, k_2 and k_3 to fit the known values of B_2^*, B_3^* and B_4^*. According to equation (4) that implies choosing a quadratic form for B_i^* as a function of i. This method will fail for very elongated molecules, as we have concluded from our discussion of figure 3. Moreover, because the form of B_i^* is quadratic, and for instance for $m = 7$ it has to fit B_2^*, B_3^* and B_4^*, negative values of higher virial coefficients will be computed and the corresponding pressure will be too low. Since this option predicts a quadratic variation of B_i^* with i, we shall denote it as a polynomial fit of second order (PF2).

4.2. *PF3*

The presence of a maximum and a minimum in B_i^* appearing in B_i^* for $m = 7$ suggests that a polynomial of third order for B_i^* (PF3) would yield better results. Let us assume that B_i^* is given by

$$B_i^* = g_0 + g_1 i + g_2 i^2 + g_3 i^3. \tag{12}$$

Then by summing the series $Z = 1 + \sum_{i=1} B_{i+1} y^i$ we obtain

$$Z = (1 + k_1' y + k_2' y^2 + k_3' y^3 + k_4' y^4)/(1 - y)^4 \tag{13}$$

where the coefficients k_1', k_2', k_3' and k_4' may be written as a linear combination of the variables g_i. As a general rule if $B_i^* = \mathrm{P}_n(\mathrm{i})$ where $\mathrm{P}_n(i)$ stands for a polynomial of order n in the variable i then the EOS will be of the form [36]:

$$Z = \left(1 + \sum_{i=1}^{i=n+1} k_i' y^i\right) \Big/ (1 - y)^{n+1} \tag{14}$$

It is possible to choose the k_i' in equation (13) or equation (14) so that the first $n + 1$ virial coefficients are reproduced. A practical limitation of equation (14) is that the numerical determination of B_6^* is difficult and the error in its estimation prevents the determination of k_5' accurately. Equation (13) may be then regarded as the highest version of equation (14) obtainable from a practical point of view.

4.3. *The Barboy and Gelbart approach*

The Barboy and Gelbart [37] approach yields an EOS of the form:

$$Z = \left(1 + \sum_{i=1}^{i=n} k_i' y^i\right) \Big/ (1 - y)^{n+1} \tag{15}$$

which is identical to equation (14) except for the absence of the last term. It can be shown that the last term in equation (14) is always

$$k_{n+1}' = (-1)^{n+1}(1 - h), \tag{16}$$

$$h = \sum_{i=0}^{i=n} g_i \tag{17}$$

where h is the summation of all the coefficients g_i appearing in equation (12) (or higher order versions). Since the BG approach sets $k_{n+1}' = 0$ that implies that

$$1 = h = \sum_{i=0}^{i=n} g_i.$$

The BG approach implies a polynomial fit to B_i^* with the restriction that the summation of the coefficients should be exactly one and, from this point of view, it is only a slightly modified version of equation (14). Therefore, the conclusions applied to equation (14) will also hold for equation (15), which is the BG approach.

4.4. *Parsons*

Parsons [38, 39] assumes that the structure of the hard body may be related to that of a hard sphere. If Z^{HS} is the compressibility factor for HS then the EOS for hard bodies arising from Parson's approach is

$$Z = 1 + [Z^{\mathrm{HS}} - 1]B_2^*/4. \tag{18}$$

If the Carnahan–Starling EOS is used for Z^{HS}, then equation (18) predicts that B_i^* is a quadratic function of i. Parsons' approach is unable to predict the negative values of B_4^* of long prolate linear models. For convex bodies equation (18) yields prolate–oblate symmetry.

Table 5. Compressibility factor Z for HLTS as obtained from the equation of state MPF2 of this work (see equation (20)), from other EOSs and from simulation results Z^{MC} [5, 22–24]. m stands for the number of tangent hard spheres.

m	y	Z^{MPF2}	Z^{PF2}	Z^{PF3}	Z^{MW}	Z^{Parsons}	Z^{MC}
1	0·0774	1·36	1·36	1·36	1·36	1·36	1·36
1	0·2097	2·53	2·53	2·52	2·52	2·52	2·53
1	0·3065	6·82	6·89	6·73	6·78	6·78	6·81
1	0·4628	10·25	10·41	9·93	10·18	10·18	10·19
2	0·1047	1·80	1·81	1·80	1·80	1·75	1·79
2	0·2094	3·35	3·37	3·33	3·33	3·07	3·36
2	0·3665	8·85	9·22	8·36	8·79	7·41	8·95
2	0·4712	17·84	19·39	14·53	17·85	14·26	18·06
3	0·100	1·99	1·99	1·99	1·98	1·89	2·00
3	0·200	3·90	3·91	3·89	3·86	3·41	3·93
3	0·300	7·55	7·67	7·43	7·52	6·09	7·71
3	0·453	21·23	22·33	19·06	21·68	15·67	21·68
4	0·205	4·75	4·75	4·75	4·75	4·02	4·85
4	0·289	8·41	8·42	8·41	8·57	6·67	8·68
4	0·359	13·38	13·40	13·36	14·00	10·22	13·81
4	0·400	17·55	17·59	17·50	18·75	13·22	*

Table 6. As in table 5 for HSP L^* stands for $L^* = l/\sigma$. Monte Carlo data were taken from [5, 7, 9].

L^*	y	Z^{MPF2}	Z^{PF2}	Z^{PF3}	Z^{Nezbeda}	Z^{Parsons}	Z^{MC}
1	0·200	2·67	2·68	2·67	2·67	2·62	2·65
1	0·300	4·56	4·60	4·52	4·56	4·42	4·48
1	0·400	8·08	8·22	7·78	8·10	7·81	8·19
1	0·446	10·69	10·98	10·01	10·74	10·38	10·74
2	0·200	3·05	3·06	3·05	3·06	2·93	3·07
2	0·300	5·34	5·41	5·27	5·41	5·09	5·40
2	0·400	9·43	9·75	8·93	9·74	9·15	9·60
2	0·455	12·63	13·26	11·13	13·24	12·13	13·00
3	0·191 7	3·28	3·28	3·28	3·31	3·12	3·30
3	0·348 5	7·96	8·04	7·87	8·36	7·72	8·26
3	0·435 6	12·8	14·42	12·31	14·02	13·23	13·68
3	0·481 8	16·43	16·93	15·32	18·59	17·97	17·54
5	0·176 70	3·65	3·59	3·68	3·72	3·43	3·67
5	0·265 10	6·27	5·89	6·57	6·51	5·87	6·33
5	0·309 22	8·09	7·28	8·90	8·46	7·67	8·18
5	0·353 40	10·38	8·78	12·38	10·90	10·05	10·26

4.5. *The new equation proposed in this work*

To study the possibilities of the EOSs of the previous section and those based on virial coefficients of this section, we shall compare theoretical predictions with Monte Carlo (MC) results. In table 5, we show the results for HLTS and in table 6 for HSP. In table 7, we compare the average deviation with respect to the MC data of different semiempirical approaches. The average deviation Δ has been

Table 7. Average deviation Δ (see equation (19)) for the compressibility factor of several theoretical EOS. The MC points correspond to those presented in tables 5 and 6. We analyse the results with α defined from equation (1) (α^R) and α defined from equation (5) (α^B).

	ΔHLTS	ΔHSP	ΔHLTS + ΔHSP
ISPT (α^B)	3·5	17·4	20·7
ISPT (α^R)	2·3	17·4	19·7
Nezbeda (α^B)	7·4	1·9	9·3
Nezbeda (α^R)	8·4	1·9	10·3
Boublik (α^B)	4·4	5·7	10·1
Boublik (α^R)	5·7	5·7	11·4
MW (α^B)	0·9	14·8	15·7
MW (α^R)	1·0	14·8	15·8
Parsons	12·2	4·5	16·7
PF2	1·8	3·5	5·3
PF3	3·8	6·2	10·0
MPF2	1·2	2·1	3·3

defined as

$$\Delta^{EOS} = (100/n_{MC}) \sum_{i=1}^{i=n_{MC}} |Z_i^{EOS} - Z_i^{MC}|/Z_i^{MC} \tag{19}$$

where n_{MC} is the number of thermodynamic states for which MC experiments were carried out. For HLTS the Wertheim (W) and its modified version MW yield the best EOS. However, only the results for $m = 3$ and $m = 4$ have been reported so far. Since the prediction of virial coefficients was poor for longer chains, we expect that W and MW EOSs will deteriorate for longer chains. Other EOSs, such as Parsons approach, and the Boublik and Nezbeda EOSs, do not provide satisfactory results the results of the ISPT being better. The PF2 yields better results than the PF3.

In the case of HSP, the Nezbeda EOS yields the best results. However, it deteriorates as the length of the molecule increases (see results for $L^* = 5$ in table 6). The W, MW, ISPT and Boublik EOSs gives results that are not quite satisfactory. Parsons' approach works better in that case than in the case of HLTS, and PF2 is again superior to PF3. This may appear surprising since PF3 incorporates correctly one additional virial coefficient (B_5^*) with respect to PF2. However, PF3 predicts a cubic variation of the virial coefficients and PF2 a quadratic one. Results of table 7 suggest that the quadratic form for B_i^* is superior to the cubic one when it is forced to fit the first virial coefficients. However, as was pointed out above, the PF2 has an important defect since for long molecules it will predict negative values of the virial coefficients beyond B_4^* and this fact does not agree with the results obtained for B_5^* and B_6^*.

The idea of a quadratic form for B_i^* is, nevertheless, appealing. It seems that at least up to $i = 6$ the virial coefficients B_i^* are increasing functions of i. The only coefficient breaking this rule in the case of prolate linear models is B_4^* which presents a singular behaviour for HLTS, HE and HSP. It should be recognized from the beginning that for linear prolate molecules a quadratic form of B_i^* may provide reasonable estimates for all i (at least up to B_6^*) except for B_4^*. So, we propose a new EOS which keeps a quadratic form for B_i^* but the coefficients k_1, k_2 and k_3 are

Table 8. EOSs for prolate ($k > 1$) and oblate ($k < 1$) HE from the MPF2 EOS of this work. For prolate molecules MPF2 is given by equation (20) and for oblate molecules by equation (25). The MC results are from [4, 41]. Virial coefficients of HE required in equation (20) and equation (25) were taken from [8]. The asterisks correspond to states where a nematic phase was found in computer simulations [41].

	$k = 3$		$k = 1/3$	
y	Z^{MPF2}	MC	Z^{MPF2}	MC
0·20	3·02	3·05	3·10	3·10
0·30	5·27	5·41	5·57	5·55
0·40	9·30	9·80	10·31	10·03
0·45	12·49	13·34	14·31	13·57

	$k = 5$		$k = 1/5$	
y	Z^{MPF2}	MC	Z^{MPF2}	MC
0·1111	2·20	2·21	2·29	2·28
0·2036	3·94	3·96	4·35	4·22
0·2592	5·45	5·54	6·25	5·79
0·3147	7·43	7·66	*	*

	$k = 10$		$k = 1/10$	
y	Z^{MPF2}	MC	Z^{MPF2}	MC
0·0555	1·90	1·90	2·01	2·00
0·1111	3·20	3·15	3·61	3·46
0·1481	4·41	4·21	4·94	4·50
0·2306	7·22	5·99	*	*

chosen to reproduce the known values of B_2^*, B_3^* and B_5^*. An EOS obtained in this way may provide a reasonable estimate of B_i^* with $i > 5$ but it gives very poor values of B_4^* for long molecules. We can correct this defect by subtracting the contribution of the predicted B_4^* and adding the correction of the numerical B_4^*. Our proposed EOS is

$$Z^{\mathrm{prolate}} = \frac{1 + k_1 y + k_2 y^2 + k_3 y^3}{(1 - y^3)} + (B_4^{*,\mathrm{exact}} - B_4^{*,\mathrm{theo}})y^3, \tag{20}$$

$$k_1 = B_2^* - 3, \tag{21}$$

$$k_2 = B_3^* - 3B_2^* + 3, \tag{22}$$

$$k_2 = (B_5^* - 6B_3^* + 8B_2^* - 3)/3, \tag{23}$$

$$B_4^{*,\mathrm{theo}} = k_3 + 3k_2 + 6k_1 + 10, \tag{24}$$

where $B_4^{*,\mathrm{theo}}$ is B_4^* as predicted by the first term on the right-hand side of equation (20). We shall denote the equation (20) as the modified polynomial of order 2 (MPF2). In tables 5, 6 and 7 we show the results of the EOS obtained that way. We see that the results are good and they do not deteriorate as the length of the molecules increases. For HLTS the deviation of MPF2 as represented by Δ is only slightly larger than that of the W and MW EOSs which are the best for this kind of molecule. For HSP, MPF2 is only slightly worse than those of Nezbeda. However, the MPF2 gives good results for the longest molecule of table 7 and it is expected that it will also provide good results for longer molecules. On the other hand, there are good reasons, as described in our discussion of the virial coefficients, to expect that both the W (or its MW) and Nezbeda EOSs will deteriorate for longer molecules.

The idea leading to equation (20) for prolate linear models can be extended to oblate molecules. For oblate molecules B_2^*, B_3^* and B_4^* are always positive and increase with the anisotropy of the molecule. However, B_5^* reaches a maximum and then goes to negative values. In fact this behaviour of the first virial coefficients has been reported for oblate [8] HE and for oblate [40] HSP. We propose for oblate molecules a quadratic form for the B_i^* with the coefficients obtained to match B_2^*, B_3^* and B_4^* and then correct the poor prediction of B_5^* with the numerical value of B_5^* The MPF2 EOS for oblate molecules is

$$Z^{\mathrm{oblate}} = \frac{1 + k_1 y + k_2 y^2 + k_3 y^3}{(1-y)^3} + (B_5^{*,\mathrm{exact}} - B_5^{*,\mathrm{theo}})y^4, \tag{25}$$

$$k_1 = B_2^* - 3, \tag{26}$$

$$k_2 = B_3^* - 3B_2^* + 3, \tag{27}$$

$$k_3 = B_4^* - 3B_3^* + 3B_2^* - 1, \tag{28}$$

$$B_5^{*,\mathrm{theo}} = 3k_3 + 6k_2 + 10k_1 + 15. \tag{29}$$

In table 8 we compare results for HE with prolate and oblate symmetry with MC data for these systems [41]. For a given density, oblate molecules have a higher pressure (i.e. Z) than prolate molecules and this fact is in agreement with computer simulations. Moreover, the general agreement between the EOS proposed here and MC, where available, is very reasonable.

The basic idea behind the new proposed EOS is to assume a quadratic form for B_i^* (as in the Carnahan–Starling EOS of HS), except for the first virial coefficient of the virial expansion showing negative values at high anisotropies (the fourth for prolate and the fifth for oblate molecules).

5. Conclusions

In this work we have evaluated the first six virial coefficients of linear tangent spheres. We show that dependence on elongation of B_3^*, B_4^* and B_5^* are similar for HLTS, HE and HSP. HE and HSP present very similar B_i^* even for high anisotropies whereas the values of HLTS differ significantly. As a consequence, different EOSs are required for HLTS and for prolate convex bodies such as HE and HSP. None of the several proposed EOSs reproduces all the features of B_i^* ($i = 3, 4, 5$) as a function of α, so they fail to reproduce the EOSs of prolate hard bodies at high anisotropies. We have analysed several attempts to build an EOS for prolate linear models from the knowledge of the first virial coefficients. We have shown that the EOS obtained by assuming a quadratic form for B_i^* plus a correction term for B_4^* yields good results for prolate linear molecules at moderate and high anisotropy. The procedure is extended to oblate molecules by admitting that the correction term should now be in B_5^*. The proposed EOS yields reliable results for HS and for intermediate elongations. Moreover, for very long molecules it does provide good results, since it incorporates the correct value of the lower virial coefficients. This is quite important since for very long molecules the range where an isotropic fluid phase is stable becomes vanishing small [42]. The proposed EOS distinguishes prolate and oblate molecules. Overall the new proposed EOS yields good predictions over a large range of anisotropies and it has proved to be very useful in theoretical studies of liquid crystal formation of hard molecules [43].

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