

**FLUIDS OF HARD NONSPHERICAL MOLECULES. I. HIGHER VIRIAL COEFFICIENTS**

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Virial coefficients of hard prolate spherocylinders and hard homonuclear diatomics are calculated up to the ninth for a number of molecule elongations. The results are fitted to an analytical formula as a function of the elongation.

**Keywords:** Virial coefficient; Hard prolate spherocylinder; Hard homonuclear diatomics; Hard dumbbell; Thermodynamics; Equation-of-state.

Hard prolate spherocylinders (HPS) and hard homonuclear diatomics (HHD, also called hard dumbbells) are prototypes of a wider class of models which describe intermolecular interactions in polyatomic molecules. It is generally known that the repulsive interaction has a dominant influence on the structure of fluids. As an example, the HPS fluid serves not only as a model of fluid of elongated molecules such as CO<sub>2</sub> or butadiene, but with a sufficient elongation it is well suited for description of nematic and smectic liquid crystals<sup>1</sup>. HHDs can be used as a model of small diatomic molecules such as N<sub>2</sub> or O<sub>2</sub> as well as a model of plastic crystals<sup>2</sup>.

The equation-of-state can be in the low-density region described by the virial expansion. This equation is believed to converge as far as a phase transition line. Because of lack of attractive forces in hard molecular models, this means that the virial equation of state describes the whole fluid range up to freezing or transition to a liquid crystal phase. Tricks like resummation, Padé and other approximants can help investigate the whole

convergence region even if a limited number of virial coefficients are known.

While the second virial coefficients of both models are known analytically<sup>3-5</sup>, higher order virial coefficients have to be calculated numerically. The first four coefficients of hard prolate spherocylinders have been calculated<sup>6-9</sup> for the length-to-width ratio  $\gamma = 1.2, 1.3, 1.4, 1.6, 1.8,$  and  $2.5$ . Virial coefficients up to  $B_5$  for higher elongations ( $\gamma = 2, 3, \dots, 6$ ) and also  $B_4$  for  $\gamma = 11$  have been reported by ref.<sup>10</sup>. For very long spherocylinders (up to  $\gamma = 10^6$ ) coefficients  $B_3$  to  $B_5$  have been determined<sup>11,12</sup>. The newest results for HPS were published quite recently<sup>13</sup>. They calculated the sixth, seventh, and eighth virial coefficients for two elongations ( $\gamma = 4$  and  $6$ ).

Only five coefficients have been determined for various hard homonuclear diatomics. For selected distances between the sphere centers reduced by the sphere diameter ( $L^* = 0.05, 0.1, 0.2, 0.4, 0.75, 0.8,$  and  $1$ ) the first four coefficients have been calculated<sup>6,14-16</sup>. The virial coefficients up to the fifth for  $L^* = 0.3$  and  $0.6$  have been reported by several authors<sup>17-19</sup>. More precise results for  $B_2$  to  $B_5$  were published<sup>20</sup> up to  $L^* = 0.8$ .

This paper is organized as follows. We first briefly summarize the method of determination of the virial coefficients for both models (HHD and HPS). Then, we present the results up to  $B_9$  and compare them with previous data up to  $B_8$ . The obtained data are also approximated as functions of elongations.

## THEORY

### Models

A HHD consists of two hard spheres of diameter  $\sigma$ . Centers of the spheres are separated by  $L$  (Fig. 1). A HPS consists of a cylinder of diameter  $\sigma$  and length  $L$  capped at each end by hemispheres of the same diameter. It is common to characterize its shape by the length-to-width ratio

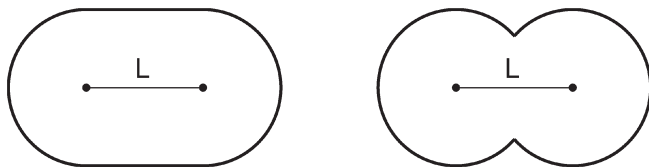


FIG. 1

The hard prolate spherocylinder (left) and hard homonuclear diatomic (right)

$$\gamma = \frac{L + \sigma}{\sigma} . \quad (1)$$

For HHD, we will use the reduced distance of centers instead,

$$L^* = \frac{L}{\sigma} . \quad (2)$$

### Virial Coefficients

The virial coefficients are coefficients in the density expansion of the compressibility factor<sup>21</sup>,  $Z$ :

$$Z = \frac{P}{k_B T \rho} = 1 + \sum_{n=2}^{\infty} B_n \rho^{n-1} \quad (3)$$

where  $\rho = N/V$  is the number density,  $P$  pressure,  $k_B$  the Boltzmann constant, and  $T$  absolute temperature. The  $n$ -th virial coefficient,  $B_n$ , can be expressed in terms of integrals whose integrands depend on the intermolecular potential energy,

$$B_n = \frac{1-n}{n!} V_n \quad (4)$$

where  $V_n$  is the sum of the cluster integrals. They can be expressed graphically by Mayer diagrams, i.e., irreducible diagrams composed of  $n$  black (field) points and  $f$ -bonds. The most compact form of  $V_n$  was provided in a pivotal work by Ree and Hoover<sup>22</sup>. They replaced the irreducible Mayer diagrams by generalized diagrams with mutually exclusive  $f$  and  $e$ -bonds,

$$V_n = \sum_k w_k^{\text{RH}} I_k \quad (5)$$

where the sum is over all unlabeled Ree–Hoover (RH) diagrams,  $w_k^{\text{RH}}$  denotes the RH weight, and the cluster integral,  $I_k$ , is an integral over black points:

$$I_k = \int \cdots \int \prod_{ij \in f\text{-bond}} f_{ij} \prod_{ij \in e\text{-bond}} e_{ij} d(1) \cdots d(n) . \quad (6)$$

Here  $e$  is the Boltzmann factor of the intermolecular potential,  $e_{ij} = e^{-u_{ij}/(k_B T)}$ , and  $f$  is the Mayer function,  $f_{ij} = e_{ij} - 1$ . Symbol  $d(i)$  denotes the integration over molecule positions and the angular average (normalized integral over orientations).

The first step in evaluating higher virial coefficients is the topological analysis which produces a list of irreducible diagrams with weights assigned. For  $n \leq 7$  these data are contained in the original papers<sup>22</sup>. Later van Rensburg<sup>23</sup> established the complement blocks contributing to  $B_8$ . In our department we proposed a computer-algebraic method to determine RH weights<sup>24</sup> up to  $B_9$ . The tables with values of RH weights obtained in this work have also been used here. The up-to-date record is  $B_{10}$  for  $D$ -dimensional spheres<sup>25</sup>.

The multi-fold integrals in Eq. (6) have been calculated by Monte Carlo (MC) integration. Technical details are described in our previous paper<sup>24</sup> dealing with the virial coefficients of hard spheres and disks. The method is based on generating configurations of the so called *spanning diagrams*, which are formed as subsets of  $f$ -bonds of a RH diagram so that the integral can be calculated analytically. The simplest examples of spanning diagrams are a linear chain or a nonlinear tree<sup>13</sup>.

Configurations of the chains are sampled by reptation<sup>26</sup>: A molecule is removed from one end of the chain and another random molecule is added at random at the other end. Here the algorithm differs from that for spheres or disks: We generate a new position at the “living” end of the chain by randomly choosing the particle center in a sphere drawn around the center of the previous particle and then check for an overlap with it; if no overlap is detected, a new trial position has to be generated. As a by-product, we get the second virial coefficient of the model.

The standard Metropolis MC method is used for nonlinear spanning diagrams. One MC step includes two kinds of moves, translation of the molecular center and rotation of the molecular axis. A move is accepted if the overlaps with other molecules correspond to the spanning tree sampled.

The second virial coefficient for any convex body (CB) model can be easily expressed analytically because the geometry of a single convex object and of a pair of such objects is quite well developed. It can be characterized by the parameter of nonsphericity<sup>3</sup>,

$$\alpha = \frac{\mathcal{R}\mathcal{S}}{3\mathcal{V}} \quad (7)$$

where  $\mathcal{V}$  is the volume,  $S$  is the surface area and  $R$  is the  $(1/4\pi)$ -multiple of the mean curvature integral of a CB particle. Its second virial coefficient is then

$$B_2^{\text{CB}} = (1 + 3\alpha)\mathcal{V}. \quad (8)$$

For spheres  $\alpha = 1$  while for all other CBs,  $\alpha > 1$ . Particularly, for HPS we have

$$\alpha = \frac{\gamma(\gamma + 1)}{3\gamma - 1} = \frac{(L^* + 1)(L^* + 2)}{3L^* + 2}. \quad (9)$$

Unlike CB models, the fused hard sphere models do not possess such generality and almost every model must be treated independently. The algorithm for the exact computation of the second virial coefficient of homonuclear diatomics is based on direct integration of the formula for  $B_2$  of nonspherical particles<sup>3</sup>. Because of the complexity of the formula, it is not shown here and we redirect the reader to the original literature<sup>4,5</sup>; the computer code is also included in the supplementary material<sup>27</sup>.

## RESULTS AND DISCUSSION

The described method was used for calculation of hard prolate spherocylinder and hard homonuclear diatomic virial coefficients. We obtained accurate data for the third to ninth coefficients. The virial coefficients of HPSs have been calculated for the length-to-width ratios  $\gamma = 1.2, 1.3, \dots, 11$  and for HHDs for the center-center distances  $L^* = 0.1, 0.2, \dots, 1$ . For testing purposes we also calculated numerically the second virial coefficients that are known analytically.

The resulting values of  $B_n$  for  $n = 3$  to  $n = 9$  for HPS and HHD, together with their uncertainty estimates and with the older literature results (if available), are shown in Tables I and II. It follows from the tables that the lower virial coefficients,  $n < 8$ , calculated in this work not only match the old data, but they are by about one order of magnitude more precise. The only exception are the data<sup>13</sup> for  $\gamma = 4$ :  $B_7$  disagrees with our result and the reported error of  $B_8$  is smaller than ours.

Because of subsequent work on equation-of-state, it is desirable to express the virial coefficients as functions of elongations by a closed analytical formula. It is not an easy task especially for higher virial coefficients where the data, as functions of elongations, have very unusual shapes. We have also

TABLE I  
 Summary of the reduced virial coefficients,  $\bar{B}_n = B_n V^{n-1}$ , of hard prolate spherocylinders for 17 length-to-width ratios,  $\gamma$ . Values in parentheses are estimated standard errors

	$\bar{B}_3$	$\bar{B}_4$	$\bar{B}_5$	$\bar{B}_6$	$\bar{B}_7$	$\bar{B}_8$	$\bar{B}_9$		
1.2	10.188690(43)	10.21(5) <sup>a</sup>	18.74760(24)	18.80(30) <sup>a</sup>	28.7558(11)	40.4663(51)	54.124(26)	69.49(15)	88.08(97)
1.4	10.106010(47)	10.64(5) <sup>b</sup>	19.54653(27)	19.26(30) <sup>b</sup>	29.7461(12)	41.5487(56)	55.243(32)	70.22(20)	87.3(1.1)
1.6	11.142770(48)	11.18(5) <sup>a</sup>	20.52461(29)	20.50(35) <sup>a</sup>	30.8330(13)	42.7047(67)	56.800(42)	72.23(23)	88.4(1.6)
1.8	11.753540(51)	11.84(6) <sup>b</sup>	21.58742(31)	21.50(30) <sup>b</sup>	31.9022(16)	43.9433(80)	58.887(50)	75.01(33)	93.7(2.0)
2.0	12.415600(40)	12.34(3) <sup>c</sup>	22.68817(31)	22.50(23) <sup>c</sup>	32.9055(19)	31.9(13) <sup>c</sup>	45.3359(97)	61.748(63)	78.35(43)
				22.82(24) <sup>e</sup>					
2.2	13.116580(61)		23.79951(37)	33.8145(20)	47.047(12)		65.739(79)	81.5(54)	96.7(42)
2.4	13.848290(64)		24.89975(43)	34.6014(23)	49.142(15)		70.39(10)	84.49(79)	101.8(57)
2.6	14.605680(71)		25.97137(46)	35.2661(25)	51.674(18)		75.32(13)	82.26(94)	96.4(83)
2.8	15.384880(76)		27.00271(52)	35.8052(30)	54.923(20)		80.49(16)	72.0(13)	56.1(109)
3.0	16.183310(81)	16.20(3) <sup>c</sup>	27.98053(56)	28.00(28) <sup>c</sup>	36.8(15) <sup>c</sup>	58.958(25)	85.52(21)	54.6(18)	107.8(87)
				28.30(44) <sup>c</sup>					
3.5	18.2510(110)		30.13473(74)	30.78(59) <sup>c</sup>	36.9187(46)	73.873(38)	88.68(34)	-33.3(31)	289(18)
4.0	20.40560(11)	20.43(4) <sup>c</sup>	31.77474(93)	31.90(32) <sup>c</sup>	37.5105(61)	39.7(16) <sup>c</sup>	97.890(56)	97.91(45) <sup>d</sup>	686.9(434) <sup>d</sup>
				32.16(76) <sup>e</sup>					-210.0(28) <sup>d</sup>
5.0	24.92476(14)	24.92(6) <sup>c</sup>	33.1278(13)	33.10(33) <sup>c</sup>	41.299(11)	39.9(16) <sup>c</sup>	181.789(94)	-253.19(98)	-339(11)
				33.02(134) <sup>c</sup>					6276(118)
6.0	29.67579(15)	29.68(6) <sup>c</sup>	31.3892(18)	31.60(32) <sup>c</sup>	55.633(18)	63.0(25) <sup>c</sup>	312.34(20)	309.1(17) <sup>d</sup>	-1323(2)
				31.66(126) <sup>e</sup>					2413(179) <sup>d</sup>
7.0	34.62032(20)		26.0565(24)	26.85(150) <sup>c</sup>	90.977(28)	45.448(30)	454.48(30)	-3788(4)	15227(60)
9.0	44.99604(30)		3.0084(39)	277.244(56)	366.7(8)		145385(259)	-15001(15)	731188(3628)
11.0	55.91620(41)		-38.6753(61)	-38.7(16) <sup>c</sup>	721.8(1)		623292(797)	-31798(40)	-645941(13848)

<sup>a</sup> Data taken from ref.<sup>8</sup> <sup>b</sup> Data taken from ref.<sup>10</sup> <sup>c</sup> Data taken from ref.<sup>13</sup> <sup>d</sup> Data taken from ref.<sup>9</sup>

TABLE II  
Summary of the reduced virial coefficients,  $\bar{B}_n = B_n/V^{n-1}$ , of hard homonuclear diatomics for 10 elongations,  $L^*$ . Values in parentheses are estimated standard errors

$L^*$	$\bar{B}_3$	$\bar{B}_4$	$\bar{B}_5$	$\bar{B}_6$	$\bar{B}_7$	$\bar{B}_8$	$\bar{B}_9$
0.1	10.060307(25)	18.49433(15)	28.42184(59)	40.0883(27)	53.659(15)	69.093(88)	86.93(49)
0.2	10.234601(25)	18.87081(15)	28.99836(65)	40.8812(30)	54.774(16)	70.273(90)	88.06(58)
0.3	10.518960(22)	19.49162(11)	29.95581(44)	42.2099(16)	56.5327(89)	72.406(54)	90.53(46)
0.4	10.917214(27)	20.36946(17)	31.31624(76)	44.1084(37)	59.093(20)	75.23(12)	94.46(82)
0.5	11.440035(29)	21.53740(18)	33.12783(83)	46.6552(41)	62.617(24)	79.95(15)	100.5(10)
0.6	12.106367(26)	23.04531(14)	35.47086(60)	49.9702(25)	67.208(15)	85.52(10)	105.66(77)
0.7	12.945143(34)	24.97247(22)	38.4561(11)	54.2213(58)	73.273(38)	92.50(26)	113.1(19)
0.8	13.999401(37)	27.43608(25)	42.2500(13)	59.6389(75)	81.184(50)	103.47(37)	125.6(28)
0.9	15.332444(40)	30.60935(29)	47.0961(16)	66.6526(98)	92.005(74)	113.51(54)	146.4(44)
1.0	17.039851(46)	34.76134(34)	53.3373(21)	75.797(13)	106.79(10)	132.22(82)	160.2(72)

<sup>a</sup> Data taken from ref.<sup>20</sup> <sup>b</sup> Data taken from ref.<sup>17</sup> <sup>c</sup> Data taken from refs<sup>14,18</sup>

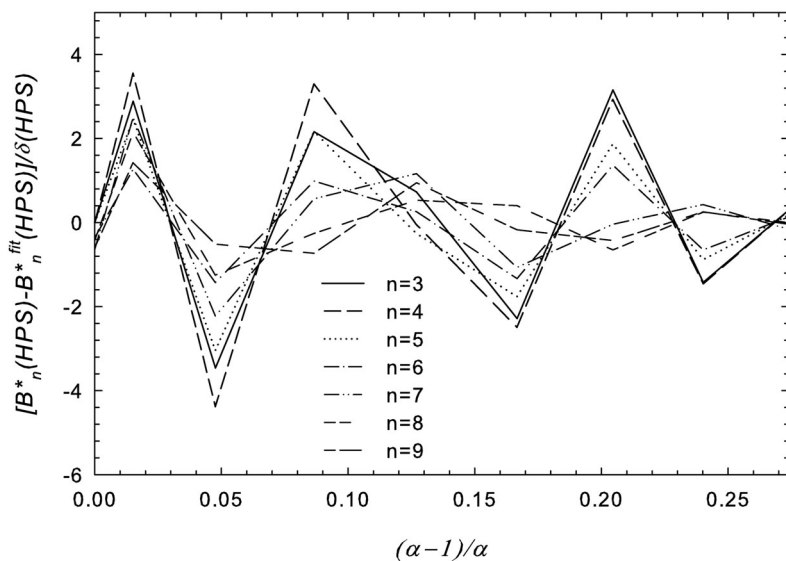


FIG. 2

Deviations of fitted  $B_n^{*,fit}$ (HPS) from the simulation data of this work,  $B_n^*$ (HPS), for hard prolate spherocylinders. Data were divided by standard errors,  $\delta$ (HPS)

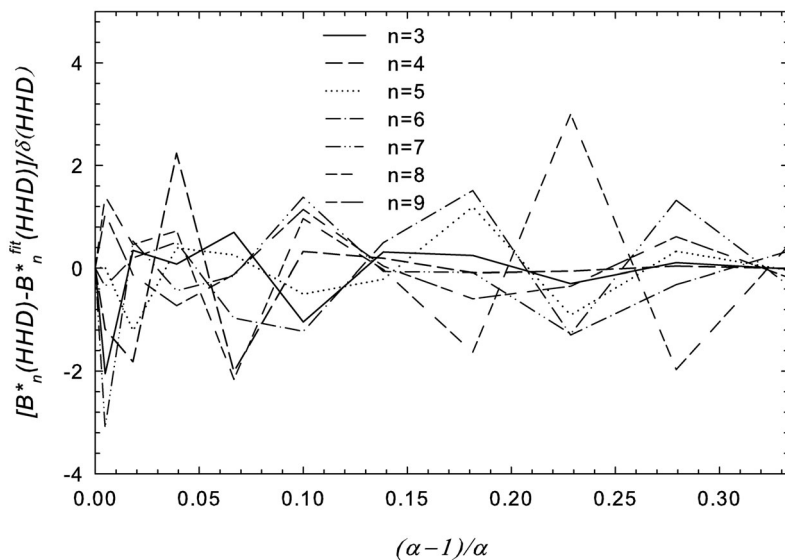


FIG. 3

Deviations of fitted  $B_n^{*,fit}$ (HHD) from the simulation data of this work,  $B_n^*$ (HHD), for hard diatomics divided by standard errors,  $\delta$ (HHD)



had a problem with the lower virial coefficients where the obtained results are so accurate that it is very difficult to approximate them within their uncertainties. The details about the correlation are given in Appendix. Comparisons of the fitted results with the simulation data of this work are given in Figs 2 and 3. It is seen that the polynomials approximate the data uniformly and with a precision only slightly worse than the theoretical best fit (68% of the data within  $\pm\delta$ ). In fact, there is a question whether it makes sense to fit the low-order coefficients which have been calculated very precisely.

## CONCLUSIONS

The recently proposed algorithm for determination of the virial coefficients of hard-body fluids<sup>24</sup> has been applied to two models of linear hard molecules, hard prolate spherocylinders and hard homonuclear diatomics. The virial coefficients were calculated for a number of elongations up to  $B_9$ . The virial coefficients were fitted to analytical expressions which can facilitate their use in developing equations-of-state.

The new data will be used in subsequent work to develop a new equation-of-state and estimate higher-order virial coefficients.

## APPENDIX: CORRELATION OF DATA

The calculated data were fitted to a polynomial in  $b = (\alpha - 1)/\alpha$ , where  $\alpha$  is the parameter of nonsphericity. It is given by Eq. (9) for HPS while for HHD it is approximated by

$$\alpha = \frac{(L^* + 2)(L^* + 1)}{2 + 3L^* - L^{*3}}. \quad (10)$$

The approximate formula for the  $n$ -th virial coefficient is

$$B_n^*, \text{fit} = \sum_{i=0}^k A_i b^i \quad (11)$$

where  $B_n^* = B_n/B_2^{n-1}$  is reduced by the second virial coefficient which is known analytically. As the weight, reciprocal values of squared standard errors,  $1/\delta^2$ , were used.

The data of HPSs were calculated for rather long molecules ( $\gamma = 11$ ). Therefore we were not able to find an accurate approximation in the whole range of elongations. Thus the results were fitted for each virial coefficient

only up to the length-to-width ratio  $\gamma = 2.6$  ( $L^* \in [0, 1.6]$ ). The resulting polynomials are presented in Table III. This problem is less severe in the case of HHD where the data could be approximated in the whole considered interval,  $L^* \in [0, 1]$  of molecular length (Table IV).

TABLE III

Orders of used polynomials for each  $B_n$  of HPS and their coefficients,  $A_i$  (see Eq. (11)). The approximation is valid for  $\gamma < 2.6$  ( $L^* \in [0, 1.6]$ )

$i$	$B_3^*$	$B_4^*$	$B_5^*$	$B_6^*$	$B_7^*$	$B_8^*$	$B_9^*$
0	0.62500	0.28695	0.11025	0.03888	0.01302	0.00418	0.00132
1	-0.16511	-0.24608	-0.18720	-0.10026	-0.04621	-0.01953	-0.00738
2	-0.75547	-1.0523	-0.68857	-0.29403	-0.03179	0.02898	0.01553
3	4.7821	7.5967	6.0110	3.7387	0.82215	0.04308	-0.00386
4	-24.078	-38.342	-28.494	-19.126	-2.7325	-0.18055	-0.03170
5	63.267	102.31	72.469	52.016	3.0039		
6	-67.231	-109.76	-74.177	-57.319			

TABLE IV

Orders of used polynomials for each  $B_n$  of HHD and their coefficients,  $A_i$  (see Eq. (11))

$i$	$B_3^*$	$B_4^*$	$B_5^*$	$B_6^*$	$B_7^*$	$B_8^*$	$B_9^*$
0	0.625000	0.286950	0.110251	0.038882	0.013023	0.004183	0.001309
1	-0.14973	-0.22293	-0.16920	-0.09038	-0.04015	-0.01653	-0.00590
2	0.07646	0.13926	0.13159	0.10197	0.05586	0.03134	0.00818
3	-0.64680	-0.93124	-0.43800	-0.23483	-0.06840	-0.04980	0.00655
4	2.6912	3.7457	1.0113	0.51835	0.06404	0.05004	-0.02295
5	-6.2707	-8.5319	-0.97363	-0.47024			
6	5.7732	7.8039					

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