Third and Fourth Virial Coefficients and the Equation of State of Hard Prolate Spherocylinders

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The self-consistency conditions (in the colloidal limit) formulated for the diluted hard convex body systems are used to discuss the third virial coefficient and to propose expressions for the individual contributions to the fourth virial coefficient of hard prolate spherocylinders. The proposed expressions yield values of the third and fourth virial coefficients in a fair agreement with the pseudo-experimental data. The equation of state formulated on the basis of expressions for the first few virial coefficients predicts the compressibility factor in full agreement with simulation data for elongations L^* as high as 5. For pure hard spheres, the derived equation of state reduces to the Carnahan−Starling form; for hard sphere mixtures, the EOS differs slightly from the BMCSL expression.

1. Introduction

Virial coefficients of hard body fluids have played an important role in the development of the hard body equations of state, in the deeper understanding of the hard body behavior, and in approximating the higher-order virial coefficients of real fluids (with realistic interaction potentials). The extension of the pure fluid expressions to mixtures is straightforward and forms a basis for the proposal of the equations of state of hard body mixtures.

Whereas numerical values and, to a lesser extent, theoretical expressions for virial coefficients of hard sphere fluids are available up to higher orders (cf. refs 1−3), in the case of nonspherical hard bodies, our knowledge of the virial coefficients is limited to numerical results for specific models (up to the fifth order), but theoretical expressions are available only for the second and third virial coefficients.

Several years ago, we studied the third[4] and fourth[5] virial coefficients of hard prolate and oblate spherocylinders with an emphasis on the determination of the numerical values of the individual contributions to the fourth virial coefficient, D, i.e., D_4, D_5, and D_6. We correlated the numerical data of D_4, D_5, and D_6 as functions of the parameter of nonsphericity, α, but we failed to characterize the behavior of these contributions in terms of the geometric quantities of the considered hard convex body.

Recently, we dealt with the behavior of the dense hard prolate spherocylinder (HPS) system in the colloidal limit[6] and found that conditions of self-consistency (SC) of the residual chemical potential of a solute and equation of state could be employed in deriving the SC equation of state.

In this paper, we consider the self-consistency constrains (for the residual chemical potential and EOS) for fluids at low densities where the state and thermodynamic functions can be expressed via the virial expansion. It is found that exact relations exist between theoretical expressions for the third and second, fourth and third, etc. hard body virial coefficients. These relations, together with exact expressions for the hard sphere

system, the simplest case of hard convex bodies, allowed us to write formulas for $(D_4 + D_5)$ and D_6 in terms of the geometric functionals of hard prolate spherocylinders. Finally we employed formulas for the first three virial coefficients to propose the hard convex body equation of state.

2. Theory

2.1. Self-Consistent Conditions in the Colloidal Limit. Self-consistent conditions between the residual chemical potential and equation of state were formulated by Henderson et al.[7] and by Matyushov and Ladanyi.[8] The binary mixture of two types of hard spheres (HS) solvent (component 1) with diameter σ_1 and solute (component 2) with σ_2 are considered at condition $x_2 \rightarrow 0$. By introducing parameter $\mathcal{R} = \sigma_2/\sigma_1$, the excluded solvent−solute volume is given as $V_{1+2} = (1 + \mathcal{R})^3 \pi\sigma_1^3/6 = (1 + \mathcal{R})^3 V_1$.

The residual chemical potential, $\Delta\mu_2$, of the solute and its derivative with respect to $\mathcal{R}$ at $\mathcal{R} = 0$ reads as

(i) $$\left[\frac{\Delta\mu_2}{kT}\right]_{\mathcal{R}=0} = -\ln(1 - \rho V_1) = -\ln(1 - y)$$

(ii) $$\left[\frac{1}{kT}\frac{\partial\Delta\mu_2}{\partial\mathcal{R}}\right]_{\mathcal{R}=0} = \frac{3y}{(1 - y)}$$

where ρ stands for the number density, V_1 denotes the solvent molecular volume and $y = \rho V_1$ is the packing fraction.

In the case of $\mathcal{R} \rightarrow \infty$, the surface of the solute molecule is planar; then

(iii) $$\left[\frac{1}{3\mathcal{R}^2}\frac{\partial\Delta\mu_2/kT}{\partial\mathcal{R}}\right]_{\mathcal{R}\rightarrow\infty} = y\left(\frac{PV}{NkT}\right)^{\text{pure}}$$

where PV/NkT stands for the compressibility factor of the solvent.

In the case of hard convex bodies (HCB), the mean volume, V_{1+2} reads as

$$V_{1+2} = \frac{1}{2}(V_1 + S_1 R_2 + R_1 S_2 + V_2) \tag{1}$$

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where V_i, S_i, and R_i denote the HCB volume, surface area, and the $(1/4\pi)$ multiple of the mean curvature integral of component i.

Instead of $\mathcal{R}$, we introduce[6,9] the dilatation coefficient, λ, which scales the size of the solute molecule, whereas its shape (e.g., its length-to breath ratio, γ) is kept constant. We denote by superscript 0 the basic geometric quantities, V_2^0, S_2^0, and R_2^0, of the parallel hard body to the solute model; further, we put $V_2^0 = V_1$. Contrary to HS systems, the corresponding ratios S_2^0/S_1 and R_2^0/R_1 generally differ from one, and we write $S_2^0/S_1 = l_S$ and $R_2^0/R_1 = l_R$.

For example, for two prolate hard spherocylinders with γ_2, σ_2 and $\gamma_1\sigma_1$

$$l_S = (\gamma_2/\gamma_1)((3\gamma_1 - 1)/(3\gamma_2 - 1))^{2/3}$$

$$l_R = (\gamma_2 + 1)/(\gamma_1 + 1)((3\gamma_1 - 1)/(3\gamma_2 - 1))^{1/3}$$

The actual values of V_2, S_2 and R_2 in terms of λ are

$$V_2 = \lambda^3 V_2^0 = \lambda^3 V_1, \; S_2 = \lambda^2 S_2^0 = \lambda^2 l_S S_1, \; R_2 = \lambda R_2^0 = \lambda l_R R_1 \tag{2}$$

The self-consistency conditions (in the concentration limit $x_2 \to 0$) then possess the following form:

$$(i) \qquad \left[\frac{\Delta\mu_2}{kT}\right]_{\lambda=0} = -\ln(1 - y) \tag{3}$$

$$(ii) \qquad \left[\frac{1}{kT}\frac{\partial\Delta\mu_2}{\partial\lambda}\right]_{\lambda=0} = \frac{sR_2}{(1-y)} = \frac{3\alpha y l_R}{(1-y)} \tag{4}$$

$$(iii) \qquad \left[\frac{1}{3\lambda^2}\frac{\partial\Delta\mu_2/kT}{\partial\lambda}\right]_{\lambda\to\infty} = y\left(\frac{PV}{NkT}\right)^{\text{pure}} \tag{5}$$

where

$$s = \rho S_1 \qquad \alpha = \frac{R_1 S_1}{3V_1}$$

We will now consider expansion of these three relationships in the variable packing fraction, y. We find

$$(i) \qquad \left[\frac{\Delta\mu_2}{kT}\right]_{\lambda=0} = y + \frac{1}{2}y^2 + \frac{1}{3}y^3 + \frac{1}{4}y^4 + \dots \tag{6}$$

$$(ii) \qquad \left[\frac{1}{kT}\frac{\partial\Delta\mu_2}{\partial\lambda}\right]_{\lambda=0} = 3\alpha l_R [y + y^2 + y^3 + y^4 + \dots] \tag{7}$$

$$(iii) \qquad \left[\frac{1}{3\lambda^2}\frac{\partial\Delta\mu_2/kT}{\partial\lambda}\right]_{\lambda\to\infty} = y[1 + B_{11}^* y + C_{111}^* y^2 + D_{1111}^* y^3 + \dots] \tag{8}$$

where B_{ij}^*, C_{ijk}^*, D_{ijkl}^* stand for the reduced virial coefficients of components i, j, k, l. Thus, we have three conditions the expression for the solute residual chemical potential should fulfill.

From the virial expansion of the residual Helmholtz energy of the binary mixture of components 1 and 2

$$\frac{\Delta A}{kT} =$$

$$\frac{\sum_{i,j=1}^{2} N_i N_j B_{ij}}{V} + \frac{\sum_{i,j,k=1}^{2} N_i N_j N_k C_{ijk}}{2V^2} + \frac{\sum_{i,j,k,l=1}^{2} N_i N_j N_k N_l D_{ijkl}}{3V^3} + \dots \tag{9}$$

one obtains for the residual chemical potential $\Delta\mu_2/kT = (\partial\Delta A/kT)/(\partial N_2)$ of solute in the concentration limit $x_2 \to 0$ the following expression:

$$\left[\frac{\Delta\mu_2}{kT}\right] = 2B_{12}\rho + \frac{3}{2}C_{112}\rho^2 + \frac{4}{3}D_{1112}\rho^3 + \dots =$$
$$2B_{12}^* y + \frac{3}{2}C_{112}^* y^2 + \frac{4}{3}D_{1112}^* y^3 + \dots \tag{10}$$

Equations 6–8 give us an important information on the form of the single cross virial coefficient. Thus, in order that eq 6 is fulfilled, the expression for each HCB virial coefficient of order j should contain terms $V_i^{(j-1)}$; from (7) we see that the expression should comprise terms $R_k S_l V_i^{(j-2)}$. Finally, (8) yields the relation between the derivative of the cross virial coefficients of the order j and the pure solvent virial coefficient of order $j - 1$. We will discuss these conclusions in detail on the example of the virial expansion of the fourth order.

The reduced second cross virial coefficient B_{12}^* in a binary mixture reads[10] as

$$2B_{12}^* = \frac{1}{V_1}[V_1 + S_1 R_2 + R_1 S_2 + V_2] =$$
$$\left[1 + \frac{S_1}{V_1}R_2 + \frac{R_1}{V_1}S_2 + \frac{1}{V_1}V_2\right] \tag{11}$$

If we express the geometric functionals of solute in terms of the dilatation coefficient, λ, we obtain the following contributions from B_{12}^* (in the considered limits)

$$[2B_{12}^*]_{\lambda=0} = 1, \qquad \left[\frac{\partial(2B_{12}^*)}{\partial\lambda}\right]_{\lambda=0} = \frac{S_1}{V_1}R_2^0 = 3\alpha l_R,$$
$$\left[\frac{1}{3\lambda^2}\frac{\partial(2B_{12}^*)}{\partial\lambda}\right]_{\lambda\to\infty} = \frac{V_2^0}{V_1} = 1 \tag{12}$$

From (12), it is obvious that these contributions correspond to the first terms in (6–8).

The reduced third cross virial coefficient, C_{112}^*, of two solvent and one solute molecule can be calculated[10–12] from

$$3C_{112}^* = \frac{1}{V_1^2}\left[V_1^2 + 2V_1 V_2 + 2V_1(R_1 S_2 + S_1 R_2) + 2R_1 S_1 V_2 + \frac{1}{3}(2Q_1 S_1 S_2 + S_1^2 Q_2)\right] \tag{13}$$

where $Q_i = R_i^2$ or other geometric functional of order $\mathcal{O}[l^2]$. Then

$$[3C_{112}^*]_{\lambda=0} = 1, \qquad \left[\frac{\partial(3C_{112}^*)}{\partial\lambda}\right]_{\lambda=0} = \frac{2S_1}{V_1}R_2^0 = 6\alpha l_R,$$
$$\left[\frac{1}{3\lambda^2}\frac{\partial(3C_{112}^*)}{\partial\lambda}\right]_{\lambda\to\infty} = 2 + 2\frac{R_1 S_1}{V_1} = 2(1 + 3\alpha) = 2B_{11}^* \tag{14}$$

If we write the fourth cross virial coefficient in the form (see next paragraph)

$$4D_{1112} = 4(D_I + D_{II}) = V_1^3 + 3V_1^2V_2 + 3V_1^2(R_1S_2 + S_1R_2) +$$
$$6V_1R_1S_1V_2 + \frac{1}{3}V_1(S_1^2Q_2 + 2Q_1S_1S_2) + \frac{1}{3}Q_1S_1^2V_2 - \frac{4}{27}W_1^3W_2 \quad (15)$$

where W_i is yet unknown geometric quantity of dimension $[l^{9/4}]$ one can obtain

$$[4D_{1112}^*]_{\lambda=0} = 1, \quad \left[\frac{\partial(4D_{1112}^*)}{\partial\lambda}\right]_{\lambda=0} = 3\frac{S_1R_2^0}{V_1} = 9\alpha l_R,$$
$$\left[\frac{1}{3\lambda^2}\frac{\partial(4D_{1112}^*)}{\partial\lambda}\right]_{\lambda\to\infty} = 3 + 6\frac{R_1S_1}{V_1} + \frac{Q_1S_1^2}{V_1^2} =$$
$$3(1 + 6\alpha + 3\alpha^2\xi) = 3C_{111}^* \quad (16)$$

From the last two equations, it is evident that if the geometric functional Q_i in eqs 13 and 15 is the same quantity and functional W_i is of $\mathcal{O}(\lambda^m)$ with $1 < m < 3$, the fourth-order virial expansion [with forms of C and D given by (13) and (15)] is self-consistent.

Thus, at least in the colloidal limit the self-consistency constrains make it possible to conjecture the form of the virial coefficient of the jth order from that of the order $j - 1$.

In the next paragraphs, we will consider expressions for the third and fourth virial coefficients which fulfill these conditions.

2.2. Third Cross Virial Coefficient. The third virial coefficient, C^{HS}, of hard spheres (HS), the simplest case of hard convex bodies (HCB), is known in an analytic form.[12,13] For hard spheres of radii a, b, and c, it holds true[13]

$$C^{HS} = \frac{16\pi^2}{27}[a^3b^3 + a^3c^3 + b^3c^3 +$$
$$3abc(a + b + c)(ab + ac + bc)] \quad (17)$$

For a triplet of HCBs, A, B, and C, Isihara[12] proposed an expression

$$3C^{HCB} = V_AV_B + V_AV_C + V_BV_C + V_A(R_BS_C + R_CS_B) + V_B$$
$$(R_AS_C + R_CS_A) + V_C(R_AS_B + R_BS_A) =$$
$$\frac{1}{3}(G_{ABC} + G_{BCA} + G_{CAB}) \quad (18)$$

In order the last expression reduces for HS to eq 17, the geometric functional G_{ijk} should be of dimension $[l_i^2 l_j^2 l_k^2]$. According to Isihara,[12] it holds

$$\frac{1}{4\pi}S_iS_jS_k \le G_{ijk} \le (4\pi)^2R_i^2 R_j^2 R_k^2$$

In the simplest approximation

$$G_{ijk} = R_i^2S_jS_k \quad (19)$$

which for a pure fluid reduces to $G_{iii} = R_i^2 S_i^2 = 9\alpha^2V_i^2$. Generally we have

$$G_{iii} = Q_iS_i^2 \quad (20)$$

($Q_i = R_i^2$ in the case of HS). For hard convex bodies[14] we write

$$Q_i = R_i^2\xi \quad (21)$$

The third virial coefficient of pure HCB fluids is then

$$C^* = C^{HCB}/V_i^2 = 1 + 6\alpha + 3\alpha^2\xi \quad (22)$$

Approximation (19) yields C^{HCB} of oblate spherocylinders in a reasonable agreement with the pseudo-experimental data; however, in the case of hard prolate spherocylinders (HPS), eq 22 with 19 overestimates experimental values. To improve the prediction of C^{HCB} of HPS, Naumann and Leland[15] (NL) assumed for G the following expression (actually the arithmetic mean of $R_i^2 S_i^2$ and $S_i^3/4\pi$):

$$G_{iii} = R_i^2 S_i^2\left[\frac{1}{2}(1 + \tau^{-1})\right] \quad (23)$$

where $\tau = 4\pi R_i^2/S_i$. Then G_{iii} can be written as

$$G_{iii} = 9\alpha^2\xi_{NL}V_i^2 \quad (24)$$

with ξ_{N-L}

$$\xi_{NL} = \frac{1}{2}(1 + \tau^{-1}) = \frac{1}{2} + \frac{1}{2}\frac{S_i}{4\pi R_i^2} \quad (25)$$

By passing we note that a similar approximation

$$\xi = \frac{2}{3} + \frac{1}{3}\frac{S_i}{4\pi R_i^2} \quad (26)$$

works even better than the original NL expression.

Besides the agreement of theoretical and pseudo-experimental values of the third virial coefficient, there is another criterion of theoretical expressions for C, namely the behavior of the ratio of the third and square of the second virial coefficients, $P = C^{HCB}/(B^{HCB})^2$, in the limit $L^* = L/\sigma = \gamma - 1 \to \infty$ (γ stands for the length-to-breadth ratio). According to Onsager[16] (cf. also discussion in ref 17)

$$\lim_{L^*\to\infty} P \approx \text{const}\frac{\ln(L^*)}{L^*} \quad (27)$$

From (22) and the expression for the reduced second virial coefficient $B^* = 1 + 3\alpha$, we have

$$\lim P_{L^*\to\infty} = \lim_{L^*\to\infty}\frac{1 + 6\alpha + 3\alpha^2\xi}{(1 + 3\alpha)^2} \approx \lim_{L^*\to\infty}\xi \quad (28)$$

Thus, ξ should approach the Onsager limit for $L^* \to \infty$, whereas for $L^* = 0$ ξ should be equal to one.

In the case of the NL approximation (as well as for its modification), we obtain

$$\lim_{L^*\to\infty}\xi_{NL} = \text{const}_1 \quad (29)$$

In this work, we assume Q_i to be the geometric mean of functionals $S_i/4\pi$ and R_i^2, i.e.

$$Q_i = \left(\frac{S_i}{4\pi}R_i^2\right)^{1/2} = (S_i/4\pi)^{1/2}R_i \quad (30)$$

so that

$$\xi = \frac{(S_i/4\pi)^{1/2}}{R_i} \quad (31)$$

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TABLE 1: Ratio of the Third and Square of the Second Virial Coefficient $\mathscr{P} = C^*/B^{*2}$ and $\mathscr{PP} = P(L^*)/P(10)$ of Hard Prolate Spherocylinders of the Length-to-Breadth Ratio $\gamma = L^* + 1$

L^*	$P_{MC}{}^a$	$P_{eq\,31}$	P_{NL}	PP_{MC}	$PP_{eq\,31}$	PP_{NL}
10	0.3383(5)	0.30217	0.3302	1	1	1
100	0.0895(3)	0.0837	0.1891	0.264	0.277	0.573
1000	0.0152(1)	0.0230	0.1690	0.045	0.076	0.512
10000	0.00215(5)	0.0069	0.1669	0.006	0.023	0.203

^{a} Reference 17.

TABLE 2: Third and Fourth Virial Coefficient C^* of Hard Prolate Spherocylinders of the Length-to-Breadth Ratio γ

γ	C^*_{NL}	C^*_{th}	$C^*_{th}{}'$	$C^*_{MC}{}^a$	D^*_{NL}	D^*_{th}	$D^*_{th}{}''$	$D^*_{MC}{}^a$
1.0	10.00	10.00	10.00	10.00	18.00	18.00	18.00	18.3648
1.4	10.56	10.56	10.58	10.64(5)	19.09	19.06	19.08	19.26(30)
1.6	11.07	11.07	11.10	11.18(5)	20.06	20.00	20.04	20.50(35)
2.0	12.28	12.27	12.35	12.34(3)	22.36	22.19	22.29	22.50(23)
2.5	14.01	13.99	14.16	14.30(7)	25.62	25.15	25.41	26.06(65)
3.0	15.91	15.85	16.13	16.20(3)	29.13	28.14	28.67	28.00(28)
4.0	20.04	19.84	20.46	20.43(4)	36.37	33.65	35.16	31.90(32)

^{a} Reference 2.

[Relation 31 is the simplest form of the semiempirical expression given by the present autor in ref 14.]

In the limit $L^* \rightarrow \infty$, parameter ξ tends to the expression

$$\lim_{L^* \rightarrow \infty} \xi = \text{const}_2 \frac{\gamma^{1/2}}{\gamma + 1} = \text{const}_3 \frac{L^{*1/2}}{L^*} \tag{32}$$

which follows reasonable well trends of P, see Table 1.

In Table 2, we compare the third virial coefficient of pure HPS calculated from (22), C_{th}, with ξ given by (31) with the pseudo-experimental values C_{MS} and results of the Leland-Naumann approximation, C_{NL}. One can see that values C_{th} differ only marginally from C_{NL}. Both sets of data are in much better accordance with the pseudo-experimental data than values determined for $\xi = 1$. In addition, we considered an approximation, similar to (31)

$$\xi = (S_i/4\pi R_i^2)^{1/3} \tag{33}$$

Values of the third virial coefficient $C^*_{th}{}'$ calculated on the basis of approximation (33) are also listed in Table 2. It appears that this approximation yields the best agreement with experimental data.

In passing, we note that eq 31 yields a fair prediction of the third virial coefficient of hard oblate spherocylinders (cf. $C^* = 11.53$, 14.34, and 17.75 for $\phi = 1$, 2, and 3 in comparison with the experimental values 11.65, 14.79, and 18.65) although Onsager's limit for the oblate spherocylinders differs from (27).

In Table 2, we list also values of the fourth virial coefficient calculated from the expression described in the next paragraph and from the Naumann-Leland prescription

$$D^*_{NL} = 1 + 9\alpha + 9\alpha^2(1 + \tau^{-1})/2 - \alpha^2(5 - 3\tau^{-1})/2 \tag{34}$$

Pseudo-experimental data are given for comparison, too.

2.3. Fourth Cross Virial Coefficient. An expression for the fourth cross virial coefficient, D_{1112} is, in comparison with C_{112}, more involved. First of all, the fourth virial coefficient, D, is given by a sum of three different terms, D_4, D_5, and D_6, corresponding to three types of cluster integrals, containing four, five and six Mayer functions, i.e.

$$D = -\frac{1}{8}(3D_4 + 6D_5 + D_6) = D_I + D_{II} \tag{35}$$

where $D_I = -(3D_4 + 6D_5)/8$. For hard spheres with radii a, b, c, and d, Blaak[13] derived expression for D_I

$$8D_I = \frac{64\pi^2}{9}\{a^3b^3c^3 + a^3b^3d^3 + a^3c^3d^3 + b^3c^3d^3 +$$
$$3abcd(ab + ac + ad + bc + bd + cd)(abc + abd +$$
$$acd + bcd)\} \tag{36}$$

This equation can be rewritten to a form

$$\frac{8}{3}D_I = V_AV_BV_C + V_AV_BV_D + V_AV_CV_D + V_BV_CV_D +$$
$$V_AV_B(R_CS_D + R_DS_C) + V_AV_C(R_BS_D + R_DS_B) +$$
$$V_AV_D(R_BS_C + R_CS_B) + V_BV_C(R_AS_D + R_DS_A) +$$
$$V_BV_D(R_AS_C + R_CS_A) + V_CV_D(R_AS_B + R_BS_A) +$$
$$\frac{1}{3}[V_A(Q_BS_CS_D + Q_CS_BS_D + Q_DS_BS_C) + V_B(Q_AS_CS_D +$$
$$Q_CS_AS_D + Q_DS_AS_C) + V_C(Q_AS_BS_D + Q_BS_AS_D + Q_DS_AS_C) +$$
$$V_D(Q_AS_BS_C + Q_BS_AS_C + Q_CS_AS_B)] =$$
$$\sum_{(4)}V_iV_jV_k + \sum_{(12)}V_iV_jR_kS_l + \frac{1}{3}\sum_{(12)}V_iQ_jS_kS_l \tag{37}$$

with $Q_i = R_i^2$ for HS; generally $Q_i = R_i^2\xi_i$.

In the special case of pure HPS, the reduced coefficient D^*_I is given by expression

$$D^*_I = \frac{D_I}{V_i^3} = \frac{3}{2}[1 + 9\alpha + 9\alpha^2\xi] \tag{38}$$

For the remaining term, $D_{II} = -D_6/8$ and four hard spheres A, B, C, and D, with radius d considerably smaller than the other ones, Blaak[13] found

$$8D_{II} = -\frac{64\pi^3}{27}\{a^3b^3c^3 + a^3b^3d^3 + a^3c^3d^3 + b^3c^3d^3 +$$
$$3abcd(ab + ac + ad + bc + bd + cd)(abc + abd +$$
$$acd + bcd)\} - \frac{64\pi^3}{3}a^2b^2c^2d^3 + \text{terms of } \mathcal{O}[d^4] \tag{39}$$

This expression yields correct limits for $\mathcal{R} = 0$ but does not allow determination of the limit for $\mathcal{R} \rightarrow \infty$. From (39), we conjecture that, in the general case of HPS, the last term of the expression for D_{II} can be written as the product of four geometric functionals W_i, i.e., $W_AW_BW_CW_D$, with W_i of the dimension $l^{9/4}$ (depending on λ^m with $m = 9/4$). Thus

$$8D_{II} = -\left\{\sum_{(4)}V_iV_jV_k + \sum_{(12)}V_iV_jR_kS_l + \frac{1}{3}\sum_{(12)}V_iQ_jS_kS_l +$$
$$\frac{8}{27}W_AW_BW_CW_D\right\} \tag{40}$$

which for the cross virial coefficient D_{1112} reduces to

$$D_{II} = -\frac{1}{8}\left\{V_1^3 + 3V_1^2V_2 + 3V_1^2(R_1S_2 + S_1R_2) + 6V_1R_1S_1V_2 +$$
$$V_1(S_1^2Q_2 + 2Q_1S_1S_2) + Q_1S_1^2V_2 + \frac{8}{27}W_1^3W_2\right\} \tag{41}$$

TABLE 3: Contributions D_I^* and D_{II}^* to the Fourth Virial Coefficient of Hard Prolate Spherocylinders of the Length-to-breadth Ratio γ

γ	D_{INL}^*	D_{Ith}^*	$D_{Ith}^{*\prime}$	D_{IMC}^* [a]	D_{IIth}^*	$D_{IIth}^{*\prime}$	$D_{IIth}^{*\prime\prime}$	D_{IIMC}^* [a]
1.0	28.50	28.50	28.50	28.521	10.17	10.17	10.50	10.156
1.5	31.15	31.15	31.25	31.35(49)	11.20	11.24	11.61	11.28(5)
2.0	36.06	36.06	36.39	36.27(68)	13.16	13.28	13.74	13.36(6)
2.5	41.89	41.78	42.54	41.6(11)	15.55	15.81	16.36	15.84(13)
3.0	48.33	48.06	49.35	46.8(16)	18.27	18.70	19.39	18.49(16)
3.5	55.26	54.73	56.69	52.2(31)	21.28	21.94	22.80	21.46(20)
4.0	62.64	61.75	64.50	56.6(24)	24.59	25.51	26.59	24.48(25)

[a] Reference 5.

W_i is yet unknown geometric quantity (of dimension $[l^{9/4}]$); we propose for it an approximative formula not containing V_i which yields D_{II} in agreement with the hard sphere experimental value and respects the self-consistency conditions [i.e., that D_{II} does not contain any further term of order λ^3 (or higher) in addition to those appearing in D_I]. Such conditions are fulfilled, if we assume

$$W_i = [R_i S_i]^{3/4} \tag{42}$$

For pure HPS, we have

$$D_{II} = -\frac{1}{2}[1 + 9\alpha + 9\alpha^2\xi + 2\alpha^3] \tag{43}$$

Values of D_I^* and D_{II}^* calculated from (38) and (43) compare well with numerical data, as can be seen from Table 3.

By passing we note that cofactor 4/3 of the last term of D_{II}^* yields better prediction of D_{II} for low values of γ but worse for higher ones and worse values of D^*.

For $D = D_I + D_{II}$, we have

$$D^* = \frac{D}{V_i^3} = 1 + 9\alpha + 9\alpha^2\xi - \alpha^3 \tag{44}$$

Values of D^* evaluated according to (44) with $\xi = (S_i/4\pi)^{1/2}/R_i$ are listed in the seventh column of Table 2, whereas the eighth column brings values od $D^{*\prime\prime}$ calculated from a similar expression in which the last term equals to $-\alpha^3/\xi$. It is evident that up to $\gamma = 2.5$ no important differences between D_{th}^* and $D_{th}^{*\prime\prime}$ are found.

2.4. Equation of State. Knowledge of the expressions for the first few virial coefficients makes it possible to write the HCB equation of state (EOS). If we consider first three virial coefficients, i.e., B^*, C^*, and D^* [eq 42], we obtain

$$\frac{P}{\rho kT} = \frac{1}{(1-y)} + \frac{3\alpha y}{(1-y)^2} + \frac{y^2(3\alpha^2\xi - \alpha^3 y)}{(1-y)^3} \tag{45}$$

However, to take into account HCB values of the fifth virial coefficient, we add a term of $\mathcal{O}(y^4)$ such that EOS for pure HS reduces to the Carnahan−Starling expression[18] (similarly as the EOSs due to Naumann and Leland[15] or Santos et al.[19] do). Then we write eq 46

$$\frac{P}{\rho kT} =$$
$$\frac{1}{(1-y)} + \frac{3\alpha y}{(1-y)^2} + \frac{y^2[3\alpha^2\xi - \alpha^3 y - (\alpha^3 - 1)y^2]}{(1-y)^3} \tag{46}$$

Results for hard prolate spherocylinders of $\gamma = 2$ and 3 are listed in Table 4 together with simulation data. In Table 5, we

TABLE 4: Compressibility Factor of Hard Prolate Spherocylinders of the Length-to-Breadth Ratio γ

	$\gamma = 2$		$\gamma = 3$	
y	Z_{th}	Z_{MC} [a]	Z_{th1}	Z_{MC} [a]
0.20	2.66	2.65(2)	3.05	3.07(3)
0.30	4.55	4.48(7)	5.40	5.40(10)
0.35	6.03		7.22	7.17(11)
0.40	8.09	8.20(20)	9.72	9.60(10)
0.45	11.00		13.19	13.10(16)
0.50	15.25	15.20(20)	18.13	18.00(40)

[a] Reference 2.

TABLE 5: Compressibility Factor of Hard Prolate Spherocylinders of the Length-to-Breadth Ratio $\gamma = 6$

y	Z_{NL}	Z_{BM}	Z_{BM}'	Z_{th}	Z_{MC} [a]
0.10	2.20	2.24	2.18	2.18	2.18
0.15	3.14	3.25	3.11	3.09	3.07
0.20	4.40	4.62	4.36	4.29	4.27
0.25	6.05	6.44	6.03	5.84	5.80
0.30	8.18	8.86	8.28	7.81	7.77
0.35	10.89	12.06	11.32	10.27	10.10

[a] References 20 and 21.

compare the compressibility factor of HPS of the length-to-breadth ratio $\gamma = 6$. In addition, we list in Table 5 also values of the compressibility factor resulting from the modified scaled particle theory EOS (denoted as BM) proposed for HSP by the present author[22]

$$\frac{P}{\rho kT} = \frac{1}{(1-y)} + \frac{3\alpha y}{(1-y)^2} + \frac{y^2[3\beta(1-2y) + 5\alpha y]}{(1-y)3} \tag{47}$$

[Values for $\beta = \alpha^2$ are denoted as Z_{BM}, those with β determined in the same way as in eq 46 as Z_{BM}'].

From Tables 4−5, fair agreement of the calculated values (from eq 46) and pseudo-experimental values is evident. For large values of γ eq 46 yields $p/\rho kT$ in fair agreement with pseudo-experimental data; (46) is superior to the MSPT[22] as well as Nezbeda[23] EOSs.

Equation 46 can be extended to mixtures. If we define

$$\alpha_s = \frac{\sum x_i R_i \sum x_i S_i}{3\sum x_i V_i} \quad \beta_s = \frac{\sum x_i Q_i (\sum x_i S_i)^2}{9(\sum x_i V_i)^2} \tag{48}$$

and

$$\delta_s = \frac{(\sum x_i W_i)^4}{27(\sum x_i V_i)^3} \text{ with } W_i = [R_i S_i]^{3/4} \tag{49}$$

then

$$\frac{P}{\rho kT} = \frac{1}{(1-y)} + \frac{3\alpha_s y}{(1-y)^2} + \frac{y^2[3\beta_s - \delta_s y - (\delta_s - 1)y^2]}{(1-y)^3} \tag{50}$$

As can be seen, in the case of hard sphere mixtures, the equation does not reduce to the BMCSL form[24,25] though the difference is small.

In Table 6, a comparison is given of the calculated and experimental values of the compressibility factor, $Z = P/\rho kT$, of the equimolar mixture of hard spheres and hard prolate

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TABLE 6: Compressibility Factor of the Equimolar Mixture of Hard Spheres and Hard Prolate Spherocylinders of the Length-to-Breadth Ratio $\gamma = 2$

y	Z_{th}	Z_{MC} [a]	y	Z_{th}	Z_{MC} [a]
0.20	2.50	2.50(6)	0.40	7.35	7.31(7)
0.30	4.19	4.11(5)	0.45	9.98	9.87(10)

[a] Reference 26.

spherocylinders of $\gamma = 2$ of the same σ. Agreement within error estimates is found.

3. Conclusion

In this paper, we dealt with the third and fourth virial coefficients of hard prolate spherocylinders, the frequently used hard body model of nonspherical molecules. From the self-consistency conditions we found general relations which hold between the virial coefficients of the order j and $j - 1$ (in the colloidal limit). These relations together with exact expressions for the hard sphere system make it possible to conjecture the form of the fourth virial coefficient (i.e., contributions D_4, D_5, and D_6) from the expression for the third-order coefficient. Next we introduced an approximation for the geometric functional Q, comprised in expressions both for C and D. This approximation yields the correct value in the case of hard spheres and a fair estimate in the case of practically infinitely long prolate spherocylinders. For hard oblate spherocylinder, $Q \approx R^2$; this explains the observation that the simpler expression for the third virial coefficient and EOS containing only one nonsphericity parameter, α, work well in the case of oblate molecules. Comparison of the theoretical values of the third and fourth virial coefficients and the compressibility factor with pseudo-experimental data shows a high precision of the new expressions even for considerably nonspherical molecules, superior to results from the so far available equations.

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