FLUIDS OF HARD NONSPHERICAL MOLECULES.
II. MONTE CARLO DATA AND EQUATION OF STATE

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Dedicated to Professor William R. Smith on the occasion of his 65th birthday.

New accurate data on the compressibility factor of the hard homonuclear diatomics with a full range of elongations and the hard prolate spherocylinders with length-to-width ratio as high as 9 are presented. The data were obtained by Monte Carlo *NpT* simulations with finite-size corrections in the range of reduced pressures $\beta p^* = 0.5–7.0$. New equations of state based on simultaneous correlation of the data with the virial coefficients up to the ninth are presented.

Keywords: Hard prolate spherocylinder; Hard homonuclear diatomics; Hard dumbbell; Equation of state; Monte Carlo simulation; Thermodynamics.

The accuracy of existing equations of state (EOS) is limited by known virial coefficients and pseudoexperimental data which are calculated only for a few selected elongations and not very accurately. In the preceding paper[1] we presented new data on the virial coefficients up to the ninth which may serve as a basis for EOS development.

The latest pseudoexperimental data for hard homonuclear diatomics (HHD) covering the full range of elongations from $L/\sigma = L^* = 0.2$ (L is the atom–atom distance and σ the sphere diameter) have been calculated in 1980 [2]. Newer data[3,4] are available only for $L^* = 0.5$ and for $L^* = 0.3$ and 0.6. Monte Carlo (MC) results on hard prolate spherocylinders (HPS) have been published[5–7] for reduced elongations $L^* = 1$ and 2 and newer molecular dynamics data for only $L^* = 5$ are available[8]. The older data are generally imprecise because of the limited computing power available.

It is interesting that theoretical work on these models is still going on[3,9–13] but it is based on old pseudoexperimental data. There is therefore need for new more accurate data.

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In this contribution we have calculated very accurate data on both models covering all reduced elongations for homonuclear diatomics and a large interval of reduced elongations for HPS up to $L^* = 8$. These data, along with precise virial coefficients from our previous article[1], serve as a basis of new accurate EOSs for both models.

METHODS

Monte Carlo Simulation

The MC simulations provide "experimental" results for model systems. We used the standard cubic periodic simulation box and the NpT ensemble[14]. The MC moves were separated into four elementary moves:

– displacement in the direction of the molecular axis,
– displacement in the direction perpendicular to the molecular axis,
– rotation around the molecular center,
– volume change (uniform in log V).

The move lengths were adjusted to give acceptance ratios of 0.2 for displacements, and 0.25 for rotations and volume changes.

The computer code uses the linked-cell list method[14] implemented efficiently in the ANSI C language by pointers. The number of cells per simulation box is optimized for speed.

The calculations started from a random configuration in a very large box and were followed by a sufficient period of equilibration until the measurements were started. The NpT ensemble for hard-body systems is controlled by a single parameter $\beta p^* = p\sigma^3/(k_B T)$ and gives the averaged volume $\langle V \rangle$. The equation of state can be equivalently expressed via the number density, $\rho = N/\langle V \rangle$, or the compressibility factor, $Z = \beta p/\rho$. It is advantageous to use the dimensionless reduced density, $\rho^* = \rho\sigma^3$, or the packing fraction, $y = V\rho$, where V is the volume of a molecule.

The calculations have been performed for systems consisting of $N = 1000$ particles, with reduced elongations L^* in the range from 0.1 to 1.0 with step 0.1 for homonuclear diatomics and from 0.2 to 2.0 with step 0.2 for prolate spherocylinders with additional reduced elongations up to 8.0. Only the fluid range was covered.

One MC cycle contained N attempted particle moves and one volume change. On average 10^5 cycles were needed to reach the equilibrium volume. The productive runs took 33×10^6 cycles at lower densities and 67×10^6 cycles at higher densities.

In simulations of both systems, the fluid can freeze, more likely at shorter elongations. This phenomenon appears on the convergence profiles (time dependence of the volume) as a jump. In addition, the crystal is visible on a playback of the simulation. Similarly, sufficiently long HPS may undergo a transition from an isotropic fluid to a nematic liquid crystal[15]. The conversion is slower and not so easily visible on the convergence profile, although still visible on a playback. To detect possible transition to the oriented state, we used the orientation order parameter defined by[14]

$$\chi = \frac{3}{2}\,\mathrm{Tr}\left[\frac{1}{N}\sum_{i=1}^{N}\left(\boldsymbol{n}_i\boldsymbol{n}_j - \frac{1}{3}\boldsymbol{I}\right)\right]^2 \qquad (1)$$

where $\boldsymbol{n}_i$ is the unit vector in the direction of the axis of molecule i and $\boldsymbol{I}$ is the unit tensor. The expectation value of χ is $1/N$ for uncorrelated orientations, small for an isotropic phase, and it approaches unity for an ordered nematic crystal.

Finite-Size Errors in the NpT Ensemble

In the *NpT* ensemble (unlike *NVT*) the efficiency decreases with increasing system size because of shorter volume-change moves possible for larger systems. It is therefore desirable to use as few particles as possible and, consequently, to correct the raw results for finite-size errors.

It has been shown[16,17] that the finite-size errors for fluid systems of hard molecules in a periodic box and the grand-canonical ensemble are completely determined by the influence of the periodic images. They decay exponentially with the box size and are negligible for moderate sizes of the system. In contrast, the finite size corrections in the *NpT* and *NVT* ensembles are subject to errors of the order of $O(N^{-1})$.

Let us consider any observable dependent on temperature T, number of particles N, and configuration $\{\boldsymbol{r}_1, ..., \boldsymbol{r}_N\}$,

$$X = X(T, N; \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\,. \qquad (2)$$

For the difference of the grand-canonical and canonical expectation values of quantity X, Eq. (*3*) holds[14,18]

$$\langle X\rangle_{\mu VT} - \langle X\rangle_{NVT} = \frac{1}{2}\,\mathrm{Var}\,N\left(\frac{\partial^2\langle X\rangle}{\partial N^2}\right)_{V,T} + O(N^{-2}) \qquad (3)$$

where $\langle\cdot\rangle_{\mu VT}$ denotes the grand-canonical expectation value (with the chemical potential $\mu = \mu_{\mu VT}$ in the μVT ensemble set so that $\langle N\rangle_{\mu VT} = N_{NVT}$) and $\langle\cdot\rangle$ denotes any (NVT or μVT) expectation value. Similarly, for the isobaric–isothermal and canonical difference, Eq. (*4*) holds

$$\langle X\rangle_{NpT} - \langle X\rangle_{NVT} = \frac{1}{2}\,\mathrm{Var}\,V\left(\frac{\partial^2\langle X\rangle}{\partial V^2}\right)_{N,T} + O(V^{-2}) \tag{4}$$

where the pressure $P = P_{NpT}$ in the NpT ensemble is set so that $\langle V\rangle_{NpT} = V_{NVT}$. The fluctuations are related to the isothermal compressibility,

$$\mathrm{Var}\,N = NkT\left(\frac{\partial p}{\partial \rho}\right)_T, \quad \mathrm{Var}\,N = \frac{N}{\rho^2}kT\left(\frac{\partial \rho}{\partial p}\right)_T . \tag{5}$$

Our main interest is the equation of state expressed via the compressibility factor $Z = p/(\rho kT)$. However, Z is not in the form of Eq. (*2*). It was shown[19] that $\rho(Z - 1)$ is such a quantity. On combining Eqs (*3*) and (*4*) for $X = \rho(Z - 1)$ most terms cancel out and the correction is as simple as

$$Z_{\mu VT} = Z_{NpT} - \frac{1}{N} . \tag{6}$$

We repeat that this value applies to $\rho = N/\langle V\rangle_{NpT}$ because we assumed $\langle V\rangle_{NpT} = V_{NVT}$ in the derivation. In addition, it is assumed that higher-order terms can be neglected, which occurs for a sufficiently large number of particles so that the volume distribution is Gaussian (asymmetry in the distribution yields the $O(N^{-2})$ term) and also the periodic error can be neglected.

NVT-Equivalent Errors

The equation of state is usually expressed in the form $Z = Z(\rho)$. However, an NpT simulation gives imprecise results for both ρ and Z and these errors are correlated. In order to facilitate the $Z = Z(\rho)$ EOS development, we provide the effective error in Z as if ρ were fixed (without any error).

The simulation result of the volume (average over the simulation run) can be written as

$$V = V_0 + u(\delta V) \tag{7}$$

where $u(\delta V)$ denotes the Gaussian distribution with zero mean and standard deviation of δV. (The true averaged volume, $V_0 = \langle V \rangle$, is approximated by the MC average along with its error estimate δV.) Then $\rho = \rho_0 - (\rho^2/N)u(\delta V)$, where $\rho_0 = N/V_0$. Similarly $Z = Z_0 + (\beta p/N)u(\delta V)$ with $Z_0 = \beta p/\rho_0$. With the given imprecise value of ρ, we correct $Z = Z(\rho)$ to $Z(\rho_0)$,

$$Z(\rho_0) = Z + \frac{\rho^2}{N} u(\delta V) \frac{\partial Z}{\partial \rho} = Z_0 + \frac{u(\delta V)}{N} \rho \frac{\partial \beta p}{\partial \rho} . \qquad (8)$$

The equivalent standard error in Z is then

$$\delta_{\text{eq}}(Z) = \frac{\delta V}{V} \frac{\partial \beta p}{\partial \rho} = \frac{\delta V}{V} \frac{1}{\rho \beta_T} \qquad (9)$$

where the isothermal compressibility is determined from a single simulation by

$$\beta_T = -\frac{1}{V} \frac{\partial V}{\partial \beta p} = \frac{\operatorname{Var} V}{V} . \qquad (10)$$

Equations of State

Many successful EOSs have a form of "generalized virial expansion" in variable $x = y/(1 - y)$ instead of the packing fraction[20] $y = \rho V$. Therefore we have chosen this form, too. The "generalized virial coefficients" A_n of this expansions are functions of molecule elongations L^*. To obtain these coefficients, we correlate simultaneously all available data, namely the virial coefficients[1] B_n, $n > 2$, and the MC compressibility factors. The second virial coefficient is known exactly for prolate spherocylinders[21], $B_2 = 1 + 3\alpha$. This formula is based on the parameter of nonsphericity α defined for hard convex bodies by

$$\alpha = \frac{\mathcal{R}\mathcal{S}}{3\mathcal{V}} \qquad (11)$$

where V is the volume of the molecule, S is its surface area, and R is the $1/(4\pi)$-multiple of the mean curvature integral. The analytical expression for the second virial coefficient for homonuclear diatomics is more complex[22,23].

It has appeared that the best results are obtained if the higher virial coefficients are first reduced by the second virial coefficient. In turn, the final explicit formula for the compressibility factor reads

$$Z = 1 + \sum_{n=2}^{9} A_n x^{n-1} \tag{12}$$

where coefficients A_n are calculated[24] from B_2 (given by analytical expressions) and higher B_n so that the y-expansion of Eq. (*12*) is up to x^8 the same as the virial expansion.

The higher virial coefficients are expressed as polynomials in $1 - 1/\alpha$ instead of L^* or the length-to-width ratio $\gamma = 1 + L^*$. It is especially advantageous for larger elongations. The nonsphericity parameter is then for prolate spherocylinders exactly

$$\alpha = \frac{(L^* + 1)(L^* + 2)}{2 + 3L^*} \, . \tag{13}$$

For homonuclear diatomics we replace R in formula (*11*) by the curvature of the convex envelope (i.e., HPS) because R is defined for convex bodies only. The result is

$$\alpha = \frac{(L^* + 1)(L^* + 2)}{2 + 3L^* - L^{*3}} \, . \tag{14}$$

The resulting second virial coefficient is an approximation.

Monte Carlo data for the compressibility factor and the MC data for the virial coefficients are correlated simultaneously. We minimize the standard objective function[25]

$$s^2 = \frac{1}{n_{\text{free}}} \left(\sum_j \left[\frac{Z_j^{\text{fit}} - Z_j}{\delta(Z_j)} \right]^2 + \sum_j \left[\frac{B_j^{\text{fit}} - B_j^{\text{MC}}}{\delta(B_j^{\text{MC}})} \right]^2 \right) \tag{15}$$

where δ are standard errors, B_j^{fit} virial coefficients calculated from the EOS and $B_j^{\text{MC}} \pm \delta(B_j^{\text{MC}})$ are virial MC data with standard errors. For $L = 0$ (hard spheres) we used the virial and pseudoexperimental data published in ref.[26]. The index j in the sums in Eq. (*15*) runs over all available data covering all elongations for HHD and a selected range of elongations for HPS (we provide two versions, one for $L^* \leq 1.0$ and other for $L^* \leq 1.6$).

RESULTS AND DISCUSSION

New MC pseudoexperimental data are presented in Tables I and II. For two selected elongations, $L^* = 0.2$ and 1.0, they are depicted in Fig. 1 along the fits. For short elongations both models are indistinguishable while for longer molecules HPS, with larger molecular volume, have larger compressibility factor. Error bars are not shown in this figure because they are 10 times smaller than the line width.

The equations of state were developed by global fitting of virial coefficients and compressibility factor data. The inaccuracies of the compressibility factor data are their *NVT*-equivalent errors, $\delta_{eq}(Z)$ according to Eq. (*9*). Since the virial data are comparably very accurate, we scaled up their errors twice. In addition, the data for hard spheres are also more accurate than for both hard bodies and thus we multiplied the errors for hard-sphere virial coefficients in addition 6 times and for hard-sphere compressibility factors 8 times (in the most demanding version of HPS up to $L^* = 1.6$, 8 and 9 times, respectively; we will consider only range $L^* \in [0,1]$ unles stated otherwise). Only fluid-phase data were used. Then the objective function (*15*) gives minimum values close to 2. The standard errors of the compressibility factor along with the fit errors are for $L^* = 1$ shown in Figs 2 and 3.

The order of polynomials describing the virial coefficients needed to correlate the data is 6 or 5 for range $L^* \leq 1.0$ for both models. If the range is en-

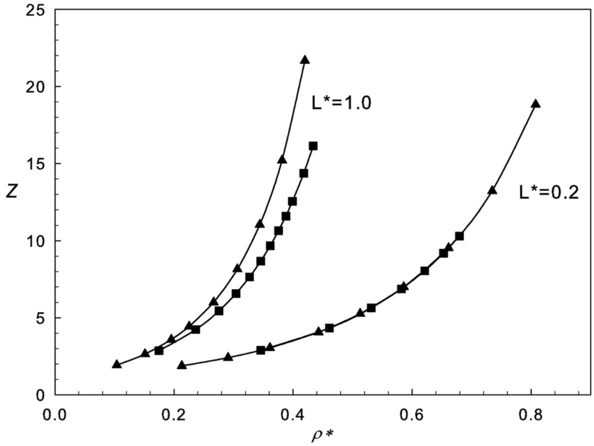

FIG. 1
Compressibility factors of both hard-body models: ▲ HPS, ■ HHD

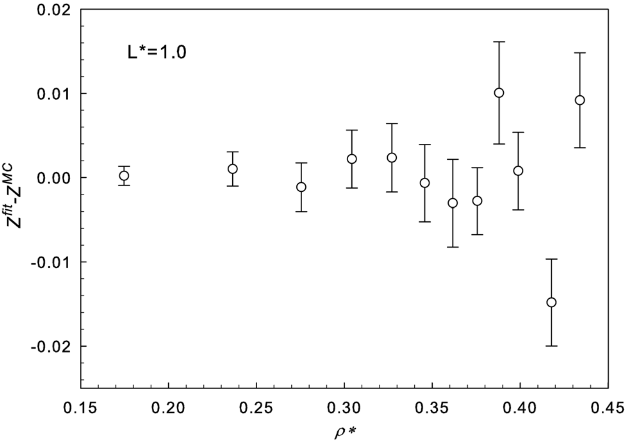

FIG. 2
Homonuclear diatomics, L^* = 1.0. Differences between Z^{fit} and Z^{MC} with errorbars in dependence on ρ*

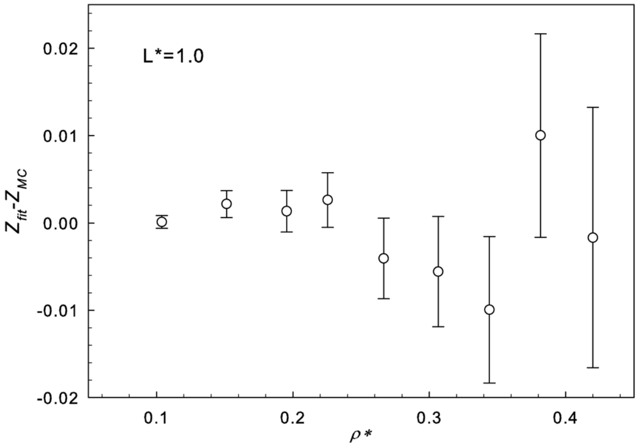

FIG. 3
Prolate spherocylinders, L^* = 1.0. Differences between Z^{fit} (fitted in range $L^* \in [0,1]$) and Z^{MC} with errorbars in dependence on ρ*

TABLE I
MC data on the compressibility factor Z of homonuclear diatomics. $L^* = L/\sigma^3$ is the reduced elongation, $\beta p^* = p\sigma^3/(kT)$ reduced pressure, ρ^* reduced number density, $\delta(Z)$ estimated standard error in Z and $\delta_{eq}(Z)$ is the NVT-equivalent standard error, Eq. (*9*)

L^*	βp^*	ρ^*	Z	$\delta(Z)$	$\delta_{eq}(Z)$
0.1	1.0	0.370210	2.70017	0.00017	0.0010
0.1	2.0	0.498866	4.00809	0.00016	0.0017
0.1	3.0	0.578431	5.18545	0.00016	0.0025
0.1	4.0	0.635153	6.29669	0.00011	0.0022
0.1	5.0	0.679498	7.35738	0.00010	0.0026
0.1	6.0	0.715465	8.38515	0.00009	0.0030
0.1	7.0	0.745745	9.38559	0.00009	0.0032
0.2	1.0	0.345827	2.89062	0.00017	0.0011
0.2	2.0	0.461147	4.33602	0.00017	0.0020
0.2	3.0	0.531468	5.64375	0.00016	0.0028
0.2	4.0	0.581977	6.87213	0.00010	0.0024
0.2	5.0	0.621166	8.04838	0.00010	0.0028
0.2	6.0	0.652760	9.19075	0.00010	0.0034
0.2	7.0	0.679611	10.29901	0.00010	0.0039
0.3	1.0	0.324689	3.07887	0.00017	0.0012
0.3	2.0	0.429098	4.65993	0.00017	0.0022
0.3	3.0	0.492550	6.008976	0.00015	0.0030
0.3	4.0	0.537752	7.43738	0.00011	0.0028
0.3	5.0	0.572800	8.72805	0.00010	0.0033
0.3	6.0	0.601190	9.97920	0.00010	0.0038
0.3	7.0	0.624977	11.19941	0.00009	0.0040
0.4	1.0	0.306233	3.26449	0.00017	0.0013
0.4	2.0	0.401728	4.97749	0.00017	0.0024
0.4	3.0	0.459340	6.53010	0.00015	0.0034
0.4	4.0	0.500610	7.98925	0.00011	0.0030
0.4	5.0	0.532544	9.38790	0.00010	0.0036
0.4	6.0	0.558303	10.74578	0.00013	0.0058
0.4	7.0	0.580068	12.06654	0.00009	0.0045

TABLE I
(*Continued*)

L^*	βp^*	ρ^*	Z	$\delta(Z)$	$\delta_{eq}(Z)$
0.5	0.5	0.209595	2.38456	0.00018	0.0008
0.5	1.0	0.290044	3.44676	0.00017	0.0014
0.5	1.5	0.340982	4.39806	0.00018	0.0020
0.5	2.0	0.378207	5.28711	0.00018	0.0027
0.5	2.5	0.407495	6.13405	0.00017	0.0032
0.5	3.0	0.431457	6.95218	0.00016	0.0037
0.5	3.5	0.451921	7.74372	0.00016	0.0043
0.5	4.0	0.469481	8.51905	0.00011	0.0033
0.5	4.5	0.484996	9.27743	0.00015	0.0050
0.5	5.0	0.498971	10.01961	0.00010	0.0037
0.5	6.0	0.522596	11.48015	0.00010	0.0043
0.5	7.0	0.542734	12.89665	0.00009	0.0047
0.6	0.5	0.200910	2.48768	0.00017	0.0008
0.6	1.0	0.276065	3.62134	0.00018	0.0016
0.6	1.5	0.323553	4.63502	0.00017	0.0022
0.6	2.0	0.358182	5.58275	0.00018	0.0030
0.6	2.5	0.385458	6.48479	0.00017	0.0035
0.6	3.0	0.407830	7.35501	0.00016	0.0040
0.6	3.5	0.426709	8.20131	0.00015	0.0043
0.6	4.0	0.443321	9.02180	0.00010	0.0035
0.6	4.5	0.457720	9.83034	0.00014	0.0053
0.6	5.0	0.470718	10.62107	0.00010	0.0040
0.6	6.0	0.492911	12.17157	0.00009	0.0045
0.6	7.0	0.511610	13.68129	0.00009	0.0052

TABLE I
(*Continued*)

L^*	βp^*	ρ^*	Z	$\delta(Z)$	$\delta_{eq}(Z)$
0.7	0.5	0.193016	2.58945	0.00019	0.0010
0.7	1.0	0.263943	3.78770	0.00019	0.0017
0.7	1.5	0.308481	4.86153	0.00019	0.0025
0.7	2.0	0.341081	5.86272	0.00018	0.0031
0.7	2.5	0.366764	6.81536	0.00016	0.0036
0.7	3.0	0.387925	7.73246	0.00016	0.0041
0.7	3.5	0.405846	8.62295	0.00015	0.0047
0.7	4.0	0.421327	9.49281	0.00010	0.0035
0.7	4.5	0.434944	10.34516	0.00014	0.0056
0.7	5.0	0.447215	11.17931	0.00010	0.0042
0.7	6.0	0.468237	12.81302	0.00009	0.0048
0.7	7.0	0.485745	14.40985	0.00009	0.0051
0.8	0.5	0.186194	2.68437	0.00018	0.0010
0.8	1.0	0.253304	3.94683	0.00019	0.0019
0.8	1.5	0.295670	5.07223	0.00019	0.0027
0.8	2.0	0.326728	6.12029	0.00019	0.0033
0.8	2.5	0.351076	7.11997	0.00017	0.0038
0.8	3.0	0.371208	8.08072	0.00015	0.0043
0.8	3.5	0.388313	9.01234	0.00015	0.0047
0.8	4.0	0.402942	9.92600	0.00010	0.0037
0.8	4.5	0.416022	10.81572	0.00013	0.0057
0.8	5.0	0.427656	11.69065	0.00010	0.0043
0.8	6.0	0.447786	13.39825	0.00009	0.0049
0.8	7.0	0.464626	15.06488	0.00009	0.0055

TABLE I
(*Continued*)

L^*	βp^*	ρ^*	Z	$\delta(Z)$	$\delta_{eq}(Z)$
0.9	0.5	0.180105	2.77515	0.00013	0.0008
0.9	1.0	0.244251	4.09315	0.00019	0.0020
0.9	1.5	0.284785	5.26614	0.00019	0.0027
0.9	2.0	0.314414	6.36004	0.00018	0.0034
0.9	2.5	0.337829	7.39919	0.00017	0.0040
0.9	3.0	0.357198	8.39770	0.00017	0.0045
0.9	3.5	0.373537	9.36888	0.00015	0.0050
0.9	4.0	0.387833	10.31273	0.00011	0.0038
0.9	4.5	0.400387	11.23813	0.00014	0.0058
0.9	5.0	0.411756	12.14213	0.00010	0.0045
0.9	6.0	0.431103	13.91679	0.00009	0.0051
0.9	7.0	0.447503	15.64136	0.00008	0.0055
1.0	0.5	0.174748	2.86026	0.00018	0.0011
1.0	1.0	0.236492	4.22748	0.00019	0.0020
1.0	1.5	0.275521	5.44323	0.00019	0.0029
1.0	2.0	0.304282	6.57185	0.00018	0.0034
1.0	2.5	0.326980	7.64474	0.00017	0.0041
1.0	3.0	0.345705	8.67693	0.00016	0.0046
1.0	3.5	0.361660	9.67660	0.00015	0.0052
1.0	4.0	0.375568	10.64953	0.00010	0.0040
1.0	4.5	0.387977	11.59762	0.00014	0.0061
1.0	5.0	0.398895	12.53361	0.00010	0.0046
1.0	6.0	0.417789	14.36031	0.00009	0.0052
1.0	7.0	0.433929	16.13066	0.00008	0.0057

TABLE II
MC data on the compressibility factor Z of prolate spherocylinders. Rows marked by * indicate a crystal or nematic phase. For other symbols see Table I

L^*	γ	βp^*	ρ^*	Z	$\delta(Z)$	$\delta(Z_{eq})$
0.2	1.2	0.4	0.213187	1.87529	0.00022	0.0007
0.2	1.2	0.7	0.290854	2.40570	0.00024	0.0011
0.2	1.2	1.1	0.361103	3.04522	0.00025	0.0017
0.2	1.2	1.8	0.442854	4.06355	0.00023	0.0025
0.2	1.2	2.7	0.512756	5.26466	0.00023	0.0036
0.2	1.2	4.1	0.585902	6.99676	0.00022	0.0052
0.2	1.2	6.3	0.661157	9.52775	0.00020	0.0071
0.2	1.2	9.7	0.734621	13.20310	0.00017	0.0101
0.2	1.2	15.2	0.807587	18.82050	0.00014	0.0142
*0.2	1.2	24.4	0.904729	26.96840	0.00013	0.0178
*0.2	1.2	40.6	0.932715	43.52784	0.00009	0.0271
0.4	1.4	0.3	0.163699	1.83163	0.00022	0.0007
0.4	1.4	0.6	0.240529	2.49350	0.00026	0.0012
0.4	1.4	0.9	0.291285	3.08876	0.00026	0.0018
0.4	1.4	1.5	0.359849	4.16741	0.00025	0.0027
0.4	1.4	2.3	0.419716	5.47890	0.00023	0.0039
0.4	1.4	3.4	0.474653	7.16212	0.00023	0.0055
0.4	1.4	5.3	0.537545	9.85864	0.00023	0.0076
0.4	1.4	8.1	0.596420	13.58003	0.00017	0.0104
0.4	1.4	12.7	0.656506	19.34383	0.00015	0.0136
*0.4	1.4	20.4	0.715742	28.50087	0.00012	0.0191
*0.4	1.4	33.9	0.773979	43.79862	0.00010	0.0261

TABLE II
(*Continued*)

L^*	γ	βp^*	ρ^*	Z	$\delta(Z)$	$\delta(Z_{\mathrm{eq}})$
0.6	1.6	0.3	0.151068	1.98486	0.00023	0.0008
0.6	1.6	0.5	0.199030	2.51118	0.00025	0.0013
0.6	1.6	0.8	0.248326	3.22057	0.00026	0.0019
0.6	1.6	1.3	0.302871	4.29126	0.00027	0.0030
0.6	1.6	2	0.353235	5.66095	0.00026	0.0042
0.6	1.6	3	0.401348	7.47381	0.00023	0.0059
0.6	1.6	4.6	0.452459	10.16566	0.00021	0.0079
0.6	1.6	7.1	0.502775	14.12064	0.00017	0.0109
0.6	1.6	11.1	0.553070	20.06879	0.00015	0.0143
*0.6	1.6	17.8	0.603173	29.50959	0.00011	0.0195
*0.6	1.6	29.5	0.652767	45.19127	0.00009	0.0278
0.8	1.8	0.3	0.140050	2.14109	0.00026	0.0010
0.8	1.8	0.5	0.182489	2.73889	0.00026	0.0015
0.8	1.8	0.7	0.212877	3.28728	0.00027	0.0021
0.8	1.8	1.1	0.256320	4.29051	0.00027	0.0029
0.8	1.8	1.8	0.305789	5.88541	0.00025	0.0042
0.8	1.8	2.7	0.347105	7.77763	0.00023	0.0061
0.8	1.8	4.1	0.389840	10.51614	0.00020	0.0084
0.8	1.8	6.4	0.434557	14.72666	0.00016	0.0111
0.8	1.8	10	0.477548	20.93930	0.00014	0.0153
*0.8	1.8	15.9	0.520190	30.56473	0.00012	0.0195
*0.8	1.8	26.4	0.563620	46.83910	0.00008	0.0303

TABLE II
(*Continued*)

L^*	γ	βp^*	ρ^*	Z	$\delta(Z)$	$\delta(Z_{eq})$
1	2	0.2	0.103831	1.92520	0.00024	0.0007
1	2	0.4	0.151334	2.64216	0.00027	0.0015
1	2	0.7	0.195358	3.58217	0.00029	0.0024
1	2	1	0.225433	4.43491	0.00026	0.0031
1	2	1.6	0.266503	6.00268	0.00024	0.0046
1	2	2.5	0.306500	8.15561	0.00023	0.0063
1	2	3.8	0.344078	11.04300	0.00021	0.0084
1	2	5.8	0.381553	15.20002	0.00016	0.0116
1	2	9.1	0.419860	21.67288	0.00014	0.0149
*1	2	14.6	0.458370	31.85097	0.00011	0.0216
*1	2	24	0.495173	48.46694	0.00009	0.0276
1.2	2.2	0.2	0.097897	2.04196	0.00025	0.0009
1.2	2.2	0.4	0.140868	2.83854	0.00026	0.0016
1.2	2.2	0.6	0.169158	3.54599	0.00028	0.0023
1.2	2.2	1	0.207296	4.82302	0.00028	0.0036
1.2	2.2	1.5	0.239018	6.27468	0.00025	0.0048
1.2	2.2	2.3	0.273084	8.42131	0.00021	0.0064
1.2	2.2	3.5	0.306688	11.41125	0.00019	0.0091
1.2	2.2	5.4	0.340752	15.84629	0.00017	0.0116
1.2	2.2	8.4	0.374669	22.41880	0.00013	0.0161
*1.2	2.2	13.5	0.409780	32.94352	0.00011	0.0212
*1.2	2.2	22.1	0.442870	49.90074	0.00007	0.0346

TABLE II
(*Continued*)

L^*	γ	βp^*	ρ^*	Z	$\delta(Z)$	$\delta(Z_{eq})$
1.4	2.4	0.2	0.092507	2.16101	0.00026	0.0010
1.4	2.4	0.3	0.114575	2.61736	0.00030	0.0015
1.4	2.4	0.6	0.157366	3.81176	0.00028	0.0026
1.4	2.4	0.9	0.184654	4.87298	0.00027	0.0036
1.4	2.4	1.4	0.215633	6.49152	0.00025	0.0051
1.4	2.4	2.2	0.248118	8.86574	0.00022	0.0069
1.4	2.4	3.3	0.277370	11.89646	0.00020	0.0089
1.4	2.4	7.9	0.339309	23.28162	0.00014	0.0160
1.4	2.4	12.5	0.371721	33.62635	0.00014	0.0185
*1.4	2.4	20.5	0.398493	51.44282	0.00014	0.0209
1.6	2.6	0.2	0.087643	2.28098	0.00027	0.0011
1.6	2.6	0.3	0.108047	2.77558	0.00027	0.0015
1.6	2.6	0.5	0.136411	3.66439	0.00032	0.0026
1.6	2.6	0.9	0.172021	5.23091	0.00026	0.0037
1.6	2.6	1.3	0.195549	6.64695	0.00025	0.0052
1.6	2.6	2	0.223687	8.94005	0.00022	0.0070
1.6	2.6	3.1	0.252552	12.27371	0.00019	0.0094
1.6	2.6	4.8	0.281290	17.06321	0.00016	0.0128
1.6	2.6	7.5	0.310401	24.16130	0.00015	0.0157
*1.6	2.6	11.8	0.352814	33.44434	0.00056	0.0054
*1.6	2.6	19.2	0.361720	53.07870	0.00011	0.0262

TABLE II
(*Continued*)

L^*	γ	βp^*	ρ^*	Z	$\delta(Z)$	$\delta(Z_{eq})$
1.8	2.8	0.2	0.083172	2.40367	0.00026	0.0012
1.8	2.8	0.3	0.102003	2.94009	0.00028	0.0017
1.8	2.8	0.5	0.128251	3.89762	0.00028	0.0026
1.8	2.8	0.8	0.154245	5.18554	0.00030	0.0040
1.8	2.8	1.3	0.182649	7.11649	0.00025	0.0055
1.8	2.8	1.9	0.205393	9.24955	0.00023	0.0072
1.8	2.8	3	0.233096	12.86926	0.00019	0.0096
1.8	2.8	4.6	0.259329	17.73712	0.00017	0.0128
1.8	2.8	7.1	0.286024	24.82210	0.00015	0.0159
1.8	2.8	11.1	0.327065	33.93716	0.00059	0.0051
*1.8	2.8	18	0.333401	53.98808	0.00016	0.0186
2	3	0.2	0.079239	2.52301	0.00030	0.0014
2	3	0.3	0.096769	3.09916	0.00027	0.0019
2	3	0.5	0.121052	4.12946	0.00029	0.0029
2	3	0.8	0.145204	5.50848	0.00027	0.0042
2	3	1.2	0.166998	7.18472	0.00025	0.0056
2	3	1.9	0.192423	9.87309	0.00022	0.0076
2	3	2.8	0.214539	13.05024	0.00019	0.0096
2	3	4.4	0.240225	18.31513	0.00016	0.0130
2	3	6.7	0.265542	25.23038	0.00015	0.0160
*2	3	10.5	0.304088	34.52845	0.00040	0.0075

TABLE II
(*Continued*)

L^*	γ	βp^*	ρ^*	Z	$\delta(Z)$	$\delta(Z_{\mathrm{eq}})$
3	4	0.1	0.044538	2.24425	0.00026	0.0011
3	4	0.2	0.063736	3.13695	0.00029	0.0019
3	4	0.4	0.086564	4.61988	0.00030	0.0033
3	4	0.7	0.107058	6.53750	0.00027	0.0050
3	4	1	0.121105	8.25629	0.00025	0.0063
3	4	1.6	0.140340	11.39985	0.00023	0.0084
3	4	2.4	0.158006	15.18828	0.00019	0.0107
*3	4	3.6	0.178937	20.11786	0.00020	0.0122
4	5	0.1	0.037998	2.63070	0.00028	0.0114
4	5	0.2	0.053317	3.75016	0.00031	0.0025
4	5	0.4	0.071378	5.60298	0.00029	0.0142
4	5	0.6	0.083149	7.21498	0.00028	0.0053
4	5	0.9	0.095830	9.39064	0.00026	0.0069
4	5	1.4	0.110990	12.61270	0.00023	0.0090
5	6	0.1	0.033072	3.02271	0.00031	0.0019
5	6	0.2	0.045823	4.36365	0.00030	0.0030
5	6	0.3	0.054340	5.51979	0.00028	0.0043
5	6	0.5	0.066244	7.54690	0.00029	0.0056
5	6	0.8	0.078684	10.16630	0.00028	0.0172
6	7	0.1	0.029293	3.41280	0.00029	0.0021
6	7	0.2	0.040176	4.97714	0.00030	0.0036
6	7	0.3	0.047541	6.30929	0.00030	0.0049
6	7	0.5	0.058119	8.60209	0.00029	0.0063
8	9	0.1	0.023833	4.19480	0.00035	0.0030
8	9	0.2	0.032397	6.17245	0.00032	0.0045
8	9	0.3	0.038534	7.78432	0.00032	0.0056

larged to $L^* \leq 1.6$ for HPS, the orders raise to 9 or 8; it is difficult to fit the data for HPS with even longer elongations by this method. In this case $s >> 1$ and the obtained EOS is much less accurate (although "less accurate" should be interpreted with respect to the MC inaccuracy and not absolutely).

The term $y/(1 - y)$ appears in the scaled particle theory (SPT) of the hard-sphere fluid as well as the Percus–Yevick theory and virial coefficient resummation. The SPT theory can be extended to a fluid of hard convex bodies so that the second virial coefficient is exactly reproduced; however, higher-order terms are approximations based on the assumption of almost spherical molecules (and cavities). Therefore it is not surprising that the accuracy of this approach decreases with increasing nonsphericity. The resulting EOSs are given by a rather complex formula and we therefore refer a possible user to our web page[24].

The obtained values are compared with other current equations of state for the reduced elongation $L^* = 1$ in Table III. Our equations of state show good agreement with the new MC data in contrast to the older EOSs. The price paid for this agreement is equation complexity.

Figures 4 and 5 present the center–center radial distribution functions (RDF) of the respective models for $L^* = 1$ and increasing pressure. It is seen that the RDF for HPS shows a jump in the second derivative, caused by T-shape conformations. For a shorter distance one of both molecules ceases free rotation and thus these conformations are less probable. Therefore at higher densities, a peak appears at this distance. At even higher pressures the molecules are forced to pack efficiently and another peak appears close to the shortest center–center distance. The behavior of RDFs at large separations indicates the periodic errors. The error is roughly given by the RDF value at the box size because at this distance the particles interact with their periodic images. Since we do not determine the RDFs at this distance,

TABLE III

Comparison of equations of state for both homonuclear diatomics and prolate spherocylinders with $L^* = 1$. Z_{fit} is the compressibility factor calculated from Eq. (*12*) with parameters fitted in range $L^* \in [0,1]$)

	ρ	y	Z_{MC}	δ(Z)	Z_{fit}	Z^a	Z^b	Z^c	Z^d
HDD	0.433929	0.454410	16.1307	0.0013	16.1398	16.0717	16.1816	–	16.3384
HPS	0.419860	0.549596	21.6729	0.0031	21.6712	–	21.4579	21.8381	–

[a] Data taken from ref.[9] [b] Data taken from ref.[10] [c] Data taken from ref.[11] [d] Data taken from ref.[13]

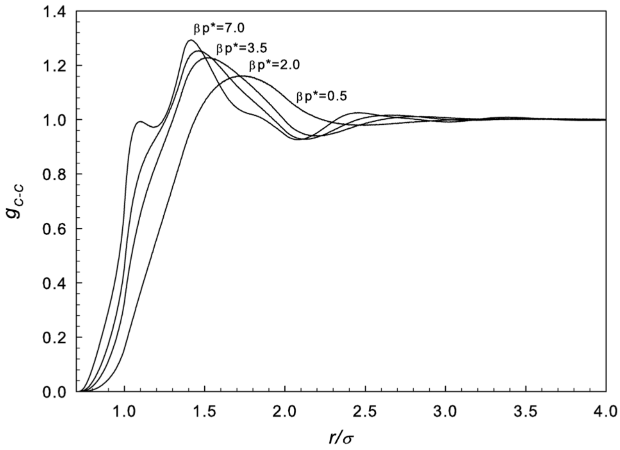

FIG. 4
The center–center distribution function of HHD for L^* = 1.0 and four values of reduced pressure βp^*

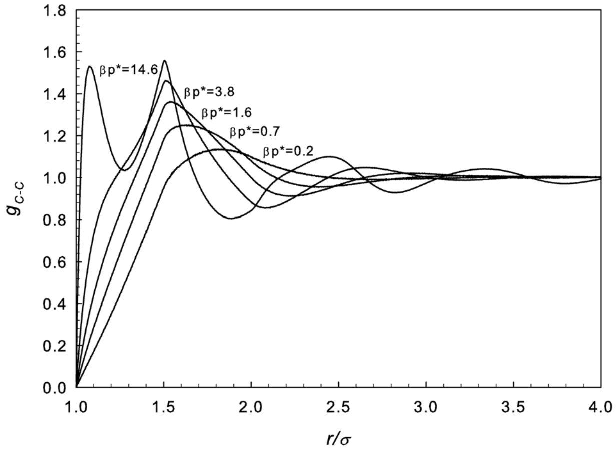

FIG. 5
The center–center distribution function of HPS for L^* = 1.0 and four values of reduced pressure βp^*

it is necessary to extrapolate. We found that the periodic error is negligible (much lower than the statistical error) with the exception of the highest densities for short molecules where it might reach 0.01, i.e., might be comparable (but not larger than) the statistical errors. The full set of RDFs is available in our web page[24].

CONCLUDING REMARKS

At present we are able to calculate Monte Carlo data on "classical" hard molecules with a much higher accuracy than in the golden age of hard-body models two or three decades ago and the same holds true for the virial coefficients. This accuracy has one disadvantage: It is difficult to correlate these data by a simple equation of state. Simple considerations like SPT have provided a deep insight into the structure of fluids and their state behavior, but cannot describe the data more accurate by one or two orders of magnitude. The fluids are more complex if we use a large magnifying glass.

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REFERENCES

1. Francová M., Kolafa J., Morávek P., Labík S., Malijevský A.: *Collect. Czech. Chem. Commun.* **2008**, *73*, 413.
2. Tildesley D. J., Street W. B.: *Mol. Phys.* **1980**, *41*, 85.
3. Largo J. R., Maeso M. J., Solana J. R.: *J. Chem. Phys.* **2003**, *119*, 9633.
4. Morávek P., Kolafa J., Hujo T., Labík S.: *J. Mol. Liq.* **2006**, *125*, 22.
5. Vieillard-Baron J.: *Mol. Phys.* **1974**, *28*, 809.
6. Boublík T., Nezbeda I.: *Czech. J. Phys.* **1976**, *26*, 1081.
7. Monson P. A., Rigby M.: *Chem. Phys. Lett.* **1978**, *58*, 122.
8. Frenkel D.: *J. Phys. Chem.* **1988**, *92*, 5314.
9. Boublík T.: *Mol. Phys.* **1989**, *68*, 191.
10. Boublík T.: *Mol. Phys.* **2002**, *100*, 3443.
11. Boublík T.: *J. Chem. Phys. B* **2004**, *108*, 7424.
12. Maeso M. J., Solana J. R.: *Mol. Phys.* **1992**, *76*, 1269.
13. Largo J., Solana J. R.: *Mol. Phys.* **1999**, *96*, 1367.
14. Allen M. P., Tildesley D. J.: *Computer Simulation of Liquids*. Clarendon Press, Oxford 1986.
15. Allen M. P., Wilson M. R.: *J. Comput.-Aided Mol. Des.* **1989**, *3*, 335.
16. Lebowitz J. L., Percus J. K.: *Phys. Rev.* **1961**, *124*, 1673.
17. Pratt L. R., Haan S. W.: *J. Chem. Phys.* **1981**, *74*, 1864.
18. Kolafa J., Labík S., Malijevský A.: *Phys. Chem. Chem. Phys.* **2004**, *6*, 2335.
19. Kolafa J., Labík S., Malijevský A.: *Mol. Phys.* **2002**, *100*, 2629.
20. Mulero A., Galán C., Cuadros F.: *Phys. Chem. Chem. Phys.* **2001**, *3*, 4991.

21. Boublík T., Nezbeda I.: *Collect. Czech. Chem. Commun.* **1986**, *51*, 2301.
22. Isihara A.: *J. Chem. Phys.* **1951**, *19*, 397.
23. Wertheim M. S.: *J. Chem. Phys.* **1983**, *78*, 4619.
24. http://www.vscht.cz/fch/papers/Jiri.Kolafa/HB.html.
25. Kolafa J., Rottner M.: *Mol. Phys.* **2006**, *104*, 3435.
26. Labík S., Kolafa J., Malijevský A.: *Phys. Rev. E* **2005**, *71*, 021105.