THERMODYNAMIC PROPERTIES OF PURE HARD SPHERE, SPHEROCYLINDER AND DUMBELL FLUIDS

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A universal equation of state for the fluid of hard bodies of an arbitrary shape is proposed. New Monte Carlo data of the hard sphere system are published and the existing pseudoexperimental data for hard spheres, spherocylinders and dumbells are critically reviewed.

The prerequisite of success of the present perturbation theories of real liquids (for the survey see *e.g.*[1,2]) is the exact knowledge of thermodynamic behaviour of simple model systems with repulsive interactions, *i.e.* the systems of hard molecules. These systems represent as well an excellent zeroth approximation when describing the structure of real liquids[3,4] and that is why they have been attracting interest of theorists all the time. Apart from a number of theoretical and semi-empirical works (*e.g.*[2,5] and references therein), great attention was paid to the pseudoexperimental study of behaviour of the systems of hard spheres, convex bodies (prolate spherocylinders) and fused hard spheres (homo- and heteronuclear dumbells). The pseudoexperiments based on the Monte Carlo (MC) or molecular dynamics (MD) methods represent today a widely spread tool for an "exact" determination of behaviour of any system with given interparticle interactions and serve consequently for verifying theoretical hypotheses. However, the fact is taken into account very rarely that the pseudoexperimental data have the character of classical experimental data, *i.e.* they are subject to random errors and in some cases even to systematic ones resulting from unsuitable algorithms used and the like. The immense complexity of the simulations and their demands on computing time (and the costs connected with) make the possibility of the error determination of pseudoexperiment difficult. Therefore the reliability of the published data can be judged mostly indirectly on the basis of their compatibility with other existing facts.

The aim of this work is twofold: *a*) To propose a universal equation of state allowing to describe the P–V–T behaviour of the system of hard bodies of an arbitrary shape simply and at the same time sufficiently accurately. *b*) On the basis of such an equation and the other known facts to assess critically all the hitherto published MC and MD data on the P–V–T behaviour of systems of hard spheres (hs), prolate

spherocylinders (sc) and homonuclear dumbells (db) and to find ranges of their applicability. The method *a*) is based on a semi-empirical equation of the Carnahan–Starling type and starts from the knowledge of first four virial coefficients of the system. Where the virial coefficients were not known from the literature they were calculated in this work.

THEORETICAL

One of the methods how to verify the correctness of pseudoexperimental data is to find generally valid relations which must be satisfied by these data. In our previous paper[5] we presented two conjectures binding together the compressibility factors of hard spheres, dumbells and spherocylinders:

1) Considering a system of N hard dumbells (fused hard spheres of a diameter σ with centres $L\sigma$ apart, $0 \leqq L \leqq 1$) confined to a volume V then it holds

$$(P/\varrho kT)_{\text{eq.hs}} \leqq (P/\varrho kT)_{\text{db}} \leqq (P/\varrho kT)_{\text{sc}} . \qquad (1)$$

In Eq. (*1*) all three compressibility factors are compared at the same density $\varrho\sigma^3$, $\varrho = N/V$ and eq.hs denotes hard spheres of the same volume as that of the dumbells studied and sc stands for the spherocylinders of breadth σ and length $(L + 1)\,\sigma$.

2) If SPT denotes the results following from the scaled particle theory[6–8] then it holds both for spheres and dumbells and spherocylinders:

$$(P/\varrho kT)^{\text{pseudoexp.}} \leqq (P/\varrho kT)^{\text{SPT}} . \qquad (2)$$

Eq. (*1*) is not the only equation of this kind. It is possible to show[9] that there exists a whole family of relations analogous to Eq. (*1*) in dependence on the reducing volume. For instance, if the dumbells and spherocylinders are compared at the same packing fraction y ($y = \varrho \times$ volume of a molecule) then it holds

$$(P/\varrho kT)_{\text{sc}} \leqq (P/\varrho kT)_{\text{db}} . \qquad (3)$$

Eqs (*1*)–(*3*) represent a very useful tool especially for the region of low and medium densities and for the dumbells not too different from spherocylinders. In the other cases they yield a good first estimate.

The best way how to compare different sets of data for the same system is to have at disposal a good equation of state. Since, however, the final validity and accuracy of the equation of state must be proved by pseudoexperiments, such an equation should be based on the facts independent of the pseudoexperiments. The immediate information on thermodynamic behaviour of an arbitrary system of interacting particles is yielded by virial coefficients which are, moreover, mostly easily available. Just

the knowledge of virial coefficients can be used advantageously to develop semi-empirical equations of state which, unlike the classical virial expansion (4),

$$P/\varrho kT = 1 + B_2 y + B_3 y^2 + \ldots , \qquad (4)$$

hold even for medium and high densities.

The semi-empirical equation, if desired to be simple and simultaneously sufficiently accurate, cannot be constructed arbitrarily but its functional form must reflect the essential theoretical knowledge. Starting from the well-known facts, we postulate, that the P–V–T behaviour of the system of hard particles of an arbitrary shape can be described with sufficient accuracy by an equation of state of the form

$$P/\varrho kT = 1/(1 - y) + f_2 y/(1 - y)^2 + f_3 y^2/(1 - y)^3 + f_4 y^3/(1 - y)^3 , \qquad (5)$$

where f_i are the numerical constants determined by the first four virial coefficients

$$f_2 = B_2 - 1 , \quad f_3 = B_3 - 2B_2 + 1 , \quad f_4 = B_4 - 3(B_3 - B_2) - 1 . \qquad (6)$$

That is to say, Eq. (5) in connection with Eq. (6) reproduces accurately the first four virial coefficients. A support for this statement can be found in the following facts:

a) By using the method of the scaled particle theory[6–8] the theoretical equations of state were derived both for the hard sphere system and for the db and sc systems in the form

$$P/\varrho kT = (1 + ay + by^2)/(1 - y)^3 . \qquad (7)$$

Moreover, from the solution of the Percus–Yevick equation for hard spheres[10] it follows that the compressibility equation of state has as well the form of Eq. (7). Therefore it is to be expected justifiably that a good semi-empirical equation shall include a term of the type (7).

b) Trying to find an accurate equation of state for the entire density region, Carnahan and Starling[11] (CS) approximated the known virial coefficients of hard spheres by a recurrent integer series and obtained the equation

$$(P/\varrho kT)^{CS} = (1 + y + y^2 - y^3)/(1 - y)^3 . \qquad (8)$$

In analogy to this equation Boublík[12] then improved in a pure empirical way the SPT equation (7) for hard convex bodies by adding the term const $\times y^3/(1 - y)^3$. Thus obtained equation was also applied with success to the dumbell fluid[13,14].

c) The form of the equation of state (5) and its unique connection to the exact values

of virial coefficients formed the starting point in our previous work[15]. The result was the hitherto best-known analytical equation for prolate spherocylinders.

Eq. (5) can be formally improved by adding the terms of the form $f_n y^{n-1}/(1-y)^3$, $n \geqq 5$ which comprise the effect of higher virial coefficients. The main reason for choosing Eq. (5) consists in the fact that for non-spherical molecules it is difficult to obtain higher virial coefficients. From a general analysis it is to be expected that Eq. (5) will yield excellent results for low and medium densities while in the region of the highest densities, it will slightly overestimate the actual compressibility factor.

RESULTS AND DISCUSSION

Hard Spheres

The hard sphere system is the simplest system of hard particles which has been studied intensively since 1954 (ref.[16]). Older data were mostly obtained using small number of particles and from comparatively short chains and therefore are unreliable (for review see[17]). The most often cited data are those due to Barker and Henderson[18] from 1971 and new data of Adams[19] from 1974 obtained on using both the NVT and μVT ensemble. For low densities, these data are essentially identical, in the region of medium and higher densities, however, they exhibit surprisingly large scattering. In Fig. 1, the difference $(P/\varrho kT)^{MC} - (P/\varrho kT)^{CS}$ is plotted in dependence on density.

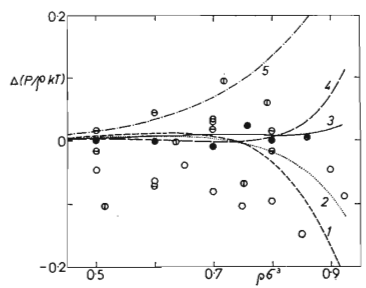

FIG. 1

Density Dependence of the Deviation of Theoretical (curves) and Pseudoexperimental (circles) Compressibility Factor of Hard Spheres from the Carnahan–Starling Equation[11]

1 Le Fevre equation[23], *2* Ree–Hoover equation[22], *3* Hall equation[21], *4* Woodcock equation[24], *5* this work, Eq. (5). Data: ○ Barker and Henderson[18], ⊖⊙ Adams[91], ● this work.

It can be seen that the data of Barker and Henderson[18] are systematically lower than the CS equation (8) and have great scattering. Similar large scattering but onto both sides from the CS equation show the Adams data from the μVT ensemble, the data from the NVT ensemble have a smaller scattering.

The reasons of such a large scattering of data can be as follows: *a*) The equation of state is determined by a radial distribution function at a contact point and this value, g^*, must be found by extrapolating the data. The effect of extrapolation on the value of g^* we studied on the Barker and Henderson data[18] on using various correlation procedures. The analysis of the results showed a relative insensitivity of the contact value g^* on the procedure used. It is possible to say that the error due to extrapolating does not exceed 0·25%. *b*) The simulations are carried out with a small set of particles. Except one value of Adams, all the others were obtained from the ensemble of 108 or 256 particles. There exists a recommendation how to correct the results for the infinitely large ensemble, this correction has not, however, a sufficient theoretical justification[18]. Another possibility is to simulate the behaviour of much greater ensemble, where the incidental corrections are negligible. This was one of the reasons why the ensemble of 864 spheres was studied in detail by the MC method. The detailed description of the simulations together with the values of the radial distribution function for the range of distances $(\sigma, 4\sigma)$ is given in the work[20]. In this work, the values of the compressibility factor for eight densities $\varrho\sigma^3$ within the range (0·3, 0·8602) are given in Table I. Considering that these data were obtained by means of such a large ensemble of particles, they exhibit considerably smaller scattering in comparison with earlier data (Fig. 1). We believe that these data are the most accurate data which are presently available.

As to the theoretical description of the hard sphere fluid the CS equation (8) is most often used. Besides, some attempts have been made all the time to develop more accurate equations; let us name here at least Hall[21], Ree and Hower[22], Le Fevre[23] and Woodcock[24]. The assertions that some of these equations is better than the

TABLE I
Monte Carlo Data of the Compressibility Factor of Hard Spheres

$\varrho\sigma^3$	$P/\varrho kT$	$\varrho\sigma^3$	$P/\varrho kT$
0·30	1·96 ± 0·01	0·70	5·70 ± 0·02
0·40	2·52 ± 0·01	0·7573	6·81 ± 0·02
0·50	3·26 ± 0·01	0·80	7·75 ± 0·03
0·60	4·28 ± 0·01	0·8602	9·41 ± 0·04

other seem to us, however, to be unjustified at present. The MC values of the compressibility factor do not form a smooth curve in the region of higher densities but are scattered in a certain band. Taking into account in addition the unavoidable experimental errors, we get a region in which, in all probability, the real value of $(P/\varrho kT)$ of hard spheres lies. As it can be seen from Fig. 1, the values of the compressibility factor of all the equations mentioned lie in the region given. As for Eq. (5) then this is in an excellent agreement with the pseudoexperimental data up to the densities $\varrho\sigma^3 \sim 0{\cdot}7$. For higher densities it shows systematically, as it can be excepted, small positive deviations.

Spherocylinders

The spherocylider is a cylinder of a length equal to $L\sigma$ capped at both ends by hemispheres with radius $\sigma/2$. The second virial coefficient of prolate spherocylinders is known exactly in the closed form[25]

$$B_2 = 1 + 3(L + 1)(L + 2)/(3L + 2). \qquad (9)$$

All the higher hitherto published virial coefficients were then obtained by numerical integration using Monte Carlo method and are summarized in Table II. For a number of eccentricities, two independently obtained values of third and fourth virial coefficients are available which agree with each other (except two cases) in limits of nume-

TABLE II
Virial Coefficients of Hard Spherocylinders

L	B_2	B_3 (ref.)	B_4 (ref.)	B_5 (ref.)
0·2	4·046	10·19 ± 0·05 (ref.[5])	19·47 ± 0·35 (ref.[5])	—
0·4	4·150	10·64 ± 0·05 (ref.[39])	19·26 ± 0·30 (ref.[39])	—
0·6	4·284	11·30 ± 0·05 (ref.[5])	21·35 ± 0·40 (ref.[5])	—
0·8	4·436	11·84 ± 0·06 (ref.[39])	21·50 ± 0·30 (ref.[39])	—
1·0	4·600	12·54 ± 0·07 (ref.[40])	22·34 ± 0·55 (ref.[15])	—
		12·34 ± 0·03 (ref.[41])	22·50 ± 0·25 (ref.[41])	31·9 ± 1·3 (ref.[41])
1·5	5·038	14·30 ± 0·07 (ref.[40])	26·06 ± 0·65 (ref.[15])	—
2·0	5·500	16·27 ± 0·08 (ref.[40])	29·15 ± 0·73 (ref.[15])	—
		16·20 ± 0·03 (ref.[41])	28·00 ± 0·30 (ref.[41])	36·8 ± 1·5 (ref.[41])
3·0	6·455	20·48 ± 0·10 (ref.[40])	—	—
		20·43 ± 0·04 (ref.[41])	31·90 ± 0·32 (ref.[41])	39·7 ± 1·6 (ref.[41])

rical errors; it is recommended, however, to use the data of Monson and Rigby[26] for they were obtained by using a much longer integration chain.

The P–V–T behaviour of the systems of spherocylinders was simulated by the MC method for $L = 1{\cdot}0$ and $2{\cdot}0$ (ref.[26–29]) and by the MD method for $L = 1{\cdot}0$ (ref.[30]). All the data given in Table III seem to be in a good mutual agreement. Besides the pseudoexperimental data, Table III presents also the values of the compressibility factor from Eq. (5) and from the Nezbeda equation[15]

$$(P/\varrho kT) = [1 + (3\alpha - 2)\,y + (\alpha^2 + \alpha - 1)\,y^2 - \alpha(5\alpha - 4)\,y^3]/(1 - y)^3\,,$$
$$\alpha = (L + 1)(L + 2)/(3L + 2)\,. \qquad (10)$$

TABLE III
Compressibility Factor of Hard Spherocylinders

L	y	$P/\varrho kT$		
		simulation (ref.)	Eq. (5)	Eq. (10)
1·0	0·20	2·69 (ref.[30])	2·67	2·67
		2·65 ± 0·02 (ref.[26])		
	0·2454	3·23 ± 0·12 (ref.[29])	3·40	3·39
		3·37 ± 0·04 (ref.[26])		
	0·30	4·48 ± 0·07 (ref.[26])	4·58	4·56
	0·3351	5·53 ± 0·14 (ref.[27])	5·59	5·55
	0·3879	7·57 ± 0·26 (ref.[27])	7·64	7·53
	0·40	8·18 (ref.[30])	8·22	8·10
		8·20 ± 0·10 (ref.[26])		
	0·4460	10·74 ± 0·24 (ref.[27])	10·98	10·74
	0·50	15·20 ± 0·20 (ref.[26])	15·76	15·28
	0·5096	16·80 ± 0·90 (ref.[27])	16·85	16·31
2·0	0·20	3·07 ± 0·03 (ref.[26])	3·06	3·06
	0·2676	4·53 ± 0·18 (ref.[29])	4·49	4·49
	0·30	5·40 ± 0·10 (ref.[26])	5·41	5·40
		5·40 ± 0·13 (ref.[28])		
	0·3058	5·52 ± 0·23 (ref.[29])	5·59	5·59
	0·3474	6·84 ± 0·30 (ref.[29])	7·13	7·13
	0·35	7·17 ± 0·11 (ref.[28])	7·24	7·23
	0·3927	8·99 ± 0·40 (ref.[29])	9·33	9·32
	0·40	9·60 ± 0·10 (ref.[28])	9·75	9·74
	0·45	13·00 ± 0·16 (ref.[28])	13·27	13·24
	0·50	18·00 ± 0·40 (ref.[28])	18·30	18·25

It is seen that for $L = 2{\cdot}0$, the both analytical results are essentially undistinguishable. For $L = 1{\cdot}0$, Eq. (*5*) yields higher values, which is caused by an inaccurate representation of the fourth virial coefficient by Eq. (*10*). In any case, Eq. (*5*) must be preferred for it results from exact values of virial coefficients whereas the Nezbeda equation is based on their approximate analytical fitting.

The comparison of Eq. (*5*) with the simulation data shows almost everywhere an excellent agreement. For $L = 2{\cdot}0$ there exists a small discrepancy for $y = 0{\cdot}40$ and $0{\cdot}45$, which is most probably due to partly the surprisingly low numerical error reported (1% for these two very high densities) and partly a slight overestimation of results by Eq. (*5*) in this region. For $L = 1{\cdot}0$, the only problematic value is the compressibility factor for $y = 0{\cdot}5$. With regard to the perfect agreement of Eq. (*5*) with the simulation data in all the other cases we are in doubts about the MC value mentioned.

Homonuclear Dumbells

Similarly to spherocylinders, also for dumbells the second virial coefficient is known exactly[31,32], whereas the third and fourth ones are obtained by numerical integration. The virial coefficients for all types of dumbells, for which the MC or MD data exist, are summarized in Table IV.

The thermodynamic behaviour or homonuclear dumbells was studied by a number of authors (Freasier[33,34], Freasier and coworkers[35], Aviram and coworkers[36], Streett and Tildesley[37] and Streett[38]). The first approximate of the behaviour of the db fluid is yielded by Eqs (*1*)–(*3*). In foregoing paper[5] we pointed out the possibility

TABLE IV
Virial Coefficients of Hard Homonuclear Dumbells

L	B_2	B_3 (ref.)	B_4 (ref.)	B_5 (ref.)
0·05	4·004	10·01 ± 0·03	18·40 ± 0·08	—
0·10	4·014	10·13 ± 0·03	18·84 ± 0·30	—
0·20	4·055	10·23 ± 0·05 (ref.[5])	19·43 ± 0·35 (ref.[5])	—
0·40	4·213	10·95 ± 0·05 (ref.[39])	20·35 ± 0·30 (ref.[39])	—
0·60	4·474	12·11 ± 0·06 (ref.[39])	22·98 ± 0·35 (ref.[39])	—
		12·13 ± 0·03 (ref.[34])	23·10 ± 0·07 (ref.[34])	35·58 ± 0·45 (ref.[34])
0·75	4·753	13·52 ± 0·05	26·26 ± 0·30	—
0·80	4·866	14·04 ± 0·08 (ref.[5])	27·61 ± 0·50 (ref.[5])	—
1·00	5·444	16·93 ± 0·25 (ref.[35])	34·88 ± 0·50 (ref.[35])	52·22 ± 1·05 (ref.[35])

that some data of Aviram and coworkers are in error; later on it was proved[38] that all the data in that work are erroneous and should be discarded. All the other data except the values for $L = 0{\cdot}10$ from the work[37], satisfy the conjectures 1 – 3 and are summarized in Table V for $L = 0{\cdot}05$, 0·20, 0·40 and 0·60. Moreover, the values of the compressibility factor calculated from Eq. (5) are as well presented in this table. The comparison of values in Table V proves that for $L \leqq 0{\cdot}40$ there exists a perfect agreement between Eq. (5) and the pseudoexperimental data. For $L = 0{\cdot}60$, two and in some cases even three different values of compressibility factor are available. In all the cases with the exception of the highest density, there is again a perfect agreement between the pseudoexperimental data and Eq. (5). For high densities, the

TABLE V
Compressibility Factor of Hard Homonuclear Dumbels

L	y	$P/\varrho kT$	
		simulation (ref.)	Eq. (5)
0·05	0·4084	7·50 ± 0·20 (ref.[37])	7·41
0·20	0·1047	1·57 ± 0·03 (ref.[38])	1·56
	0·1571	2·03 ± 0·04 (ref.[38])	1·99
	0·2094	2·61 ± 0·05 (ref.[38])	2·56
	0·2618	3·38 ± 0·08 (ref.[38])	3·35
	0·2714	3·55 ± 0·08 (ref.[38])	3·52
	0·3142	4·50 ± 0·09 (ref.[38])	4·44
	0·3665	6·02 ± 0·12 (ref.[38])	6·00
	0·4189	8·26 ± 0·17 (ref.[38])	8·26
0·40	0·4084	8·10 ± 0·25 (ref.[37])	8·00
0·60	0·1047	1·64 ± 0·01 (ref.[33])	1·63
	0·1877	2·46 ± 0·02 (ref.[34])	2·48
	0·2094	2·80 ± 0·06 (ref.[38])	2·78
		2·84 ± 0·03 (ref.[33])	
		2·76 ± 0·02 (ref.[34])	
	0·2815	4·14 ± 0·04 (ref.[34])	4·13
		4·04 ± 0·02 (ref.[34])	
	0·3141	5·02 (ref.[33])	4·97
		4·95 ± 0·05 (ref.[34])	
		4·86 ± 0·04 (ref.[34])	
	0·4189	9·42 ± 0·19 (ref.[38])	9·44
		9·24 (ref.[33])	
	0·4691	12·95 ± 0·26 (ref.[38])	13·22
		12·70 ± 0·16 (ref.[34])	

Freasier data[33,34] seem to be systematically lower. Analogous situation exists also for $L = 1{\cdot}0$ where, unfortunately, there is only one set of data[35]. The data of Freasier and coworkers[35] lie always below the values of Eq. (5) and this difference increases with increasing density. The difference for $\varrho\sigma^3 = 0{\cdot}45$ is approximately 15%, which strongly exceeds the assumed positive deviation of Eq. (5). There remains a question whether this discrepancy is a consequence of the trend observed with the data of this author already for $L = 0{\cdot}60$ or of the inaccuracy of Eq. (5) for $L \to 1$ or the combination of both effects. The definitive answer to this question can be provided only by new simulation data.

The agreement between the compressibility factor given by Eq. (5) and the majority of simulation data for three systems of different hard particles proves the justification of its use to describe the thermodynamic behaviour of these systems. To prove even the general validity of this equation we applied it as well to the calculation of the compressibility factor of systems of the hard heteronuclear dumbells for which it is possible to find both the MC data and virial coefficients in the literature. The agreement of the values given by Eq. (5) and the MC data was excellent even in this case.

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LIST OF SYMBOLS

L	length of the core of a nonspherical molecule
B_i	i-th virial coefficient reduced by an appropriate power of the volume of the molecule
y	packing fraction
ϱ	number-density
σ	breadth of a molecule
$P/\varrho kT$	compressibility factor

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