

Monte Carlo simulation of the equation of state of hard tetrahedral molecules

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The equation of state of a simple but rather general hard model for tetrahedral molecules at different densities and elongations is investigated through Monte Carlo simulation. Molecular volumes and surfaces as well as the second virial coefficients are also evaluated. This enables estimations of the anisotropic factor α . Nevertheless, semi-empirical pressures so obtained show only fair agreement with our pseudoexperimental data. Conversely, a very accurate equation—similar to that used by Tildesley and Streett for hard dumb-bells—is obtained by a nonlinear least squares fitting procedure. Interestingly, it requires only five parameters from which two are needed to reproduce the second virial coefficients. The parametrization makes available an accurate equation of state for a wide variety of hard tetrahedral systems which can be useful in perturbative approaches to real fluids.

1. Introduction

In the past decade, considerable attention has been paid to the study of poly-atomic fluids. The existence of a common geometry for a wide variety of substances stimulates its investigation because it is possible to attack the problems in a general manner. Besides, it allows the isolation of the influence of a given variable in the properties of the system. In particular, great attention has been paid to analysing the effect of the anisotropy in the simplest polyatomic fluids, namely, those made up of linear molecules. Nowadays, these systems are relatively well known. This is not the case for tetrahedrally coordinated liquids. The pioneer study of Lowden and Chandler [1] using the RISM equation gave theoretical support to neutron diffraction experiments [2-4]. Hard core models were proposed to account for the structural properties, but it seems that more sophisticated models are needed to give accurate predictions. With regard to the thermodynamic properties, the situation is somewhat different. It is widely accepted that the study of hard polyatomic fluids is specially relevant in terms of perturbation theories. Irrespective of the perturbation scheme used [5, 6], the final formulations almost invariably rely on a hard core reference system. The perturbation treatments need both the equation of state and the structure of the hard fluid. It has already been shown [7] that the errors induced by the RISM approximation to the reference system atomic pair distribution function are not important. On the other hand, an accurate knowledge of the *PVT* behaviour of the (hard) reference system is crucial. Hence the importance of having acceptable analytical equations of state (EOS). Since, as far as we are aware, the available data are rather scarce [8, 9], we attempt in the present paper to augment our knowledge of the EOS of hard tetrahedral particles. In this paper, we report the pressures obtained by MC simulation for a

Table 1. Diameters and X–Y distances of representative hard XY_4 systems. Asterisks denote magnitudes deduced with d_Y .

System	d_Y	d_X	L_{XY}	L^*	$(1 + d_X^*)/2$	h^*	Ref.
$C(CH_3)_4$	3.94	3.78	1.55	0.39	0.98	1.06	[10]
CF_4	2.95	3.35	1.32	0.45	1.07	1.06	[11]
CCl_4	3.50	3.20	1.77	0.51	0.96	1.05	[12]
$SiCl_4$	3.40	3.48	2.01	0.59	1.01	1.03	[4]
$GeCl_4$	3.40	2.70	2.12	0.62	0.90	1.02	[4]
$SnCl_4$	3.40	2.57	2.27	0.67	0.88	1.00	[4]

simple model which can be described by the reduced density and a single reduced elongation.

2. Hard models: shapes and second virial coefficients

Our choice for the hard models of tetrahedral molecules XY_4 attempts to maximize the simplicity while retaining a satisfactory degree of generality. In this regard, it is illuminating to analyse the geometry of a number of models already proposed to account for the structural and thermodynamic properties of different XY_4 systems. When the potential models are soft we have substituted them by approximate hard reference bodies. For these, we used the simple prescription (supported by WCA-like perturbation theories for site–site systems [5, 7]) that the hard body diameters are roughly equal to the σ 's of the corresponding Lennard–Jones interaction. Let us examine the systems considered in table 1. There, the molecular shape is defined mainly by the diameter d_Y of the outer atoms and by their distance L_{XY} to the central one. The X atoms play only a minor role in defining both the volume and the relative elongation. Moreover, it has been reported [3, 4] that they are only of marginal influence on the outcome of structural calculations. Bearing in mind that for the systems in table 1 d_X is of comparable size to d_Y , one may ask whether the atoms X and Y of different molecules may touch. The closest approach of a Y site to the central atom X of another molecule occurs when the former atom is simultaneously in contact with three Y atoms of the latter molecule. In such a case, the distance h between sites X and Y of the molecules involved (see figure 1) is given by

$$h^* = L^*/3 + (1 - 8L^{*2}/9)^{1/2}, \quad (1)$$

Here and in the remainder of the paper, the diameter d_Y of the outer atoms has been used to reduce all the geometrical quantities, which are then denoted by an asterisk. Then, the reduced elongation L^* is

$$L^* = L_{XY}/d_Y \quad (2)$$

Therefore, X–Y contacts will never take place if the sum of the X and Y radii are lower than h . Since, by definition, $d_Y^* = 1$, the condition

$$(1 + d_X^*)/2 < h. \quad (3)$$

ensures that the central atom will not be reachable by the outer atoms of the other molecules.

We have presented both sides of equation (3) in table 1. From the hard systems considered, X–Y encounters can occur only in extremely rare configurations of CF_4 . We can then suppress the need for a d_X^* parameter by taking it as the maximum

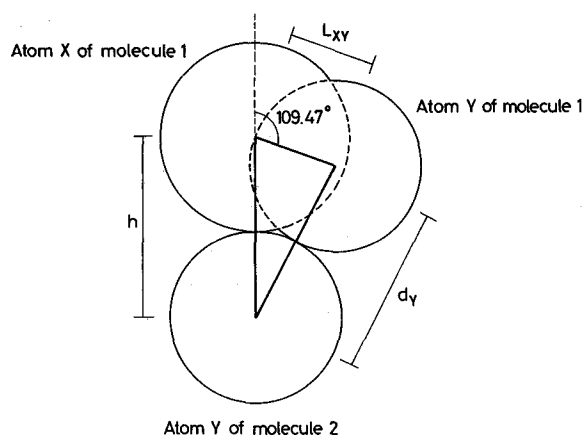


Figure 1. Intramolecular distances.

diameter which fulfils equation (3). In this way, as long as only one reduced length suffices to define the model, it is both simple and general, thus allowing an unambiguous investigation of the effects of the molecular anisotropy. Although it cannot deal with the case of methane (equation (3) is not fulfilled) our results might provide useful information for the theoretical treatment of this important system. On the other hand, there is another advantage derived from the choice made for the Y diameters, namely, the physical consistency. For a given L^* , all the systems satisfying equation (3) have an identical equation of state. This means that all of them have the same effective volume [13, 14], even if the hard envelopes defining the apparent volume are different. The best agreement between apparent and effective volumes obviously corresponds to the models for which the central atom diameter has the maximum value allowed by the above stated condition.

Table 2 presents the reduced elongations of the models investigated in this paper. Also given are the molecular surfaces S_m and volumes V_m , leading to the estimation of the anisotropic factor α . For the evaluation of these quantities we used numerical methods. The algorithm for the volumes is a slight modification of the usual one, i.e. it is based on the generation of random points within a cubic box containing the molecule. But, if a high precision is wanted, simple random generators are not valid since they produce cyclic sequences, so increase in the number of points does not improve the accuracy of the results. By using a test system made up of four spheres

Table 2. Shape (molecular surface and volume) and low density properties of the hard tetrahedral models used in this work. The second column lists the central atom diameters while the fifth and the last ones show the anisotropic factors calculated through equations (10) and (12), respectively.

L^*	d_X^*	S_m^*	V_m^*	α_{BN}	$B/4V_m^*$	α_R
0.35	1.1213	7.013	1.5345	1.159	1.1141	1.152
0.40	1.1190	7.676	1.6876	1.210	1.1492	1.199
0.45	1.1111	8.370	1.8345	1.270	1.1904	1.254
0.50	1.0972	9.099	1.9713	1.342	1.2387	1.318
0.55	1.0768	9.844	2.0940	1.425	1.2961	1.395
0.60	1.0492	10.558	2.1996	1.515	1.3634	1.485
0.65	1.0138	11.279	2.2847	1.620	1.4427	1.590

in contact (for which the volume is exactly known) we have observed that a better alternative consist of dividing the main box into smaller ones. In this way, the number of points in each subbox is reduced and so is the possibility of generating cyclic sequences. It is also convenient to use an odd number of small boxes, since this disrupts the symmetry of the molecule. With respect to the molecular surface algorithm, the standard von Neumann method is used [15]. This proceeds in three steps: first, random points are generated on the surface of each of the atoms; then the calculation of the distances to the remainder atoms allows them to be defined as truly superficial or internal points (i.e. inside an overlapping region); and, finally, the contributions of each atom are added.

It is to be noted that the geometrical quantities displayed in table 2 refer to models with d_x satisfying equation (3). The interpolation for $L^* = 0.5057$ (the reduced elongation for a widely used model for CCl_4) will produce slightly different results from that reported in the literature. In particular, the interpolated volume for that elongation ($d_x^* = 1.0952$) gives $V_m^* = 1.9854$, which may be compared with the value $V_m^* = 1.9685$ calculated by Nezbeda and Vörtler [8] for the model described in table 1 ($d_x^* = 0.9143$). We have repeated the calculation of the geometrical quantities of the latter model, obtaining $V_m^* = 1.9694$ and $\alpha_{\text{BN}} = 1.386$ (in the above quoted paper $\alpha_{\text{BN}} = 1.384$). Not only are the geometrical quantities different, but also the semi-empirical equations using such quantities will predict different results. This might throw some doubt on the conclusion based on the use of a particular value for the central atom diameter (we recall that the actual pressure of the system is independent of d_x provided that equation (3) is fulfilled). Nevertheless, as long as an increase in the molecular volume implies a higher packing fraction but also a lower anisotropic factor, the global effect of the different choice for d_x on the pressure is very small.

In the evaluation of the second virial coefficients,

$$B(T) = -\frac{2\pi}{\Omega^2} \int r^2 \int \{\exp(-u(r, \Omega_1, \Omega_2)/kT) - 1\} dr d\Omega_1 d\Omega_2, \quad (4)$$

the use of quaternions for the angular integration [16] speeds up the calculation by a factor of ≈ 4 with respect to the Euler angles method. Besides, it ensures nonbiased sampling of the relative molecular orientations. The numerical results at different elongations have been parametrized by using a least squares fit to a third order polynomial in L^* ,

$$\frac{B^*}{4V_m^*} = 1 + \frac{UL^* + VL^{*3}}{4}, \quad (5)$$

yielding $U = 0.72477$ and $V = 4.730$. The predictions are in good agreement with the numerical results (table 3). Also, the interpolation for $L^* = 0.5057$ gives $B^* = 9.884$, which agrees well with the value 9.889 reported by Nezbeda and Vörtler [8].

3. The simulation

The simulations were performed by using the standard Monte Carlo method with Metropolis sampling and periodic boundary conditions. Depending on the reduced densities and anisotropies, the sample consisted of 108, 216 or 500 particles in a cubic box. Trial runs showed some size-dependence of the results at the higher densities and elongations. This is because, even at not too high densities, the relative molecular

Table 3. Second virial coefficients. Comparison between numerical results and the predictions of equation (5) with $U = 0.72477$ and $V = 4.730$.

L^*	$B^*/4V_m^*$		Δ
	Eqn (5)	Numeric	
0.30	1.0863	1.0843	0.0020
0.35	1.1141	1.1141	0.0000
0.40	1.1482	1.1492	-0.0010
0.45	1.1893	1.1904	-0.0011
0.50	1.2384	1.2387	-0.0003
0.55	1.2964	1.2961	0.0003
0.60	1.3641	1.3634	0.0007
0.65	1.4425	1.4427	-0.0002

orientations are considerably restricted. As a consequence, the correlations are longer than that corresponding to a simple fluid at the same packing fraction, forcing the use of larger samples. The steric hindrance also makes difficult the generation of the initial configuration. The centres of mass were placed in the positions of a FCC lattice, but we have deliberately avoided the use of a particular orientational arrangement spanning the full box. Instead, the initial positions of the atoms were randomly chosen from a restricted set of orientations. When the procedure caused overlaps between particles, the MC program was used to produce random rotations until an acceptable configuration was reached.

For the rotation of the particles, a variant of the algorithm based on the Euler angles has been devised. Two are the main inconvenience which have restricted the use of such methods in MC simulations. First, the dependence of an axis rotation upon the result of the previous one leads to biased sampling of the orientational space: the most serious drawback of the usual definitions of the Euler angles [17] comes from the fact that two consecutive rotations along the (approximately) same axis are produced when one of the three angles is small. It is easy to avoid most effects of this problem by changing the order of the rotations. For a transformation through three consecutive rotations along the X , Y , and Z axes resulting from the immediate one we can obtain the new position of a point by multiplying the matrix

$$A = \begin{pmatrix} \cos \phi \cos \psi - \sin \phi \sin \theta \sin \psi & -\sin \phi \cos \psi - \cos \phi \sin \theta \sin \psi & -\cos \theta \sin \psi \\ \sin \phi \cos \theta & \cos \phi \cos \theta & -\sin \theta \\ \cos \phi \sin \psi + \sin \phi \sin \theta \cos \psi & -\sin \phi \sin \psi + \cos \phi \sin \theta \cos \psi & \cos \theta \cos \psi \end{pmatrix} \quad (6)$$

by the old coordinates of the atom. Generally speaking, this does not completely solve the problem, since the three rotation axes are not completely independent. But, as long as the molecules considered are highly symmetrical, the angular displacements will be small. In this case, the consecutive gyration axes will be almost orthogonal and the transformation acceptable for our purposes. Equation (6) is not useful yet because of the trigonometrical functions concerned. We can make further use of approximations connected with the small values needed for the angular moves ($\sin x \simeq x$) to

write

$$A = \begin{pmatrix} c_\phi c_\psi - \phi\theta\psi & -\phi c_\psi - c_\phi\theta\psi & -c_\theta\psi \\ \phi c_\theta & c_\phi c_\theta & -\theta \\ c_\phi\psi + \phi\theta c_\psi & -\phi\psi + c_\phi\theta c_\psi & c_\theta c_\psi \end{pmatrix}, \quad (7)$$

with $c_t = (1 - t^2)^{1/2}$, $t = \phi, \psi, \theta$.

Now ψ, ϕ, θ , can be obtained simply from a random number generator. Besides, we write the matrix in terms of the c_t s to emphasize that the quantities inside the square root signs are always close to unity, so it is possible to use fast algorithms for these calculations [15]. We have checked the mean value of the absolute displacements along each of the Cartesian coordinates, verifying that they all are essentially identical. In contrast, under the same conditions, the usual Euler angles produced $\Delta x \simeq 1.3 \Delta z$ and $\Delta y \simeq 1.8 \Delta z$. In summary, this is a simple and efficient method useful for highly symmetrical systems (more precisely, globular-like molecules).

In addition to the well known neighbours list, another computational time saving scheme has been employed. It relies again on the molecular shape features. In a first pass of every trial move, only the translational displacements of the selected molecule centre of mass are generated. A possible overlap of the molecule with the neighbour ones is checked by comparing the centres of mass distance r_{12} with the smaller and the greater separations at which, irrespective of the mutual orientation, they *do necessarily* and *cannot* overlap, namely $r_{\min} = h^*$ and $r_{\max}^* = 1 + 2L^*$. If the new configuration cannot be acceptable, i.e., $r_{12} < r_{\min}$, the move is rejected, so there is no need to calculate or compare the 24 remaining atom-atom distances. When an overlap cannot occur ($r_{12} > r_{\max}^*$ is fulfilled for all the distances to the particles in the neighbours list) the new configuration is accepted. In such a case the rotation of the target molecule is performed, but the calculation of the site-site distances can again be neglected. Finally, the occurrence of an overlap might depend on the mutual orientation. Then a record of the molecule concerned is made in a second neighbouring list. The evaluation of the interatomic distances is needed only when none of the particles necessarily produces overlap and the secondary list is not empty. In this way, the implementation of all of the saving tricks makes the overall algorithm only marginally more time consuming than that of a simple fluid.

Translational order parameters [15] have served to elucidate when the equilibration phase can be considered completed. For systems with higher elongation there have been some difficulties in destroying the solid lattice. This is an indication of the vicinity of a plastic phase. As an example, let us cite the point at $\rho^* = 0.18$ for the model with $L^* = 0.65$ which needed about 8 millions trial moves (16 000 per molecule) to reach the production phase or the state at $\rho^* = 0.25$, $L^* = 0.50$ which was finally discarded due to the difficulties of melting the lattice.

The compressibility factors have been calculated [17] through the limiting value of the function

$$\beta p/\rho = 1 + \langle r_{12}(\partial r_{\alpha\gamma}/\partial r_{12}) \rangle g_{\alpha\gamma}(r) \quad (8)$$

as $r_{\alpha\gamma}$ approaches $d_{\alpha\gamma}$. Here r_{12} is the distance between the centres of mass of molecules 1 and 2, $r_{\alpha\gamma}$ is the distance between site α on molecule 1 and γ on molecule 2, and $g_{\alpha\gamma}$ is the site-site radial distribution function. The pointed brackets indicate an ensemble average. In our program, a linear extrapolation of the mean results for three equidistant shell provides the desired limit. Some care is needed for the choice of the

intervals to ensure the validity of the linear behaviour. Small values of the shell thickness increase the statistical uncertainty but eliminate possible systematic errors. In this work, we have used different values but they always ranged (according to the elongation and density of the state point) between 0.01 and 0.02 in reduced units.

4. Results

Compressibility factors have been calculated for 35 state points covering a wide range of elongations and the full range of fluid densities. The results are shown in table 4 together with the number of configurations and the sample size used in each experiment. The statistical uncertainty is given as the 95% confidence interval estimated from typically 20 subaverages. The anisotropic effects greatly increase at high elongations, as can be seen in figure 2. There, we present the relative deviations of the compressibility factor from that of a hard sphere at the same packing fraction calculated through the Carnahan–Starling equation [19]. We note that the slopes of the curves at constant L^* increase with the molecular anisotropy.

In table 5 the pseudoexperimental pressures are compared with the predictions of some semiempirical equations. The Boublik–Nezbeda equation is based on a hard convex body equation of state [20] which is an extension of the ideas of scaled particle theory (SPT)

$$\frac{\beta p}{\rho} = \frac{1 + (3\alpha - 2)y + (3\alpha^2 - 3\alpha + 1)y^2 - \alpha^2 y^3}{(1 - y)^3}, \quad (9)$$

to fused hard spheres models [21] by a suitable definition of the nonsphericity parameter, α_{BN} , in terms of the surface and volume of the actual molecule and the means curvature R of an enveloping convex body

$$\alpha_{\text{BN}} = RS_{\text{m}}/3V_{\text{m}}. \quad (10)$$

For our hard tetrahedral model, R is given by [22]

$$R^* = 1/2 + L^* \sqrt{6} \arccos(-1/3)/2\pi. \quad (11)$$

Rigby [23] proposed a definition of α based on the low density behaviour of equation (9)

$$\alpha_{\text{R}} = (B/V_{\text{m}} - 1)/3. \quad (12)$$

Both α_{BN} and α_{R} are trivially obtained from the results of the preceding section. The values for different elongations are displayed in table 2.

The so-called [24, 25] modified thermodynamic perturbation theory (MTPT) uses the TPT equation of state originally proposed [26, 27] for hard chain molecules

$$\frac{\beta p}{\rho} = 1 + v \frac{(4y - 2y^2)}{(1 - y)^3} + (v - 1) \left(\frac{y}{(2 - y)} - \frac{3y}{(1 - y)} \right). \quad (13)$$

Boublik [25] and, independently, Walsh and Gubbins [24] extended the equation to molecules made of overlapping spheres by replacing the number v of tangent spheres by an effective v_{e} obtained through the identification of the second virial coefficients given by the TPT and the SPT equations. This simply reduces to

$$v_{\text{e}} = 2\alpha - 1 \quad (14)$$

Semiempirical results are given in table 5. It is well known that Rigby's definition

Table 4. Monte Carlo results for the equation of state. The second and third columns are the number of particles and the number of configurations used in each run. The last column represents the error estimated for a 95% confidence interval.

ρ^*	N_p	$N_c/10^6$	$\beta p/\rho$	Δ
$L^* = 0.35$				
0.10	108	1.0	2.09	± 0.03
0.15	108	1.3	3.08	± 0.05
0.20	256	1.2	4.72	± 0.08
0.25	256	2.0	7.48	± 0.07
0.30	500	3.0	12.20	± 0.13
$L^* = 0.40$				
0.10	108	1.2	2.29	± 0.04
0.15	108	1.2	3.64	± 0.04
0.20	256	1.5	5.98	± 0.07
0.25	256	2.0	10.06	± 0.10
0.27	500	3.0	12.70	± 0.10
$L^* = 0.45$				
0.10	108	1.3	2.58	± 0.04
0.15	256	1.5	4.32	± 0.04
0.20	256	1.8	7.59	± 0.07
0.23	256	2.6	10.75	± 0.09
0.25	500	3.0	13.86	± 0.10
$L^* = 0.50$				
0.05	108	1.0	1.67	± 0.02
0.10	108	1.2	2.88	± 0.03
0.15	256	1.5	5.16	± 0.08
0.20	256	1.9	9.75	± 0.09
0.23	500	3.0	14.40	± 0.12
$L^* = 0.55$				
0.05	108	1.0	1.77	± 0.02
0.10	256	1.0	3.27	± 0.04
0.15	256	1.5	6.23	± 0.06
0.18	256	2.5	9.45	± 0.07
0.20	256	2.6	12.43	± 0.10
0.215	500	3.0	15.55	± 0.10
$L^* = 0.60$				
0.05	108	1.0	1.87	± 0.02
0.10	256	1.2	3.68	± 0.05
0.15	256	1.8	7.51	± 0.09
0.18	256	2.0	11.67	± 0.06
0.20	500	3.0	16.05	± 0.12
$L^* = 0.65$				
0.05	108	1.5	1.99	± 0.02
0.10	256	2.0	4.18	± 0.05
0.15	256	2.5	9.06	± 0.05
0.18	500	3.0	14.70	± 0.14

of α leads to an underestimation of the pressures. Tetrahedral systems are no exception to this rule. More satisfactory are the BN predictions, specially at low elongations. But, when the reduced length and packing fractions increase, the departures become important. Although the MTPT equation of state is slightly more accurate, its general behaviour is close to the BN equation. It seems that the similarity

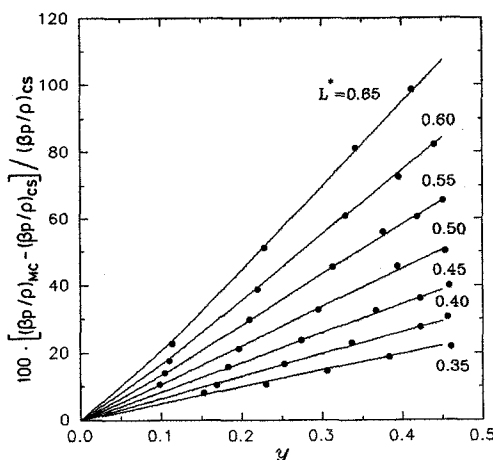


Figure 2. Relative deviations of the compressibility factor from that of a hard sphere at the same packing fraction.

lies in the functional dependence, since the TPT equation also produces essentially the same results (this is why they do not appear in table 5) that Rigby's equation does when v_e is obtained from the low density limit of equations (13)

$$B/V_m = (3v + 5)/2. \quad (15)$$

The conclusions drawn do not contradict previous findings. Good agreement between BN predictions and simulation results have been reported [8] for $L^* = 0.5057$. But, the departures of the BN equation from pseudoexperimental data greatly increases with elongation. So the BN equation is accurate enough at low anisotropies but not at the higher ones. On the other hand, the accuracy does not depend on the values used for d_x . For the above reduced length, the difference between the results obtained with V_m^* and α_{BN} interpolated from table 2 and that reported by Nezbeda and Vörtler is always less than 1%.

In view of the relatively poor accuracy of semiempirical equations at the highest elongations, we have tried to parametrize the simulation data. We have chosen a functional form close to that proposed by Tilesley and Streett [28] for homonuclear dumb-bells. It is based on the SPT function but with the nonsphericity factor dependence replaced by polynomials in L^*

$$\frac{\beta p}{\rho} = \frac{1 + F(L^*)y + G(L^*)y^2 - H(L^*)y^3}{(1 - y)^3}. \quad (16)$$

When F, G and H are the unity it reduces to the Carnahan–Starling equation. We have found that the simplest function providing satisfactory accuracy needs only five coefficients

$$\frac{\beta p}{\rho} = \frac{1 + (1 + UL^* + VL^{*3})y + (1 + WL^* + XL^{*4})y^2 - (1 + ZL^{*3})y^3}{(1 - y)^3}. \quad (17)$$

The parameters U and V are simply those obtained in the fitting of the second virial coefficients. The remainder have been obtained by a nonlinear least squares fitting procedure with all points equally weighted, giving the following values (U and

Table 5. A comparison of the MC compressibility factors with semiempirical predictions (MTPT, Boublik–Nezbeda (BN) and Rigby (R) equations) and the least squares fit of the simulated data (equation (17)). The last column is the relative difference between fitted and MC values.

L^*	y	MC	MTPT	BN	R	Eqn (17)	$\Delta(\%)$
0.35	0.1534	2.09	2.08	2.07	2.07	2.08	-0.5
0.35	0.2302	3.08	3.11	3.08	3.07	3.10	0.8
0.35	0.3069	4.72	4.75	4.69	4.66	4.75	0.6
0.35	0.3836	7.48	7.46	7.34	7.29	7.49	0.1
0.35	0.4603	12.20	12.17	11.95	11.86	12.28	0.7
0.40	0.1688	2.29	2.31	2.29	2.28	2.30	0.6
0.40	0.2531	3.64	3.65	3.60	3.58	3.64	0.0
0.40	0.3375	5.98	5.92	5.83	5.78	5.94	-0.7
0.40	0.4219	10.06	9.98	9.79	9.68	10.07	0.1
0.40	0.4557	12.70	12.46	12.21	12.08	12.61	-0.7
0.45	0.1835	2.58	2.58	2.55	2.53	2.57	-0.3
0.45	0.2752	4.32	4.31	4.25	4.20	4.32	0.0
0.45	0.3669	7.59	7.46	7.32	7.22	7.54	-0.7
0.45	0.4219	10.75	10.58	10.38	10.22	10.76	0.1
0.45	0.4586	13.86	13.51	13.25	13.03	13.81	-0.3
0.50	0.0986	1.67	1.67	1.67	1.66	1.67	-0.1
0.50	0.1971	2.88	2.88	2.86	2.82	2.89	0.3
0.50	0.2957	5.16	5.12	5.04	4.95	5.17	0.3
0.50	0.3943	9.75	9.43	9.26	9.07	9.67	-0.8
0.50	0.4534	14.40	13.96	13.72	13.40	14.47	0.5
0.55	0.1047	1.77	1.77	1.77	1.75	1.77	0.0
0.55	0.2094	3.27	3.23	3.20	3.15	3.26	-0.2
0.55	0.3141	6.23	6.06	5.98	5.85	6.23	0.0
0.55	0.3769	9.45	9.02	8.89	8.66	9.38	-0.7
0.55	0.4188	12.43	11.87	11.71	11.39	12.47	0.4
0.55	0.4502	15.55	14.70	14.51	14.10	15.56	0.0
0.60	0.1100	1.87	1.88	1.87	1.85	1.88	0.7
0.60	0.2200	3.68	3.61	3.58	3.52	3.70	0.4
0.60	0.3299	7.51	7.12	7.05	6.89	7.51	0.0
0.60	0.3959	11.67	10.93	10.84	10.57	11.76	0.8
0.60	0.4399	16.05	14.72	14.63	14.25	16.07	0.1
0.65	0.1142	1.99	1.98	1.98	1.96	2.01	0.8
0.65	0.2285	4.18	4.01	3.99	3.92	4.19	0.2
0.65	0.3427	9.06	8.27	8.26	8.09	9.02	-0.4
0.65	0.4112	14.70	13.06	13.09	12.78	14.63	-0.5

V are also included for completeness)

$$U = 0.72477 \quad V = 4.730 \quad W = 1.3296 \quad X = 24.78 \quad Z = 7.69$$

From table 5 it follows that the compressibility factors evaluated from the proposed equation of state are in very good agreement with our MC data for the whole range of elongations and densities (see also figure 2). The greatest of the relative (absolute) deviations is 0.8%, with 0.4% the mean value. It is to be noted that only four coefficients suffice to fit the results at elongations up to $L^* = 0.60$ within a 1% error interval. Indeed, this is illustrative of the great effects of steric hindrance at high elongations already shown in figure 2. An independent test both of the quality of our simulation results and of the predictive ability of equation (17) is presented in table 6, where we compare the simulation results reported by Nezbeda and Vörtler [8] with those from the above equation. The agreement is again satisfactory.

Table 6. Comparison of the predictions of the parametrized equation (17) with the MC simulation of Vörtler and Nezbeda [8].

L^*	γ	MC [8]	Eqn (17)
0.5057	0.2017	2.94	2.98
0.5057	0.3026	5.39	5.44
0.5057	0.3586	7.70	7.73
0.5057	0.4034	10.26	10.38

We can thus conclude that the proposed equation of state represents a satisfactory description of the PVT behaviour of hard tetrahedral particles which can be useful in perturbative approaches to real fluids.

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