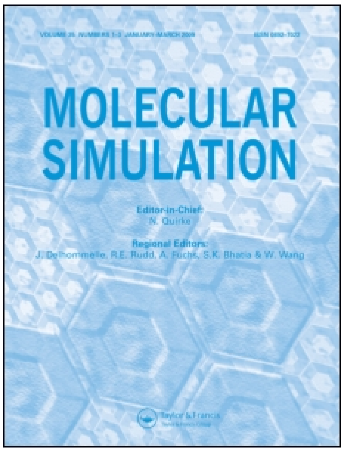

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MD Simulations of Liquids with *T_d*, O_h Molecular Symmetry

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MD SIMULATIONS OF LIQUIDS WITH T_d, O_h MOLECULAR SYMMETRY: A TWO MODEL POTENTIALS APPROACH

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A new method is proposed for the calculation of intermolecular interactions in Molecular Dynamics simulations of liquids with T_d, O_h molecular symmetry. The new algorithm is based on the separation of the pair potential into a short-range and a long-range contribution described by a site-site and a spherical centre-centre potential model respectively using an additional cutoff distance. Test calculations for the Lennard-Jones fluids CCl_4 and SF_6 show significant savings in CPU time. We compare thermodynamic properties, pair correlation functions and a few dynamic autocorrelation functions obtained with the novel strategy with results of the commonly used algorithm for systems containing 864 molecules. Since no significant differences appear the new algorithm may be suggested as a useful contribution to the area of Molecular Dynamics simulation of liquids with these rather high molecular symmetries.

KEY WORDS: High molecular symmetry, intermolecular interactions, Molecular Dynamics

1 INTRODUCTION

A central problem in Molecular Dynamics (MD) simulation is the location of interacting pairs of particles. Their separation may be determined applying different strategies (e.g., neighbour list, and cell list) depending on the size of the system and the range of the used potential model [1]. In this paper we consider the commonly adopted all-pairs method with a double-loop calculation of distances and forces between each pair of particles in the system. Savings in CPU time may be achieved ignoring pairs separated by a distance larger than the range of interaction (spherical cutoff). The missing long-range part of the potential will be taken into account by an appropriate correction. In molecular systems the anisotropic nature of the potential implies additional loops over different sites or atoms in each pair of molecules. The requirement in CPU time increases proportional to the square number of particles and sites in a molecule.

In MD simulations of liquids the application to large systems allows a more accurate calculation of ensemble fluctuations, dynamic autocorrelation functions and interaction-induced phenomena. However, a compromise between economy in CPU time and reliable statistics obtained by using an appropriate ensemble size must be achieved. In the case of "spherical" molecules with, e.g., T_d- or O_h-symmetry, we propose to introduce an additional cutoff distance r_{ca} for the orientational dependent contribution of the pair potential. Thus the potential between a considered pair of molecules may be separated by two cutoff distances into a short-range and a long-range part. Up to the first cutoff r_{ca} an anisotropic potential model, for instance a Lennard-Jones potential of the site-site form, describes short-range intermolecular interaction. Beyond this sphere an isotropic potential function, e.g., a centre-centre Lennard-Jones model, is used to evaluate the orientational independent long-range forces as far as the second cutoff r_{ci}. This distance truncates the range of interaction and a common technique [1] to correct the isotropic pair potential becomes useful to compensate the missing long-range parts of potential energy and virial function. Thus we split the total pair potential function into three parts:

$$\phi(r_{ij}, \omega_i, \omega_j) = \begin{cases} U(r_{ij}, \omega_i, \omega_j) & \text{for } r_{ij} < r_{ca} \\ U(r_{ij}) & \text{for } r_{ca} \leqslant r_{ij} < r_{ci} \\ \text{Long-range correction} & \text{for } r_{ij} \geqslant r_{ci} \end{cases} \tag{1}$$

with

$$U(r_{ij}, \omega_i, \omega_j) = \sum_{\alpha} \sum_{\beta} 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{6}\right] \tag{2}$$

and

$$U(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{3}$$

where α, β are indices labelling the Lennard-Jones centres corresponding to the molecules i and j, respectively, and $r_{\alpha\beta}$ denotes the distance between them.

Making use of this strategy, it is possible to save significant CPU time, which otherwise would be required for the computation of all atom-atom interactions between the two cutoffs. We were motivated to try this approach for "spherical" molecules by consideration of their centre-centre and atom-atom pair correlation functions. These functions connect the structure of a liquid with ensemble averages of any pair function [2, 3]. Assuming a pairwise interaction model, the pair correlation function of a liquid shows a one-to-one correspondence to their pair potential [4]. This theorem also indicates that a unique set of atom-atom potentials corresponds to a given set of atom-atom pair correlation functions [5].

In order to discuss the structure of the molecular liquids one can use the site-site correlation functions $g_{\alpha\beta}(r)$ or the more general approach of expanding the full angle dependent pair correlation functions $g(r, \omega_1, \omega_2)$ into the Wigner rotational matrices D^l_{km} [5]

$$g(r, \omega_1, \omega_2) = \sum (2l_1 + 1)^{1/2}(2l_2 + 1)^{1/2} g^{l_1 l_2}_{m_1 m_2 k}(r) D^{l_1}_{km_1}(\omega_1) D^{l_2}_{-km_2}(\omega_2) \tag{4}$$

The summation being over all indices. On account of their simplicity we choose to use site-site correlation functions although these functions contain orientational correlations only implicitly.

$$g_{\alpha\beta}(r) = \frac{1}{4\pi N\rho}\left\langle \sum_{j \neq i} \frac{\delta(r - |r_{\alpha\beta}|)}{r^2} \right\rangle \tag{5}$$

The centre-centre pair correlation function $g(r)$ is an unweighted average over all corresponding angular distributions irrespective of molecular orientations. In the case of "spherical" molecules geometric considerations show that site–site correlations vanish at shorter distances compared with centre–centre correlations. For this reason it becomes evident that anisotropic interaction may be neglected at distances where centre–centre potentials describe the interaction with sufficient accuracy.

In order to introduce the new strategy into a MD program we consider the double-loop algorithm for explicit computation of intermolecular interactions [1]. The first approach to this method is to calculate the distance r_{ij} between two molecules. Neglecting pairs of molecules with r_{ij} longer than the truncation value r_{ci} we compare r_{ij} with the anisotropic cutoff r_{ca}. In the case of $r_{ij} - r_{ca} > 0$ the interaction is treated to be isotropic and the forces on molecule number i and j are evaluated using the centre–centre potential (Equation 3). Otherwise, forces and torques are computed by a set of site–site potentials (Equation 2). In a system of N molecules this procedure has to be repeated for each of the $(N(N - 1)/2)$ pairs of particles. We emphasize that both cutoffs are defined with respect to centre of mass distances.

The remainder of the paper is organized as follows: Section 2 shows an application to the test fluids CCl_4 and SF_6. These molecules have been selected because they have been extensively studied previously. Details of the simulations with the new algorithm and the usual one are given in Section 3. We conclude with a comparative discussion of the results obtained by the two methods.

2 APPLICATION TO CCl_4 AND SF_6

Since the first detailed study of the structure [6] of CCl_4 was published a large number of experimental studies [7–9] and computer simulations [10–12] have led to a rather detailed knowledge of structure factors and pair correlation functions of this liquid. Also, statistical mechanical theories of intermolecular pair correlation of CCl_4 are available both for a hard-core interaction [13] and a site–site Lennard-Jones potential model [14]. Nevertheless, a disagreement regarding the arrangement of the two nearest neighbour CCl_4 molecules is not yet settled. Also, none of these orientation models can exactly explain the size of the peaks in the C—Cl pair correlation function. However, each class of the presented correlation functions shows a similar dependence on interatomic distance r. A typical shape of pair correlation functions for liquid CCl_4 is illustrated in Figure 1.

All three correlation functions differ both in the first peak as well as in their long-range behaviour. The oscillations in the Cl—Cl and C—Cl correlation functions vanish at 0.9 nm and 1.2 nm, respectively. On the other hand oscillations in $g_{CC}(r)$ persist for values of r larger than 1.4 nm. The oscillations in $g_{CCl}(r)$ and $g_{ClCl}(r)$ is due to the interlocking structure of nearest neighbour molecules [6, 13] in liquid CCl_4 for distances below 1.0 nm. When at larger distances interlocking is no more active, due to the high symmetry of the molecule a large part of the angular configuration space is occupied. This leads to the vanishing of the site–site correlation. It is reasonable to generalize these considerations to molecules with a similar symmetric structure, e.g., other tetrahedral and octahedral molecules.

We notice that a MD simulation using a cutoff radius in the region of non-vanishing site–site correlation may produce computational inaccuracies, since the assumptions allowing a long-range correction on the potential energy and the virial function are not fulfilled. On the other hand, the explicit calculation of these properties at distances where oscillations of the centre–centre pair correlation function are

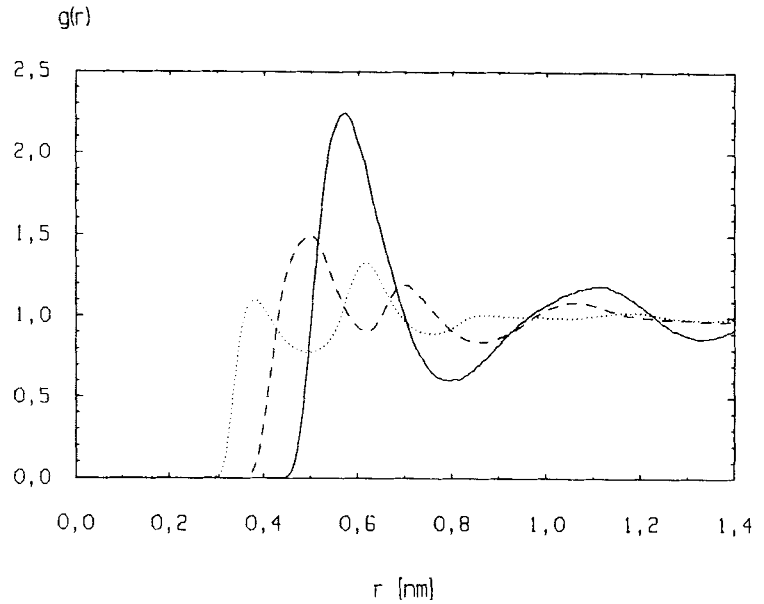

Figure 1 Atom-atom pair correlation functions of liquid CCl_4 from MD simulation (A) $g_{CC}(r)$ (———), $g_{CCl}(R)$ (– – –) and $g_{ClCl}(r)$ (· · ·) (T = 298 K, ρ = 1.5847 g/cm^3).

negligible using an anisotropic potential model is more accurate, but the additional expense of CPU time considerable. This situation can be improved if we use a centre–centre pair potential for the region between the decay of site–site and the centre–centre correlation functions. Considering CCl_4 at small distances as a five-site molecule and replacing this at larger distances by an isotropic only centre of mass dependent potential we obtain a good compromise. This method saves the CPU time required for 24 computations of distances per pair of molecules compared with the anisotropic model.

Our second test molecule is the O_h symmetric SF_6. Although, experimental data on intermolecular liquid structure is not available in the literature, we choose this molecule, because a simple anisotropic pair potential model has been presented in MD simulation studies [15, 16].

The anisotropic potential yields the largest contribution to the internal energy and, thus, it determines the conditions for the isotropic interaction model. Since potential energy is a continuous function the one-centre model has to join smoothly to the site–site model at the first cutoff distance. Describing only long-range forces the isotropic potential can be characterized as a long-range contribution to the translational equations of motion.

We suggest that the two potential approach may not be restricted to molecules with "spherical" symmetry. We argue that with vanishing site–site and centre–centre correlations we may use a long-range correction for the intermolecular pair potential model. It seems possible to generalize this algorithm to all classes of molecules, where site–site correlation is of shorter range than the centre–centre correlation. In the case of "non-spherical" molecular geometries our approach is often not necessary, since site–site and centre–centre correlations vanish at the same distance.

We stress that we intend to retain the complete anisotropic character of the potential model and to simplify it only in the range, where the interactions become mainly isotropic. This increase of the interaction radius may be very important for the calculation of dynamical properties and collision-induced phenomena.

In order to use the two potential approach we propose to regard the following aspects:

(1) Perform a short test simulation with the anisotropic potential model (Equation 2) in order to estimate the long-range behaviour of the site–site and centre–centre pair correlation functions.

(2) Choose the anisotropic cutoff r_{ca} at the distance where the site–site correlations vanish.

(3) Choose the second cutoff r_{ci} at a distance where the centre–centre correlation vanishes.

(4) Fit the isotropic potential model (Equation 3) in the range of r_{ca} to the anisotropic model (Equation 2). Note that it is sufficient to consider only the r^{-6} term of (Equation 3). Alternative procedures to obtain an effective central potential are discussed in the literature [17].

3 COMPUTATIONAL DETAILS

We have carried out four MD simulations (A, B, C, D) in the microcanonical ensemble (N, V, E) containing 864 molecules in a cubic box with periodic boundary conditions. All runs were initiated with the molecules arranged in a fcc lattice. Translational and rotational velocities were chosen randomly in direction and magnitude, both agreeing with the initial temperature. The orientation of each molecule was selected also randomly. The equations of motion were solved with a Gear–Predictor–Corrector scheme [1] (fifth order for translational motion and fourth order for rotational motion) using the quaternion formalism. The integration time-step in all MD runs was $5 \cdot 10^{-15}$ s. Equilibrium was achieved after 10 ps for CCl_4 and after 5 ps for SF_6 and the production runs were extended subsequently to 50 ps. The energy drift was lower than 1 in 10^4 for the whole simulations. In intervals of 27 steps all pair correlation functions were calculated. In order to study the influence of the two potential model approach on the translational and rotational behaviour, we computed the velocity autocorrelation function and angular velocity autocorrelation function in intervals of 10 time-steps.

The simulations A and B correspond to liquid CCl_4 at the same thermodynamic state ($T = 298$ K, $\rho = 1.5847\,\mathrm{g/cm^3}$) [18]. The bond lengths were $d_{\mathrm{CCl}} = 1.76$ Å. Simulation A was carried out with a five-centre (12-6)-Lennard–Jones model (Equation 2) which was applied in previous successful MD studies of pure CCl_4 [11] and CCl_4/CS_2 liquid mixtures [19].

Simulation B is carried out with the same potential but at a distance of 1.33 nm we switch to a one-centre-model (Equation 3). Since the isotropic potential has to be valid only for great distances, its repulsive contribution is unimportant. Thus, we constructed a (12-6)-LJ model with parameters of an (18-6)-LJ model [20]. The accuracy of the new isotropic potential is quite satisfactory. We find no significant deviation of a continuous function in the region of potential change.

The simulations C and D describe the liquid SF_6 at the thermodynamic state

Table 1 Computational parameters for the MD simulations (A, B, C, D). x and y refer to the considered molecules of type XY_n. U denotes the negative long-range correction of the configurational energy.

	CCl_4		SF_6	
	A	*B*	*C*	*D*
ε_{xx} [K]	51.2	51.2	0.0	0.0
ε_{xy} [K]	72.4	72.4	0.0	0.0
ε_{yy} [K]	102.4	102.4	60.0	60.0
ε [K]	–	320.0	–	145.0
σ_{xx} [nm]	0.460	0.460	0.0	0.0
σ_{xy} [nm]	0.405	0.405	0.0	0.0
σ_{yy} [nm]	0.350	0.350	0.270	0.270
σ [nm]	–	0.525	–	0.440
r_{ca} [nm]	1.81	1.30	1.70	1.07
r_{ci} [nm]	–	1.81	–	1.70
U [kJ/mole]	0.37	0.484	0.089	0.112

($T = 240\,\mathrm{K}$, $\rho = 1.826\,\mathrm{g/cm^3}$) [15]. The bond lengths were $d_{SF} = 1.561$ Å. In simulation C a six-site LJ model (Equation 2) of F–F interaction, which has been applied in previous MD studies [15, 16] was used. The simulation D was based on the same potential, but at a distance of 1.07 nm a one-centre LJ model (Equation 3) is introduced instead of the F–F site-site model. The isotropic potential is found by fitting the anisotropic interaction model to the one-centre function. This procedure enables a quantitative description of the total potential model for the SF_6 molecule.

Potential parameters for the used (12-6)-Lennard-Jones models are given in Table 1 together with the spherical cutoff distances and their corresponding long-range corrections for the configurational energy.

4 RESULTS

Liquid CCl_4

Thermodynamic properties

The derived mean potential energy $U = -32.2$ kJ/mole (A) and -32.3 kJ/mole (B) are in quite satisfactory agreement with previous simulations [11]. This result indicates that the used potential combination (B) can provide an acceptable prediction of the total internal energy which is very sensitive to the potential parameters. The predicted pressure of model (B) was in better agreement with the experimental one than those predicted of model (A). However, the pressure data should not be overrated since such disagreements often appear between experimental and MD pressures.

The calculated kinetic energies T of 7.6 (A) and 7.5 kJ/mole (B) are equivalent and the ratios of the translational and rotational contributions to T are 0.995 (A) and 0.999 (B) and, thus, very close to the theoretical value of 1.0. Comparing these results we find no significant differences between the thermodynamic properties of both MD studies.

Pair correlation functions

The computed pair correlation functions g_{CC}, g_{CCl}, and g_{ClCl} are given in Figure 1 (A) and Figure 2 (B). We renounce to a comparison with experimental data and refer to other simulations [11, 12] since our correlation functions are very similar to previous MD results. Positions and heights of the first two maxima and minima in the atomic pair correlation functions from simulation (A) and (B) are given in Table 2. g_{CCl} and g_{ClCl}

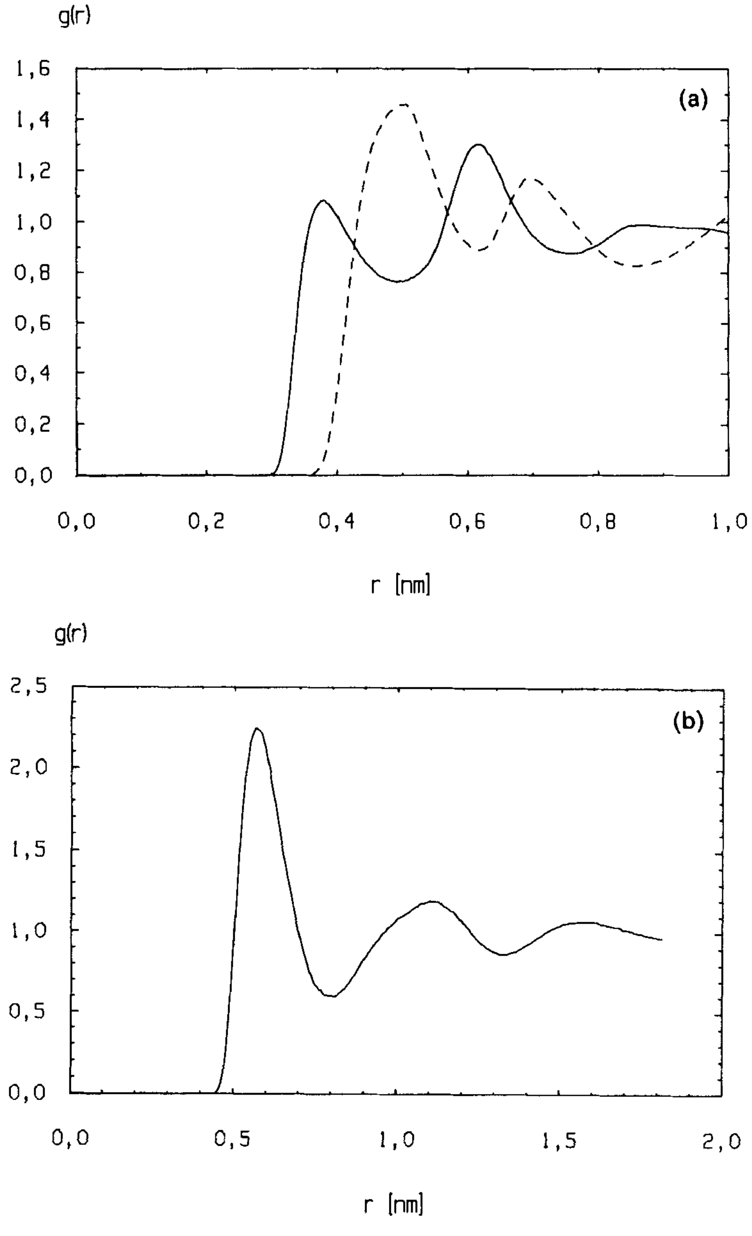

Figure 2 (a) $g_{\mathrm{CCl}}(r)$ (— — —) and $g_{\mathrm{ClCl}}/r)$ (———) of CCl_4 from simulation (B) using the two potential model approach ($T = 298$ K, $\rho = 1.5847\ \mathrm{g/cm^3}$). (b) Centre–centre pair correlation function of liquid CCl_4 from the two potential model approach (B) ($T = 298$ K, $\rho = 1.5847\ \mathrm{g/cm^3}$).

Table 2 The first two maxima and minima of the computed pair correlation functions of CCl_4 (A, B).

		A		*B*	
		r [*nm*]	$g(r)$	r [*nm*]	$g(r)$
g_{CC}	1. Max.	0.57	2.25	0.57	2.25
	1. Min.	0.80	0.60	0.80	0.60
	2. Max.	1.13	1.19	1.10	1.20
	2. Min.	1.32	0.87	1.33	0.86
g_{CCl}	1. Max.	0.50	1.49	0.51	1.46
	1. Min.	0.62	0.91	0.62	0.89
	2. Max.	0.70	1.19	0.70	1.17
	2. Min.	0.86	0.85	0.86	0.82
g_{ClCl}	1. Max.	0.38	1.10	0.38	1.09
	1. Min.	0.49	0.78	0.49	0.76
	2. Max.	0.62	1.33	0.62	1.30
	2. Min.	0.76	0.89	0.75	0.87

were calculated from atomic distances. Both simulations use the same site–site separation. Thus, small differences in peak positions and heights may arise from computational inaccuracies. g_{CC} was established from centre of mass distances up to the second cutoff in both runs. The agreement in g_{CC} between simulation (A) and (B) is quite satisfactory. That is the change of potential at $r = 1.33$ nm in run (B) does not affect the centre–centre pair correlation function.

Dynamical properties

The translational diffusion coefficients D computed by mean-square displacements is in good agreement with an experimental value [21] of $D = 1.3 \cdot 10^{-5}$ cm^2/s. We found $D = 1.35 \cdot 10^{-5}$ (A) and $D = 1.34 \cdot 10^{-5}$ cm^2/s (B). The influence of the two potential model approach also on translational and rotational behaviour may be examined by comparison of the time dependent autocorrelation functions. In Table 3 the integrated correlation times of the velocity and angular velocity autocorrelation functions are given as well as the mean-square forces F^2 and torques T^2. The agreement between the results is quite satisfactory. The corresponding diffusion coefficients from the velocity autocorrelation functions are $D = 1.55 \cdot 10^{-5}$ (A) and $D = 1.50 \cdot 10^{-5}$ cm^2/s (B). The difference to the experimental data is quite acceptable since another MD simulation [10] yields $1.75 \cdot 10^{-5}$ cm^2/s.

Table 3 Integrated correlation times of the velocity τ_v and angular velocity autocorrelation functions τ_ω and the corresponding mean-square forces F^2 and mean-square torques T^2 of the simulations (A, B, C, D).

	CCl_4		*SF_6*	
	A	*B*	*C*	*D*
τ_v [10^{-13}s]	0.95	0.92	2.53	2.49
τ_ω [10^{-13}s]	1.40	1.40	3.58	3.56
F^2 [10^{-20}N^2]	20.09	19.75	9.46	9.64
T^2 [10^{-39}J^2]	3.30	3.24	1.10	1.13

Liquid SF_6

Thermodynamic properties

The SF_6 simulations (C, D) yield configurational energies of $U = -10.7$ kJ/mole (C) and $U = -10.9$ kJ/mole (D). The same agreement may be found in the kinetic energies T of 6.0 kJ/mole for both MD runs. Also, the ratio of translational and rotational energies is identical (1.003, theoretical value: 1.0). Comparing the predicted pressures of 290 bar (C) and 300 bar (D) we find a quite satisfactory agreement between the one and two potential model approach in all thermodynamic properties. The calculated pressures are closer to the experimental value of 120 bar than the MD results of a previous study [16].

Pair correlation functions

The calculated centre–centre pair correlation functions of liquid SF_6 are given in Figure 3 for the MD runs (C) and (D). Between both ensembles no differences arise in $g_{SS}(r)$. Peak maxima and minima of these functions are depicted in Table 4. The area below the first peak of $g_{SS}(r)$ corresponds to a coordination number of 12.2 (C) and 12.0 (D). To our knowledge, no pair correlation function of liquid SF_6 is available in the literature. Our results indicate the spherical character of the SF_6 molecules, because their centre–centre pair correlation function is very similar to liquid noble gases.

Dynamical properties

For the liquid density of $\rho = 1.766\,\mathrm{g/cm^3}$ an experimental diffusion coefficient is estimated with $D = 3.35 \cdot 10^{-5}\,\mathrm{cm^2/s}$ at 240 K [22]. The computed values of $D = 2.75 \cdot 10^{-5}\,\mathrm{cm^2/s}$ (C) and $D = 2.64 \cdot 10^{-5}\,\mathrm{cm^2/s}$ (D) are in quite satisfactory agreement. The difference with the experimental result is due to the higher density of the simulated systems ($\rho = 1.826\,\mathrm{g/cm^3}$). Considering the integrated correlation times of velocity and angular velocity autocorrelation functions of Table 3 the two potential model approach shows no influence on translational and rotational motion of liquid SF_6. Small differences between mean-square forces and mean-square torques (Table 3) of the MD runs (C) and (D) may arise from computational inaccuracies.

CPU Time

The MD runs were carried out on a Convex C240 using the optimization option O2. Since we compute all pair correlation functions and time correlation functions within the simulation the CPU times can not be compared with other MD programs. The CPU time for 1000 configurations of our CCl_4 ensembles takes 4450 s (A) and 3150 s (B). Thus, introducing an additional anisotropic cutoff radius for CCl_4 savings in CPU time are about 30%. In the case of SF_6 the savings in CPU time is 45%. Due to the small first cutoff distance in run (D), we are able to reduce the CPU time for 1000 configurations from 7600 s (C) to 4040 s (D).

5 CONCLUSIONS

A new strategy is proposed for the calculation of intermolecular interactions in MD simulations of molecules with high symmetry. It is based on separating the range of interaction into a short-range anisotropic and a long-range isotropic contribution to

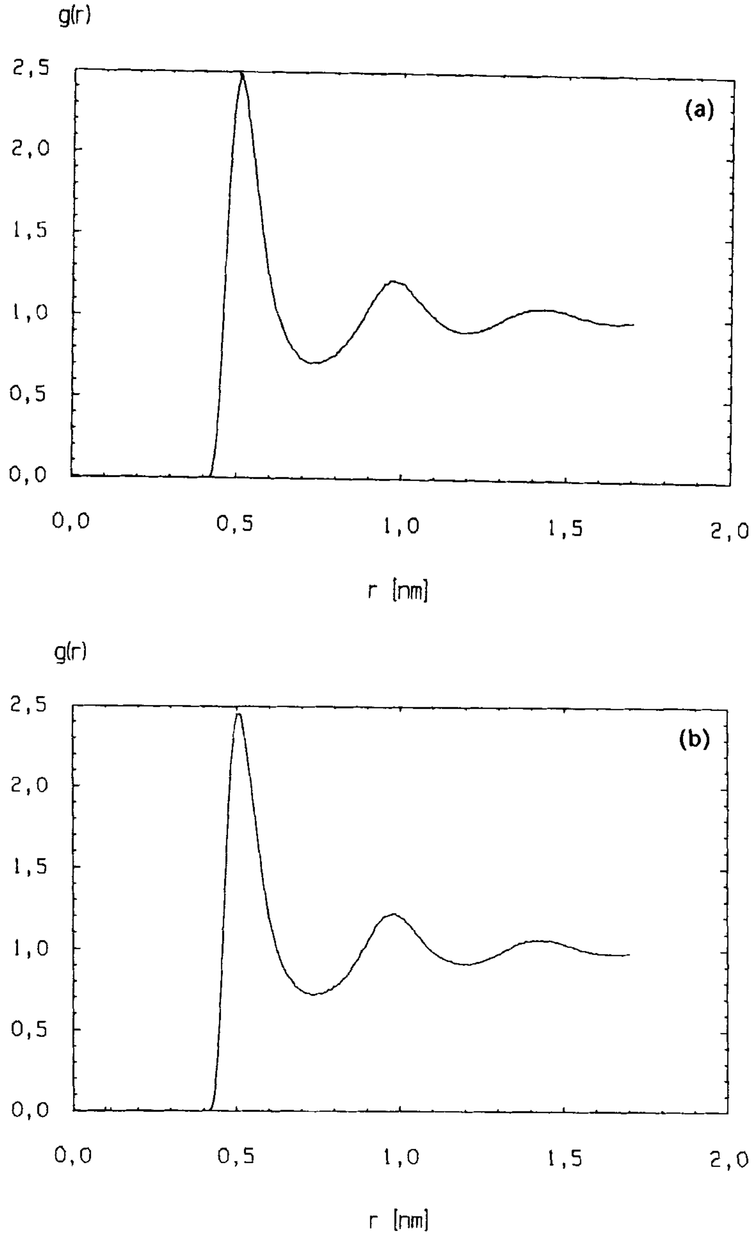

Figure 3 (a) Centre-centre pair correlation function of liquid SF_6 ($T = 240\,K$, $\rho = 1.826\,g/cm^3$) from MD run (C). (b) Centre-centre pair correlation function of liquid SF_6 ($T = 240\,K$, $\rho = 1.826\,g/cm^3$) from MD run (D) with the two potential model approach.

Table 4 The first two maxima and minima of the computed $g_{SS}(r)$ for liquid SF_6 from MD runs (C, D).

	C		*D*	
	r [*nm*]	*g*(*r*)	*r* [*nm*]	*g*(*r*)
1. Max.	0.51	2.46	0.50	2.46
1. Min.	0.74	0.71	0.73	0.72
2. Max.	0.97	1.23	0.98	1.22
2. Min.	1.18	0.91	1.20	0.91

potential energy, virial function and force between two particles. The new method is shown to be accurate in the case of the tetrahedral T_d and octahedral O_h molecular liquids. The computed thermodynamic properties, pair correlation functions, and dynamical data agree with results predicted by the commonly adopted "one cutoff" algorithm. Savings in CPU time of about 30% (CCl_4) and 45% (SF_6) point to the fact that the "two cutoff" method is a convenient elaboration in the field of MD simulation of isotropic molecules.

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References

[1] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford (1987)

[2] F. Kohler, *The Liquid State*, Verlag Chemie, Weinheim (1972) ch. 4.

[3] P.A. Egelstaff, *An Introduction to the Liquid State*, Academic Press, London (1967) ch. 2.

[4] R.L. Henderson, "A uniqueness theorem for fluid pair correlation functions", *Phys. Lett.*, **49A**, 197 (1974).

[5] C.G. Gray and K.E. Gubbins, *Theory of Molecular Fluids. I. Fundamentals*, Clarendon Press, Oxford (1984) ch. 3.

[6] A.H. Narten, M.D. Danford and H.A. Levy, "Structure and intermolecular potential of liquid carbon tetrachloride derived from X-ray data", *J. Chem. Phys.*, **46**, 4875 (1967).

[7] P.A. Egelstaff, D.I. Page and J.G. Powles, "Orientational correlations in molecular liquids by neutron scattering. Carbon tetrachloride and germanium tetrachloride", *Mol. Phys.*, **20**, 881 (1971).

[8] A.H. Narten, "Liquid carbon tetrachloride: Atomic pair correlation functions from neutron and X-ray diffraction", *J. Chem. Phys.*, **65**, 573 (1976).

[9] M. Misawa, "Temperature dependence of structure of liquid carbon tetrachloride measured by pulsed neutron total scattering", *J. Chem. Phys.*, **91**, 5648 (1989).

[10] O. Steinhauser and M. Neumann, "Structure and dynamics of liquid carbon tetrachloride. A molecular dynamics study", *Mol. Phys.*, **40**, 115 (1980).

[11] I.R. McDonald, D.G. Bounds and M.L. Klein, "Molecular dynamics calculations for the liquid and cubic plastic phases of carbon tetrachloride", *Mol. Phys.*, **45**, 521 (1982).

[12] C. Kölmel, R. Ahlrichs and B. Karch, "MD simulations of liquid CCl_4 with a new pair potential", *Mol. Phys.*, **66**, 1015 (1989).

[13] L.J. Lowden and D. Chandler, "Theory of intermolecular pair correlations for molecular liquids. Applications to the liquids carbon tetrachloride, carbon disulphide, carbon diselenide, and benzene", *J. Chem. Phys.*, **61**, 5228 (1974).

[14] O. Steinhauser and H. Bertagnolli, "Pair correlation functions of liquid CCl_4. A comparison between statistical mechanical theories and computer simulation", *Z. Phys. Chem., N.F.*, **124**, 33 (1981).

[15] C. Hoheisel, "Transport coefficients of dense fluids composed of globular molecules. Equilibrium molecular dynamics investigations using more-centre Lennard-Jones potentials", *J. Chem. Phys.*, **89**, 3195 (1988).

[16] C. Hoheisel, "Transport coefficients of liquid CF_4 and SF_6 computed by molecular dynamics using polycenter Lennard-Jones potentials", *Int. J. Thermophys.*, **10**, 101 (1989).

[17] C.G. Gray and C.G. Joslin, "Effective central potentials for molecular liquids", *Chem. Phys. Lett.*, **101**, 248 (1983).

[18] F. Mopsik, "Dielectric properties of slightly polar organic liquids as a function of pressure, volume, and temperature", *J. Chem. Phys.*, **50**, 2559 (1969).

[19] U. Mittag, J. Samios and Th. Dorfmüller, "Molecular dynamics simulation of the liquid mixture CCl_4/CS_2. I. Thermodynamic and structural properties", *Mol. Phys.*, **66**, 51 (1989).

[20] C. Hoheisel and C. Deiters, "A molecular dynamics study of the liquid mixture $CHCl_3/CCl_4$ on the basis of Lennard-Jones type potentials", *Ber. Bunsen. Phys. Chem.*, **81**, 1225 (1977).

[21] A.F. Collings and R. Mills, "Temperature-dependence of self-diffusion for benzene and carbon tetrachloride", *Trans. Faraday Soc.*, **66**, 2761 (1970).

[22] J.K. Tison and E.R. Hunt, "Self-diffusion, spin-lattice relaxation, and density of SF_6 near the critical point", *J. Chem. Phys.*, **54**, 1526 (1971).