

# Test of effective pair potential models by molecular dynamics simulation on liquid OCS

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Molecular Dynamics simulation on liquid carbonyl sulphide has been used to develop a new effective atom–atom intermolecular potential in the form of a (12-6) Lennard-Jones equation. This model has been used to study thermodynamic properties, self-diffusion coefficients and intermolecular pair correlation functions at three thermodynamic states between 243 and 300 K.

## 1. Introduction

Although the geometry of the linear molecules CO<sub>2</sub>, OCS and CS<sub>2</sub> is very similar, most of the bulk thermodynamic properties of these liquids are very different [1]. It is obvious, that the dissimilar behaviour of these liquids is predominantly due to differences of the intermolecular interactions.

As might be expected, this series of compounds has been extensively studied experimentally [2–8], as well as theoretically [9–13]. In addition, molecular dynamics (MD) simulation studies on liquid CS<sub>2</sub> and CO<sub>2</sub>, based on effective potential models, have been published by several groups in the past [14–17]. In these MD studies molecular interactions responsible for the bandshapes and intensities of forbidden FIR, IR, Rayleigh and Raman spectra have also been investigated [18–22].

In this paper we shall be concerned with the MD simulation of the liquid OCS, and our main purpose has been to find an effective atom–atom potential model, which first will reproduce the thermodynamic properties of the liquid. We then have studied the structure of this liquid and compared it with the structure of liquid CS<sub>2</sub> and CO<sub>2</sub>. Information about differences or similarities in the structure of liquids belonging to the same class may be very useful to

check theories in statistical mechanics. Finally, if the potential model can predict accurately equilibrium properties of this liquid, we aim at obtaining simple dynamical properties and spectral lineshapes.

## 2. The potential model

The crystal structure of carbonyl sulphide has been investigated by Vegard [23] and later by Overell et al. [24]. Both studies find a rhombohedral structure of the crystal group type R3m ( $C_{3v}^3$ ) with one molecule per unit cell. The characteristic cell dimensions are  $a=4.06$  Å and  $b=98.8^\circ$ . The bond lengths are  $d_{CO}=1.21$  Å and  $d_{CS}=1.51$  Å. The molecule lies along the crystal threefold axis. The lattice energy has been estimated to approximately  $-28.1$  kJ/mol [25,26].

For the first time and on the basis of these results, Deakin et al. [26] reported a lattice dynamics study on carbonyl sulphide. Their purpose was to evaluate an intermolecular effective potential model, which should be able to fit the experimental lattice energy, the lattice parameters and the fundamental IR–Raman frequencies [27,28]. In this study several potential models were tested and the authors concluded, that “the conventional atom–atom model is never suitable without augmentation and that, out of

the range of possibilities considered, the effect of the high molecular octupole moment must be included, either directly or indirectly". They also point out that a type of potential model, first introduced by Berne and Pechukas [29], with an octupole electrostatic contribution is satisfactory. Finally, they were not successful in reproducing the crystal properties using atomic charges to mimic the molecular octupole electrostatic contribution.

In our treatment we have tested by MD simulation two models of effective pair potentials for the liquid OCS. The first one is the model proposed by Deakin et al., which is proved to give reasonable  $\epsilon$  values and real normal mode frequencies of crystalline OCS. It is a three centre Lennard-Jones potential plus octupole–octupole electrostatic interaction. This means that the potential energy between a pair of OCS molecules is given by

$$U_{12}(r_{ij}, \omega_1, \omega_2) = \sum_{\alpha=1}^3 \sum_{\beta=1}^3 u_{\alpha\beta}^{12}(r_{\alpha\beta}) + U_{\Omega_1\Omega_2}^{12}, \quad (1)$$

where

$$u_{\alpha\beta}^u(r_{\alpha\beta}) = 4\epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^6 \right] \quad (2)$$

is a (12–6) LJ potential function and  $U_{\Omega_1\Omega_2}^{12}$  the octupole–octupole energy of the molecular pair. The first term of eq. (1) includes nine distinct site–site interactions between two OCS molecules, and one thus needs a set of six pairs of the potential parameters ( $\epsilon_{\alpha\beta}$ ,  $\sigma_{\alpha\beta}$ ), corresponding to SS, CC, OO, CS, CO and SO pairs of atoms.

The parameter values are shown in table 1. These values are those used in [26], they have been modified however to fit our form of the LJ potential as given in eq. (2). As we can see, the three like–like atom pair SS, CC and OO length potential param-

eters  $\sigma_{\alpha\alpha}$  and their potential well-depths  $\epsilon_{\alpha\alpha}$  are equal to each other and take the values 0.329 nm and 31.502 K, respectively. Another point which must be noted here, is the physical sense of the potential parameters for the unlike pairs CO, SO, and CS. The lengths  $\sigma_{\alpha\beta}$  have equal values and the well-depths  $\epsilon_{\alpha\beta}$  are different.

Actually, these site–site potential parameters, which characterize the repulsive and dispersive part of the molecular interactions, seem to be unrealistic in the sense of representing the shape of the carbonyl sulphide. However, in order to test to what extent the thermodynamic properties of the liquid dependent on the site–site potential parameters, we have carried out a MD simulation using this LJ potential first without electrostatic interactions. In a second run the octupole–octupole interactions have been also directly included in addition to the LJ part as indicated in eq. (1). Results from both MD simulations are shown in table 3.

For a given pair of OCS molecules, called 1 and 2, the octupole–octupole electrostatic interactions have been calculated taking into account the following data. It is well known, that the ground state of the OCS molecule has an  ${}^1\Sigma^+$  symmetry in  $C_{\infty v}$  configurations and in this case the charge distribution is axially symmetric. According to the one-point multipole expansion theory [30] for a given charge distribution, we obtain the potential energy  $U_{\Omega_1\Omega_2}^{12}$  from

$$U_{\Omega_1\Omega_2}^{12} = -T_{\alpha\beta\gamma\delta\epsilon\lambda}^{21} \left[ \frac{1}{225} \Omega_{\alpha\beta\gamma}^1 \Omega_{\delta\epsilon\lambda}^2 \right], \quad (3)$$

where the tensor  $T_{\alpha\beta\gamma\delta\epsilon\lambda}^{21}$  is given by

$$T_{\alpha\beta\gamma\delta\epsilon\lambda}^{21} = \nabla_{\alpha} \nabla_{\beta} \nabla_{\gamma} \nabla_{\delta} \nabla_{\epsilon} \nabla_{\lambda} (r_{12}^{-1}), \quad (4)$$

where  $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$  is the vector between the centres of mass of the molecules 1 and 2.  $\Omega_{\alpha\beta\gamma}^1$  and  $\Omega_{\delta\epsilon\lambda}^2$  are the octupole tensor components of the molecules as given,

Table 1  
Atom–atom LJ potential parameters and molecular octupole moment for the liquid OCS from ref. [26]

Parameter	OCS–OCS					
	S–S	C–S	S–O	C–O	C–C	O–O
$\epsilon$ [K]	31.502	103.706	24.809	168.481	31.502	31.502
$\sigma$ [nm]	0.329	0.347	0.347	0.347	0.329	0.329

$$\Omega_{\text{OCS}} = 10 \text{ D } \text{\AA}^2.$$

$$\Omega_{\alpha\beta\gamma} = \frac{1}{2}\Omega_0(5l_{\alpha}l_{\beta}l_{\gamma} - l_{\alpha}\delta_{\beta\gamma} - l_{\beta}\delta_{\alpha\gamma} - l_{\gamma}\delta_{\alpha\beta}). \quad (5)$$

$l_{\alpha}$  is a component of the unit vector  $\mathbf{u}$  along the axis of symmetry and  $\Omega_0$  represents the molecular octupole moment. We note that the calculations of the octupole–octupole intermolecular interactions were extremely time consuming due to the high dimensionality of eqs. (3) and (4).

The second potential model, which is used throughout this treatment is an effective 12–6 LJ potential model for liquid OCS. For each molecule we have employed three interaction centres located on the atomic nuclei, where the bond lengths  $d_{CS}$  and  $d_{CO}$  were taken from gas phase experimental results to be equal to 1.561 and 1.164 Å [9,31], respectively. In order to determine the six potential parameter pairs  $(\sigma, \epsilon)$  used in this model, we have taken into account the potential parameters of the molecules  $CS_2$  and  $CO_2$ . In fact, the geometry of the molecule OCS is intermediate between the geometries of  $CS_2$  and  $CO_2$ . This motivated us to use as starting values for  $(\sigma_{SS}, \epsilon_{SS})$  and  $(\sigma_{OO}, \epsilon_{OO})$  the values from previous successful MD studies of the pure liquids  $CS_2$  and  $CO_2$ , respectively. The most difficult choice is that of the starting values for carbon–carbon  $\sigma_{CC}$  and  $\epsilon_{CC}$ . As we can see in table 2, in the MD study of liquid  $CS_2$  the  $\sigma_{CC}$  and  $\epsilon_{CC}$ , which have been taken from the five centre potential model of liquid methane [32], are greater than the estimated corresponding values of liquid  $CO_2$  [14]. On the other hand, the carbon–carbon  $\sigma_{CC}$  and  $\epsilon_{CC}$  of OCS must be physically reasonable, i.e. both must be lower than the  $\sigma_{SS}$  and  $\epsilon_{SS}$  of  $CS_2$  and also lower than the  $\sigma_{OO}$  and  $\epsilon_{OO}$  values of  $CO_2$ . Because the  $\sigma_{CC}$  of  $CS_2$  is greater than the  $\sigma_{OO}$  of  $CO_2$  and the  $\sigma_{CC}$  of  $CO_2$  is small than  $\sigma_{SS}$  and  $\sigma_{OO}$ , we have chosen as starting parameters  $\sigma_{CC}$

and  $\epsilon_{CC}$  for OCS those of the  $CO_2$  molecule.

A few MD computation tests sufficed to readjust the starting parameters in order to obtain internal energy and pressure in satisfactory agreement with experiment. The atom–atom potential parameters for this model are shown in table 2. The cross interaction parameters are obtained by the usual Lorentz–Berthelot combining rules, i.e.  $\epsilon_{ij} = [\epsilon_{ii}\epsilon_{jj}]^{1/2}$  and  $\sigma_{ij} = \frac{1}{2}[\sigma_{ii} + \sigma_{jj}]$ . Finally, the potential models are represented in fig. 1.

### 3. MD computational details and thermodynamic results

Our MD calculations were carried out in the microcanonical ensemble (N, V, E) containing 864 molecules in a cubic box with the usual periodic boundary conditions. We have chosen three thermodynamic states at the temperatures 243, 273 and 300 K and corresponding densities for which experimental data are available [1]. In all simulations the cut-off radius was equal to the half box length  $L$ . The translational and rotational equations of motion were integrated by using a fifth- and a fourth-order predictor–corrector algorithm based on the quaternion method. Several thousand integration steps were necessary in order to ensure equilibrium. Each simulation was extended subsequently to 52.5 ps with an integration time step  $\Delta t = 3.5 \times 10^{-15}$  s. The relative energy drift was lower than  $1/10^4$  for the total simulation. A few supplementary runs have also been performed in order to check the accuracy of the results. All MD runs were performed on a CONVEX C240 four processor computer. The important computational data are tabulated in table 3.

Table 2  
Atom–atom LJ potential parameters for the liquids OCS<sup>a)</sup>,  $CS_2$ <sup>b)</sup> and  $CO_2$ <sup>c)</sup>

Parameter	OCS–OCS <sup>a)</sup>						$CS_2$ – $CS_2$ <sup>b)</sup>			$CO_2$ – $CO_2$ <sup>c)</sup>		
	S–S	C–C	C–S	O–O	S–O	C–O	S–S	C–C	C–S	O–O	C–C	C–O
$\epsilon$ [K]	178.0	29.0	71.85	78.0	117.83	47.66	183.0	51.2	96.8	83.1	29.0	49.1
$\sigma$ [nm]	0.360	0.284	0.322	0.302	0.331	0.293	0.352	0.335	0.344	0.301	0.278	0.289

<sup>a)</sup> This work.

<sup>b)</sup> Tildesley and Madden in ref. [17], model A.

<sup>c)</sup> Murthy et al. in ref. [14]: the parameter values are transformed to the LJ potential form used in this work (eq. (2)).

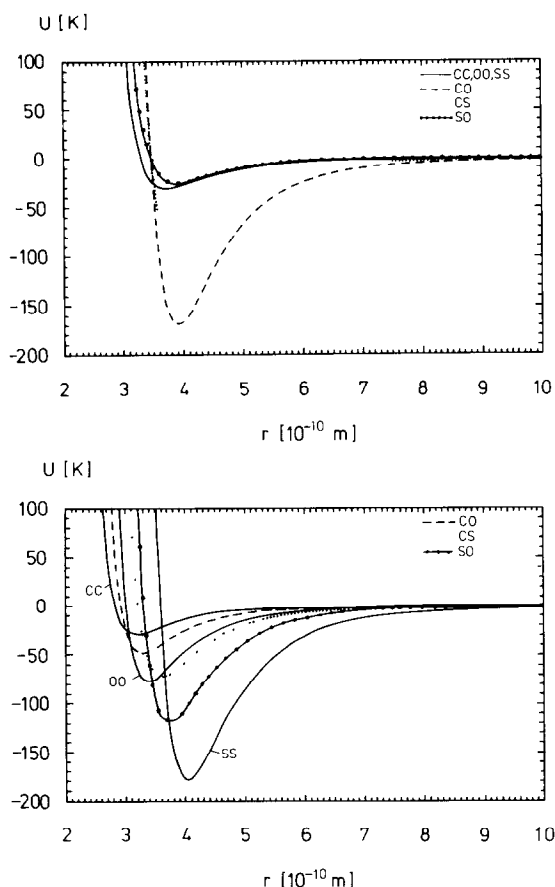


Fig. 1. Atom-atom Lennard-Jones potential models for the liquid OCS. Upper curve: LJ models with the parameters of the lattice dynamics study (table 1). Lower curve: LJ models with the parameters of this work (table 2).

On the basis of the results presented in table 3, agreement with experimental internal energy and pressure is quite satisfactory for our simple three-centre LJ model. Similar very small disagreements between computed and experimental values in the internal energy and pressure have been also found in the most successful MD simulation studies of other small molecules.

On the contrary, the results show that the LJ part of the lattice dynamics potential yields a less adequate description of OCS at liquid densities. The internal energy is too low by about 1 kJ/mol, which indicates too strong attractive forces in the liquid phase. Also, the calculated pressure is unrealistic, because it was found to take a too low value. A MD run with the

full lattice dynamics potential (LJ plus  $\Omega$ - $\Omega$  interaction) yields an additional contribution of 0.9 kJ/mol to the internal energy using an octupole moment of  $10 \text{ D } \text{\AA}^2$ .

#### 4. The self-diffusion coefficients

The self-diffusion coefficients  $D$  were calculated in the MD runs for each temperature using the well-known Einstein relation

$$2D = \lim_{t \rightarrow \infty} \frac{1}{3Nt} \sum_{i=1}^N \langle |r_i(t) - r_i(0)|^2 \rangle, \quad (6)$$

where  $r_i(t)$  and  $\langle |r_i(t) - r_i(0)|^2 \rangle$  is the centre-of-mass molecular position and its mean-square displacement of molecule  $i$ . The calculated values are shown in table 3.

To our knowledge, at the present time no experimental data about the diffusion coefficients and viscosities are available in the literature for the liquid OCS. However, the change of the predicted values with temperature shows the correct tendency. Comparing our diffusion coefficients with experimental and simulated values of liquid  $\text{CS}_2$  [33] and with calculated results of liquid  $\text{CO}_2$  [34], we estimate the predicted OCS data to be realistic.

#### 5. Intermolecular pair correlation functions

A complete description of the liquid intermolecular structure requires the evaluation and analysis of the atom-atom pair correlation functions (PCFs)  $g_{\alpha\beta}(r)$  and of the orientation correlation functions. The functions  $g_{\alpha\beta}(r)$  give the normalized probability of finding an atom  $\beta$  in one molecule a distance  $r$  apart from an atom  $\alpha$  located in a second molecule. For each simulated state the six atom-atom and the centre of mass (COM) pair correlation functions have been calculated and discussed. The characteristic extrema of all COM-COM pair correlation functions are given in table 4. Also the peak positions and heights of the atom-atom PCFs of the thermodynamic state at  $T = 273 \text{ K}$  are listed.

The COM pair correlation function is studied first. As we can see in fig. 2, this function exhibits two distinct peaks. The first peak is centered about  $4.7 \text{ \AA}$  and

Table 3

Temperature, molar volume, diffusion coefficients, internal energy and the pressure of the MD simulation. The experimental  $V_m$ ,  $U$  and  $p$  are from ref. [1]. The experimental internal energy is approximated by  $U = RT - \Delta H_{\text{vap}}$ . Fluctuations in  $U$  and  $T$  are 0.07 kJ/mol and 3.5 K. The error in  $D$  lies within 10 percent approximately

Run <sup>a)</sup>	$T$ (K)	$V_m$ (cm <sup>3</sup> /mol)	$D$ (10 <sup>-5</sup> cm <sup>2</sup> /s)	$U$ (kJ/mol)		$P$ (bar)	
				sim.	exp.	sim.	exp.
A	243	53.16	3.52	-15.3	-15.7	-13	2.1
A	273	57.264	4.51	-14.0	-14.4	1	6.2
A	300	62.14	5.17	-12.7	-12.5	32	12.8
B	300	62.14	5.01	-13.6	-12.5	-53	12.8
C	300	62.14	4.94	-14.4	-12.5	-460	12.8

<sup>a)</sup> A: This work. B: LJ potential model of the lattice dynamics study ref. [26]. C: LJ potential model of ref. [26] plus octupole–octupole interaction with a molecular octupole moment of 10 D Å<sup>2</sup>.

Table 4

Positions in (Å) and amplitudes ( $r/g(r)$ ) of the extrema of the computed atom–atom pair correlation functions ( $T=273$  K) and of the COM–COM pair correlation functions for all temperatures <sup>a)</sup>. Peaks denoted with “s” are small sholders of the following maxima

$g_{\alpha\beta}(r)$	Maxima		Minima		
S–S	3.96/1.80	6.04/0.97	7.78/1.05	5.41/0.93	6.57/0.93
C–C	4.25/1.20s	4.83/1.29	8.45/1.04	6.52/0.90	
O–O	3.24/1.49	5.99/1.09		4.64/0.86	
S–O	3.62/1.62	6.86/1.06		4.98/0.90	
C–S	4.15/1.32s	4.35/1.35	8.07/1.04	6.28/0.90	
C–O	3.86/1.20s	4.11/1.24	7.39/1.05	5.65/0.92	
COM (A)	4.62/1.45	8.20/1.06		6.45/0.82	
COM (B)	4.78/1.43	8.45/1.06		6.57/0.84	
COM (C)	4.81/1.41	8.64/1.05		6.65/0.86	
COM (D)	4.62/1.46	8.59/1.06		6.75/0.83	

<sup>a)</sup> The COM–COM pair correlation functions are calculated with the potential of this work at 243 K (A), 273 K (B) and 300 K (C). “D” denotes the LJ potential model without octupole–octupole interaction of ref. [26] at 300 K.

the second smoother peak at about 8.5 Å. The first coordination shell contains  $12.1 \pm 0.2$  molecules at 243 K, and  $11.7 \pm 0.3$  molecules at 300 K. The coordination number shows a very small temperature dependence. The shapes of the three functions do not change dramatically in the studied temperature range. A comparison between the correlation functions at 243 and 300 K shows this situation clearly.

At very short distances the three correlation functions show a number of small local structures, which are more distinct at low temperature. This feature has also been found in the study of the liquid structure of CS<sub>2</sub> [17,35].

Finally, we have calculated the COM–COM relation function at 300 K with the lattice dynamics LJ potential model. Fig. 2d shows this function, which

is similar in all details to the other three functions.

More information on the intermolecular ordering may be supplied by using the site–site pair correlation functions. For the molecules OCS there are six independent site–site PCFs:  $g_{SS}$ ,  $g_{CC}$ ,  $g_{OO}$ ,  $g_{SO}$ ,  $g_{CS}$  and  $g_{CO}$ . These functions are illustrated in fig. 3 at 273 K. We should note that they do not change significantly in the studied temperature range. The functions  $g_{SS}$ ,  $g_{OO}$  and  $g_{SO}$  exhibit a sharp first peak at distances shorter than 4.0 Å (table 4) followed by a minimum. The other three PCFs display a broad peak of weaker amplitude in contrast to the SS-, OO- and SO-functions.

Comparing our  $g_{SS}$  with the corresponding function of CS<sub>2</sub> [14] we find a significant difference in the region of the first minimum. In OCS a very weak

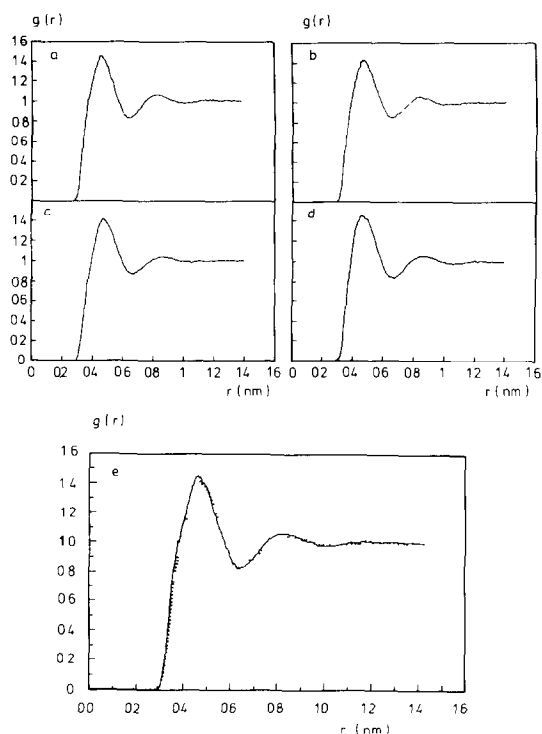


Fig. 2. Centre-of-mass pair correlation functions of liquid OCS at 243 K (a), 273 K (b) and 300 K (c) of our potential model; (d) denotes the centre-of-mass pair correlation function of the lattice dynamics LJ model [26]. In (e) the functions at 243 K (—) and 300 K (...) of our potential model are plotted to show the temperature dependence of  $g(r)$ .

maximum appears at 6.04 Å, which has not been observed in the case of  $\text{CS}_2$ . Without regard to peak heights the  $g_{\text{SO}}$  of OCS may be described like the SS-PCF of  $\text{CS}_2$  at the high temperature state. Due to the different bond lengths in the OCS molecule the two peaks of the first maximum in the  $g_{\text{CS}}$  and  $g_{\text{CC}}$  of  $\text{CS}_2$  merge to a broad peak in the corresponding OCS functions. All three PCFs CO, CC, CS, are, as expected, very similar in shape due to the similarity of the steric situation. On the other hand the PCFs SS, OO, SO, are distinctly sharper peaked as a consequence of the position of these atoms in the OCS molecule. The  $g_{\text{OO}}$  of OCS differs from the corresponding  $\text{CO}_2$ -function [15] in the range of the second maximum.

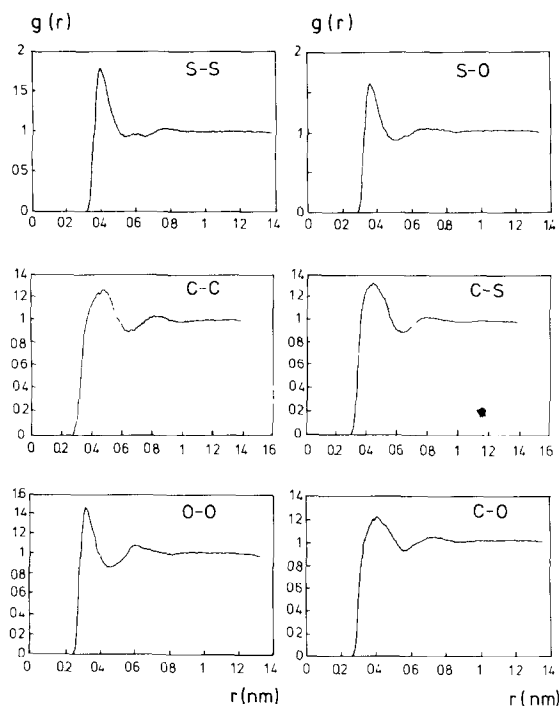


Fig. 3. Atom-atom pair correlation functions of liquid OCS at 273 K.

## 6. Summary and conclusions

In this paper we reported the first MD simulation on the liquid OCS at three temperatures. The obtained results can be summarized as follows:

(a) The three centre Lennard-Jones model, which has been proposed in this study, gives a very good description of the equilibrium properties (internal energies and pressures) of the system in the temperature range from 243 to 300 K. The potential model of previous lattice dynamics studies, which is a site-site Lennard-Jones model plus octupole-octupole interaction, has also been tested. The results show that this model can not predict the internal energy and pressure of liquid OCS.

(b) The calculated self-diffusion coefficients are found to have realistic values compared with results for molecules of similar shape.

(c) The intermolecular pair correlation functions have been obtained. The centre of mass and the site-site pair correlation functions show similarities with those of the liquids  $\text{CO}_2$  and  $\text{CS}_2$ . In order to confirm

this computed intermolecular structure neutron scattering investigations of this liquid are encouraged.

Finally, a very small correction of our predicted site-site potential model by introducing electrostatic interactions may be considered. However, test calculations with our LJ model taking into account the small dipole moment on the OCS molecule, have shown, that this electrostatic contribution does not affect the above results significantly. Obviously our effective LJ potential is to some extent able to accommodate the electrostatic interactions with reasonable values of its parameters. Work on a possible combination of the predicted LJ model with electrostatic interactions is in progress.

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