

This article was downloaded by:

On: 14 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Molecular Simulation

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713644482>

### A Molecular Dynamics Simulation Study of Liquid Carbon Tetrachloride

Ilario G. Tironi<sup>a</sup>; Patrick Fontana<sup>a</sup>; Wilfred F. van Gunsteren<sup>a</sup>

<sup>a</sup> Laboratorium für Physikalische Chemie, ETH Zentrum, Zürich, Switzerland

**To cite this Article** Tironi, Ilario G. , Fontana, Patrick and van Gunsteren, Wilfred F.(1996) 'A Molecular Dynamics Simulation Study of Liquid Carbon Tetrachloride', *Molecular Simulation*, 18: 1, 1 – 11

**To link to this Article:** DOI: 10.1080/08927029608022351

**URL:** <http://dx.doi.org/10.1080/08927029608022351>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# A MOLECULAR DYNAMICS SIMULATION STUDY OF LIQUID CARBON TETRACHLORIDE

ILARIO G. TIRONI, PATRICK FONTANA and  
WILFRED F. VAN GUNSTEREN

*Laboratorium für Physikalische Chemie, ETH Zentrum,  
CH-8092 Zürich, Switzerland.*

*(Received April 1996; accepted April 1996)*

We present an all-atom force field model for liquid carbon tetrachloride for use in molecular dynamics simulations. The model is rigid with tetrahedral symmetry and the molecular interactions are represented in terms of site-site Lennard-Jones potential energy functions. With the molecular dynamics method we are able to accurately predict physical quantities of  $\text{CCl}_4$  including shear viscosity, the excess Helmholtz energy and the surface tension.

**Keywords:** Carbon tetrachloride; molecular dynamics; viscosity; surface tension.

## 1. INTRODUCTION

Computer simulation studies have gained increasing importance within many areas of current research [1]. The molecular dynamics method is being applied standardly for simulations of molecular liquids and fluids. In many cases these fluids are modelled by simple pair-wise additive potential energy functions. The advantages of simple interaction functions are manifold: the ease of implementation, the rapid evaluation on general purpose hardware, the relatively modest number of parameters and the possibility to generalize to macromolecules and large molecular systems. Although each interaction function has its intrinsic limitations in describing molecular systems, its correct parametrization is of fundamental importance for an accurate representation of the system.

In a recently performed MD simulation of carbon tetrachloride, some shortcomings of the  $\text{CCl}_4$  force field used emerged [2]. The  $\text{CCl}_4$  model considered in the calculation was a one-site united atom model [3]. During the course of a constant pressure simulation it was noticed that the solvent had a tendency to expand to low density (gas). The subsequent inspection of the phase diagram of a Lennard-Jones fluid showed that a united atom force field is not able to fulfil the thermodynamic constraints (density, heat of vaporization, pressure, temperature) implicit in the state points of liquid  $\text{CCl}_4$ . Therefore it was decided to investigate a model force field for  $\text{CCl}_4$  using an all-atom description.

Several all-atom  $\text{CCl}_4$  interaction functions have been proposed in the literature so far [4–7]. Chang *et al.* [7] have reported a polarizable force field which includes partial charges on five interaction sites. Although polarizability is of major concern in polar molecules and contributes significantly to the interaction energy, we refrain from using polarizable atoms in this specific case. The introduction of polarizability induces an increment in the computational effort of at least a factor of two. Further, using polarizability in simulations consisting of a macromolecule solvated by a small-molecule liquid, such as carbon tetrachloride, would necessitate the incorporation of polarizability also for the atoms of the macromolecule. Also, due to the tetrahedral symmetry of the  $\text{CCl}_4$  molecule, the first non-vanishing term in the electrostatic multipole expansion is the octopole moment. An octopole-octopole interaction scales with  $r^{-7}$  which compares to induced dipole induced dipole (polarizability) that scales with  $r^{-6}$  (e.g. Lennard-Jones dispersion term). Therefore, the inclusion of electrostatic terms will have a minor influence on the energy of the system and as a first approximation can be accounted for by the normal Lennard-Jones term.

The purpose of this study is to present a pair-wise additive force fields for liquid carbon-tetrachloride and to extend the calculation of properties to thermodynamic relevant quantities which have been neglected so far in the literature [3–7]. The force field has been designed to allow for a simulation of a general macromolecule in a  $\text{CCl}_4$  solvent environment. Thus, the intermolecular potential energy is of the general GROMOS87 form [8]. The parameters were fitted to the experimental heat of vaporization and density. With the optimal parameter set, a series of classical molecular dynamics simulations were performed to validate the force field.

## 2. MOLECULAR INTERACTION FUNCTION AND SIMULATIONS

The interaction function for a pair of atoms  $a$  and  $b$  belonging to two distinct molecules  $i$  and  $j$  is of the form

$$U(r_{iajb}) = \sum_{i=1}^{N-1} \sum_{j>i}^N \sum_{a=1}^5 \sum_{b=1}^5 \left( \frac{C_{12}(ab)}{r_{iajb}^{12}} - \frac{C_6(ab)}{r_{iajb}^6} \right) \quad (1)$$

in which  $r_{iajb}$  is the distance between sites  $ia$  and  $jb$ . The Lennard-Jones parameters  $C_{12}(ab)$  and  $C_6(ab)$  for  $a \neq b$  are obtained as the geometrical mean of the parameters  $C_{12}(aa)$  and  $C_{12}(bb)$  and of  $C_6(aa)$  and  $C_6(bb)$ . The interaction between two molecules is only computed if their centre of mass distance is less than  $R_{\text{cut}} = 1.4$  [nm]. Internal degrees of freedom were not treated and each molecule was constrained to adopt a fixed geometry (Tab. I) by using the SHAKE method [9] with a relative precision of  $10^{-5}$ . In view of the tetrahedral symmetry imposed on the  $\text{CCl}_4$  molecule no partial charges were taken into account. A cubic box of 3.259 [nm] length with 216  $\text{CCl}_4$  molecules served as simulation system. Simulations were performed in the NVT and NPT ensemble using the Berendsen thermostat and manostat [10]. The coupling constant for the heat bath was set to 0.1 [ps]. A relaxation time of 0.2 [ps] with a compressibility of  $1.041 \cdot 10^{-9}$  [ $\text{m}^2 \text{N}^{-1}$ ] was used for the pressure bath. The mass of  $\text{CCl}_4$  was taken as 153.82 [u]. The trajectories were integrated using a time step of 2 [fs]. All simulations were carried out with the GROMOS87 MD program [8].

Starting from the van der Waals parameters given in [11] the potential energy surface was explored by performing trial simulations in the NVT ensemble at a temperature of 293 [K] and at an experimental density of

TABLE I Parameters of the Lennard-Jones 6-12 potential energy function and geometry of the rigid carbon tetrachloride model

	$C_6(ab)$ [ $10^{-3} \text{ kJ mol}^{-1} \text{ nm}^6$ ]	$C_{12}(ab)$ [ $10^{-6} \text{ kJ mol}^{-1} \text{ nm}^{12}$ ]
C – C	2.6309	7.600
C – Cl	4.4727	9.8507
Cl – Cl	7.604	12.768
$d_{\text{C-Cl}}$ [nm]	0.1760	
$d_{\text{C-Cl}}$ [nm]	0.2874	
$\angle_{\text{Cl-C-Cl}}$ [°]	109.47	

1595 [kgm<sup>-3</sup>]. The target value for the potential energy was the experimental heat of vaporization,  $-32.4$  [kJmol<sup>-1</sup>] [12]. For each parameter set, the configuration was energy minimized before performing a 50 [ps] molecular dynamics simulation. The refined Lennard-Jones parameter values and the geometry of the CCl<sub>4</sub> molecule are listed in Table I.

### 3. PHYSICAL PROPERTIES OF CCl<sub>4</sub> FROM COMPUTER SIMULATION

#### 3.1. Radial Distribution Functions

Structural properties can be obtained by calculating the different pair radial distribution functions. The pair correlation functions  $g(r)$  as computed from a 50 [ps] NPT simulation are shown in Figure 1. The pair correlation functions derived from experimental data [13] are shown as dashed curves. It is interesting to note the differences in agreement between the calculated  $g(r)$  and the one derived from experiment for the Cl-Cl and the C-Cl pairs. While in the case of the Cl-Cl pair correlation function the disagreement is within an acceptable range, the C-Cl curve is too far off from the one derived from experiment. Although the positions of the peaks compare well for MD and experiment in both cases, the discrepancies in the minima and maxima of Figure 1b are unacceptably large. This cannot be explained in terms of usual statistical errors. The computation of pair distribution functions from a MD trajectory is a trivial task and the precision is the same for all types of atom pairs. This is not true for the experimentally determined pair distribution functions. The neutron or X-ray diffraction data has to be deconvoluted using isotope substitution in order to obtain the different pair correlation functions. Since the agreement between experiment and MD is satisfactory for the Cl-Cl pair, and the chlorine-chlorine pair contributes more than 70% to the structure factor, there is only little room to bring the molecular dynamics results closer to the experimentally derived functions for the C-Cl case.

#### 3.2. Translational and Rotational Diffusion

The translational self-diffusion coefficient  $D$  and the rotational correlation times  $\tau_1$  and  $\tau_2$  were calculated from a NPT trajectory over 50 [ps] and are

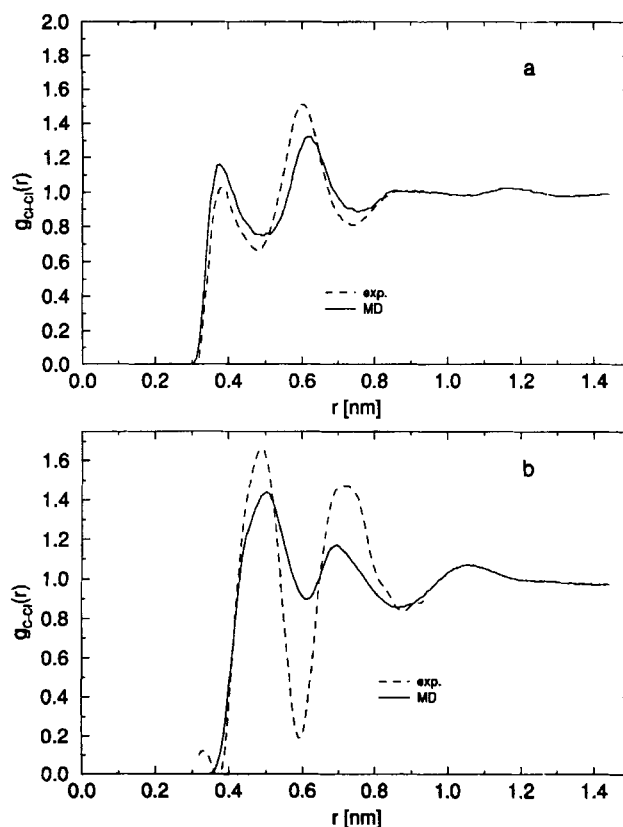


FIGURE 1 Radial distributions functions for the chlorine-chlorine and the carbon-chlorine pairs calculated from a 50 [ps] MD simulation of 261  $\text{CCl}_4$  molecules and as derived from experiment.

given in Table II. Considering the diffusion coefficient, the mobility of the  $\text{CCl}_4$  molecule is overestimated compared to the experimental value. The neglect of polarization interaction could serve as an explanation for the underestimated molecular attraction. However, comparing with the diffusion coefficient of the polarizable force field of Chang *et al.* [7], which is reported to be  $1.8 [10^{-1} \text{ m}^2\text{s}^{-1}]$ , this argument loses its weight.

### 3.3. Free Energy

The excess Helmholtz energy is the change in free energy for transferring a sample of  $\text{CCl}_4$  from the liquid to the gas phase under constant volume. In

TABLE II Physical properties of the  $\text{CCl}_4$  force field at 293[K] calculated from different molecular dynamics simulations (MD) and data obtained from experiment (Exp.). The surface tension has been calculated from the mean value quoted in Table III plus the tail correction.  $^a)\Delta H_{\text{vap}} = -E_{\text{pot}} + RT$  and quantum corrections have been neglected

		MD	Exp.
density	$[\text{kgm}^{-3}]$	1601	1595.0 <sup>[15]</sup>
heat of vaporization <sup>a)</sup>	$[\text{kJmol}^{-1}]$	32.45	32.40 <sup>[12]</sup>
diffusion coefficient	$[10^{-9}\text{m}^2\text{s}^{-1}]$	1.8	1.15 <sup>[16]</sup>
rotational correlation times	$[\text{ps}]$		
$\tau_1$		5.1	4.5 <sup>[16]</sup>
$\tau_2$		2.0	1.8
excess Helmholtz energy	$[\text{kJmol}^{-1}]$	15.8	16.3 <sup>[16]</sup>
shear viscosity	$[\text{cP}]$	0.88	0.96 <sup>[16]</sup>
surface tension	$[10^{-3}\text{Nm}^{-1}]$	28.8	26.8 <sup>[16]</sup>

the thermodynamic integration formalism this quantity can be calculated by MD using Equation (2)

$$\Delta A = \int_1^0 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_{\lambda} d\lambda. \quad (2)$$

The potential energy function  $U$  is now a function of a new parameter  $\lambda$ , which forces the system from a thermodynamic state at  $\lambda = 1$  (liquid) to an other state at  $\lambda = 0$  (gas) in the course of a simulation. The functional form of  $U$  is

$$U(r_{iajb}; \lambda) = \lambda^5 \sum_{i,j,a,b} \frac{C_{12}(ab)}{r_{iajb}^{12}} - \lambda^3 \sum_{i,j,a,b} \frac{C_6(ab)}{r_{iajb}^6}. \quad (3)$$

Changing  $\lambda$  from 1 to 0 in a 200 [ps] NVT simulation gives ensemble averaged  $\langle \partial U / \partial \lambda \rangle_{\lambda}$  values which can be integrated to yield the excess Helmholtz energy. To test for the reversibility of the calculation (and thus the accuracy), a reversed simulation was performed where  $\lambda$  was changed back from 0 to 1. The Helmholtz energy obtained from these two paths differed by 0.4  $[\text{kJmol}^{-1}]$ , indicating a small hysteresis. The mean of the two values is given in Table II. We note that the Helmholtz energy is not just equal to the heat of vaporization of the system but that there is in fact an entropic contribution which lowers the potential energy value by about 50%.

### 3.4. Shear Viscosity

The shear viscosity  $\eta$  was calculated during a 1 ns equilibrium simulation in the NVT ensemble using

$$\eta = \frac{V}{2k_B T} t^{-1} \left\langle \left[ \int_0^t p_{\alpha\beta}(t') dt' \right]^2 \right\rangle \quad \alpha, \beta = x, y, z \quad \alpha \neq \beta \quad (4)$$

where  $V$  is the volume of the box,  $T$  the temperature and  $k_B$  Boltzmann's constant. The off-diagonal elements  $p_{\alpha\beta}$  of the pressure tensor were computed using the molecular definition of the virial.

$$p_{\alpha\beta} = \frac{1}{V} \left[ \sum_{i=1}^N M_i (\mathbf{V}_i \cdot \mathbf{u}_\alpha) (\mathbf{V}_i \cdot \mathbf{u}_\beta) + \sum_{i=1}^{N-1} \sum_{j>i}^N \sum_{a=1}^5 \sum_{b=1}^5 \mathbf{R}_{ij} \cdot \mathbf{u}_\alpha \left( \frac{-\mathbf{r}_{iajb} \cdot \mathbf{u}_\beta}{r_{iajb}} \right) \frac{dU}{dr_{iajb}} \right] \quad (5)$$

In Equation (5),  $\mathbf{R}_{ij}$  denotes the centre of mass distance between molecules  $i$  and  $j$ ,  $M_i$  and  $\mathbf{V}_i$  are the molecular mass and the centre of mass velocity respectively and  $\mathbf{u}_\alpha$  denotes the  $\alpha$  unit vector. Expression (4) is plotted in Figure 2, for the three components  $xy$ ,  $xz$  and  $yz$ . The individual components start diverging after a few tens of ps, despite the fact that these lines were obtained as averages over half a million points. It is a problem inherent to computing pressure quantities that the fluctuations are quite large and the statistics bad. The mean value for  $\eta$  over the three slopes is given in Table II. The MD result underestimates the shear viscosity compared to the experimental value.

### 3.5. Surface Tension

The surface tension is obtained by direct simulation of the corresponding liquid-vapour coexistence region. For this purpose a special box containing 512 molecules was constructed by increasing the length of a normal simulation box in the  $z$ -direction. In this way a free volume zone is created next to the slice containing the particles in the centre of the box. The cell dimensions in the  $x$ - and  $y$  directions were held fixed at  $L_x = L_y = 4.3453$  [nm]. The length in the  $z$ -direction was varied from  $L_z = 8$  to 43 [nm] in order to check for size dependencies in the computed surface tension (Tab. III). After an equilibration period of 50 [ps] in the NVT ensemble each system was simulated for another 200 [ps] in the NVE ensemble. From this last simulation the diagonal elements of the pressure tensor were



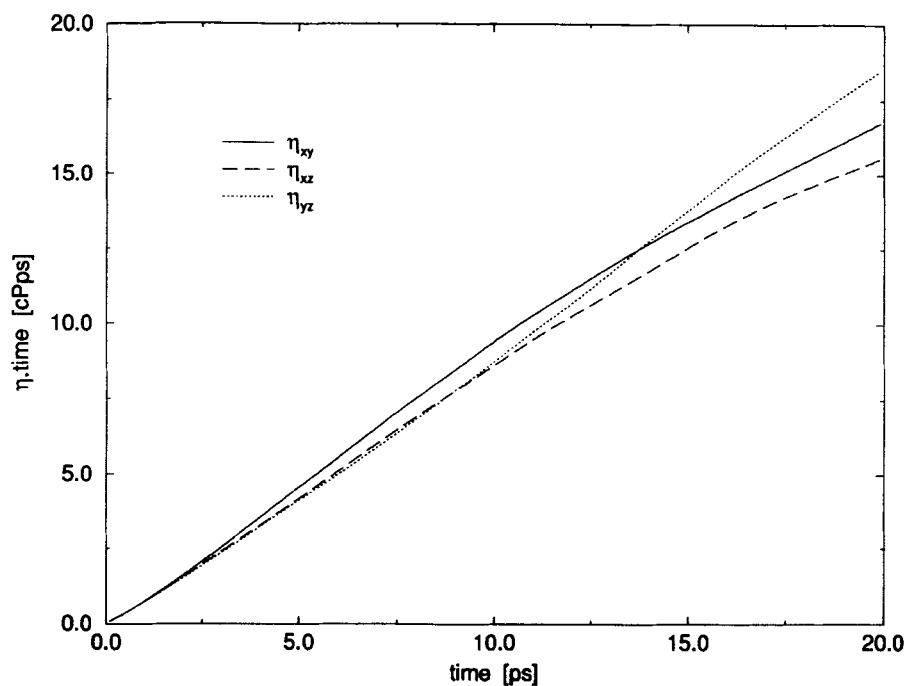


FIGURE 2 Shear viscosity components times time as a function of time calculated using off-diagonal elements of the pressure tensor according to Equation (4) from a 1 [ns] MD simulation of 216  $\text{CCl}_4$  molecules.

TABLE III Calculated surface tension coefficients  $\gamma$  (without tail correction) at 293 [K] for different  $z$  box-dimensions  $L_z$ . The length of the simulation cell in the  $x$ - and  $y$ -directions was kept constant at 4.3453 [nm]

$L_z$ [nm]	$L_x/L_z$	$\gamma [10^{-3} \text{Nm}^{-1}]$
8.691	0.5	21.6
10.863	0.4	23.9
14.484	0.3	22.2
21.727	0.2	23.8
43.453	0.1	24.0
mean		23.1

used to calculate the surface tension according to (6)

$$\gamma = \frac{L_z}{2} \left\langle p_{zz} - \frac{1}{2} (p_{xx} + p_{yy}) \right\rangle. \quad (6)$$

Surface tensions were determined at 293 [K] for box-size ratios  $L_x/L_z$  ranging from 0.1 to 0.5 and for 3 temperatures at a  $L_x/L_z$  ratio of 0.2. For different  $L_z$  box lengths the values of the surface tension are distributed evenly around  $23 \cdot 10^{-3}$  [Nm<sup>-1</sup>] ( see Tab. III). Thus, there is no trend which would indicate a size dependence in the  $zz$ -component of the pressure tensor. There is a systematic error in the so calculated values for the surface tension arising from using a finite cut-off radius. One can account for that by using a long range correction to the surface tension [14]. For a LJ interaction the correction is

$$\gamma_{\text{tail}} = 3\pi(\rho_L - \rho_V)^2 \sum_a^5 \sum_b^5 C_6(ab) \int_0^1 \int_{R_{\text{cut}}}^{\infty} \coth\left(\frac{rs}{D}\right) (3s^3 - s) r^{-3} dr ds \quad (7)$$

in which  $\rho_L$  and  $\rho_V$  are the (number) densities of the liquid and the gas phase respectively,  $D$  denotes the thickness of the interface and  $C_6(ab)$  are the LJ parameters given in Table I. The three parameters  $\rho_L$ ,  $\rho_V$  and  $D$  can be obtained by fitting the density profile  $\rho_L(z)$  to

$$\rho(z) = \frac{1}{2}(\rho_L + \rho_V) - \frac{1}{2}(\rho_L - \rho_V) \tanh\left(\frac{z - z_0}{D}\right) \quad (8)$$

where  $z_0$  is the position of the interface. In Figure 3 the density profiles are shown for 293 and 393 [K]. The circles and triangles denote the MD results, the solid and dashed lines are the fitted curves. The fitted parameters for three different temperatures are given in Table IV. The surface tension decreases with temperature which trend is reproduced by the MD calculation. The model gives slightly higher values for the surface tension than experiment.

#### 4. DISCUSSION AND CONCLUSIONS

An all-atom force field for liquid carbon tetrachloride has been refined to reproduce the experimental heat of vaporization and density at room temperature. Various quantities have been obtained from classical molecular dynamics simulations. The radial distribution functions describing the structure of liquid CCl<sub>4</sub> are only partially consistent with the ones derived from neutron and X-ray diffraction measurements. The diffusion coefficient and the shear viscosity indicate that the model slightly overestimates the translational mobility of the CCl<sub>4</sub> molecule. The rotational mobility is well

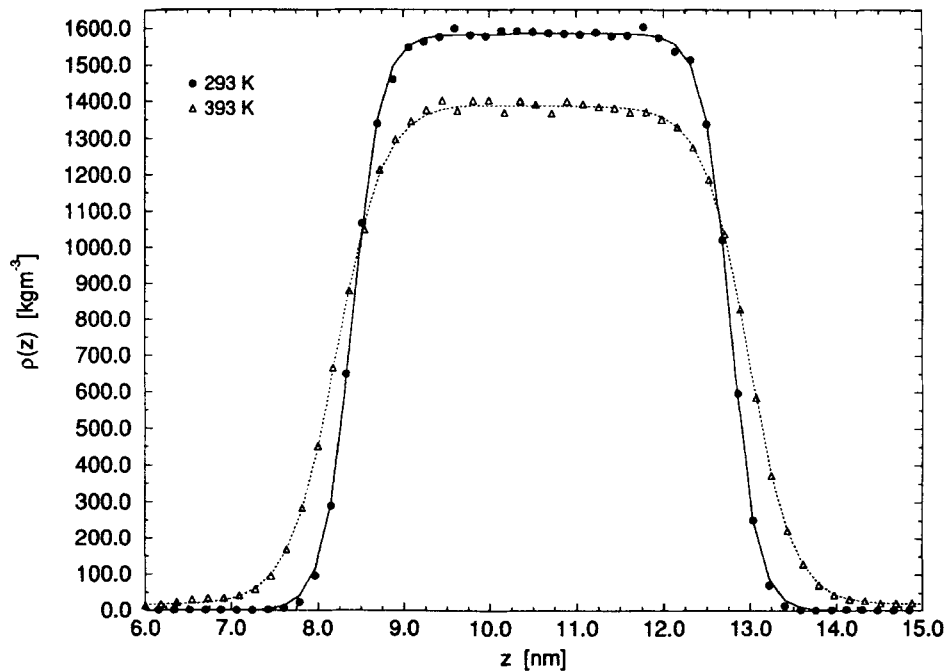


FIGURE 3 Density profiles across a box of size 4.3453-4.3453-21.727 [nm<sup>3</sup>] containing 512 CCl<sub>4</sub> molecules. The filled circles (T=293 [K]) and open triangles (T=393 [K]) are values obtained from 200 [ps] MD simulations. The solid and the dashed lines are fitted curves obtained using Eq. (8).

TABLE IV MD simulation results for the densities of the liquid and gas phase, the thickness of the interface  $D$ , the tail correction to the surface tension  $\gamma_{tail}$  and the total surface tension  $\gamma$  for 3 different temperatures at an  $L_x/L_z$  ratio of 0.2. The corresponding experimental values for the surface tensions are also given. a) Linear extrapolation from values at lower temperature

		293[K]	343[K]	393[K]
$\rho_L$	[kgm <sup>-3</sup> ]	1584	1495	1390
$\rho_V$	[kgm <sup>-3</sup> ]	1	7	17
$D$	[nm]	0.32	0.39	0.53
$\gamma_{tail}$	[10 <sup>-3</sup> Nm <sup>-1</sup> ]	5.7	4.9	3.9
$\gamma$	[10 <sup>-3</sup> Nm <sup>-1</sup> ]	29.5	21.7	17.8
Exp.	[10 <sup>-3</sup> Nm <sup>-1</sup> ]	26.8	20.3	15.0 <sup>(a)</sup>

reproduced. The calculated surface tension compares well with experimental data and shows the right temperature dependence. We conclude that the model is fit to adequately describe liquid carbon tetrachloride in a classical molecular dynamics simulation.

## References

- [1] Allen, M. P. and Tildesley, D. J. (1991) in *Computer Simulation of Liquids*, Oxford University Press, Oxford.
- [2] Beutler, T. C. and Mark, A. E. personal communication.
- [3] Rebertus, D. W. and Berne, B. J. (1979) "A molecular dynamics and Monte Carlo study of solvent effects on the conformational equilibrium of *n*-butane in  $\text{CCl}_4$ ", *Journal of Chemical Physics*, **70**, 3395.
- [4] Steinhäuser, O. and Neumann, M. (1980) "Structure and dynamics of liquid carbon tetrachloride. A molecular dynamics study", *Molecular Physics*, **40**, 115.
- [5] McDonald, I. R., Bounds, D. G. and Klein, M. L. (1982) "Molecular dynamics calculations for the liquid and cubic plastic crystal phases of carbon tetrachloride", *Molecular Physics*, **45**, 521.
- [6] Strassen, H. and Dorfmueller, T. (1991) "Molecular Dynamics Simulations of the Depolarized Rayleigh Spectra of  $\text{CS}_2/\text{CCl}_4$  Liquid Mixtures", *Berichte Bunsengesellschaft Physikalische Chemie*, **95**, 995.
- [7] Chang, T., and Peterson, K. A. (1995) "Molecular dynamics simulations of liquid, interface and ionic solvation of polarizable carbon tetrachloride", *Journal of Chemical Physics*, **95**, 7502.
- [8] van Gunsteren, W. F. and Berendsen, H. J. C. (1987) *Molecular Simulation (GROMOS) Library A. Manual*, Biomos, Groningen.
- [9] Ryckaert, J.-P., Ciccotti, G. and Berendsen, H. J. C. (1977) "Numerical Integration of the cartesian Equations of Motion of a System with Constraints: Molecular Dynamics of *n*-Alkanes", *Journal of Computational Physics*, **23**, 327.
- [10] Berendsen, H. K. C. Postma, J. P. M. van Gunsteren, W. F. DiNola A. and Haak, J. R. (1984) "Molecular dynamics with coupling to a heat bath", *Journal Chemical Physics*, **81**, 3684.
- [11] Tironi I. G. and van Gunsteren, W. F. (1994) "A molecular dynamics simulation study of chloroform", *Molecular Physics*, **83**, 381.
- [12] Riddick, J. A. Bunger W. B. and Sakand, T. K. (1986) *Organic Solvents Physical Properties and Methods of Purification*, John Wiley & Sons New York.
- [13] Narten, A. H. (1976) "Liquid carbon tetrachloride: Atom pair correlation functions from neutron and x-ray diffraction", *Journal of Chemical Physics*, **65**, 573.
- [14] Alejandre, J. Tildesley D. J. and Chapela G. A. (1995) "Molecular dynamics simulation of the orthobaric and surface tension of water", *Journal of Chemical Physics*, **102**, 4574.
- [15] Weast, R. C. (1986) *CRC Handbook of Chemistry and Physics*, CRC Press.
- [16] Landolt-Börnstein (1969) "Zahlenwerte und Funktionen aus Physik und Chemie", Vol. II, Part 2a, 5a and 3, Springer, Heidelberg.