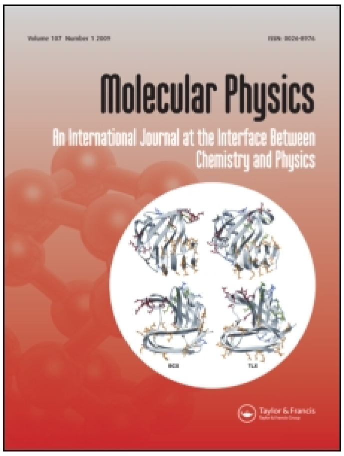
This article was downloaded by: *[HEAL-Link Consortium]*
On: *8 July 2009*
Access details: *Access Details: [subscription number 772725613]*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Physics
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713395160

Molecular dynamics simulation of the liquid mixtures CCl_4/CS_2

U. Mittag [a]; J. Samios [ab]; Th. Dorfmüller [a]
[a] University of Bielefeld, Faculty of Chemistry, Bielefeld, Germany [b] Department of Chemistry, Theor.—Phys. Chemistry, University of Athens, Athens, Greece

Online Publication Date: 10 April 1994

To cite this Article Mittag, U., Samios, J. and Dorfmüller, Th.(1994)'Molecular dynamics simulation of the liquid mixtures CCl_4/CS_2',Molecular Physics,81:5,1143 — 1154
To link to this Article: DOI: 10.1080/00268979400100761
URL: http://dx.doi.org/10.1080/00268979400100761

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.

MOLECULAR PHYSICS, 1994, VOL. 81, No. 5, 1143–1154

Molecular dynamics simulation of the liquid mixtures CCl_4/CS_2

II. Concentration dependence of the translational and rotational motion

By U. MITTAG, J. SAMIOS† and TH. DORFMÜLLER
University of Bielefeld, Faculty of Chemistry, 4800 Bielefeld, Germany
†Department of Chemistry, Theor.–Phys. Chemistry, University of Athens,
Pamepistimiopolis 157-71 Athens, Greece

(*Received 8 September 1992; accepted 21 October 1992*)

Previous molecular dynamics studies on the liquid mixture CCl_4/CS_2 at three mole fractions and at room temperature have been extended to the molecular translation and rotation in this system. The linear and angular velocity, and the first and second order reorientational autocorrelation functions have been calculated and discussed in terms of the CCl_4 concentration in the mixture. Diffusion coefficients and rotation relaxation times $\tau_{1,s}$, $\tau_{2,s}$ and τ_ω have been evaluated for both species and were compared with experimental data. The agreement is found to be very good. This study also shows that, by increasing the CCl_4 concentration in the mixture, the dynamics of the CS_2 molecules become increasingly restricted as compared with the dynamics of the CCl_4 molecules. This effect is less pronounced for the dynamics of the CCl_4 molecule in the mixtures.

1. Introduction

Only scant systematic information on structural and dynamical properties at the molecular level is available on both molecular components of binary liquid mixtures. This is partly due to the difficulties in deriving these properties from those of pure substances. It is also due to experimental problems arising in attempts to disentangle the data, in view of obtaining information separately for both species in the mixture. For this purpose, it is highly desirable to perform combined experiments and molecular dynamics (MD) simulations at the same *PVT* and composition state points. In this paper, we report an MD simulation of the translation and rotation motion in the liquid mixture CCl_4/CS_2 at the three mole fractions $\chi = 0{\cdot}25$, $0{\cdot}50$, $0{\cdot}75$ and at room temperature. In two previous papers [1, 2], thermodynamic and structural properties (experimental and simulated) were reported for this system. Good agreement between experimental and simulated data has been obtained, and it seems reasonable, therefore, to assume that the dynamic properties also of the simulated model liquid mixture will to some degree approach the dynamic behaviour of the real system. It should, however, be borne in mind that, as a consequence of the stronger model dependence of the interpretation of dynamic data, a direct comparison between experiment and simulation is less clear than in the case of static data. Translational and rotational motion have been studied by calculation of the corresponding autocorrelation functions (ACFs) and the single particle dynamics has been analysed and discussed.

2. Computational aspects

An analytical description of the model and the atom–atom potential parameters has been given in part I of the work [1]. The simulations of the pure liquids CS_2 and CCl_4 after achieving equilibrium were subsequently extended to 90 ps and those of the three mixtures to 140 ps. All centre of mass (COM) molecular positions, orientations and velocities were stored on magnetic tape in equal time intervals of eight time steps over the total simulation time. One time step was equivalent to 5×10^{-15} s. The stored data were used as primary data for the calculation of the time dependent ACFs, based on the direct approach [3]

$$C_a(t) = \frac{\langle \boldsymbol{a}(t) \cdot \boldsymbol{a}(0) \rangle}{\langle \boldsymbol{a}(0) \cdot \boldsymbol{a}(0) \rangle}, \tag{1}$$

$$\tau_c = \int_0^\infty C_a(t)\, \mathrm{d}t \tag{2}$$

where $\boldsymbol{a}(t)$ is a dynamic property of the system and τ_c is the correlation time which corresponds to the ACF $C_a(t)$. The calculated translational and rotational ACFs are presented in the following sections.

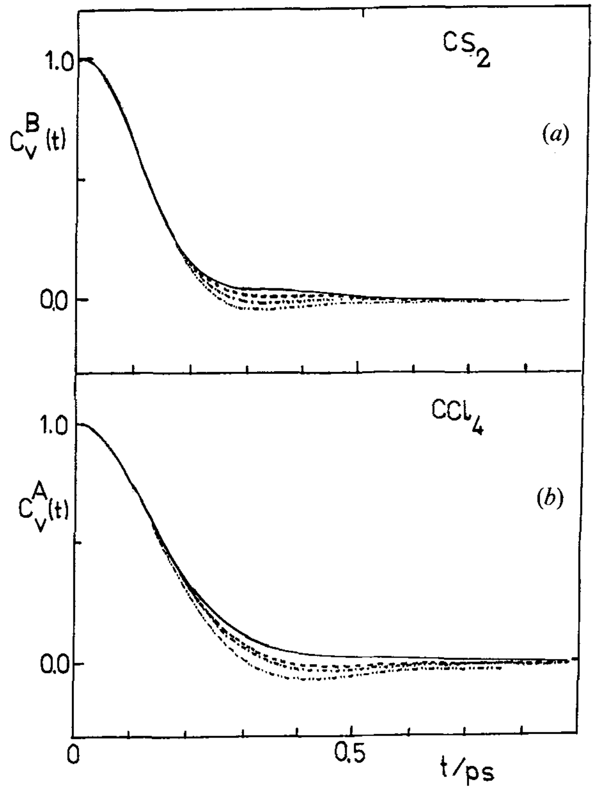


Figure 1. The COM velocity ACFs obtained from this MD simulation study. (a) ——, pure CS_2; – – –, 25% CCl_4; –. – .–, 50% CCl_4; –.. – ..–, 75% CCl_4. (b) ——, 25% CCl_4; – – –, 50% CCl_4; –. – .–, 75% CCl_4; –.. – ..–, pure CCl_4.

3. Single molecule motion

3.1. *Translation*

We first studied the concentration dependence of the single-molecule translational motion of the two components at room temperature. The ACFs of interest were $C_v^{\mathrm{A}}(t)$ and $C_v^{\mathrm{B}}(t)$, the COM linear velocity ACFs

$$C_v^{\mathrm{A}}(t) = \frac{\langle \boldsymbol{v}_i^{\mathrm{A}}(0) \cdot \boldsymbol{v}_i^{\mathrm{A}}(t) \rangle}{\langle \boldsymbol{v}_i^{\mathrm{A}}(0) \cdot \boldsymbol{v}_i^{\mathrm{A}}(0) \rangle} \tag{3}$$

$$C_v^{\mathrm{B}}(t) = \frac{\langle \boldsymbol{v}_i^{\mathrm{B}}(0) \cdot \boldsymbol{v}_i^{\mathrm{B}}(t) \rangle}{\langle \boldsymbol{v}_i^{\mathrm{B}}(0) \cdot \boldsymbol{v}_i^{\mathrm{B}}(0) \rangle} \tag{4}$$

$\boldsymbol{v}_i^{\mathrm{A}}$ and $\boldsymbol{v}_i^{\mathrm{B}}$ are the COM velocity of the molecule A and B. A and B stand for the two components CCl_4 and CS_2, respectively. The two ACFs calculated for each composition of the mixtures are illustrated in figure 1(*a*, *b*). The correlation times τ, corresponding to the velocity ACFs, have been calculated by means of integrals corresponding to equation (2), and their values are shown in table 1. The ACFs $C_v^{\mathrm{A}}(t)$ and $C_v^{\mathrm{B}}(t)$ show the following qualitative behaviour. The $C_v^{\mathrm{B}}(t)$ ACFs for all concentrations practically overlap up to $t \simeq 0{\cdot}2$ ps and the $C_v^{\mathrm{A}}(t)$ up to $t \simeq 0{\cdot}15$ ps. As the CS_2 molecules are gradually diluted in CCl_4, all corresponding ACFs display a characteristic concentration dependence. With the exception of pure CS_2, they first go through a shallow minimum and then converge to zero after approximately 1 ps. In order to obtain more information on the negative portion of the $C_v^{\mathrm{B}}(t)$ ACFs, we have computed the $C_v^{\mathrm{B},\parallel}(t)$ and $C_v^{\mathrm{B},\perp}(t)$ ACFs with the following expressions.

$$C_v^{\mathrm{B},x}(t) = \frac{\langle \boldsymbol{v}_i^{\mathrm{B},x}(0) \cdot \boldsymbol{v}_i^{\mathrm{B},x}(t) \rangle}{\langle \boldsymbol{v}_i^{\mathrm{B},x}(0) \cdot \boldsymbol{v}_i^{\mathrm{B},x}(0) \rangle}, \tag{5}$$

Table 1. Correlation times τ_c/ps of the COM velocity ACFs of both components. The times $\tau_c^{\parallel}$ and $\tau_c^{\perp}$ correspond to the ACFs $C_{v,\parallel}^{\mathrm{B}}(t)$, $C_{v,\perp}^{\mathrm{B}}(t)$, respectively (see text). All correlation times have been calculated with upper integrated limit. $t_{\max} = 1{\cdot}5$ ps. The error bars are smaller than 1%.

Concn mol % CCl_4	00	25	50	75	100
CS_2					
τ_c	0·127	0·120	0·108	0·103	–
$\tau_c^{\parallel}$	0·167	0·163	0·164	0·151	–
$\tau_c^{\perp}$	0·091	0·088	0·077	0·073	–
$\tau_c^{\parallel}/\tau_c^{\perp}$	1·8(1·9)[a]	1·9	2·1	2·1	–
CCl_4					
τ_c		0·173	0·150	0·148	0·134

[a] Reference [23]

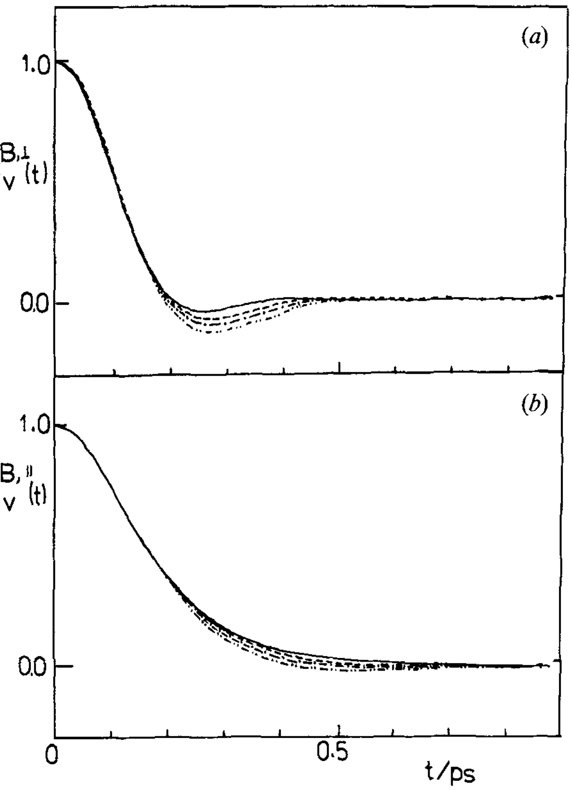


Figure 2. The COM velocity components ($v_B^{\perp}$, $v_B^{\parallel}$) ACFs of the CS_2 molecule: (*a*) $C_v^{B,\perp}(t)$, and (*b*) $C_v^{B,\parallel}(t)$: ——, pure CS_2; – – –, 25% CCl_4; –. – .–, 50% CCl_4; –.. – ..–, 75% CCl_4.

with $x = \perp$ or $\parallel$

$$v_i^{\parallel}(t) = [v_i(t) \cdot \hat{u}_i(t)] \cdot \hat{u}_i(t) \tag{6}$$

$$v_i^{\perp}(t) = v_i(t) - v_i^{\parallel} \tag{7}$$

where $\hat{u}_i$ is the unit vector along the molecular axis of the *i*th CS_2 molecule. The $C_v^{B,\perp}(t)$ and $C_v^{B,\parallel}(t)$ ACFs are shown in figure 2(*a*, *b*) and the corresponding relaxation times $\tau_c^{\parallel}$ and $\tau_c^{\perp}$ plus the ratio $\tau_c^{\parallel}/\tau_c^{\perp}$, are given in table 1. We can see that all three quantities τ_c, $\tau_c^{\perp}$ and $\tau_c^{\parallel}$ decrease in the intermediate time range with increasing concentration of CCl_4. It is interesting to note furthermore that the values of the dynamic anisotropy, defined as the ratio $\tau_c^{\parallel}/\tau_c^{\perp}$ show a slight increase with increasing concentration of CCl_4. This effect indicates that, as the concentration changes, the average structure of the environment of CS_2 molecules is modified. In fact, changes in the dynamic anisotropy of a given molecule produced by changes in the composition of the system can be considered as reflecting structural changes in the environment. As can be inferred from the values of $\tau_c^{\parallel}/\tau_c^{\perp}$, the cage around a linear molecule is less restricting with respect to a movement in the direction of the axis than vertical to it. In the latter case, the effective collision cross-section is larger, and the probability of a recoil from the cage wall is found to be significantly larger indeed. The recoil on the cage walls is also reflected in the observed negative value of

Table 2. Self-translational diffusion coefficients $D_s/10^{-5}\,\mathrm{cm^2\,s^{-1}}$ of both components, from mean-square displacement (MSD) and from the linear velocity ACF (VACF).

	MSD	VACF	Experimental	Other simulations
$D_s^B(CS_2)$				
0% CCl_4	3·9 ± 0·5	4·11	4·2[a]	3·85[b] 3·90[c]
25% CCl_4	3·26 ± 0·1	3·90		
50% CCl_4	2·79 ± 0·3	3·52		
75% CCl_4	2·34 ± 0·1	3·31		
$D_s^A(CCl_4)$				
25% CCl_4	2·21 ± 0·1	2·81		
50% CCl_4	1·62 ± 0·3	2·43		
100% CCl_4	1·45 ± 0·1	2·21	1·4[d]	1·75[e]

[a] From reference [27].
[b] From reference [23].
[c] From reference [24].
[d] From reference [25].
[e] From reference [26].

$C_v^{B,\perp}(t)$ around 0·3 ps. Negative regions in the ACF lower the value of the integral of the normalized ACF which is equivalent to increased perturbation of the motion. The increase of τ_c of both species with increasing CS_2 concentration is a consequence of reduced caging in spite of the concomitant increase of the number density around the CS_2 molecules. Actually, the number of neighbours in the first shell rises with the concentration of CS_2, as is shown in table 4 of reference [1], but the structural restrictions for the lateral motion of the CS_2 molecules obviously decrease.

3.2. *Translational diffusion coefficients*

The translational self-diffusion coefficients D_s^A and D_s^B of the two molecular species CCl_4 and CS_2, have been calculated, and are presented together with experimental values in table 2. All calculations were based on the well known equations:

$$D_s = \frac{1}{3}\int_0^{\infty} \langle \dot{\boldsymbol{R}}(0)\cdot\dot{\boldsymbol{R}}(t)\rangle\,\mathrm{d}t \tag{8}$$

$$6D_s = \lim_{t\to\infty}\frac{\partial}{\partial t}\langle|\boldsymbol{R}_i(t)-\boldsymbol{R}_i(0)|^2\rangle \tag{9}$$

where $\boldsymbol{R}_i(t)$ is the COM molecular position at time t. From equation (9) we have calculated the slopes of the mean-square displacement versus t for times greater than 30 ps for all molecules, and starting from 25 different initial points in phase space. The mean values and the corresponding errors are given in table 2. The difference between the diffusion values obtained from the mean-square displacement (MSD) and from the linear velocity ACF (VACF), may be explained on the basis of the rather low accuracy of the VACF method. This has been discussed amply in the literature and it is well known that results obtained by this method may be affected by problems arising from continuing to take into account the long negative tails of the ACFs. Unfortunately, values for the self-diffusion coefficients of the components in CCl_4/CS_2 liquid mixtures are not available in the literature. From the data in table 2 we may conclude that the self-diffusion coefficients of both species decrease with increasing concentration of CCl_4. This result also reflects the mentioned increase of caging in mixtures richer in CCl_4.

In this study, the mutual diffusion coefficient D_{AB} has been calculated only for the equimolar mixture by using the Green–Kubo formalism as done in a previous paper [21]. We found good agreement with the corresponding experimental value [22].

3.3. *Rotation*

The rotational motion of the CS_2 molecules in the neat liquid has been the subject of a number of experimental studies [4–11]. Less experimental data are available for CCl_4 rotational motion in the liquid [12, 13]. In the case of liquid mixtures, two depolarized Rayleigh light scattering studies have been reported [4, 14]. To shed some light on the rotational dynamics of the CCl_4 and CS_2 molecules in the mixtures, we have calculated the most important ACFs $C_\omega(t)$, $C_2(t)$ and $C_1(t)$ of both components for each simulated system. The following sections briefly show the results.

3.3.1. *The angular velocity ACFs*

The following functions have been calculated

$$C_\omega^{\mathrm{A}}(t)=\frac{\langle\omega_i^{\mathrm{A}}(0)\cdot\omega_i^{\mathrm{A}}(t)\rangle}{\langle\omega_i^{\mathrm{A}}(0)\cdot\omega_i^{\mathrm{A}}(0)\rangle} \tag{10}$$

$$C_\omega^{\mathrm{B}}(t)=\frac{\langle\omega_i^{\mathrm{B}}(0)\cdot\omega_i^{\mathrm{B}}(t)\rangle}{\langle\omega_i^{\mathrm{B}}(0)\cdot\omega_i^{\mathrm{B}}(0)\rangle}. \tag{11}$$

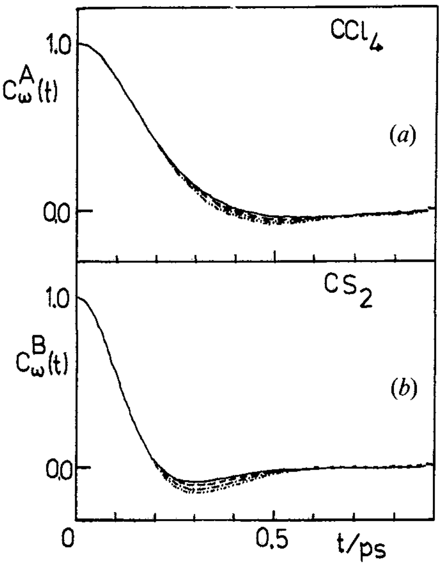


Figure 3. The angular ACFs obtained from this study. (*a*) ——, 25% CCl_4; – – –, 50% CCl_4; –. – .–, 75% CCl_4; –.. – ..–, pure CCl_4. (*b*) ——, pure CS_2; – – –, 25% CCl_4; –. – .–, 50% CCl_4; –.. – ..–, 75% CCl_4.

Table 3. Correlation times τ_c/ps of the angular ACFs and the mean-square torques $T^2/10^{-39}\,J^2$. All correlation times have been calculated with upper integrated limit. $t_{max} = 1{\cdot}5$ ps. The error bars are smaller than 1%.

Concn mol % CCl_4	00	25	50	75	100
CS_2 τ_c	0·084 0·088[a]	0·081	0·075	0·068	–
T^2	2·76 2·40[a]	2·60	2·55	2·49	
CCl_4 τ_c		0·161	0·164	0·157	0·159 0·185[b]
T^2		3·45	3·34	3·23	3·34

[a] From reference [23].
[b] From reference [26].

The results are shown in figure 3(*a*, *b*) and the corresponding correlation times calculated by means of equation (12)

$$\tau_c = \int_0^\infty C_\omega(t)\,dt \tag{12}$$

are displayed in table 3. In this table the mean square torques are also given. From figure 3 we can see that the angular velocity ACFs display a behaviour reminiscent of the linear velocity ACFs. We thus observe a minimum at negative values which, in the case of CS_2, is localized at $t \simeq 0{\cdot}3$ ps and for the CCl_4 curves at $t \simeq 0{\cdot}48$ ps. The negative portions of the ACFs decay rather slowly to zero and display a concentration dependence which, reflecting the high isotropy of this molecule, is very weak for CCl_4. In fact, it is known that, in molecular liquids with high torques, the angular momentum ACFs display non-exponential behaviour [15], often exhibiting negative portions. This feature amounts to describing the motion in terms of a librational motion, which results in a reversal of the angular momentum after a time which can be described roughly as the time between successive collisions. The rotational correlation function of the CS_2 molecule, in the pure liquid as well as in the mixture, display an analogy to the translational correlation function discussed above. Finally, it also appears that no indication of strong librational motion of the CS_2 molecule is observed which would give rise to a shoulder in the reorientation correlation functions $C_1(t)$ [16, 17]. Such behaviour has not been observed in the simulated CS_2 ACFs (see figure 4(*d*, *e*)).

3.3.2. *The reorientation ACFs*

In order to study the reorientational molecular dynamics of the system, the corresponding self and cross ACFs of the first and second Legendre functions

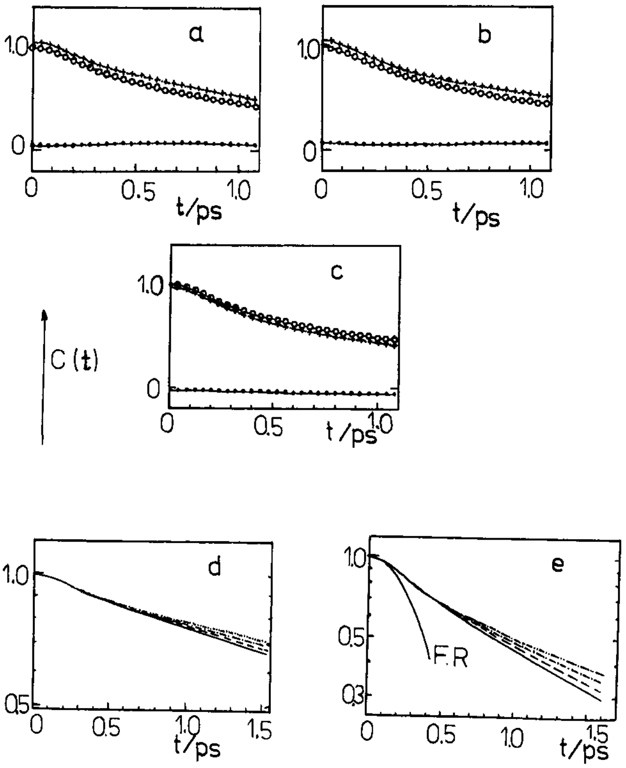


Figure 4. The first and second order reorientation ACFs of the CS_2 molecule obtained from this MD simulation study. (*a*) o, single ACF $C^{B}_{2,s}(t)$; •, cross ACF $C^{B}_{2,s}(t)$; +, sum of the single and cross ACFs; 25% CCl_4. (*b*) As for (*a*) but 50% CCl_4. (*c*) As for (*a*) but 75% CCl_4. (*d*) Logarithmic plots of the single first order ACFs: ——, pure CS_2; – – –, 25% CCl_4; –. – .–, 50% CCl_4; –.. – ..–, 75% CCl_4. (*e*) Logarithmic plots of the single second order ACFs: symbols as in (*d*). FR is the free-rotor curve.

$P_1(\hat{u}(0)\cdot\hat{u}(t))$ for both molecules have been obtained.

$$C^{A}_{l,s}(t) = \langle P_l(\hat{u}^{A}_i(0)\cdot\hat{u}^{A}_i(t))\rangle \tag{13}$$

$$C^{A}_{l,c}(t) = \langle P_l(\hat{u}^{A}_i(0)\cdot\hat{u}^{A}_j(t))\rangle \tag{14}$$

$$C^{B}_{l,s}(t) = \langle P_l(\hat{u}^{B}_i(0)\cdot\hat{u}^{B}_i(t))\rangle \tag{15}$$

$$C^{B}_{l,c}(t) = \langle P_l(\hat{u}^{B}_i(0)\cdot\hat{u}^{B}_j(t))\rangle. \tag{16}$$

The index l takes the values 1 and 2, while s and c stand for the self and cross terms, respectively. $\hat{u}^{B}_i$ and $\hat{u}^{A}_i$ are unit vectors along a symmetry axis of CCl_4 and CS_2. Figure 4(*a*, *b*, *c*) shows the self and cross second order ACFs of the CS_2 in the mixtures. In figure 4(*d*, *e*) the logarithmic curves of the first and second order reorientation ACFs are also displayed. In order to obtain reliable results, especially for the cross ACFs, we have used trajectories of about 90 ps with many initial zero times. In spite of these precautions, the calculated errors of the cross ACFs were quite large precluding a reliable calculation of Kirkwood's g^2 factor, which is generally calculated from the second order $C^{B}_{2,c}(t)$ correlation functions. However, we observe a basic similarity between our predicted cross reorientation ACFs of CS_2

Table 4. Single reorientational times $\tau_{1,s}^{A}$, $\tau_{2,s}^{A}$, $\tau_{1,s}^{B}$ and $\tau_{2,s}^{B}$ (in ps) at different CCl_4 concentrations from this study. The symbol i means calculation with the integral method (upper integration limit = 8 ps) and the upper symbol s with the method of linear fit on the logarithmic ACFs. *, experimental values from [4].

Concn mol % CCl_4	00	25	50	75	100
CS_2 $\tau_{1,s}^{B,s}$	3·88	4·09	4·65	5·02	–
$\tau_{1,s}^{B,i}$	3·83	4·03	4·49	4·80	–
$\tau_{2,s}^{B,s}$	1·49(1·5)[a]	1·61	1·86	2·11	–
	1·54*	1·68*	1·87*	2·14*	–
$\tau_{2,s}^{B,i}$	1·35	1·44	1·59	1·75	–
	1·30[a]				
CCl_4 $\tau_{1,s}^{A,s}$		3·78	4·03	4·03	3·9[b]
$\tau_{1,s}^{A,i}$		3·81	4·02	4·02	3·75[b]
$\tau_{2,s}^{A,s}$		1·52	1·68	1·79	1·70[c]
$\tau_{2,s}^{A,i}$		1·45	1·54	1·58	1·8[d]

[a] From reference [23], simulation.
[b] From reference [26], simulation.
[c] From reference [13], experimental.
[d] From reference [12], experimental.

and those of less anisotropic molecules like N_2 [18] and Cl_2 [19] calculated in previous MD simulations. In the following discussion we focus on logarithmic plots (see figure 4(*d*, *e*)) of the self CS_2 reorientation first and second order Legendre polynomial ACFs. Unfortunately, experimental functions for CS_2 in this mixture are not available in the literature. On the other hand, concentration-dependent depolarized Rayleigh relaxation times $\tau_{1,s}$ for CS_2 in CCl_4/CS_2 liquid mixtures have been published [4, 14]. In one of these papers [4], single particle reorientation relaxation times $\tau_{2,s}$ for CS_2 have been obtained from the $\tau_{1,s}$ time at fixed η/T extrapolated to zero solute concentration. These experimental results, together with our predicted reorientation times $\tau_{2,s}^{B}$, are given in table 4. The agreement between experimental and simulated single reorientation times is remarkably good. The simulated times, presented in table 4, have been derived by numerical integration of the corresponding ACFs, and also by a linear fit procedure on the logarithmic plots of the same functions. In the case of the $\tau_{1,s}^{A}$ and $\tau_{1,s}^{B}$, the uncertainty may amount approximately to $\simeq 7\%$ whereas, for the relaxation times $\tau_{2,s}^{A}$ and $\tau_{2,s}^{B}$, the uncertainty is significantly smaller. The first and the second order reorientation ACFs, which are plotted in the figure (4(*d*, *e*)), show the well known behaviour of the reorientational motion, as in the case of simple liquids. After a free inertial motion for very short times ($t \simeq 0{\cdot}15$ ps), deviation from free rotor behaviour can be observed and, for relatively long times, the ACFs display the exponential régime typical of rotational diffusion. The ACFs $C_{2,s}^{B}(t)$ decay also more rapidly than the $C_{1,s}^{B}(t)$ ACFs. From table 4 and figure 4 we also see that the relaxation times $\tau_{1,s}^{B}$, $\tau_{2,s}^{B}$ increase with increasing concentration of CCl_4 in the mixture. The CCl_4 rotational motion, on

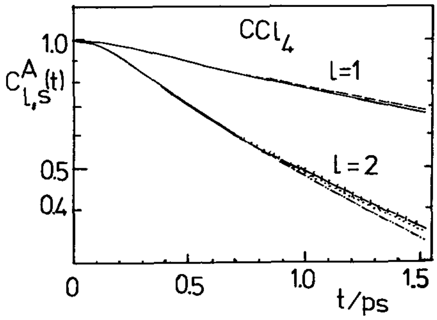


Figure 5. The first ($l = 1$) and the second ($l = 2$) order ACFs of CCl_4 in logarithmic plots $l = 1$: ——, 25% CCl_4; – – –, 50% CCl_4. $l = 2$: –.. – ..–, 25% CCl_4; ......, 50% CCl_4; – + –, 75% CCl_4.

the other hand, seems to be almost independent of its concentration in the mixture. This result may be observed from the calculated reorientation times (see table 4) $\tau_{1,s}^A$ and $\tau_{2,s}^A$ and from figure 5. On the basis of the Debye rotational diffusion model, these data yield the rotational diffusion coefficients D_R calculated by:

$$\tau_{l,s}^{-1} = -\frac{\partial}{\partial t} \ln C_{l,s}(t) \equiv l(l+1)D_R \qquad (17)$$

or by the integral formula from the angular ACF $C_\omega(t)$

$$D_R = \frac{KT}{I}\int_0^\infty C_\omega(t)\,dt \equiv \frac{KT}{I}\tau_\omega \qquad (18)$$

The values obtained for the CS_2 molecule in the mixture are given in table 5.

4. Conclusion

In the present MD simulation study of CCl_4/CS_2 mixtures, the single-particle dynamics of both species have been analysed and discussed. The conclusions from

Table 5. Rotational diffusion coefficients $D_R^B/10^{11}\ s^{-1}$ of the CS_2 in the mixture at different concentrations.

Concn mol % CCl_4	00	25	50	75	100
From τ_ω^B	1·33	1·27	1·17	1·06	–
From $\tau_{2,s}^{B,s}$	1·12	1·04	0·90	0·79	–
From $\tau_{1,s}^{B,s}$	1·29	1·22	1·08	1·00	–

this work can be summarized as follows. (a) The single molecule translation of both molecules in the mixtures becomes increasingly restricted by increasing the CCl_4 concentration. From previous analysis of the mobility of the CS_2 molecule in the pure liquid [20], it was shown that the mobilities parallel and normal to the molecular axis are different. This was also observed in the mixtures. It was furthermore shown that, by increasing the CCl_4 concentration, translation normal to the symmetry axis becomes significantly more restricted than parallel to the axis. (b) The calculated self-diffusion coefficient of both species decreases with increase in the CCl_4 concentration. For the pure substances, excellent agreement was found between experimental and simulated values. We also calculated the mutual diffusion coefficient D_{AB} for the equimolar mixture. The calculated value is in good agreement ($D_{AB}^{sim} = 2{\cdot}4 \times 10^{-5}$, $D_{AB}^{exp} = 2{\cdot}35 \times 10^{-5}\,cm^2\,s^{-1}$) with experiment. (c) The angular velocity ACFs show negative minima whose depths are concentration dependent. This effect is stronger in the case of the CS_2 ACFs than in CCl_4. This apparently reflects the librational character of the motion, especially of the CS_2 molecule. (d) The reorientational ACFs $C_{1,s}(t)$ and $C_{2,s}(t)$ for both molecules decay monotonically and very slowly. The reorientation ACFs of CS_2 are more affected by the CCl_4 concentration than the ACFs of CCl_4. The single-molecule reorientation relaxation times $\tau_{2,s}^{B}$ of CS_2 from this simulation have been found to be in good agreement with those obtained experimentally.

This work was carried out within the project Molekulare induzierte Wechselwirkungen und spektrale Linienformen between the Universities of Bielefeld (Germany) and Athens (Greece). The financial support of the Stiftung Volkswagenwerk is gratefully acknowledged. We also acknowledge the financial support of the Fonds der Chemischen Industrie.

References

[1] Mittag, U., Samios, J., and Dorfmüller, Th., 1989, *Molec. Phys.*, **66**, 51.
[2] Mittag, U., Samios, J., Dorfmüller, Th., Günster, St., Zeidler, M. D., and Chieux, D., 1989, *Molec. Phys.*, **67**, 1141.
[3] Allen, M. P., and Tildesly, D. J., 1987, *Computer Simulation of Liquids* (Clarendon Press).
[4] Higashigaki, Y., Whittenburg, S. L., and Wang, C. H., 1978, *J. chem. Phys.*, **69**, 3297.
[5] Langer, H., and Versmold, H., 1979, *Ber. Bunsenges. Phys. Chem.*, **83**, 510.
[6] Cox, T. T., Battaglia, M. R., and Madden, P. A., 1979, *Molec. Phys.*, **38**, 1539.
[7] Hegeman, B., and Jonas, J., 1985, *J. chem. Phys.*, **82**, 2845.
[8] Spies, H. W., Schweitzer, D., and Halberlen, U., 1978, *J. magn. Reson.*, **5**, 101.
[9] Vold, R. R., Sparks, S. W., and Vold, R. C., 1978, *J. magn. Reson.*, **30**, 497.
[10] Kohles, N., and Laubereau, A., 1987, *Chem. Phys. Lett.*, **138**, 365.
[11] Zalpouzos, C., Lotshow, W. T., McMorrow, D., and Kenney-Wallace, G. A., 1987, *J. chem. Phys.*, **91**, 2028.
[12] Bartoli, F. J., and Litovitz, T. A., 1972, *J. chem. Phys.*, **56**, 404.
[13] O'Reilly, D. E., and Schader, G. E., 1963, *J. chem. Phys.*, **39**, 1968.
[14] Versmold, H., 1978, *Ber. Bunsenges. Phys. Chem.*, **82**, 451.
[15] Lynden-Bell, R. M., and Steele, W. A., 1984, *J. phys. Chem.*, **88**, 6514.
[16] Härtl, W., and Versmold, H. J., 1983, *J. chem. Soc. Faraday Trans.* 2, **79**, 1143.
[17] Impey, R. W., Madden, P. A., and Mcdonald, I. R., 1982, *Molec. Phys.*, **46**, 513.
[18] Levesque, D., and Weiss, J. J., 1975, *Phys. Rev.* A, **12**, 2584.
[19] Singer, K., Singer, J. K. L., and Taylor, A. J., 1979, *Molec. Phys.*, **37**, 1239.
[20] Steinhauser, O., 1981, *Chem. Phys. Lett.*, **82**, 153.

[21] Schön, M., and Hoheisel, C., 1984, *Molec. Phys.*, **52,** 33.
[22] Siddigi, M. A., Krahn, W., and Lucas, K., 1987, *J. Chem. Engng. Data*, **32,** 48.
[23] Tildesley, D. J., and Madden, P. A., 1983, *Molec. Phys.*, **48,** 129.
[24] Steinhauser, O., and Neumann, M., 1979, *Molec. Phys.*, **37,** 1921.
[25] Watts, H., Alder, B. J., and Hildebrand, 1965, *J. chem. Phys.*, **23,** 659.
[26] Steinhauser, O., and Neumann, M., 1980, *Molec. Phys.*, **40,** 115.
[27] McCall, D. W., Douglas, D. C., and Anderson, E. W., 1959, *Phys. Fluids*, **2,** 87.