

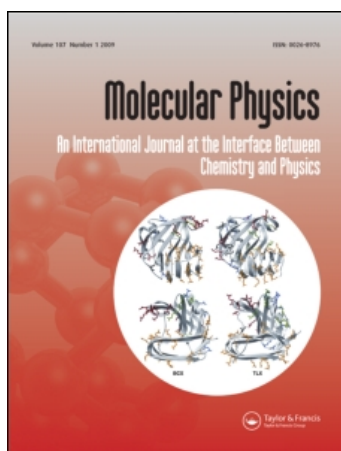
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Molecular Physics

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713395160>

A comparative molecular dynamics and neutron scattering study of the liquid mixture carbon tetrachloride/carbon disulphide

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Online Publication Date: 10 August 1989

To cite this Article Mittag, U., Samios, J., Dorfmueller, Th., Guenster, St., Zeidler, M. D. and Chieux, P.(1989)'A comparative molecular dynamics and neutron scattering study of the liquid mixture carbon tetrachloride/carbon disulphide',Molecular Physics,67:5,1141 — 1151

To link to this Article: DOI: 10.1080/00268978900101691

URL: <http://dx.doi.org/10.1080/00268978900101691>

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A comparative molecular dynamics and neutron scattering study of the liquid mixture carbon tetrachloride/carbon disulphide

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(Received 3 January 1989; accepted 13 February 1989)

Neutron diffraction studies on the equimolar liquid mixture CCl_4/CS_2 with three different isotopic chlorine compositions (99.35 per cent, 75.77 per cent—natural composition—1.79 per cent of ^{35}Cl ; the complementary isotope is ^{37}Cl) were carried out under ambient conditions. The data were corrected for background, absorption, multiple scattering and inelastic effects (Placzek correction) and then were normalized to absolute differential cross-section by comparison with vanadium standard. The absolute coherent distinct differential cross-section was separated into intramolecular and intermolecular contributions. A molecular dynamics simulation with 500 molecules was performed. The interaction between molecules was described by a five-centre and a three-centre Lennard-Jones potential for CCl_4 and CS_2 respectively. For the cross interactions the Lorentz-Berthelot mixing rule was used. An algorithm based on the quaternion method was adapted to this two-component system. Intermolecular pair correlation functions were then calculated for this system. The comparison of the experimental and simulated pair-correlation functions shows very good agreement.

1. Introduction

The aim of the present work is the determination of the liquid structure for the equimolar mixture of carbon tetrachloride CCl_4 in carbon disulphide CS_2 . This system is of particular interest in far-infrared spectroscopy since interaction-induced spectra are observed [1]. The pure components of course possess no permanent electric dipole moments, the lowest multipole moment being the quadrupole for CS_2 and the octupole for CCl_4 . Thus in the mixture strong interactions must occur between the molecules which should reflect in the structure. Since no experimental determinations of the structure up to now had been done, computer simulation studies were performed in order to provide the necessary information [2]. Thus it seemed desirable to carry out neutron diffraction experiments and to compare the structural information obtained from these scattering data with the simulation results.

We considered this as an important issue given the uncertainties involved in both methods. Thus, neutron scattering experiments suffer from inaccuracies due to the applied correction procedures, while the basic uncertainty of the simulation is our poor knowledge of atom–atom potentials. This system was chosen because of its small excess free energy and enthalpy [3] at room temperature and for its perfect miscibility at all concentrations. Furthermore, both pure liquids have been extensively studied experimentally, theoretically and by numerous MD simulations [4, 5]. In addition, careful experimental measurements of the thermodynamic properties at different temperatures and compositions, diffusion coefficients, and a large number of spectroscopic studies have been published by several groups in the last decade [6–8].

We employ the method of isotopic substitution in neutron diffraction, details of which may be found in previous reviews [9, 10]. In this particular system the isotopes ^{35}Cl , ^{37}Cl , ^{37}S and ^{33}S are basically of interest, but the very high price of the sulphur isotopes prohibits their use. Only the chlorine isotopes were measured in our diffraction experiments.

2. Experimental

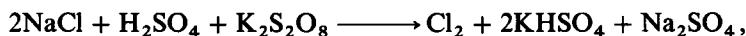
2.1. The neutron scattering experiment

Neutron diffraction experiments were carried out with the two-axis diffractometer D4B of the Institute Laue-Langevin. The following samples were prepared and measured:

- 0.498 mole per cent C^{35}Cl_4 + 0.502 mole per cent CS_2
- 0.501 mole per cent C^{37}Cl_4 + 0.499 mole per cent CS_2
- 0.513 mole per cent $\text{C}^{\text{nat}}\text{Cl}_4$ + 0.487 mole per cent CS_2

where $^{\text{nat}}\text{Cl}$ signifies the natural isotopic composition of chlorine which is 75.77 mole per cent ^{35}Cl and 24.23 mole per cent ^{37}Cl .

The samples were prepared from commercially available sodium chloride (Oak-Ridge National Laboratory, U.S.A.) with isotopic contents of 99.35 per cent ^{35}Cl and 98.21 per cent ^{37}Cl respectively. In a first step chlorine was produced by the reaction [11]



which proceeds at 60–80°C with a yield of 95 per cent. In a second step chlorine reacts with carbon disulfide in the presence of an iron catalyst [12, 13]



Chlorine, carbon tetrachloride and a small amount of iron powder were sealed in a glass vessel and kept at 80°C for 60 hours. The reaction mixture was then treated with aqueous sodium hydroxide to decompose the sulphur chlorides and CCl_4 together with CS_2 was distilled off. After determination of the composition in the distillate the missing amount of CS_2 was added to obtain the equimolar mixture. The overall yield was 50–70 per cent.

The samples were filled into a vanadium container of 5 mm diameter and 0.1 mm wall thickness. Due to the limited amount of liquid only 20 mm of height were

obtained, the same volume was kept, however, also for the inexpensive natural isotopic composition. Measurements were performed at the wavelength $0.7046 \pm 0.0005 \text{ \AA}$. The detection system consisted of two arms with 64-cell ^3He -multidetectors each, one covering the range $1.7\text{--}64.8$ degrees in steps of 0.1 degree at a distance of 1445 mm from the sample, the other covering the range $46.3\text{--}134.1$ degrees in steps of 0.2 degree at a distance of 727 mm . The dwell time at each detector position was monitored by a counter in the incident beam which was preset to $8 \cdot 10^5$. In addition measurements of the empty container, background, vanadium and cadmium rods with the same dimensions as the container were performed, in these cases the monitor rate was selected between $1 \cdot 10^5$ and $6 \cdot 10^5$.

The raw scattering data of the three samples are shown in figure 1.

The diffraction data were corrected for background, absorption and container as described previously [14] employing the procedure of Paalman and Pings [15]. Multiple scattering was calculated by Monte Carlo simulation using a program of Meardon [16]. For this calculation the total angular range ($0\text{--}180$ degrees) was subdivided into 223 grid points. Since the measuring grid was finer intermediate

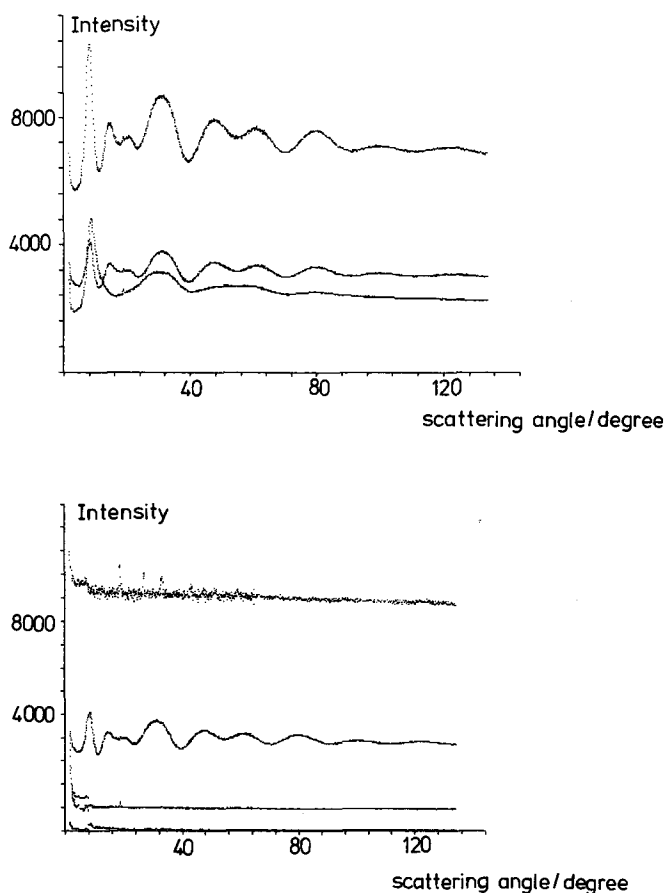


Figure 1. Experimental neutron scattering curves of $\text{C}^{\text{nat}}\text{Cl}_4/\text{CS}_2$, $\text{C}^{35}\text{Cl}_4/\text{CS}_2$, $\text{C}^{37}\text{Cl}_4/\text{CS}_2$, vanadium rod, $\text{C}^{35}\text{Cl}_4/\text{CS}_2$, container, background and cadmium rod (from top to bottom).

angular values had to be obtained by spline interpolation. As input for the program we used the scattering curve corrected for background and absorption and extrapolated to 180 degrees which of course includes multiple scattering. Therefore in an iterative way we took the single scattering output as a new input and repeated the calculation. It was verified for the vanadium rod sample that the program yields the same result as the analytic procedure for an isotropic scatterer worked out by Sears [17]. The inelasticity correction (Placzek correction) was done in the same way as described previously [18] using the spline-fitting procedure in combination with the Placzek parabola.

All data that are required for carrying out the correction procedures are summarized in table 1.

2.2. The molecular dynamics simulation

Although considerable advances have been made recently in computer simulation of molecular liquids little work has been done on molecular liquid mixtures. One major barrier to this is the problem of constructing an 'effective' potential which is capable of reproducing experimental features. In a previous (NPT) MD simulation study Coon *et al.* [19] used the same potential model as Bohn *et al.* [20] in their early theoretical paper for the mixture CCl_4/CS_2 . In both papers the calculated thermodynamic properties did not agree with the experimental data, probably on account of the inadequacy of describing the interactions with only one and two centres. Previous successful MD studies of the pure liquids CCl_4 and CS_2 using atom-atom L-J potentials motivated us to adopt this potential.

In the present simulation the interactions between $\text{CCl}_4\text{-CCl}_4$ are described by a five-centre and those of $\text{CS}_2\text{-CS}_2$ by a three-centre 12-6 L-J potential. For the cross interaction terms the Lorentz-Berthelot mixing rules were used.

The MD simulations were carried out in the microcanonical ensemble using 500 molecules in a cubic box with periodic boundary conditions. All runs were initiated with the molecules arranged in an f.c.c. lattice. In the case of mixtures the molecules with the smaller concentration were located in free sites randomly created within the lattice. The equations of motion were integrated by using an algorithm based on the quaternion method and adapted to a two-component system of linear and tetra-

Table 1. Data for correction procedures.

Substance	$\text{C}^{35}\text{Cl}_4/\text{CS}_2$	$\text{C}^{\text{nat}}\text{Cl}_4/\text{CS}_2$	$\text{C}^{37}\text{Cl}_4/\text{CS}_2$	V
$\rho/10^{27} \text{ m}^{-3}$	7.657	7.635	7.654	72.3
$\sigma_{\text{abs}}/10^{-28} \text{ m}^2$	34.405	26.451	0.545	1.88
$\sigma_{\text{scat}}/10^{-28} \text{ m}^2$	49.658	40.685	8.990	4.997
$A_{\text{S, sc}} (\theta = 0^\circ)$	0.8808	0.8915	0.9735	1.0000
$A_{\text{S, sc}} (\theta = 100^\circ)$	0.8818	0.8924	0.9735	1.0000
$A_{\text{C, sc}} (\theta = 0^\circ)$	0.9020	0.9097	0.9682	0.8115
$A_{\text{C, sc}} (\theta = 100^\circ)$	0.9042	0.9115	0.9683	0.8147
$(d\sigma/d\Omega)_{\text{coh}}^{\text{self}}/10^{-30} \text{ m}^2$	305.7	241.7	73.4	
$(d\sigma/d\Omega)_{\text{inc}}/10^{-30} \text{ m}^2$	71.2	48.4	1.3	39.6
$(d\sigma/d\Omega)_{\text{coh}} (\theta = 0^\circ)/10^{-30} \text{ m}^2$	32.78	25.75	7.45	

ρ , molecular number density; σ_{abs} , absorption cross-section; σ_{scat} , scattering cross-section; $A_{i,jk}$, Paalman-Pings absorption correction factors; $(d\sigma/d\Omega)_{\text{coh}}^{\text{self}}$, self-part of the coherent scattering cross-section; $(d\sigma/d\Omega)_{\text{inc}}$, incoherent scattering cross-section; $(d\sigma/d\Omega)_{\text{coh}} (\theta = 0^\circ)$, limiting value of the coherent scattering cross-section at scattering angle zero.

hedral molecules. The relative energy drift was lower than 1 in 10^6 for the whole simulation. Equilibrium was achieved at about 8 ps and the simulations were extended subsequently to 90 ps. All molecular positions, orientations and velocities were stored on magnetic tape in intervals of 8 time steps (1 step = 0.005 ps) over the total simulation time.

The calculated internal energy of the system was 28.6 kJ mol^{-1} which is almost equal to the experimental one (28.5 kJ mol^{-1}). The results indicate that the used potential model can provide indeed an acceptable prediction of the total internal energy which is very sensitive to this parameter. All atom-pair correlation functions have been calculated.

3. Results

The coherent differential cross-sections obtained after normalization of the neutron scattering curves and subtraction of the incoherent contributions are shown in figure 2 and tabulated in table 2. The extrapolation to $k \rightarrow 0$ was obtained by use of the isothermal compressibility of the components assuming an ideal mixture, an even polynomial of fourth degree was employed in the range $0 < k < 1.7 \text{ \AA}^{-1}$. Included in figure 2 are the coherent self-terms as horizontal lines around which the distinct terms oscillate.

The intramolecular contribution to the coherent cross-section was estimated from the molecular parameters of the mixture components [21, 22] collected in table 3. These served as a start but the intramolecular contribution was finally adjusted to the coherent scattering curve at large k . Then the difference gives the intermolecular contribution which is included in table 2.

This intermolecular coherent differential cross-section contains the information on the liquid structure. It can be described by atom-pair correlation functions of which we have ten different ones in the present mixture (see table 4). We have the relations

$$G(r) = 1 + (2\pi^2\rho)^{-1} \left(\sum_{i,j=1}^n x_i x_j b_i b_j \right)^{-1} \int_0^\infty (d\sigma/d\Omega)_{\text{inter}} \sin(kr)/(kr) k^2 dk$$

and

$$G(r) = \sum_{i=1}^n \sum_{j=1}^n x_i x_j b_i b_j g_{ij}(r) / \sum_{i=1}^n \sum_{j=1}^n x_i x_j b_i b_j \quad (1)$$

where x_i mole fraction of atomic species i , b_i coherent scattering length of atomic species i taking account of the isotopic composition, ρ number density of the sample (total number of molecules per m^3), $(d\sigma/d\Omega)_{\text{inter}}$ intermolecular coherent differential cross-section, and n total number of atomic species in the sample. The values of ρ in the different mixtures are included in table 1. We see that the $g_{ij}(r)$ s enter with different weights into the experimental quantity $G(r)$. By changing the chlorine isotopes in the sample we can form difference curves $\Delta G(r)$ in which all $g_{ij}(r)$ which do not refer to chlorine are excluded, thus only a weighted sum of four g_{ij} s remains.

The relevant data to be substituted into (1) for $G(r)$ are given in table 5. These data gives weights for the use in equation (1) which have been tabulated in table 6. We note that for calculation of $G(r)$ all terms in the double sum are involved, and the weights of the non-diagonal terms in table 6 must be doubled since the atom-pair correlation functions g_{ij} and g_{ji} are equal.

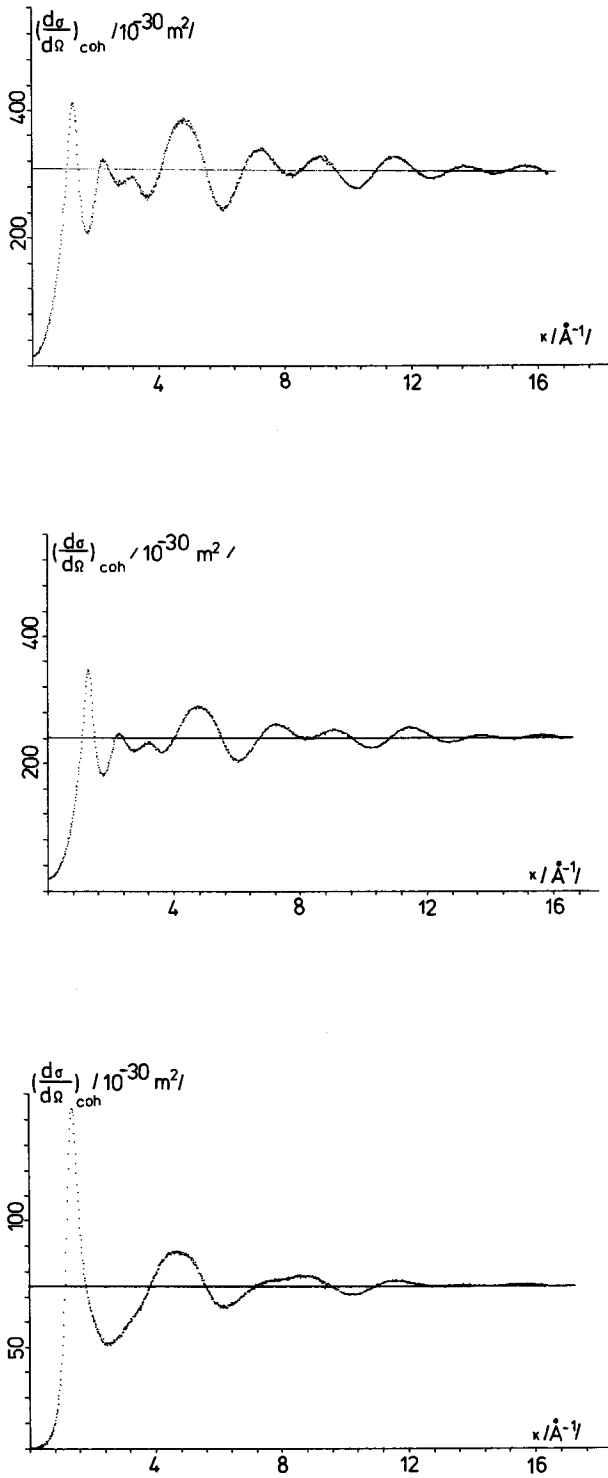


Figure 2. Normalized coherent differential cross-sections of $\text{C}^{35}\text{Cl}_4/\text{CS}_2$, $\text{C}^{\text{nat}}\text{Cl}_4/\text{CS}_2$ and $\text{C}^{37}\text{Cl}_4/\text{CS}_2$ (from top to bottom). The horizontal line indicates the coherent self-term.

Table 2. Corrected coherent differential cross-section and intermolecular contribution.

$k/\text{\AA}^{-1}$	$(d\sigma/d\Omega)_{\text{coh}}/10^{-30} \text{ m}^2$			$(d\sigma/d\Omega)_{\text{inter}}/10^{-30} \text{ m}^2$		
	$\text{C}^{37}\text{Cl}_4/\text{CS}_2$	$\text{C}^{\text{nat}}\text{Cl}_4/\text{CS}_2$	$\text{C}^{35}\text{Cl}_4/\text{CS}_2$	$\text{C}^{37}\text{Cl}_4/\text{CS}_2$	$\text{C}^{\text{nat}}\text{Cl}_4/\text{CS}_2$	$\text{C}^{35}\text{Cl}_4/\text{CS}_2$
0.2	9.33	23.80	36.61	-254.60	-1027.06	-1322.96
0.4	9.87	39.73	58.77	-234.75	-908.75	-1163.85
0.6	12.56	69.42	98.37	-203.15	-728.39	-923.15
0.8	18.88	117.57	159.39	-162.53	-506.50	-631.17
1.0	39.24	193.62	255.67	-107.06	-260.82	-310.84
1.2	99.98	310.23	384.76	-14.53	-2.11	3.87
1.4	141.67	304.00	374.14	52.72	90.98	120.31
1.6	98.48	199.44	236.81	27.53	38.17	45.76
1.8	73.13	182.89	214.64	12.86	31.14	30.22
2.0	61.72	211.96	267.57	6.24	40.30	51.88
2.2	54.46	245.44	319.97	-0.10	40.59	57.60
2.4	50.22	239.78	308.01	-5.26	3.50	4.20
2.6	51.03	224.56	289.08	-5.72	-30.97	-37.10
2.8	52.70	221.19	278.23	-4.96	-37.48	-46.77
3.0	56.65	226.91	283.24	-1.67	-21.25	-21.51
3.2	58.93	230.87	287.04	-0.36	-0.03	10.87
3.4	62.97	226.15	273.32	1.66	10.75	21.35
3.6	66.34	217.79	255.14	1.49	9.03	12.62
3.8	72.22	223.47	265.29	2.31	8.99	12.59
4.0	77.89	239.39	286.67	2.01	7.81	6.05
4.2	83.33	259.83	322.10	1.53	4.61	3.47
4.4	86.11	277.26	350.30	-0.42	-1.21	-5.62
4.6	86.31	287.24	370.85	-2.83	-7.29	-11.11
4.8	86.29	289.14	378.63	-2.86	-9.72	-11.03
5.0	85.73	284.59	368.30	-0.90	-5.81	-9.03
5.2	83.23	274.12	353.61	0.98	2.41	4.80
5.4	78.27	254.45	322.47	1.27	6.40	10.25
5.6	73.00	228.76	281.27	1.03	3.12	3.98
5.8	68.02	211.38	252.95	-0.03	1.45	0.37
6.0	65.59	205.41	241.44	-0.20	1.35	-1.74
6.2	65.03	207.61	246.92	-0.24	-0.64	-2.67
6.4	66.52	220.21	264.57	0.33	0.20	-3.43
6.6	67.71	233.26	288.86	-0.27	-1.88	-2.99
6.8	69.67	245.83	314.05	-0.37	-3.29	0.12
7.0	71.82	257.55	330.53	-0.08	-0.92	1.94
7.2	73.53	262.20	333.13	0.23	0.64	-0.01
7.4	74.70	260.11	330.81	0.48	1.21	2.48
7.6	75.17	255.19	317.94	0.37	2.50	0.27
7.8	75.78	247.00	306.39	0.51	1.18	0.38
8.0	75.63	240.95	298.33	-0.15	0.00	0.50
8.2	76.71	240.79	296.11	0.33	1.17	0.27
8.4	77.04	241.26	298.18	0.05	-0.57	-2.03
8.6	77.31	244.76	306.60	-0.08	-1.49	-2.19
8.8	77.04	248.53	317.69	-0.35	-2.21	-0.28
9.0	76.92	251.57	323.95	0.08	-1.62	-0.06
9.2	76.01	252.89	325.48	0.27	0.65	1.16
9.4	72.80	249.36	322.10	-1.44	1.63	3.77
9.6	72.68	241.97	308.12	0.08	1.23	0.57
9.8	71.52	234.65	295.54	0.37	1.43	0.42
10.0	70.22	228.00	284.56	0.06	0.67	-0.17
10.2	70.05	225.14	278.91	0.23	0.33	-0.54
10.4	70.13	225.96	279.45	-0.01	-0.44	-1.36
10.6	70.77	230.92	288.82	-0.25	-0.79	0.45

Table 2 (continued).

$k/\text{\AA}^{-1}$	$(d\sigma/d\Omega)_{\text{coh}}/10^{-30} \text{ m}^2$			$(d\sigma/d\Omega)_{\text{incoh}}/10^{-30} \text{ m}^2$		
	$\text{C}^{37}\text{Cl}_4/\text{CS}_2$	$\text{C}^{\text{nat}}\text{Cl}_4/\text{CS}_2$	$\text{C}^{35}\text{Cl}_4/\text{CS}_2$	$\text{C}^{37}\text{Cl}_4/\text{CS}_2$	$\text{C}^{\text{nat}}\text{Cl}_4/\text{CS}_2$	$\text{C}^{35}\text{Cl}_4/\text{CS}_2$
10.8	71.94	239.02	300.20	-0.27	-0.26	0.26
11.0	73.54	246.80	312.64	0.11	-0.33	0.37
11.2	74.44	253.02	322.64	0.00	-0.26	0.57
11.4	74.98	255.72	325.66	-0.08	-0.61	-1.29
11.6	75.47	256.89	326.81	0.23	1.09	0.70
11.8	75.14	252.48	320.76	0.10	0.28	0.45
12.0	74.63	247.88	312.67	0.05	1.08	0.96
12.2	74.02	241.00	303.09	-0.02	-0.17	0.13
12.4	73.68	236.93	296.81	0.13	0.15	0.33
12.6	73.31	234.26	292.86	0.11	-0.29	-0.89
12.8	73.07	234.95	295.01	0.02	0.29	0.05
13.0	72.91	236.19	298.27	-0.14	-0.42	-0.81
13.2	72.91	238.79	304.12	-0.23	-0.66	-0.25
13.4	72.98	241.62	309.68	-0.28	-0.47	0.77
13.6	73.39	244.30	310.43	0.06	0.59	-0.89
13.8	73.37	244.46	310.75	0.04	0.52	-0.33
14.0	73.19	243.11	308.49	-0.06	0.17	-0.15
14.2	73.14	241.12	306.34	-0.03	-0.18	1.19
14.4	73.17	239.36	302.66	0.06	-0.41	0.60
14.6	73.01	238.68	300.11	-0.12	-0.32	-0.41
14.8	72.98	238.07	301.01	-0.24	-1.26	-0.07
15.0	73.09	240.22	303.91	-0.29	-0.43	0.46
15.2	73.64	242.65	306.53	0.08	0.16	-0.13
15.4	73.66	243.63	308.84	-0.02	-0.48	-0.57
15.6	73.75	245.33	310.72	0.06	0.48	0.18
15.8	73.83	245.05	309.75	0.30	0.75	0.35
16.0	73.63	243.62	307.11	0.41	1.17	1.05

Table 3. Intramolecular parameters of CCl_4 and CS_2 .

	CCl_4	T/K	CS_2	T/K	
$R_{\text{CCl}}/\text{\AA}$	1.7667		$R_{\text{CS}}/\text{\AA}$	1.56	
$R_{\text{ClCl}}/\text{\AA}$	2.8881		$R_{\text{SS}}/\text{\AA}$	3.12	
$\Delta_{\text{CCl}}/\text{\AA}$	0.0505	295	$\Delta_{\text{CS}}/\text{\AA}$	0.0387	298
$\Delta_{\text{ClCl}}/\text{\AA}$	0.0696	295	$\Delta_{\text{SS}}/\text{\AA}$	0.0412	298

R_{AB} , length of the bond A-B; Δ , mean-square vibrational amplitude.

Table 4. Atom-pair correlations for the CCl_4/CS_2 mixture.

		CCl_4		CS_2	
		C	Cl	C'	S
CCl_4	C	g_{CC}	g_{CCl}	$g_{\text{CC}'}$	g_{CS}
	Cl		g_{ClCl}	$g_{\text{ClC}'}$	g_{ClS}
CS_2	C'			$g_{\text{C}'\text{C}'}$	$g_{\text{C}'\text{S}}$
	S				g_{SS}

Table 5. Data for the calculation of weight factors in equation (1).

	CCl_4				CS_2			
	C		Cl		C'		S	
	$b/10^{-15}$ m	x	$b/10^{-15}$ m	x	$b/10^{-15}$ m	x	$b/10^{-15}$ m	x
$\text{C}^{35}\text{Cl}/\text{CS}_2$	6.65	0.498	11.65†	1.992	6.65	0.502	2.85	1.004
$\text{C}^{37}\text{Cl}/\text{CS}_2$	6.65	0.501	3.24†	2.004	6.65	0.499	2.85	0.998
$\text{C}^{\text{nat}}\text{Cl}/\text{CS}_2$	6.65	0.513	9.61	2.052	6.65	0.487	2.85	0.974

† This scattering length takes into account the ^{35}Cl respectively ^{37}Cl concentration of our samples (99.35 per cent ^{35}Cl , 0.65 per cent ^{37}Cl ; 98.21 per cent ^{37}Cl , 1.79 per cent ^{35}Cl) and the scattering length of ^{35}Cl (11.7×10^{-15} m) and ^{37}Cl (3.08×10^{-15} m).

In figure 3 the intermolecular G -functions for the three samples are plotted. The full curves show the results from neutron scattering, they were obtained by Fourier-transformation of the data in figure 2; the crosses are the results from computer simulation obtained by adding the atom-pair correlation functions with the proper weights given in table 6. The figure shows a remarkable good agreement between the experimental and simulated G s. The steep initial increase, the location and the shape of the first and of the second peak are in excellent agreement. The agreement also extends to some of the local structure in the region of the first peak.

A further technique for analysing $G(r)$ to obtain the ten atom-pair correlation functions is by forming differences of the scattering curves, for example of the intermolecular contributions of the coherent cross-sections shown in figure 2. From

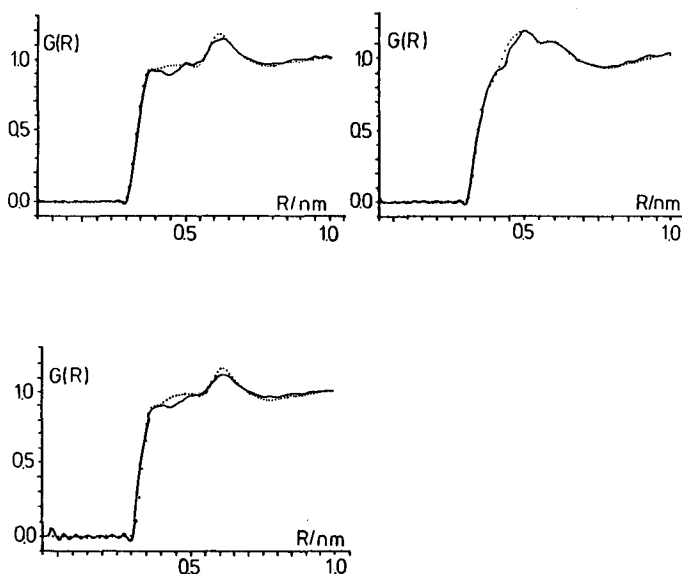


Figure 3. Intermolecular G -functions from neutron scattering (full curves) and computer simulation (dotted curves): $\text{C}^{35}\text{Cl}_4/\text{CS}_2$ (upper left), $\text{C}^{37}\text{Cl}_4/\text{CS}_2$ (upper right) and $\text{C}^{\text{nat}}\text{Cl}_4/\text{CS}_2$ (lower left).

Table 6. Weight factors for use in equation (1). The three figures in each box refer to the three samples $C^{35}Cl_4/CS_2$, $C^{37}Cl_4/CS_2$ and $C^{nat}Cl_4/CS_2$ respectively.

		CCl ₄		CS ₂	
		C	Cl	C'	S
CCl ₄	C	0.010	0.072	0.010	0.009
		0.043	0.085	0.043	0.037
		0.014	0.079	0.013	0.011
Cl			0.503	0.072	0.062
			0.165	0.084	0.072
			0.458	0.075	0.064
CS ₂	C'			0.010	0.009
				0.043	0.037
				0.012	0.011
S					0.008
					0.032
					0.009

the weights of the atom-pair correlation functions contained in the functions G as given in table 6, we can derive the following differences:

$$\frac{4.193G(C^{35}Cl_4/CS_2) - G(C^{37}Cl_4/CS_2)}{3.190}$$

$$= 0.609g_{ClCl} + 2 \cdot 0.068g_{CCl} + 2 \cdot 0.068g_{C'Cl} + 2 \cdot 0.059g_{SCl}$$

$$\frac{1.265G(C^{35}Cl_4/CS_2) - G(C^{nat}Cl_4/CS_2)}{0.262}$$

$$= 0.679g_{ClCl} + 2 \cdot 0.046g_{CCl} + 2 \cdot 0.061g_{C'Cl} + 2 \cdot 0.053g_{SCl}$$

$$\frac{3.315G(C^{nat}Cl_4/CS_2) - G(C^{37}Cl_4/CS_2)}{2.333}$$

$$= 0.580g_{ClCl} + 2 \cdot 0.076g_{CCl} + 2 \cdot 0.071g_{C'Cl} + 2 \cdot 0.063g_{SCl}$$

These differences are shown in figure 4 together with the computer simulation results obtained by adding the atom-pair correlation functions as indicated above. Also in this case the agreement between experimental and simulated curves is remarkably good. These results amply justify the use of the described potential model and indicate that the structural data of the mixture can be considered as quite reliable.

We gratefully acknowledge financial support by the project 'Complex Liquids' of the 'Zentrum für interdisziplinäre Forschung' and by the Fonds der Chemischen Industrie. We thank Dr. J. Schulz, Institut für Physikalische Chemie der RWTH Aachen, for help with the neutron scattering measurements. Dr. C. Albayrak, Schering AG Berlin, gave assistance during the preparative work.

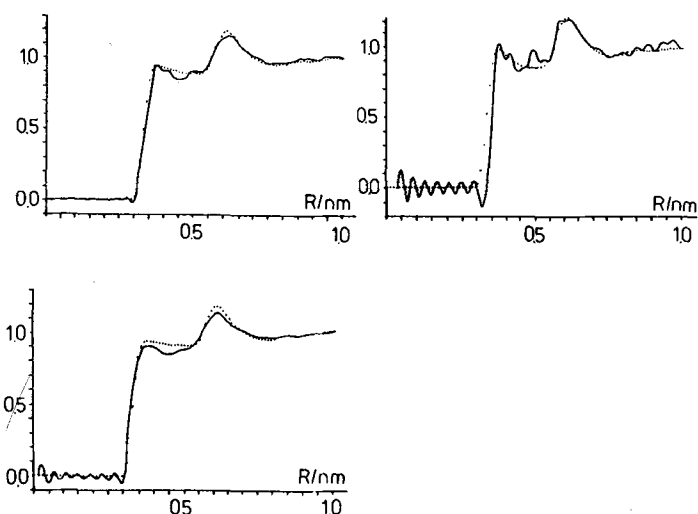


Figure 4. Intermolecular difference functions of $\text{C}^{35}\text{Cl}_4/\text{CS}_2 - \text{C}^{37}\text{Cl}_4/\text{CS}_2$ (upper left), $\text{C}^{35}\text{Cl}_4/\text{CS}_2 - \text{C}^{\text{nat}}\text{Cl}_4/\text{CS}_2$ (upper right) and $\text{C}^{\text{nat}}\text{Cl}_4/\text{CS}_2 - \text{C}^{37}\text{Cl}_4/\text{CS}_2$ (lower left) from neutron scattering (full curves) and computer simulation (dotted curves).

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