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## Molecular dynamics studies and neutron scattering experiments on methylene chloride

### I. Structure

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Molecular dynamics (MD) simulations of methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) with two different potentials are used to calculate the intermolecular static structure factor  $\mathcal{S}_{\text{inter}}(q)$  for a series of isotopic substituted mixtures  $\text{CX}_2\text{Cl}_2$ . The intermolecular structure factors are compared with corresponding experimental data obtained from neutron diffraction. We discuss the validity of the rigid molecule approximation in the MD simulation and show that the quantitative comparison of the static structure factors of molecular liquids obtained from neutron diffraction experiments and MD simulation must be considered with some care for molecules containing hydrogen atoms with low effective masses.

### 1. Introduction

The ultimate goal of neutron diffraction experiments on molecular fluids is a complete description of the liquid structure, usually described by a set of atom pair correlation functions. It has to be remarked that this description is not really complete, because it contains the information about angular correlations between the molecules in the liquid only implicitly. In principle, for molecules consisting of  $N$  non-equivalent atoms, the atom pair correlation functions can be extracted from diffraction experiments by performing a series of  $N(N + 1)/2$  diffraction experiments on different isotopic mixtures yielding a linear system of equations from which the partial structure factors can be calculated. The atom pair correlation functions are essentially the Fourier-Bessel transforms of the partial structure factors.

In practice the method of isotopic substitution fails for larger molecules, because the number of constructable isotopic mixtures is limited by the number of isotopes available for each atom. In addition, the differences between the diffraction patterns of different isotopic mixtures are often very small and so two or more of the linear equations for the partial structure factors are nearly dependent. As a consequence the solution may become unstable and therefore not reliable.

Molecular dynamics (MD) simulations, combined with neutron diffraction experiments, offer an excellent tool for the determination of the atom pair correlation functions: Given an intermolecular MD potential, one can calculate a 'fictitious' diffraction pattern for one or more isotopic mixtures. If the experimental patterns can be reproduced one can assume, although not prove, that the MD

potential is realistic, and it is then a simple matter to get all structural information from the MD simulation.

Although this procedure is in principle very simple one has to be aware of some essential points when comparing simulated and measured diffraction patterns:

beside assuming the validity of classical mechanics for the liquid motion in the MD simulation, the molecules are usually idealized by rigid rotators, non-trivial inelasticity corrections of the experimental data have to be applied, because the neutron is not an ideal probe and cannot map an instantaneous picture of the liquid.

Nevertheless the intermolecular structure factors for methylene chloride, shown by Jung *et al.* [1], to which we refer in this article, can be reproduced quite well by MD for all isotopic mixtures. Therefore the calculated atom pair correlation functions can be assumed to be close to reality.

## 2. MD simulation of methylene chloride

The molecules of methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) have the geometry shown in figure 1. From the moments of inertia,  $I_a = 2.62 \times 10^{-46} \text{ kg m}^2$ ,  $I_b = 2.53 \times 10^{-45} \text{ kg m}^2$ ,  $I_c = 2.74 \times 10^{-45} \text{ kg m}^2$  it can be seen, that a  $\text{CH}_2\text{Cl}_2$  molecule behaves like a nearly symmetric top molecule, because the relation  $I_b \approx I_c$  holds. The total mass of a  $\text{CH}_2\text{Cl}_2$  molecule equals 85 atomic mass units and its characteristic bond lengths and angles are given in (1) according to [2].

$$\left. \begin{aligned} r_{\text{C-Cl}} &= 1.767 \pm 0.002 \text{ \AA}, \\ r_{\text{C-H}} &= 1.085 \pm 0.002 \text{ \AA}, \\ \angle_{\text{H-C-H}} &= 112.1 \pm 0.2^\circ, \\ \angle_{\text{Cl-C-Cl}} &= 112.2 \pm 0.1^\circ. \end{aligned} \right\} \quad (1)$$

We used two different MD potentials from the literature [3, 4] which had already been employed in previous MD simulations [3, 4, 5]. The simulation runs were carried out with the program MDMPOL from the CCP5 program library [6] which had to be modified for the implementation of the second potential [7]. An excellent introduction into the technique of MD simulations and a detailed description of the MD simulation algorithm in MDMPOL is given in [8].

### 2.1. Potentials

Both potentials we used for the simulation of methylene chloride are so-called 'site-site-potentials', in which the molecules are treated as *rigid rotators* consisting of atoms that are modelled by mass points (see figure 1). Each molecule carries a number of force centres (sites), which are identical with the atomic positions in the first potential [3], called 'potential A', and shifted towards the centre of mass by a small amount in the second potential [4], called 'potential B'. The interaction between the molecules is described by intermolecular site-site *pair interactions* and is split up into a Coulombic and a non-Coulombic part. The latter is given by a Lennard-Jones-potential in potential A and by a 'exp-6-potential' in potential B. In

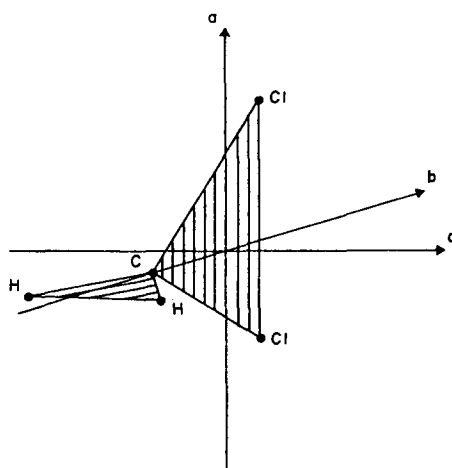


Figure 1. Geometry of a  $\text{CH}_2\text{Cl}_2$  molecule. The axes  $a$ ,  $b$ ,  $c$  are principal axes of inertia.

both potentials the Coulomb interaction is described by fractional point charges on the interaction sites.

If we denote two sites on different molecules by ' $\alpha$ ' and ' $\beta$ ' we have for the site-site interaction potential  $\Phi_{\alpha\beta}(r)$  in the case of potential  $A$  (see [3])

$$\Phi_{\alpha\beta}^{(A)}(r) = 4\varepsilon_{\alpha\beta} \cdot \left( \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^6 \right) + \frac{1}{4\pi\varepsilon_0} \cdot \frac{q_\alpha q_\beta}{r}. \quad (2)$$

The parameters  $\sigma_{\alpha\beta}$  and  $\varepsilon_{\alpha\beta}$  are combined according to the mixing rules

$$\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_\alpha + \sigma_\beta), \quad (3)$$

$$\varepsilon_{\alpha\beta} = \sqrt{(\varepsilon_\alpha \varepsilon_\beta)}. \quad (4)$$

All parameters  $\sigma_\alpha$ ,  $\varepsilon_\alpha$ , and the fractional charges  $q_\alpha$  are listed in table 1. It should be remarked that in [3] no hint on the molecular geometry can be found. We assumed an exact tetrahedral geometry with respect to the angles  $\angle_{\text{X-C-X}}$ , because the MD program used in [3] is TETRA, which is designed for the simulation of tetrahedral five-centre Lennard-Jones fluids [9]. The difference between the molecular geometry given in (1), see also [4], and the geometry used in [3] is small:

$$\left. \begin{aligned} r_{\text{C-Cl}} &= 1.770 \text{ \AA}, \\ r_{\text{C-H}} &= 1.090 \text{ \AA}, \\ \angle_{\text{H-C-H}} &= 109.5^\circ, \\ \angle_{\text{Cl-C-Cl}} &= 109.5^\circ. \end{aligned} \right\} \quad (5)$$

Table 1. Parameters for potential  $A$ .

Site ( $\alpha$ )	$(\varepsilon/k_B)/\text{K}$	$\sigma/\text{\AA}$	$q/ e $
Cl	175.0	3.35	-0.109
H	13.4	2.75	0.098
C	51.0	3.20	0.022

Table 2.  $C_{6,\alpha\beta}$ -parameters for potential  $B$  in a.u.

Interaction	$C_{6,\alpha\beta}$
C-C	24.748
C-Cl	54.578
C-H	9.509
Cl-Cl	121.203
Cl-H	21.265
H-H	3.745

The intermolecular site-site potential reads for potential  $B$  (see [4]):

$$\Phi_{\alpha\beta}^{(B)}(r) = \exp\left(-\frac{r - \sigma_\alpha - \sigma_\beta}{\rho_\alpha + \rho_\beta}\right) - C_6 f(r) \frac{C_{6,\alpha\beta}}{r^6} + \frac{q_\alpha q_\beta}{r}, \quad (6)$$

$$f(r) = \begin{cases} \exp\left[\left(1 - \frac{1.28R_{\alpha\beta}^0}{r}\right)^2\right], & r \leq 1.28R_{\alpha\beta}^0, \\ 1, & r > 1.28R_{\alpha\beta}^0. \end{cases} \quad (7)$$

In tables 2 and 3 all parameters for this 'exp-6-potential' can be found. They are given in atomic units (a.u.), i.e. lengths are measured in Bohr-radii ( $a_0 = 5.292 \times 10^{-11}$  m), energies in Hartree (1 Hartree =  $4.36 \times 10^{-18}$  J), and charges in proton charges ( $e = 1.60 \times 10^{-19}$  C) [10].

## 2.2. Simulation runs

We carried out two MD simulations of methylene chloride at 293 K, one for each potential, with 108 molecules in the (cubic) simulation box and 65 536 time steps of 5 fs, giving a total length of  $\approx 320$  ps for each MD run in real time. For both MD runs a separate equilibration run of 3000 time steps was performed.

According to the simulation algorithm implemented in MDMPOL [6] the MD runs were performed with constant total energy  $E$ , volume  $V$ , and number of molecules  $N$  (simulation of an  $(N, V, E)$ - or microcanonical ensemble). MDMPOL uses a *leap-frog algorithm* for the integration of the translational equation of motion and a *leap-frog quaternion algorithm* for the integration of the rotational equation of motion.

The size of the MD box was set to 22.56 Å. This is equivalent to the density of  $\text{CH}_2\text{Cl}_2$  at 293 K on the liquid-vapour coexistence line, which is equal to 1.326 g/cm<sup>3</sup> [11]. For both potentials table 4 shows the average values of some important quantities and their rms fluctuations calculated by MDMPOL during the simulation run. From the rms fluctuations of the total energy it can be seen that the integration algorithm is quite stable (only for the first 5000 time steps energy scaling

Table 3. Potential parameters of the interaction sites for potential  $B$  in a.u.

Site ( $\alpha$ )	$q$	$\rho$	$\sigma$	$R_{\alpha\beta}^0$	$C_6$
C	-0.487	0.12898	1.60502	3.2125	
Cl	-0.037	0.26756	1.69610	3.3070	1.327
H	0.280	0.27646	0.28849	2.2677	

Table 4. Averages and rms-fluctuations from MDMPOL for potential A/B.

Quantity	Average (A)	Rms-fluct. (A)	Average (B)	Rms-fluct. (B)
$\langle U \rangle / \text{kJ mol}^{-1}$	-25.43	0.25	-28.60	0.27
$\langle T \rangle_{\text{trans}} / \text{kJ mol}^{-1}$	3.67	0.24	3.66	0.24
$\langle T \rangle_{\text{rot}} / \text{kJ mol}^{-1}$	3.69	0.24	3.69	0.24
$\langle E \rangle / \text{kJ mol}^{-1}$	-18.08	0.10	-21.25	0.07
virial / $\text{kJ mol}^{-1}$	1.63	6.15	2.53	5.56
pressure / MPa	29.65	31.19	24.97	28.06
temperature / K	295.04	10.21	294.89	10.56

was performed). Another simple check of the ‘quality’ of the simulation runs can be carried out by comparing the mean potential energy per mole  $\langle U \rangle$  with the experimental value  $\langle U \rangle \approx \Delta_v H - RT$ , where  $\Delta_v H$  is the molar vapourization enthalpy. From that relation one obtains, with  $\Delta_v H = 29.16 \text{ kJ mol}^{-1}$  [12],  $\langle U \rangle = -26.7 \text{ kJ mol}^{-1}$ . This shows that the MD runs for both potentials give reasonable values for  $\langle U \rangle$ .

### 3. The static structure factor: theoretical relations and calculation from MD simulations

In general the distribution of neutrons scattered by an isotropic target such as a molecular liquid or an amorphous solid, is described by the double differential cross section (flux per incident current density, unit solid angle, and unit energy interval)

$$\frac{d^2\sigma}{d\Omega dE} = N \frac{k}{k_0} \mathcal{S}(q, \omega), \tag{8}$$

where the *dynamic structure factor*  $\mathcal{S}(q, \omega)$  is given by

$$\mathcal{S}(q, \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \mathcal{F}(q, t), \tag{9}$$

$$\mathcal{F}(q, t) = \frac{1}{N} \sum_{\alpha, \beta} \sum_{i, j} \Gamma_{\alpha\beta ij} \langle \exp[-i\mathbf{q} \cdot \mathbf{R}_{\alpha i}(0)] \exp[i\mathbf{q} \cdot \mathbf{R}_{\beta j}(t)] \rangle, \tag{10}$$

$$\Gamma_{\alpha\beta ij} = \bar{b}_{\alpha}^* \bar{b}_{\beta} + \delta_{\alpha\beta ij} \{ |\bar{b}_{\alpha}|^2 - |\bar{b}_{\beta}|^2 \}. \tag{11}$$

In (10) Latin symbols denote molecules, Greek symbols denote atoms in one molecule, and  $N = N_m \cdot N_a$ .  $N_a$  is the total number of atoms/scatterers in the target. ( $N_m$  is the number of molecules and  $N_a$  is the number of atoms per molecule.) The position of atom  $\alpha$  in molecule  $i$  is therefore denoted by  $\mathbf{R}_{\alpha i}$ . As usual,  $\bar{b}_{\alpha}$  and  $|\bar{b}_{\alpha}|^2$  stand for the mean and mean square scattering length of atom  $\alpha$  in an arbitrary molecule. The quantity  $\mathcal{F}(q, t)$  is called ‘intermediate scattering function’ and its Fourier transform, the dynamic structure factor, is the basic quantity of interest in *inelastic* neutron scattering experiments: It contains the total information about the structure and dynamics of the probed liquid [13].

In neutron diffraction experiments the basic quantity of interest is the *static structure factor*  $\mathcal{S}(q)$ , given by

$$\mathcal{S}(q) = \int_{-\infty}^{\infty} d\omega \mathcal{S}(q, \omega) = \mathcal{F}(q, 0). \tag{12}$$

If the *static approximation*,  $\mathcal{F}(q, t) \approx \mathcal{F}(q, 0)$ ,† can be assumed to be valid,  $\mathcal{S}(q)$  is related to the measured differential cross section by

$$\frac{d\sigma}{d\Omega} = N\mathcal{S}(q). \quad (13)$$

In equations (8) and (13) it is tacitly assumed that multiple scattering and absorption of neutrons in the specimen can be neglected. Those effects will be treated in part II of this publication.

According to equations (10), (11), and (12)  $\mathcal{S}(q)$  splits into a *coherent* and an *incoherent* part

$$\mathcal{S}_{\text{coh}}(q) = \frac{1}{N} \sum_{\alpha, \beta} \sum_{i, j} \bar{b}_{\alpha}^* \bar{b}_{\beta} \langle \exp(-i\mathbf{q} \cdot [\mathbf{R}_{\alpha i} - \mathbf{R}_{\beta j}]) \rangle, \quad (14)$$

$$\mathcal{S}_{\text{inc}}(q) = \frac{1}{N_a} \sum_{\alpha} \{ |\bar{b}_{\alpha}|^2 - |\bar{b}_{\alpha}|^2 \}. \quad (15)$$

It is evident that  $\mathcal{S}_{\text{inc}}(q)$  does not contain structural information and therefore in the following we consider only the coherent structure factor  $\mathcal{S}_{\text{coh}}(q)$  which can be separated into an *intermolecular* and an *intramolecular* part. The latter one can be separated again into a ‘distinct’ and a ‘self’ (index ‘d’ and ‘s’) part:

$$\mathcal{S}_{\text{coh}}(q) = \mathcal{S}_{\text{intra, s}}(q) + \mathcal{S}_{\text{intra, d}}(q) + \mathcal{S}_{\text{inter}}(q). \quad (16)$$

The functions  $\mathcal{S}_{\text{intra, s}}(q)$ ,  $\mathcal{S}_{\text{intra, d}}(q)$ , and  $\mathcal{S}_{\text{inter}}(q)$  are given by

$$\mathcal{S}_{\text{intra, s}}(q) = \frac{1}{N_a} \sum_{\alpha} |\bar{b}_{\alpha}|^2, \quad (17)$$

$$\mathcal{S}_{\text{intra, d}}(q) = \frac{1}{N_a} \sum_{\alpha \neq \beta} \bar{b}_{\alpha}^* \bar{b}_{\beta} \exp(-\frac{1}{6} \langle \mathbf{u}_{\alpha\beta}^2 \rangle q^2) j_0(qR_{\alpha\beta}^{(0)}), \quad (18)$$

$$\mathcal{S}_{\text{inter}}(q) = \frac{1}{N_a} \sum_{\alpha, \beta} \bar{b}_{\alpha}^* \bar{b}_{\beta} h_{\alpha\beta}(q). \quad (19)$$

Here is  $j_0(qr)$  the zeroth spherical Bessel function,  $R_{\alpha\beta}^{(0)}$  the intramolecular equilibrium distance of atoms  $\alpha$  and  $\beta$ , and  $\langle \mathbf{u}_{\alpha\beta}^2 \rangle$  the corresponding mean square displacement. The set of functions  $h_{\alpha\beta}(q)$  is related to the *atom pair correlation functions*  $g_{\alpha\beta}(r)$  [15, 16] and contains the same information about the structure of the liquid:

$$h_{\alpha\beta}(q) = \rho \int_0^{\infty} dr 4\pi r^2 \{g_{\alpha\beta}(r) - 1\} j_0(qr) \quad (20)$$

with  $\rho$  defined as the molecular number density. In principle the set  $h_{\alpha\beta}(q)$  can be obtained from a series of  $N_a(N_a + 1)/2$  diffraction patterns from different isotopic mixtures [15].

To get an empirical guess of the size of the ‘error bars’ which must be assigned to the values of  $\mathcal{S}_{\text{inter}}(q)$  calculated by MD we calculated the static intermolecular structure factor in two different ways from our MD simulations.

† Here  $t$  stands for the interaction time of the neutron with the target [14]. The static approximation may be also written in the form  $\mathcal{S}(q, \omega) \approx \mathcal{S}(q) \cdot \delta(\omega)$  which is also known as ‘elastic scattering approximation’.

- (a) Direct calculation according to (12). (This calculation can be regarded as a byproduct if one is interested in the dynamics of the liquid)
- (1) Construct an appropriate number of  $q$ -vectors on a cubic lattice with lattice constant  $L$  (box size of the cubic MD box):  $\mathbf{q} = 2\pi/L(l, m, n)$ , with integer  $l, m, n$ .
  - (2) Calculate  $D(\mathbf{q}, t) = 1/\sqrt{N} \sum_{\alpha, i} \bar{b}_{\alpha} \exp [i\mathbf{q} \cdot \mathbf{R}_{\alpha i}(t)]$ ;  $t = n_t \Delta t$ , from the position coordinates of all atoms, generated by the MD program.
  - (3) Calculate the time correlation function  $\mathcal{F}_{\text{coh}}(\mathbf{q}, t) = \langle D(-\mathbf{q}, 0)D(\mathbf{q}, t) \rangle$ .
  - (4) Average  $\mathcal{F}_{\text{coh}}(\mathbf{q}, t)$  over an appropriate number of  $q$ -vectors in the same channel  $q = n_q \Delta q$  to get  $\mathcal{F}(q, t)$  on an equidistantly spaced  $(q, t)$ -mesh.
  - (5) Extract  $\mathcal{S}'_{\text{coh}}(q)$  according to  $\mathcal{S}'_{\text{coh}}(q) = \mathcal{F}_{\text{coh}}(q, 0)$ . The prime indicates that the corresponding quantities refer to a rigid molecule.
  - (6) Calculate  $\mathcal{S}_{\text{inter}}(q) = \mathcal{S}'_{\text{coh}}(q) - \mathcal{S}_{\text{intra, s}}(q) - \mathcal{S}'_{\text{intra, d}}(q)$ .
- (b) Indirect method: Calculate  $\mathcal{S}_{\text{inter}}(q)$  from the atom pair correlation functions according to equations (19), (20).

It should be pointed out that, although most of the information contained in  $\mathcal{F}_{\text{coh}}(q, t)$  is not used in  $\mathcal{S}_{\text{coh}}(q)$ , the direct method is about four times faster than the indirect method if the *fast correlation algorithm* for the calculation of  $\mathcal{F}_{\text{coh}}(q, t)$  is applied [16, 17], using the number of configurations and  $q$ -vectors specified below.

#### 4. Results

Here we show the results for the static correlation functions  $\mathcal{S}_{\text{inter}}(q)$  and  $g_{\alpha\beta}(r)$  obtained from MD simulations of methylene chloride with potential  $A$  and  $B$ . All calculations were performed for a series of four different isotopic mixtures  $CX_2Cl_2$ , as studied in [1], where  $X$  stands for 'H', 'Z', 'M', or 'D':

'H' means pure  $\text{CH}_2\text{Cl}_2$ .

'Z' means  $\bar{b}_Z = 0$  ('zero mixture'). This can be achieved by mixing  $\text{CZ}_2\text{Cl}_2 = 64$  per cent  $\text{CH}_2\text{Cl}_2 + 36$  per cent  $\text{CD}_2\text{Cl}_2$ .

'M' means a mixture of 50 per cent  $\text{CH}_2\text{Cl}_2$  and 50 per cent  $\text{CD}_2\text{Cl}_2$ .

'D' means completely deuterated methylene chloride.

When using the 'direct method' the intermolecular structure factor  $\mathcal{S}_{\text{inter}}(q)$  is calculated as follows: First, the total scattering function  $\mathcal{S}_{\text{coh}}(q)$  is computed by using statistically averaged scattering lengths (assuming random distribution of the H and D). Then we subtract the intramolecular part, which we calculate exactly the same way. By this, we obtain the correct intermolecular structure factor  $\mathcal{S}_{\text{inter}}(q)$  for the molecular mixtures, which are random with respect to the molecular, but not with respect to the intramolecular H/D distribution.

For the direct calculation of  $\mathcal{S}_{\text{inter}}(q)$  and  $\mathcal{S}_{\text{coh}}(q)$  we used 8192 MD configurations with a time distance of 40 fs in real time (each eighth time step of the simulation) and 600  $q$ -vectors in 60 equidistant  $q$ -channels of  $0.2 \text{ \AA}^{-1}$ .

The atom pair correlation functions  $g_{\alpha\beta}(r)$  were calculated from 500 MD configurations for  $0 \text{ \AA} \leq r \leq 10 \text{ \AA}$  and a channel width  $\Delta r$  of  $0.1 \text{ \AA}$ .

For the calculation of  $\mathcal{S}_{\text{inter}}(q)$  according to equations (19) and (20) we used a 70 per cent (gaussian) taper window [18] with a standard deviation of  $1.5 \text{ \AA}$  to suppress truncation effects in the Fourier-Bessel transform.

Figure 2 shows the so-called 'reduced intensity'  $q\mathcal{S}_{\text{inter}}(q)$ , calculated from MD simulation, using the direct and the indirect method (solid line and dashed



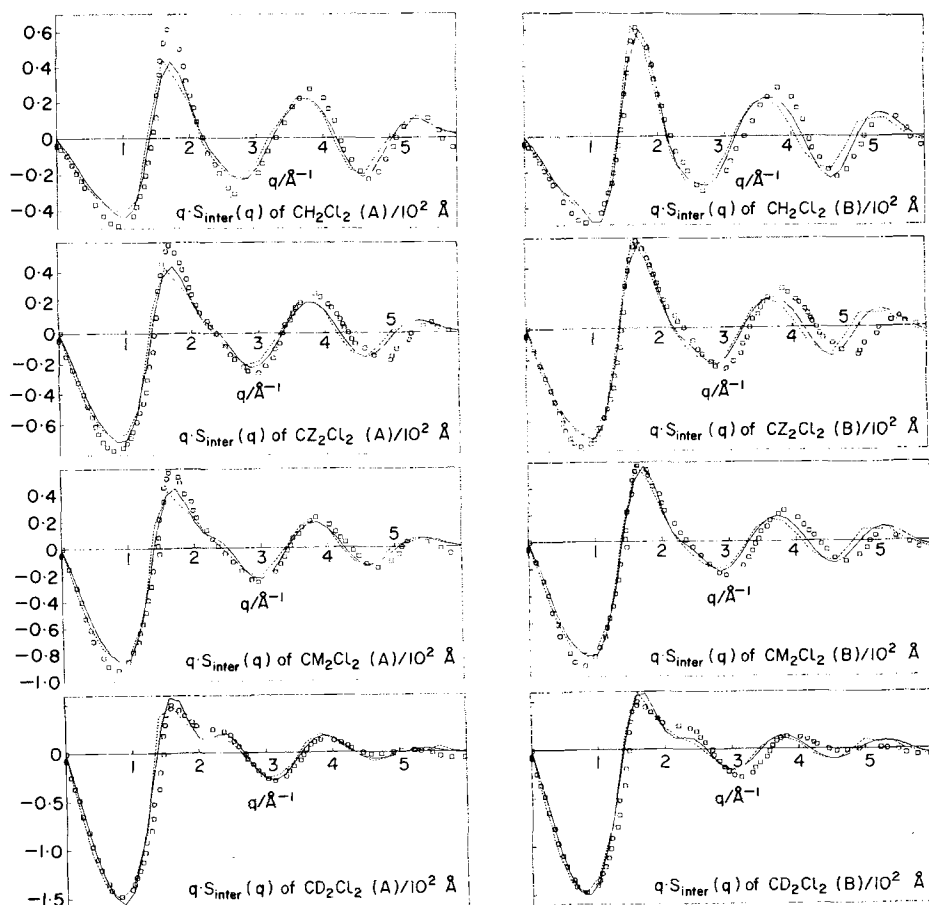


Figure 2. Intermolecular structure factor for different isotopic mixtures of  $\text{CH}_2\text{Cl}_2$ . Squares denote experimental values, solid and dashed lines values obtained from MD-simulations (further explanations are given in the text).

line), and for comparison the experimental values (squares) from [1]. In figure 3 the computer generated atom pair correlation functions are presented.

We remark at this point that the undamped oscillations in the reduced intensities shown in [1] for  $q > 6 \text{ \AA}^{-1}$  do not show up in the MD results. They might be caused by a correction step usually applied after correcting for inelastic scattering [15, 19, 20].

## 5. Discussion

As mentioned in the introduction, there are two points which have to be brought into focus when comparing simulated and measured static structure factors:

The basic assumptions that are made for the calculation of  $\mathcal{S}_{\text{inter}}(q)$  from the MD simulations described in § 2.1,

The error in  $\mathcal{S}_{\text{coh}}(q)$ , extracted from diffraction experiments, that is due to correction for inelasticity (Placzek-correction).

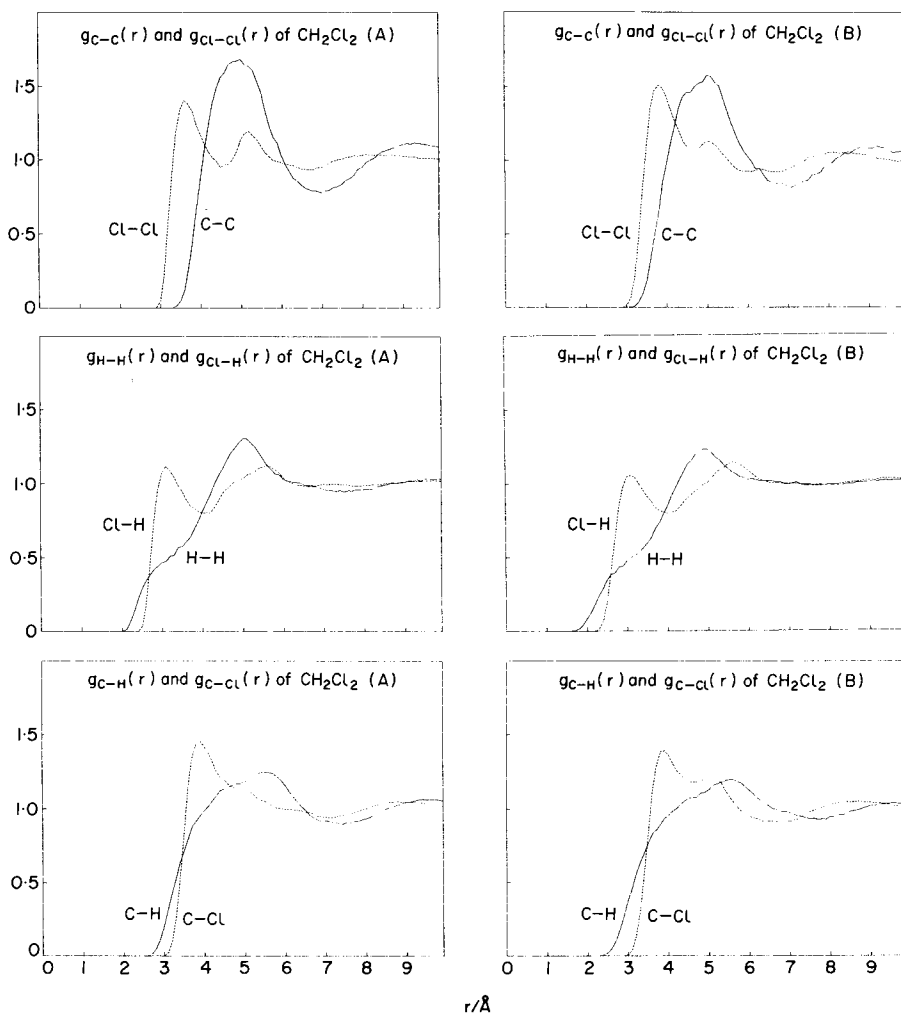


Figure 3. Atom pair correlation functions for  $\text{CH}_2\text{Cl}_2$  from MD simulations.

To consider the first point we concentrate on the intermolecular structure factor and split the position of atom  $\alpha$  in molecule  $i$  into an equilibrium position  $\mathbf{R}_{i\alpha}^{(0)}$  and a displacement vector  $\mathbf{u}_{i\alpha}$ :

$$\mathbf{R}_{i\alpha} = \mathbf{R}_{i\alpha}^{(0)} + \mathbf{u}_{i\alpha}. \tag{21}$$

Assuming (a) decoupling of vibrational and rotational motion and (b) harmonic vibrations, we have [21]:

$$\begin{aligned} \mathcal{L}_{\text{inter}}(q) = \frac{1}{N} \sum_{i \neq j} \sum_{\alpha(i)\beta(j)} \bar{b}_\alpha^* \bar{b}_\beta \exp \left\{ -\frac{1}{2} \langle [\mathbf{q} \cdot (\mathbf{u}_{i\alpha} - \mathbf{u}_{j\beta})]^2 \rangle \right\} \\ \times \langle \exp [-i\mathbf{q} \cdot (\mathbf{R}_{i\alpha}^{(0)} - \mathbf{R}_{j\beta}^{(0)})] \rangle. \end{aligned} \tag{22}$$

The two basic approximations are now that the thermal average involving the equilibrium positions can be calculated according to the rules of classical mechanics

and the vibrational terms can be neglected (rigid molecule approximation)

$$\mathcal{S}_{\text{inter}}(q) = \frac{1}{N} \sum_{i \neq j} \sum_{\alpha(i)\beta(j)} \bar{b}_\alpha^* \bar{b}_\beta \langle \exp[-i\mathbf{q} \cdot (\mathbf{R}_{i\alpha}^{(0)} - \mathbf{R}_{j\beta}^{(0)})] \rangle_{\text{cl}}. \quad (23)$$

The first approximation produces an error in the order of 1 per cent [22], which can be neglected with respect to the precision of the experimental data (see below).

The second approximation is valid for  $\text{CH}_2\text{Cl}_2$ , because the typical *intermolecular* distances are between 3 and 5 Å (see figure 3) and typical values for  $\langle (\mathbf{u}_{i\alpha} - \mathbf{u}_{j\beta})^2 \rangle \approx \langle (\mathbf{u}_{i\alpha})^2 \rangle + \langle (\mathbf{u}_{j\beta})^2 \rangle$  ( $i \neq j$ ) are between  $10^{-3} \text{ \AA}^2$  and  $10^{-2} \text{ \AA}^2$  [23].

We come now to the inelasticity corrections performed in [1] to determine the static structure factor from neutron diffraction data. Let us first summarize some basic formulae: In a real diffraction experiment the measured differential cross section is given by (neglecting multiple scattering and absorption)

$$\frac{d\sigma}{d\Omega} = N \cdot \int_{-\infty}^{E_0/\hbar} d\omega \varepsilon(k) \frac{k}{k_0} S(q(\Theta), \omega), \quad (24)$$

$$q = k_0 \sqrt{\left[ 2 - \frac{\hbar\omega}{E_0} - 2 \sqrt{\left( 1 - \frac{\hbar\omega}{E_0} \right) \cos \Theta} \right]}, \quad (25)$$

whereas one wants to measure

$$\left. \frac{d\sigma}{d\Omega} \right|_{\text{id}} = N \cdot \int_{-\infty}^{+\infty} d\omega \varepsilon(k) \mathcal{S}(q_{\text{el}}(\Theta), \omega) \equiv \varepsilon(k_0) \mathcal{S}(q_{\text{el}}(\Theta)), \quad (26)$$

$$q_{\text{el}}(\Theta) = 2k_0 \sin\left(\frac{\Theta}{2}\right). \quad (27)$$

Here  $\Theta$  is the scattering angle,  $E_0$  the energy of the incident neutrons,  $\omega$  their energy loss in the scattering process, and  $\varepsilon(k)$  stands for the efficiency of the detector as a function of the neutron velocity. With  $k_0$  and  $k$  we denote the momentum of the neutrons before and after scattering in units of  $\hbar$ . The static approximation  $\mathcal{F}(q, t) \approx \mathcal{F}(q, 0)$  can be assumed to be valid if the inequality

$$\frac{q}{k_0} \frac{m}{M} \ll 1, \quad (28)$$

holds [14, 16], where  $m$  denotes the neutron mass and  $M$  the (effective) mass of the scattering atom. The effective mass of an atom in the rigid molecule approximation is known as *Sachs-Teller mass*  $M_{\text{S-T}}$  [24]. The S-T masses of the  $H$ -isotopes are between 4.82  $m$  and 6.26  $m$  for the different isotopic mixtures  $\text{CX}_2\text{Cl}_2$ . Equation (28) shows that the static approximation is not valid for  $\text{CH}_2\text{Cl}_2$  if  $q$  is of the order of  $k_0$  ( $k_0 = 9.1 \text{ \AA}^{-1}$  in [1]) and therefore an inelasticity correction, formally defined by [1]

$$\frac{d\sigma}{d\Omega} = \left. \frac{d\sigma}{d\Omega} \right|_{\text{id}} \left( 1 + \frac{\Delta(\Theta)}{\mathcal{S}(q_{\text{el}}(\Theta))} \right), \quad (29)$$

$$\Delta(\Theta) = \int_{-\infty}^{E_0/\hbar} d\omega \frac{\varepsilon(k)}{\varepsilon(k_0)} \frac{k}{k_0} \mathcal{S}(q(\Theta), \omega), \quad (30)$$

has to be applied. The authors of [1] used the dynamic structure factor of an ideal gas to calculate  $\Delta(\Theta)$ , because the usual *Placzek correction* [25], which is essentially

an expansion in  $m/M$ , cannot be applied. The mass of the gas atoms was taken as an adjustable parameter.

It is hard to decide whether this correction, which is quite drastic for pure  $\text{CH}_2\text{Cl}_2$  (see [1]) due to the large incoherent scattering cross section of hydrogen, is sufficiently precise with respect to the requirements for the test of MD potentials. In particular, the question arises, whether the assumption of no structural effects being present in the correction function  $\Delta(\Theta)$  is justified. Unfortunately this question cannot be answered by using in (29) and (30) the dynamic structure factor calculated from our MD simulations: The validity of the semiclassical correction, which must be applied to the dynamic structure factor, calculated as classical ensemble average from MD simulations to ensure detailed balance, is confined to the region [16]

$$|\hbar\omega| < k_{\text{B}} T, \quad (31)$$

$$\frac{\hbar^2 q^2}{2M} \ll 2k_{\text{B}} T, \quad (32)$$

i.e.  $|\hbar\omega| < 25 \text{ meV}$  and  $q < 5 \text{ \AA}^{-1}$ , if one takes  $M \approx 5m$ , which is the S-T mass of the protons in methylene chloride (see above). The knowledge of  $\mathcal{S}(q, \omega)$  in this  $(q, \omega)$ -region is not sufficient to calculate  $\Delta(\Theta)$  according to equation (30).

Since the quality of the inelasticity correction applied in [1] cannot be checked, we think that  $\mathcal{S}_{\text{coh}}(q)$  and  $\mathcal{S}_{\text{inter}}(q)$  of completely deuterated methylene chloride should be preferred for quantitative comparisons with MD simulations, because the correction for inelastic scattering is by far the smallest in that case. As a consequence the genuine dynamical information contained in MD simulations should be used to calculate realistic *inelastic* neutron scattering intensities in the low  $q$ -region [16]. Corresponding results are published in part II of this publication.

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