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MOLECULAR DYNAMICS COMPUTER SIMULATION OF LIQUID DICHLOROMETHANE . I. EQUILIBRIUM PROPERTIES

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The molecular dynamics of CH_2Cl_2 in the liquid state have been simulated with two model representations of the intermolecular potential. These consist of a three-interaction site model and a five-interaction site one with or without fractional electrical charges at the atomic sites. The MD algorithms used in the simulation are described in detail. Equilibrium thermodynamic properties are calculated and compared with experimental data. In part two some dynamical properties are presented and some attention is given to the reproduction of the experimental far infrared spectra.

roduction

Molecular dynamics and interactions in the liquid e can now be investigated with an ever-increasing e of techniques. It is essential that a coordinated of a suitable species be carried through before can hope to assimilate the different viewpoints able. A particularly favourable liquid in this ect is dichloromethane, whose molecular dynami- properties have recently been reviewed in detail -3]. This is particularly suitable for many areas of ctroscopy including inelastic neutron scattering, nfrared, microwave, infrared, NMR, light scatter- non-linear electrooptics and Raman scattering. In ciple these are all capable of providing time cor- tion functions [2] of various vectors or tensors ciated with the movement of the molecule. Pro- ed we know approximately the pair interaction po- al between CH_2Cl_2 molecules then the technique olecular dynamics simulation can be used to pute these correlation functions from the equa- s of motion. The problem of describing a range of ctra at a given state point is thus reduced to op- sing the form of the pair interaction potential, refining the techniques of computer simulation. If this process were then to be repeated at state points over the *complete* range of existence of the liquid we would be in a better position to produce a predictive theory of the liquid state of molecular matter.

Unfortunately at present our knowledge of the potential energy surface between two interacting molecules the size of CH_2Cl_2 is very poor, despite the amount of painstaking work on the subject. This is due to a number of factors, not least among which is the difficulty of relating the pair potential to spectra from the liquid in a self-consistent manner, i.e. the *need* for a better potential has been obscured by the mathematical difficulties posed by liquid state molecular dynamics. Phenomenological theories (e.g. the generalised Langevin equation and variations) approach the pair-potential problem, if at all, at a glancing angle (e.g. some hydrodynamic approaches do not go into any detail about molecular interaction). However, one of the most sensitive methods of testing an intermolecular pair potential is through the second pressure B_p and dielectric B_ϵ virial coefficients in the gas phase. Work in this direction is in progress and a direct measurement of B_ϵ is being undertaken. A reliable model is that where the interaction between each atom of two distinct molecules is represented by a Lennard-Jones form. The complete pair potential is the sum of atom–atom terms.

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Various ~~values~~ of the Lennard-Jones parameters are available in the literature [4–7] for C, Cl and H atom–atom interactions in the same hybridisation states as in CH_2Cl_2. The electrostatic component is mainly due to dipole–dipole interaction, and may be represented conveniently by fractional charges [8] situated at each atomic site, in a simpler way than by expanding the electrostatic force field in multipoles. The drawback of using charges has its roots in the technical difficulty at present of dealing with long-ranged interaction in a molecular dynamics simulation using periodic boundary conditions.

In this paper we describe a computer simulation of liquid CH_2Cl_2 using atom–atom forms for the pair potential. We assume that the forces in the liquid are molecularly pairwise additive and produce a variety of atom–atom distribution functions suitable for comparison, at the same state points, with freshly measured neutron-scattering spectra of various kinds, should these become available. The paper is organised as follows. In section 2 we describe the two algorithms used: with respectively a three-site atom–atom potential (taking CH_2 as a moiety) and a fuller five-site atom–atom potential. In section 3 we present thermodynamic results with and without charge interactions.

2. Description of the molecular dynamics algorithms

The two representations of the CH_2Cl_2 potential (3 X 3 and 5 X 5 atom–atom) were used with the algorithms "TRI2" and "TETRA" respectively with the aim of seeing which representation is the more accurate, and in what respects. This is important, and not merely an exercise in numerical simulation, because it allows us to see, for example, whether spectra or equilibrium thermodynamics are sensitive to details of the pair potential. It also allows us to find out which type of spectrum is sensitive to changes in the pair potential.

Both TRI2 and TETRA are modifications of an algorithm written originally by Singer and Renaud. In practice the same algorithm is used to integrate rotational and translational equations of motion. Differences within the two are to be found mainly in the calculation of the pair interactions (3 X 3 against 5 X 5), the geometrical shape of the molecules and a slightly more accurate integration in TETRA for rotational motion, because a fourth order predictor is taken into account for the angular momentum J.

Table 1

	H	C	Cl	CH_2
3 X 3 LJ σ (Å)			3.35	3.96
3 X 3 LJ ϵ/k (K)			173.5	70.5
3 X 3 electrostatic			$-0.151\,e$	$0.302\,e$
5 X 5 LJ σ (Å)	2.75	3.35	3.35	
5 X 5 LJ ϵ/k (K)	13.4	51.0	175	
5 X 5 electrostatic	$0.098\,e$	$0.022\,e$	$-0.109\,e$	

2.1. The 3 X 3 potential model

A molecule of CH_2Cl_2 is represented as three interactions sites, one for the CH_2 group and two for the chlorine atoms. The model potential has been taken from a preliminary study of McDonald [4] and from the literature [5]. It is composed of a Lennard-Jones site–site core, described by the parameters in table 1. Mixed site interactions are obtained following the usual Lorentz–Berthelot rule of geometric means for ϵ-parameters and arithmetic ones for the σ. Electrostatic interactions are described by partial charges, see table 1, at the same interaction sites as the Lennard-Jones parameters. They are chosen to reproduce correctly the dipole moment of the CH_2Cl_2 molecule, d = 1.6 D. This full potential had been tested in the case T = 287 K, V_m = 62.92 cm^3/mol and gave a mean potential energy of 6.2 kcal/mol, similar to measured values in the range 6.2 to 6.3 kcal/mol, as estimated from an experimental value of the heat of vapourisation ΔH = 6.69 to 6.83 kcal/mol ‡.

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† For energy of vapourization see ref. [9]. At 760 mmHg [illegible] K, ΔH = 6.69 kcal mol^{-1}; ΔS = 21.4 cal $(mol\ K)^{-1}$.

The 5 X 5 site model potential

As for the previous model the interaction between
) CH_2Cl_2 molecules consists of a Lennard-Jones
: plus an electrostatic one. Starting values for the
m–atom Lennard-Jones parameters $\epsilon_{\alpha\alpha}, \sigma_{\alpha\alpha}$ were
ermined on the basis of the ones already known in
literature – the optimised values actually used are
wn in table 1. We took the ϵ and σ parameters for
chlorine–chlorine interaction from the work of
ger et al. [5] on the computer simulation of di-
mics. Values for the carbon–carbon and hydrogen–
lrogen interactions come from the model potential
ermined by Williams [6] from a study of lattice
operties of hydrocarbons. We remark that originally
lliams defined an exp-5 potential used sebsequently
Murad et al. [7] in the computer smiulation of
uid methane. We have adapted Williams potential to
2-6 form by deriving from its data σ_{CC} and σ_{HH},
C and ϵ_{HH}. As for the three-sites case the Lorentz–
rthelot mixing rules have been followed to fix σ_{CH},
Cl, σ_{ClH} and the relative ϵ. Electrostatic interactions
e again represented by fractional charges placed at
e atomic sites. The values, shown in table 1, have
en taken from a molecular orbital calculation by del
e [8].

Some preliminary runs were made for three differ-
t densities, corresponding to the experimental
te points at 1 atm respectively with temperature T
77 K (fp), 293 K, 323 K (bp), to refine the model
tential by monitoring of equilibrium properties.

In both TETRA and TRI2 interactions have been
uncated at a distance R_c equal to half the size of
e cubic box. For $T = 293$ K and $V_m = 64.0$ cm^3/
ol one has $R_c = 11.28$ Å which is 3.3 times the
rgest σ, σ_{ClCl}, of the Lennard-Jones interactions.

Separate minimum image criteria have been em-
oyed for Lennard-Jones interactions and electro-
atic ones. In the case of Lennard-Jones interactions
omic sites have been considered independently of
hat molecule they belonged to. For electrostatic
teraction we tried to consider the interaction as a
olecular property and so the minimum image con-
ention and the cutoff have been applied to the
entre of mass–centre of mass distance accounting
r all 25 contributions for each pair of molecules.
here is evidence that this is a better choice, although
ere is now a tendency to prefer Ewald sum methods to account fully for long-range interactions [10]. (We plan to introduce the Ewald sum in the near future, together with second virial tests for the model potential.)

2.3. Integration scheme for the equations of motion

2.3.1. Translation

The translational motion of each molecular centre of mass is integrated with the usual two-step Verlet algorithm

$$R_i(t + \Delta t) = 2\, R_i(t) - R_i(t + \Delta t)$$
$$+ (\Delta t^2/M) F_i(t) + O(\Delta t^4),$$

where $F_i(t)$ is equal to the total force on molecule i and M is the total mass of the molecule – velocities are computed with an error of $O(\Delta t^3)$.

2.3.2. Rotation

Rotational equations of motion are integrated in two distinct steps. Once the total torque $N_i(t)$ has been computed from atomic forces, the angular momentum J at time t is computed with

$$J_i(t) = J_i(t - \Delta t) + \int_{t-\Delta t}^{t} N_i(t)\, \mathrm{d}t,$$

where $N_i(t)$ is replaced by a quadratic interpolation over its three last values. In TETRA a cubic interpolation using the last four points of $N_i(t)$ has been used increasing the accuracy of $J_i(t)$ to order Δt^4.

The orientation of the molecule is described by means of the coordinates in the laboratory system of the intrinsic system of reference defined by the three unit vectors e_A, e_B, e_C directed along the principal axes of the molecule. The equation of motion is given by the kinematical relation

$$\dot{e}_\alpha^{(i)}(t) = \boldsymbol{\omega} \times e_\alpha^{(i)}(t), \quad \alpha = A, B, C \tag{3}$$

for each molecule i. A predictor algorithm including terms of Δt^3 order is combined with a restoring of the orthonormality relation within each molecule.

This algorithm has been already tested widely by one of us for triatomic molecules. The site model has been checked in the case of no electrostatic interaction with the help of a shifted potential, i.e. continuously shifting to zero from $R = R_c$ leaving forces unchanged. We had a total energy conservation of 1 part over 10^4 on segments of about a thousand steps, with fluctuation of the total kinetic energy of little less than 10% and on average an equipartition between the translational and rotational parts well within the 1% figure. These results refer to a simulation of a system of 108 molecules in a box of side $L = 22.56$ Å ($V_m = 64.0$ cm^3/mol) and a time step $\Delta t = 0.005$ ps. Equilibration took about 2000 steps for melting of the initially, random-disturbed, lattice configuration. The Verlet parameter $S(K_x)$ for the centre of mass has been monitored to follow the melting from the lattice configuration. Long-range corrections to the virial sum and to the potential energy have been taken into account for the LJ interactions only, due to the divergence of such sums of the electrostatic contributions. This results in high values for pressure, computed with the formulae described by Cheung [11].

3. MD simulation results

3.1. Equilibrium properties

After the potential adjustment runs two main MD runs have been performed recording instantaneous values of thermodynamical quantities and average values on the equilibrium trajectories have been computed. Values of pressure and specific heat have been calculated following Cheung [11]. Table 2 contains a complete outline of the results collected up to now. Both the total and potential energy are significantly affected by inclusion of electrostatic explicit interactions. Also, the atomic pair distribution functions (fig. 1), are very sensitive to charge–charge effects. In particular it appears that the liquid at room temperature (20°C) is not highly structured, and a weak chlorine bonding can be represented by the charge distribution, resulting in the enhancement of the first peak at $R = 3.20$ Å of the H–Cl pair distribution. However, it should be noted that due to the shape of CH_2Cl_2 which is almost a symmetric top with the dipole perpendicular to the quasi-symmetry axis (parallel to the Cl–Cl direction), the dipoles tend to a parallel relative orientation, which can also explain the double peak feature of the H–Cl pair distribution. In general all pair distributions become more structured following the inclusion of the electrostatic part of the potential.

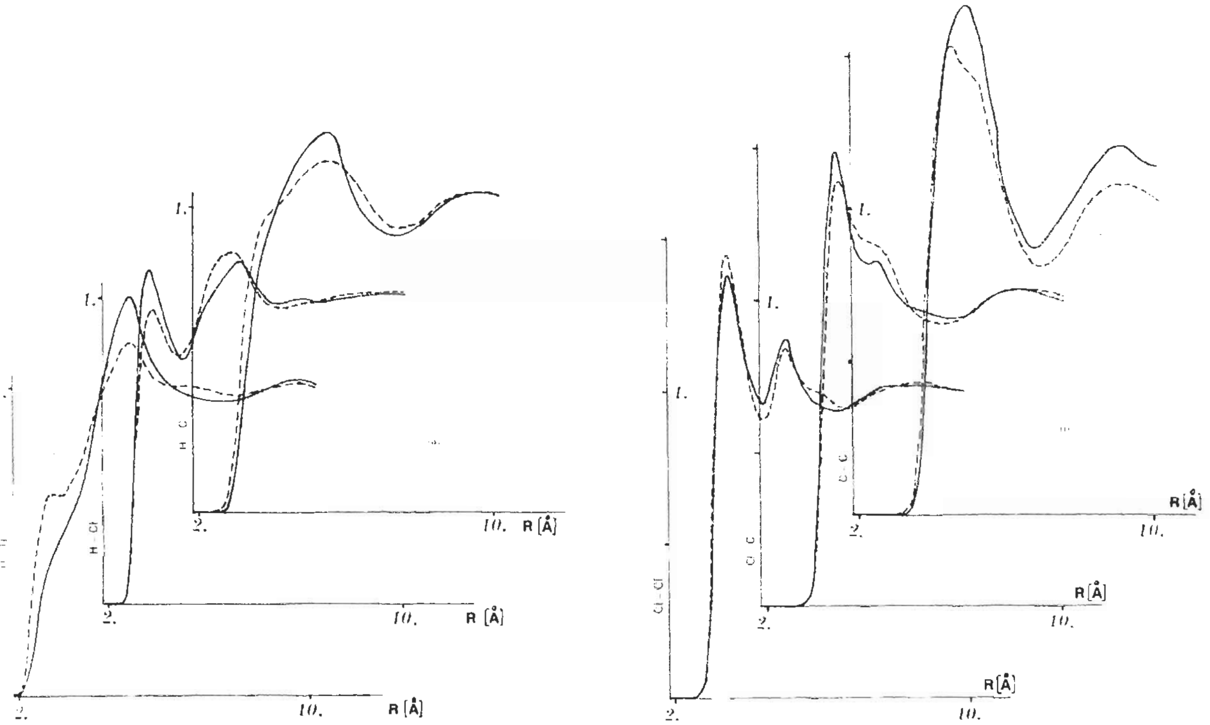
Thermodynamic averages are of course ameliorated by the full model, in particular the pressure value. Still, there is a large discrepancy with the experimental value of the specific heat at room temperature [12] which is around 100 J mol^{-1} K^{-1}. Such a discrepancy was *not* observed however in the lower temperature cases on adjusting the potential.

4. Conclusion

A potential function has been developed for CH_2Cl_2 which reproduces the thermodynamical properties of the liquid adequately well. In the next part of this series [13] we apply the simulation algorithm to the calculation of molecular dynamical properties (auto-correlation functions and spectra).

Table 2

MD run	3-site potential model	5 sites/ no charges	Full 5 sites
molar volume (cm^3)	64	64	64
temperature (K)	287 ± 10	298.5 ± 8.5	296.2 ± 10.0
potential energy (kJ/mol)	26.0 ± 0.5	24.64 ± 0.21	26.46 ± 0.25
total energy conservation (relative fluctuations)	2.7 × 10^{-2}	0.16 × 10^{-2}	0.5 × 10^{-2}
C_V (J mol^{-1} K^{-1})	–	33.2	41.0
% rotaional kinetic energy	51	50.3	50.8



g. 1. (a) Atom–atom pair distribution functions: bottom to top: H–H; H–Cl; H–C. (b) As for (a): bottom to top: Cl–Cl; l–C; C–C. —— no charges; --- with charges.

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