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MOLECULAR DYNAMICS SIMULATION OF LIQUID METHYLENE DICHLORIDE (EMLG PUBLICATION)

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ABSTRACT

The molecular dynamics and interactions of liquid methylene dichloride (CH_2Cl_2) have been computer simulated with atom-atom interaction potentials, with and without charges, at three EMLG pilot project state points, 293K 1 bar; 177K, 1 bar; and 323K, 5 k bar. A wide variety of static and dynamic results have been lodged in the EMLG data bank and in this paper we summarise the work to date and suggest areas of further investigation.

INTRODUCTION

Methylene chloride (CH_2Cl_2) is a C_{2v} asymmetric top which is accidentally an inertial symmetric top (ref. 1,2). The liquid is particularly suitable for a wide range of relaxation, absorption and diffraction measurements which all have a bearing on the molecular dynamics. It is also possible to investigate the pair potential with a variety of methods, including measurements on pressure (B_p) and dielectric (B_E) second virial coefficients. The latter in particular are very sensitive to the form of the pair potential and it is often the case that the empirical formulae (e.g. atom-atom Lennard-Jones) gives the wrong sign for B_E.

In what follows we have space only for a brief description of the two algorithms used to computer simulate the molecular dynamics and interactions of liquid CH_2Cl_2 and for a resume of the results.

The Algorithms

We have used a 3 x 3 and 5 x 5 site-site model for the intermolecular potential using algorithms TRI2 and TETRA respectively.

TRI2

This was developed from an algorithm written initially by Singer and Renaud (ref.3). The equations of motion for 108 molecules are solved using a two-step predictor method with periodic boundary conditions. The core atom-atom interaction is Lennard-Jones in type with parameters: $\sigma(Cl - Cl) = 3.35\text{Å}$; $\sigma(CH_2 - CH_2) = 3.96\text{Å}$; $\epsilon/k(Cl - Cl) = 173.5K$; $\epsilon/k(CH_2 - CH_2) = 70.5K$ taken from the literature. Partial charges were added to produce a total dipole moment of 1.6D. Thus the charge on the Cl unit is $- 0.151|e|$ and that on the CH_2 unit is $+ 0.302|e|$. This provides a mean

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potential energy comparable with that observed.

TETRA

This was developed from a CCP5 algorithm written by Thomson (ref. 4) and based on the quaternion method of D. J. Evans. The 108 molecules interact via a 5 x 5 atom-atom potential (with or without charges). The Lennard-Jones parameters are as follows: $\sigma(H - H) = 2.75\text{Å}$; $\sigma(Cl - Cl) = 3.35\text{Å}$; $\sigma(C - C) = 3.2\text{Å}$; $\varepsilon/k(H - H) = 13.4K$; $\varepsilon/k(Cl - Cl) = 175.0K$; $\varepsilon/k(C - C) = 51.0K$ with fractional charges (when incorporated) of $+ 0.098|e|$ on H; $- 0.109|e|$ on Cl; and $+ 0.022|e|$ on C.

Both algorithms were run at the same (EMLG) state prints of 293K, 1 bar; 177K, 1 bar; and (3 x 3 only) 322K, 5000 bar. Greater detail will be available in forthcoming EMLG publications.

RESULTS AND DISCUSSIONS

Given the trajectories of 108 interacting molecules it is in principle possible to compute any recquired average using the statistical laws governing the behaviour of a microcanonical molecular ensemble. We have lodged in the EMLG data bank[†] information concerning: atom-atom pair distribution functions; thermodynamical averages (e.g. specific heat at constant volume); a wide variety of auto and cross correlation function of vectors such as $\underline{v}$ (c. of m. linear velocity), $\underline{J}$ (the angular momentum), $\underline{e}_A$, $\underline{e}_B$ and $\underline{e}_C$ (unit vectors along the principal moment of inertia axes), $\dot{\underline{e}}_A$, $\dot{\underline{e}}_B$ and $\dot{\underline{e}}_C$ (their time derivatives), $\underline{F}$ the force, $\underline{T}_q$ the torque and many more. Mode-mode coupling has been investigated via mixed autocorrelation functions such as $\langle F^2(t)Tq^2(o)\rangle$ which show strong rotation/translation coupling (ref. 5).

These results are suitable for direct comparison with a range of experimental data including: far infra-red/dielectric, i.-r., Raman, Rayleigh, NMR, neutron scattering, and picosecond time resolved spectroscopies.

The far infra-red spectrum in particular is a sensitive barometer of the liquid state molecular dynamics, being essentially (ref. 6) the Fourier transform of the correlation function of $\dot{\underline{e}}_A(t)$, the time derivative of the dipole unit vector. Fig.(1) is a direct comparison of the real and computer simulated spectra. It is clear that the 5 x 5 is the more realistic potential but for further improvement a great deal of painstaking measurement is needed on quantities such as B_E (ref. 7) and improvements are required in the theory relating this to the intermolecular pair potential. Finally fig. (2) shows that the macro-micro theorem relating auto and multiparticle correlation functions in CH_2Cl_2 seems to work well, resolving some problems in the theory of dielectric spectroscopy.

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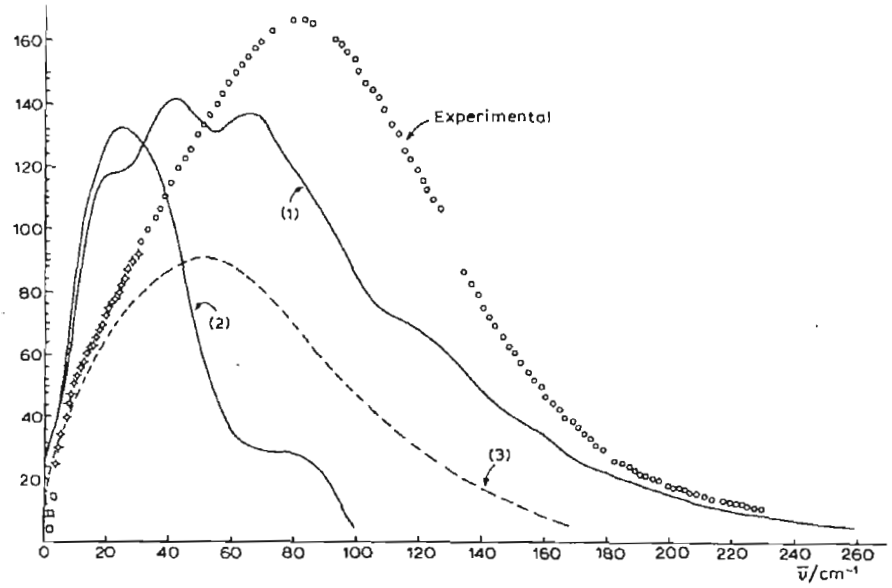

Fig. 1. Far Infra-red spectra of CH_2Cl_2 at 293 K, 1 bar. Experimental, Klystrons and interferometry. (1) 5 x 5 simulation, with charges; (2) 3 x 3 simulation, no charges; (3) spectrum of 10% CH_2Cl_2 in CCl_4; O, experimental.

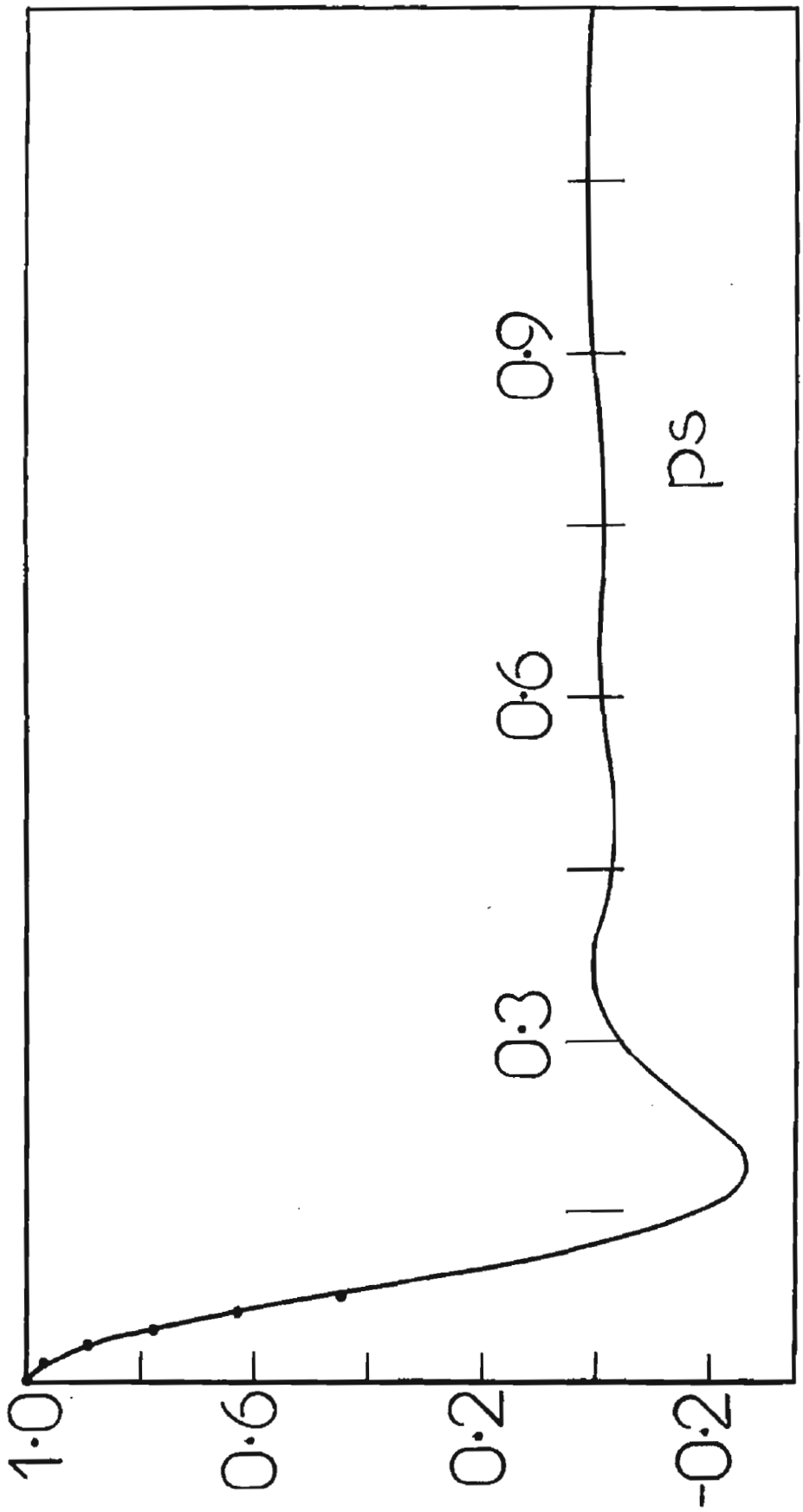

Fig. 2. Normalized auto (——) and cross (or microscopic) ( ) correlation functions for CH_2Cl_2 at 177K, 1 bar, 3 x 3 potential. The function is calculated inside a Kirkwood sphere of ~8Å radius. The box edge is 22.56 Å.