

## COMPUTER SIMULATION OF DICHLOROMETHANE . II. MOLECULAR DYNAMICS

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The technique of computer simulation is used to compute some molecular dynamical properties of liquid  $\text{CH}_2\text{Cl}_2$ . The results are compared with experimental data from a variety of spectral sources, and emphasize the importance of keeping to an accurate representation of the shape of  $\text{CH}_2\text{Cl}_2$  through a five-atom Lennard-Jones potential. The nature of the interaction between a tagged molecule and its thermal bath gives rise to non-gaussian statistics in the interval  $t = 0$  to a few picoseconds. The same source is responsible for rotation-translation coupling, clearly observable in the moving frame of reference defined by the three principal moment of inertia axes of the asymmetric top  $\text{CH}_2\text{Cl}_2$ .

### 1. Introduction

In this paper we focus our attention on the molecular dynamics [1] of  $\text{CH}_2\text{Cl}_2$ , and compare correlation times from the computer simulation with those available experimentally [2; 1, ch.12] using spectra from various sources. Having checked the algorithm in this way at two or more widely separated thermodynamic state points we proceed to discuss the nature of the transient statistics of the time evolution from  $t = 0$  to a few picoseconds. We find that these are not gaussian, and suggest an explanation in the non-linear nature [3-6] of the interaction between a tagged molecule and its surroundings. This is carefully distinguished from the non-gaussian nature [1, ch. 2] of the rotational Euler (or Euler/Langevin) equations of motion for interacting molecules. The subtle details of rotation-translation coupling [7] are observable in a moving frame of reference, and an attempt is made to reproduce these computer simulation results using a rototranslational Euler/Langevin system [8] of equations written in the moving frame defined by the principal moments of inertia axes. Numerical integration of this system, using a stochastic molecular

dynamics technique developed by Ferrario [9] produces none of the computer simulated effects. It is therefore conjectured that these can only be reproduced analytically by, in the simplest case, a model such as the non-linear rototranslational itinerant oscillator/librator [4,8]. *The algorithms* are described fully in part I [11].

### 2. Results and discussion

To indicate the need for a  $5 \times 5$  rather than the oversimplified  $3 \times 3$  potential we illustrate the effects on the far infrared spectrum of adding hydrogens in fig. 1. The  $5 \times 5$  potential is clearly the more realistic, and this is corroborated by the fitting of atom-atom potentials at individual atomic sites to ab initio calculations [10] of the intermolecular potentials in molecules such as  $\text{C}_2\text{H}_4$ . This type of potential has also been used successfully [10] in lattice dynamics calculations of the molecular crystal structure and crystalline heats of sublimation. It is also accepted that the electrostatic energy can be represented well by the use of point-charges if these are allowed to shift away from the nuclei. However, we have chosen *not* to use this degree of flexibility in our calculations because we wish to adhere to Lennard-Jones and frac-

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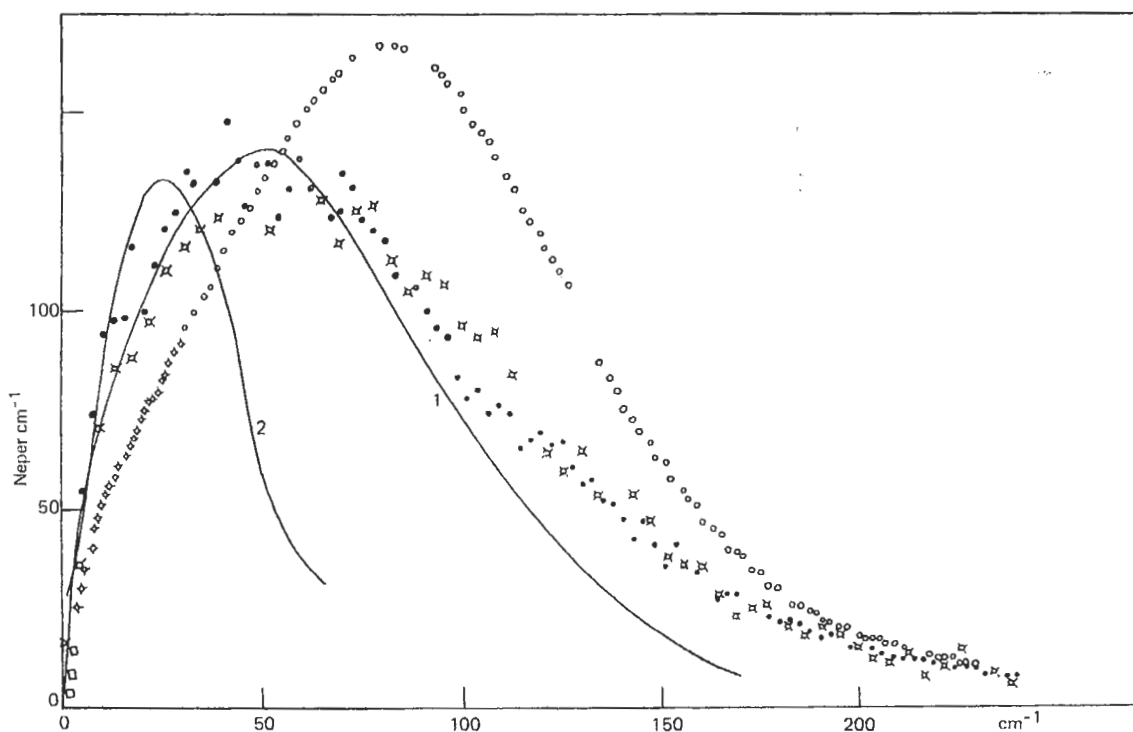


Fig. 1. Far infrared spectra.  $\square$ ,  $\diamond$  and  $\circ$ . Experimental (klystrons and interferometry).  $\bullet$   $5 \times 5$  simulation, no charges.  $\times$   $5 \times 5$  simulation, with charges. — (2)  $3 \times 3$  simulation, no charges. — (1) Spectrum of 10%  $\text{CH}_2\text{Cl}_2$  in  $\text{CCl}_4$ . Scaled up to match the intensity of  $\bullet$ .

tional charge parameters available in the literature (for a fuller description, see part I [11]), and which can be transferred between molecules, i.e. from one MD simulation to another.

Further evidence for the importance of the hydrogens comes from the illustration in fig. 1 of the spectrum of 10%  $\text{CH}_2\text{Cl}_2$  in dilute  $\text{CCl}_4$  (the experimental curve in dilute decalin is very similar). The microwave correlation time measured by Reid and Evans [12] (see also ref. [1], ch. 4) for 10% v/v decalin solution is  $1.2 \pm 0.3$  ps, and the area beneath the simulated autocorrelation function  $\langle e_A(t) \cdot e_A(0) \rangle$  (where  $e_A$  is the dipole unit vector) is also 1.2 ps. From these results we may suppose:

(i) That the hydrogen atoms play an important part in the dynamics of  $\text{CH}_2\text{Cl}_2$ .

(ii) In dilute solution the electrostatics are effectively isolated from the kinematics. In other words, in dilute  $\text{CH}_2\text{Cl}_2$ /decalin solution we may suppose that we are looking at the autocorrelation function of  $\text{CH}_2\text{Cl}_2$  with negligible multipole-

multipole interaction between  $\text{CH}_2\text{Cl}_2$  molecules.

(iii) The similarity of bandshape suggests that *induced* absorption effects are minimal in affecting the spectrum of  $\text{CH}_2\text{Cl}_2$  in dilute decalin solution. To corroborate these results we need experimental spectra of still higher quality.

We have computed the usual orientational autocorrelation functions (a.c.f.)  $P_1$  and  $P_2$  for the three vectors  $e_A$ ,  $e_B$  and  $e_C$  of the five-site  $\text{CH}_2\text{Cl}_2$  model representation.  $P_1(t)$  and  $P_2(t)$  are very nearly exponential except near the origin. Some correlation times of interest are compared with the available experimental results in table 1. The correlation times have been evaluated from the time it takes the relevant a.c.f. to decay to  $1/e$  of its  $t = 0$  value, normalised to one.

There are correlation times available in the literature [13] from infrared [14] and Raman [15] spectroscopy, Rayleigh scattering [15], inelastic and incoherent neutron scattering [13]; various forms of NMR relaxation [16–20], and from dielectric/far

Table 1  
Correlation times for liquid CH<sub>2</sub>Cl<sub>2</sub> (293 K, 1 bar)

Technique	Vector	Correlation time (ps)	
<sup>1</sup> H (intra) [13]	H-H (   to e <sub>C</sub> )	0.53 ± 0.06	P <sub>2</sub>
<sup>2</sup> D (quadrupole) [13]	C-D	0.80 ± 0.10	
<sup>13</sup> C-H (dipolar) [13]	C-H	0.70 ± 0.07	
<sup>35</sup> Cl (quadrupole relaxation) [13]	C-Cl (≈e <sub>B</sub> )	1.20 ± 0.10	
computer simulation	e <sub>A</sub>	0.50	
	e <sub>B</sub>	0.9	
	e <sub>C</sub>	0.51	
	centre of mass to H	0.56	
neutron scattering [13]			
Dielectric relaxation [12; 1, ch. 4]	e <sub>A</sub>	1.45	P <sub>1</sub>
infrared [14]	e <sub>A</sub>	0.5	
	e <sub>B</sub>	1.1	
infrared [15]	e <sub>A</sub>	1.1	
computer simulation	e <sub>A</sub>	1.2	
	e <sub>B</sub>	3.8	
	e <sub>C</sub>	1.21	
Rayleigh scattering [15]	e <sub>A</sub>	1.85	P <sub>2</sub>

frared spectroscopy [12; 1, ch. 4]. The most detailed study has been carried out by NMR spectroscopy, and these results have been analysed critically by Brier and Perry [13]. The diffusion of CH<sub>2</sub>Cl<sub>2</sub> is isotropic, as may be discerned by <sup>1</sup>H (proton) NMR relaxation, <sup>2</sup>D nuclear quadrupole relaxation and <sup>35</sup>Cl nuclear quadrupole relaxation. Table 1 summarises the data available.

There are some fairly consistent features of this molecule. For example, the <sup>1</sup>H (intramolecular) correlation time of 0.53 ± 0.06 ps agrees with the computer simulation result for motion about the e<sub>C</sub> vector of 0.50 ps. The latter has been calculated as the time taken for the P<sub>2</sub>(e<sub>C</sub>) correlation function to fall to 1/e of its initial (t = 0) value, when this is normalised to unity. The <sup>35</sup>Cl (quadrupole relaxation, magnetic resonance) correlation time is a measure of the motion about the C-Cl axis, roughly parallel to the e<sub>B</sub> vector in the computer simulation. The two correlation times are, respectively, 1.20 ± 0.10 ps and 0.90 ps. The NMR times refer, theoretically, to strictly single particle a.c.f.'s, as for the computer simulations.

The inverse of the dielectric loss peak frequency (the dielectric relaxation time, τ<sub>D</sub>) is, on the other hand, multi-molecular in origin [1, ch. 3]. For pure liquid CH<sub>2</sub>Cl<sub>2</sub> at 293 K, 1 bar, τ<sub>D</sub> (exp.) is 1.45 ps.

The single-particle correlation time of the a.c.f. ⟨e<sub>A</sub>(t) · e<sub>A</sub>(0)⟩ of the computer simulation is 1.2 ps. We have attempted to calculate a multi-particle correlation time in the computer simulation using four small sub-spheres, and this is 1.3 ps. Even this is not directly comparable with τ<sub>D</sub> for a variety of reasons, foremost among which is the necessity for correcting the experimentally measurable τ<sub>D</sub> for the internal field effect. This correction is frequency and cavity-shape dependent. An excellent account of the relationship between the dielectric relaxation time and single-particle correlation time is given by Kluk [21] in an important recent paper. Bearing these factors in mind we record without further comment that the experimental τ<sub>D</sub> is 1.45 ps and the simulated auto-correlation time is 1.2 ps.

Van Konijnberg and Steele [15] have extracted a P<sub>2</sub> correlation time for the e<sub>B</sub> vector from Rayleigh scattering to 100 cm<sup>-1</sup> shift from the exciting line. This type of spectrum is also multimolecular in origin and is probably more significantly affected by collision-induced effects because it deals directly with reorientations of the polarisability tensor. Van Konijnberg and Steele have attempted to correct for collision-induced effects and have indicated a P<sub>2</sub>(e<sub>A</sub>) correlation time of ≲1.85 ps. This compares

Table 2  
Correlation times: the effect of hydrostatic pressure (3 × 3 algorithm)<sup>a)</sup>

Temperature	Pressure		$\tau_A$ <sup>b)</sup> (ps)	$\tau_B$ (ps)	$\tau_C$ (ps)
293 K	1 bar	$P_1$	0.5	1.8	0.5
		$P_2$	0.3	0.8	0.3
		$P_3$	0.1	—	—
		$P_4$	—	—	—
323 K	5 kbar	$P_1$	0.8	3.8	0.8
		$P_2$	0.4	1.2	0.4
		$P_3$	0.15	0.5	0.15
		$P_4$	—	0.3	—

a) The correlation times in this table are for purposes of internal intercomparison only, they are *not* meant to be compared with the experimental data. For that purpose see table 1 (the 5 × 5 algorithm).

b)  $e_A$  = dipole unit vector ( $C_{2v}$  symmetry axis).

with a single particle NMR time of only 0.5 ps and a  $P_2(e_A)$  (single particle) correlation time from the present computer simulation also of 0.5 ps.

The most inconsistent features of table 1 are those involved with near infrared bands. The experimentally derived correlation times are different. Rothschild's correlation times [14] are over 100% too short in comparison with those from other sources (see table for details).

In contrast to the results in table 1 the  $P_1(t)$  to  $P_4(t)$  orientational a.c.f.'s for the  $e_A$  vector from the 3 × 3 model [11] and algorithm are non-exponential, and decay too quickly in comparison with the experimentally available data. Bearing this in mind, it is nevertheless quite interesting to look at the difference between the  $P_1(t)$ ,  $P_2(t)$ ,  $P_3(t)$  and  $P_4(t)$  correlation times from the 3 × 3 algorithm at 293 K, 1 bar and 5 kbar, 323 K. This provides a rough indication of what would be observable experimentally under hydrostatic pressure. These correlation times are collected in table 2. The anisotropy of the rotational diffusion is greater at 5 kbar, 323 K, and the correlation times are much longer.

Rotational velocity autocorrelation functions [1, chs. 1, 4], are illustrated in fig. 2, and the curves of fig. 1 were obtained from these by Fourier transformation. These exhibit the characteristically long negative tail familiar from literature curves derived from far infrared spectroscopy [12; 1, ch. 4].

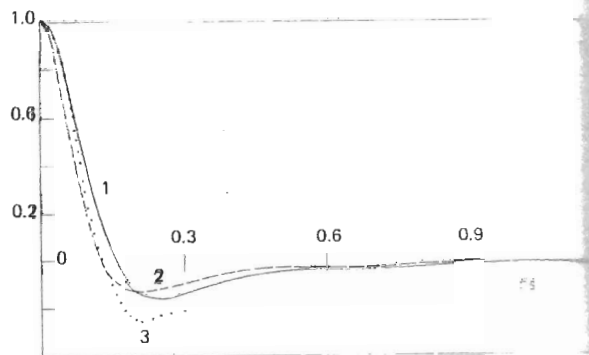


Fig. 2. Rotational velocity a.c.f.'s from (1) the 3 × 3 algorithm (no charges); (2) the 5 × 5 algorithm (no charges); (3) for comparison, a spectrum of a 10% dilute solution of CH<sub>2</sub>Cl<sub>2</sub> in decalin directly Fourier transformed into the time domain. Ordinate:  $C(t)$ ; Abscissa: time (ps).

### 3. Angular momentum autocorrelation functions -- non-gaussian effects

The molecular dynamics simulation produces information which may be difficult to obtain in other ways. An example is the second-moment a.c.f. of angular momentum [22] ( $J$ ):

$$\langle J(t) \cdot J(t) J(0) \cdot J(0) \rangle,$$

and the cross-correlation:

$$\langle J(t) \cdot J(t) \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle,$$

where  $\mathbf{v}$  is the centre of mass linear velocity of the CH<sub>2</sub>Cl<sub>2</sub> molecule. These and similar second order correlation functions may be used [23] to check the nature of the transient statistics in the simulation. If these are gaussian, it follows that:

$$\langle J(t) \cdot J(t) \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle = \langle J(t) \cdot J(t) \rangle \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle$$

$$= \langle J(0) \cdot J(0) \rangle \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle, \quad (1)$$

$$\langle J(t) \cdot J(t) J(0) \cdot J(0) \rangle / \langle J^4(0) \rangle$$

$$= \frac{(I_1 + I_2 + I_3)^2 + 2 \sum_{i=1}^3 I_i^2 \chi_i^2(t)}{(I_1 + I_2 + I_3)^2 + 2(I_1^2 + I_2^2 + I_3^2)}, \quad (2)$$

where

$$\chi_i(t) = \langle J_i(t) J_i(0) \rangle / \langle J_i^2(0) \rangle$$

and

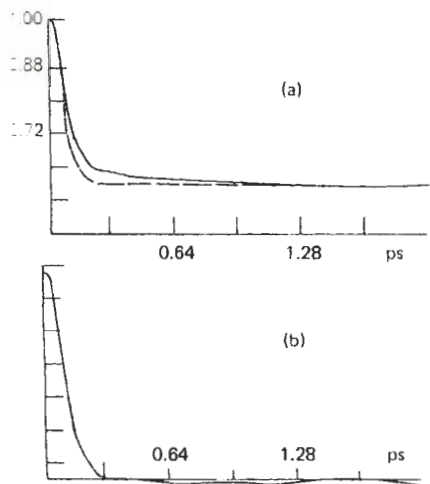


Fig. 3. (a) —  $(J(t) \cdot J(t)J(0) \cdot J(0))/\langle J^4(0) \rangle$ , --- gaussian result. (b)  $(\mathbf{v}(t) \cdot \mathbf{v}(t)\mathbf{v}(0) \cdot \mathbf{v}(0))/\langle v^4(0) \rangle$ , computer simulation at 293 K, ordinate scale as in (a).

$$J_1i + J_2j + J_3k,$$

where  $i, j$  and  $k$  are unit vectors and  $J_1, J_2$  and  $J_3$  components of  $J$  in the molecule frame.  $I_1, I_2$  and  $I_3$  are the three principal moments of inertia of CH<sub>2</sub>Cl<sub>2</sub>, defined about the axes of  $i, j$  and  $k$  respec-

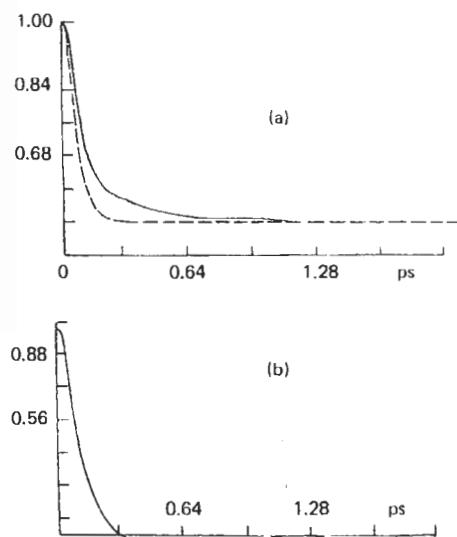


Fig. 4. (a) —  $(\mathbf{v}(t) \cdot \mathbf{v}(t)\mathbf{v}(0) \cdot \mathbf{v}(0))/\langle v^4(0) \rangle$ , computer simulation, --- gaussian result. (b)  $(\mathbf{v}(t) \cdot \mathbf{v}(t))/\langle v^2(0) \rangle$ , computer simulation.

tively. For linear velocity Berne and Harp [24] deduced:

$$\langle \mathbf{v}(t) \cdot \mathbf{v}(t)\mathbf{v}(0) \cdot \mathbf{v}(0) \rangle / \langle v^4(0) \rangle$$

$$= \frac{3}{5} \left\{ 1 + \frac{2}{3} [\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle^2] / \langle v^2(0) \rangle^2 \right\}. \quad (3)$$

The computer results (figs. 3, 4 and 5) are clearly different from the predictions in eqs. (1)–(3). The maximum deviation in each case occurs at around 0.3 ps after  $t = 0$ .

In the rotational case there are two sources of non-

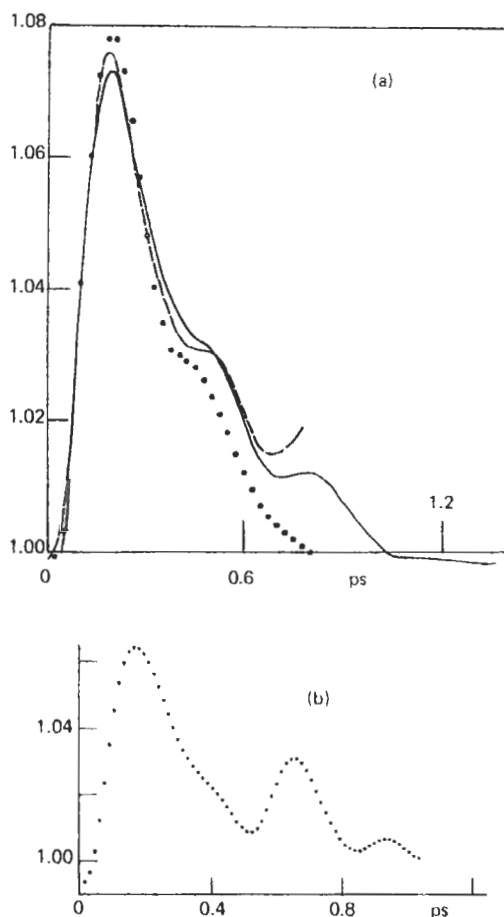


Fig. 5. (a) The non-gaussian nature of transient statistics in CH<sub>2</sub>Cl<sub>2</sub>, 293 K, 1 bar. The ordinate  $(J(t) \cdot J(t)\mathbf{v}(0) \cdot \mathbf{v}(0))/\langle J^2(0) \rangle \langle v^2(0) \rangle$ , where  $J$  is the molecular angular momentum and  $\mathbf{v}$  the centre of mass linear velocity. For gaussian statistics this remains at one for all  $t$ . • 5 × 5 algorithm, no charges, 12.5 ps running time-span, — 3 × 3, no charges, 12.5 ps span, --- 3 × 3, no charges, 9 ps span. (b) As for (a) 5 × 5 algorithm + site-charges.



gaussian transient statistics [3–6]. Even in the limit of free rotation, the orientational probability density function of an asymmetric top rotating in space is a wrapped gaussian [12]. This implies that the rotation between the first and second moment a.c.f.'s of angular momentum should be described with this in mind, and also with the added factor of non-gaussian effects arising from the interaction of molecular fields of force.

Euler–Langevin equations [25]:

$$\dot{\omega}_i = \tau_i \omega_j \omega_k - B_i \omega_i + A_i(t) \equiv -E_i(\omega) + A_i(t), \quad (4)$$

where  $\tau_i = (I_k - I_i)/I_i$ , and where the  $i, j, k$  indices are permuted cyclically among 1, 2, and 3.  $A_i(t)$  are stochastic forces and  $B_i$  friction coefficients. These may be estimated from the areas  $\gamma_i$  beneath the three  $P_1$  orientational a.c.f.'s of the unit vectors  $e_A, e_B$  and  $e_C$  defined earlier. Classical Euler–Langevin theory provides the relations [7]:

$$1/\gamma_i = kT(1/I_j B_j + 1/I_k B_k), \quad (5)$$

and are tabulated at two state points of the  $5 \times 5$  simulation in table 3. Numerically integrating [9] eq. (4) with these values we find that the difference between the right and left hand sides of eq. (2), with the parameters of table 3, is negligibly small, less than 5 parts in 1000 throughout the whole range of  $t$ . This means that:

(a) eqs. (4) do not reproduce the computer simulation results;

(b) the implied generalisation of eqs. (4) must be structured so as to produce transiently non-gaussian effects.

In order to examine the source of those non-gaussian effects that are known to be due to interactions rather than the nature of rotational motion we must construct phenomenological diffusion equations more general than eqs. (4). One of the ways of exploring

these new possibilities is to make the restoring frictional term in eqs. (4) *non-linear* in angular velocity  $\omega$ , and in general, this implies that the asymmetric top CH<sub>2</sub>Cl<sub>2</sub> diffuses rotationally according to an equation such as [26]

$$\partial P(A, g, t)/\partial t = \Gamma P(A, g, t), \quad (6)$$

where  $P$  is a probability density function,  $J$  is the rotation generator operator,  $g$  the vector defining asymmetric top orientation and  $A$  a column vector:

$$A = \begin{bmatrix} \omega_0 \\ \omega_1 \\ \vdots \\ \omega_n \end{bmatrix} \quad (7)$$

The first component,  $\omega_0$ , of  $A$  is the molecular angular velocity, and the other components are defined in sub-spaces generated by projection operators acting on  $\omega_0$ . They simulate the non-markovian nature of  $\omega_0$ . The last component  $\omega_n$  interacts stochastically with the thermal bath. We may define  $\Gamma$  as:

$$\Gamma = -i\omega \cdot J + \Gamma_A, \quad (8)$$

where  $\Gamma_A$  is the generalised Fokker–Planck operator defined by Ferrario and Grigolini [27]. The diffusion equation (6) is non-linear both in the rotational and interactive senses, and may be used to generate non-linear versions of the well-known itinerant oscillator model [28,29]. Eq. (6) implies non-gaussian transient behaviour as a consequence of this type of interactive non-linearity, which is also responsible for

$$\langle J(t) \cdot J(t) \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle \neq \langle J(t) \cdot J(t) \rangle \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle. \quad (9)$$

Note that  $\langle J(t) \cdot J(t) \rangle = \langle J(0) \cdot J(0) \rangle$  for a stationary process. This implies that the curves of fig. 5 are accurately one for all  $t$  in the gaussian limit.

The new phenomenon of “interactive non-linearity” may be defined conveniently in terms of the inter-

Table 3  
Correlation times and friction coefficients ( $5 \times 5$  algorithm), from eq. (5)

Temperature (K) (at 1 bar)	$\tau_1 (= 1/\gamma_1)$ a) (ps)	$\tau_2$ (ps)	$\tau_3$ (ps)	$\beta_1$ (THz)	$\beta_2$ (THz)	$\beta_3$ (THz)
293	1.2	3.8	1.2	11.7	22.0	11.7
177 b)	4.2	10.1	4.2	18.8	49.4	18.8

a) Dipolar orientation axis. b) Freezing point.

molecular pair potential itself. The torque on a molecule is the derivative of this potential with respect to rotation, and, as in the non-linear itinerant oscillator [28,29], may be approximated roughly by a co-linear (non-linear) form.

### Rotation-translation coupling

The computer simulation result summarised in fig. 1 by eq. (9), has profound implications for the physical theory of diffusing molecules. This is because the theory must describe the numerical deduction

$$\frac{\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle}{\langle v^2(0) \rangle} \neq 1; \quad t \neq 0; \quad (10)$$

must also obey the parity symmetry theorem

$$\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle = 0 \quad \text{for all } t. \quad (11)$$

Furthermore, following a suggestion of Ryckaert [7], we have computed the correlation function of the variables  $J(t)$  and  $\mathbf{v}(0)$  [or, alternatively,  $\mathbf{v}(t)$  and  $J(0)$ ] in a *moving frame of reference* defined as follows. Let  $v_x, v_y$  and  $v_z$  be the components of  $\mathbf{v}$ , for example, in the laboratory (fixed) frame. Define a rotating (molecular) frame of reference with respect to the unit vectors  $e_A, e_B$  and  $e_C$  along the principal axes of inertia axes of CH<sub>2</sub>Cl<sub>2</sub>. The components in the moving frame are then:

$$\begin{aligned} v_x &= v_1 e_{Ax} + v_2 e_{Ay} + v_3 e_{Az}, \\ v_y &= v_1 e_{Bx} + v_2 e_{By} + v_3 e_{Bz}, \\ v_z &= v_1 e_{Cx} + v_2 e_{Cy} + v_3 e_{Cz}, \end{aligned} \quad (12)$$

By applying parity reversal [7] to the C<sub>2v</sub> symmetry of CH<sub>2</sub>Cl<sub>2</sub>, we deduce that the correlation func-

$$\langle v_3(0) \rangle \quad \text{and} \quad \langle v_B(t) J_A(0) \rangle \quad (13)$$

vanish, except at  $t = 0$  and  $t \rightarrow \infty$ . We have computed them at 293 K, 1 bar and they are not mirror images. The  $(AB)$  element, defined by:

$$(AB) = \frac{[\langle v_A(t) J_B(0) \rangle + \langle v_A(0) J_B(t) \rangle]}{2 \langle v_A^2(0) \rangle^{1/2} \langle J_B^2(0) \rangle^{1/2}} \quad (14)$$

to reduce the statistical noise in the simulation, peaks with a value of  $-0.12$ . The  $(BA)$  element peaks at just below  $+0.02$ .

These correlation function elements do not exist (de facto) in any theory of a diffusing molecule referred to a static frame of reference. In order to describe the results of figs. 3-5 self-consistently we will have to rewrite eq. (6) in the moving frame, adding linear velocity components to the column vector  $A$ . The solution of the resulting diffusion equation is a task which involves the construction of a long continued fraction, numerically tractable in the manner of Evans et al. [31] through the use of Dupuis's renormalisation techniques [25,32]. In the simplest case [the rototranslational equivalent of eq. (4)] we have, in the moving frame:

$$\begin{aligned} \dot{\omega}_i &= [(I_i - I_k)/I_i] \omega_j \omega_k \\ &\quad - \sum_{l=1}^3 [\gamma_{il}^{(t)} v_l + \gamma_{il}^{(tr)} \omega_l] + F_i(t), \\ \dot{v}_i &= v_j \omega_k - \omega_j v_k - \sum_{l=1}^3 (\gamma_{il}^{(t)} v_l + \gamma_{il}^{(tr)} \omega_l) + F_i(t), \end{aligned} \quad (15)$$

where  $i, j, k$  are permuted cyclically among 1, 2 and 3. This may be integrated numerically using the computer random number generator for the stochastic force and torque [ $F_i(t)$  and  $\tau_i(t)$  respectively].

We have pursued the implications of this set of moving frame rototranslational Euler/Langevin equations by numerical integration, using a method developed by Ferrario [9]. The results of this numerical integration show that the Euler/Langevin structure of eq. (15) *cannot* account for the observed computer simulation results without the incorporation of non-linear characteristics into the stochastic torque and force terms. We need something akin to the non-linear rototranslational itinerant-oscillator [8] even to begin to explain [33] the moving frame computer simulation results.

## 5. Conclusions

(1) A  $5 \times 5$  atom-atom Lennard-Jones representation of the CH<sub>2</sub>Cl<sub>2</sub>, with added charges, has been



used in an attempt to reproduce spectral data pertaining to the molecular dynamics of CH<sub>2</sub>Cl<sub>2</sub> in the liquid state.

(2) The computer simulation is accurate enough to reveal the inconsistencies in the experimental literature, and to indicate which data are the more reliable.

(3) The computer simulation has revealed subtle details of molecular dynamics and interaction which need new analytical hypotheses for their explanation.

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