The Diffusional Dynamics of Liquid Methanol
New Cross-correlation Functions

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The application of a new rotating frame theory for asymmetric-top diffusion to methanol has produced, via computer simulation, a range of cross-correlation functions with which to measure the fine details of the molecular dynamics. Two of these cross-correlation functions have been examined in this paper together with autocorrelation functions of accelerations such as that of Corio which involve simultaneously the linear and angular motion of the molecule. The inertia distribution in the free-methanol molecule plays a dominant role in the liquid-state molecular dynamics. For example, the anisotropy of the inertia distribution in methanol causes one element of one of the cross-correlation functions investigated to be a hundred times greater in normalized magnitude than the element corresponding to the axis of the least moment of inertia. This type of cross-correlation function is therefore extremely sensitive to the details of simultaneous rotational and translational diffusion in a hydrogen-bonded liquid such as liquid methanol at 293 K.

The rapid increase in power, speed and availability of computer systems has made Newton's equations available for the study of condensed-phase molecular dynamics. It is now possible to release the constraints imposed by the historical dependence on the theory of Brownian motion. In no area is this clearer than in the statistical inter-relations of molecular rotation and translation. This is fundamental physics which immediately puts the original theory of 'rotational' and 'translational' diffusion in considerable difficulty, both conceptual and analytical. The reluctance of specialists to meet this problem mathematically is understandable from the complexity of the problem once we depart from the extreme over-simplifications of Debye. No satisfactory theoretical treatment has emerged, and the existence of the problem is often ignored by experimentalists. It follows that our state of the art in this field is at a primitive level. Part of the problem is that simple, intuitive ideas in this area lead to large, insoluble, differential equations and no progress. It is much easier to go back to Newton via the computer.

Computer simulation is already capable of providing much greater insight than some of the normal diffusion equations available, such as those of Condiff and Dahler,1 Hwang and Freed,2 T. C. Evans3 and Steiger and Fox.4 The latter seem to have found inconsistencies in other papers of this group. It is easy to see that molecules must both rotate and translate, and that these motions take place simultaneously, but to progress any further it is essential to find out which statistical cross-correlation functions may be used to make this quantitative. The first such cross-correlation function (c.c.f.) was discovered by Ryckebusch et al. using the frame of the principal molecular moments of inertia to correlate the centre-of-mass velocity and the molecular angular velocity through the simple tensor product. This c.c.f. was discovered by computer simulation, and was not known previously from the theory of molecular diffusion. This fact alone shows clearly the extent of the failure of analytical theory. Subsequently some attempts have been made to patch up the theory5 and to form a new analytical framework on which to construct a coherent explanation of the data now available6 from the computer. In order to do this it is necessary to re-examine the simple equations at the root of the

1967
Molecular Dynamics of Liquid Methanol

matter and then to use the computer to explore the existence or otherwise of c.c.f.
composed of terms which appear in these equations. This simple but revealing exercise
has been reported recently for the $C_2$-symmetric top dichloromethane having $C_2$
symmetry, and the symmetry characteristics of a number of c.c.f. have been tabulated.
The original simple c.c.f. discovered by Ryckaert et al. has been supplemented by
others, and it has become possible to begin to explore the dynamics of interacting
molecules in terms of the symmetry group and inertia distribution of the molecule
itself. These results have also stimulated progress in other directions: analogue circuit
simulation has been adapted to solve the fundamental Langevin equations of the
new theory through the use of electrical circuitry designed especially for this purpose,
and some care has been taken with the proper definition of reference frames in which
to write the equations themselves.

This paper extends the work to liquid methanol. The molecular dynamics are
simulated using a pair potential based on the ST2 of Stillinger and Rahman originally
developed for water. An analytical section examines the rotational and translational
Langevin equations in three different frames of reference, with a view to examining
their structure for non-vanishing c.c.f. and also for autocorrelation functions (a.c.f.) of
accelerations, such as that of Coriolis, which automatically involve the linear and
angular velocities simultaneously. The time dependence and relative normalised ampli-
tudes of elements of these new c.c.f. allow us to see clearly the way in which the
rotational motion of the molecule affects the mean position of its own centre of mass,
or alternatively its velocity. This is achieved using the frame (1, 2, 3) of the principal
molecular moments of inertia. Under certain conditions the cross-correlation becomes
observable directly in the laboratory frame ($x$, $y$, $z$), for example in the presence of
an electric field $E$.

Methanol is a particularly favourable asymmetric top with which to study these
dynamics, because one principal moment of inertia of the molecule is very much smaller
than the other two, making it possible to pick out the different kinds of motions by
inspection of diagonal or off-diagonal elements of non-vanishing c.c.f. tensors in
frame (1, 2, 3). It is anticipated that these dynamical effects will provide in future a
recognisable picture of phase transitions and related phenomena which cannot be
described with the contemporary theory of molecular diffusion. An example of these is
the simple liquid-to-crystal phase change, where the molecular dynamics become
highly coherent over a very small interval of temperature. It is expected that c.c.f.
amplitudes will vary dramatically near the normal melting point. In this paper evidence
is presented for a variation of two orders of magnitude or more between the diagonal
elements of the same c.c.f. in liquid methanol at 300 K. The c.c.f. are therefore
extremely sensitive to the fine details of molecular dynamics, much as are, in this
context, simple a.c.f. such as those of the resultant angular or linear velocity in the
laboratory frame itself.

The Langevin Equations in Different Reference Frames

Whatever the frame of reference, there should be a link between the translational
Langevin equation and the rotational counterpart when written for the same diffusing
asymmetric top. This link has been forged rather artificially in the literature using
the concept of cross-coefficients of friction and cross-diffusion coefficients. However,
it is not necessary to use this idea in any frame. For example, in the laboratory frame
the rotational Langevin equation is

$$ J(t) + \gamma \cdot J(t) = \Gamma(t) $$

(1)

where

$$ J = \sum_{i} m_i \mathbf{x} (\mathbf{\Omega} \cdot \mathbf{x}_i) $$

(2)
\[ J = \sum \frac{d}{dt} (m_i \times r_i) \]
\[ = \sum m_i \times \frac{d}{dt} r_i \]
\[ = \sum (m_i \times (\Omega \times r_i) + m_i \times (\Omega \times \dot{r}_i)) \]
\[ \text{with} \]
\[ \Omega \times r_i = \Omega \times (\Omega \times r_i) \]
The term \( \Omega \times r_i \) can be regarded as an intramolecular Coriolis term equal to the centripetal term \( \Omega \times (\Omega \times r_i) \) by the kinematic equation
\[ \dot{r}_i = \Omega \times r_i \]
The matrix in eqn (1) is a friction matrix assumed to be definable in such a way that it contains only diagonal components. \( \Gamma(t) \) is a random term which is statistically stationary and Gaussian in the simple Langevin equation.\(^1\) It is a Wiener process with an infinitely short correlation time:
\[ \langle \Gamma(t) \Gamma(0) \rangle = -2D \delta(t) \]
where \( D \) is a \( 3 \times 3 \) diagonal matrix termed the diffusion matrix and \( \delta(t) \) is the delta function.
If the molecule is simultaneously translating then eqn (1) must be supplemented by a translational equivalent, usually written in terms of the centre of mass velocity \( u \) as
\[ m \dot{u} + m \delta_i \dot{r}_i(t) = W(t) \]
where \( m \) is the mass of the molecule and \( \delta_i \dot{r}_i \) is the translational friction coefficient (a scalar in frame \( \{x, y, z\} \)) and \( W \) is a Wiener process describing the stochastic force in the laboratory frame. Eqn (6) can be written as
\[ \sum m_i \dot{u} + \delta_i \dot{r}_i \]
where the sum extends over all the atoms in the molecule. This comes from the basic dynamical principle that the momentum of a moving object can always be represented by that of the centre of mass. Comparing eqn (1) and (7) it is clear that time derivatives of atomic coordinates appear in both, and that the equations are not independent.

Rotating Frame of Reference
This concept has already been introduced and described elsewhere. The rotating frame \( (1, 2, 3') \) rotates at the origin of frame \( (x, y, z) \) with the molecular angular velocity \( \Omega \). The elementary dynamics\(^2\) of frame transformation then imply the equivalence relations between vectors defined in frame \( (x, y, z) \) and \( (1, 2, 3') \):
\[ [x]_{1,2,3'} = [x + \Omega \times R]_{1,2,3'} \]
\[ [a]_{1,2,3'} = [a + 2 \Omega \times u + \Omega \times \dot{R} + \Omega \times (\Omega \times R)]_{1,2,3'} \]
The laboratory frame is rotating with respect to frame (1, 2, 3) with the same angular velocity, and this implies that the equivalence is fully reversible:

\[ \theta_{10.3} = \theta_{10.2} \hat{\Omega} \times \hat{R}_{3} \times \hat{R}_{2} \times \hat{R}_{1} \]

(10)

\[ \theta_{11.3} = \theta_{11.2} \hat{\Omega} \times \hat{R}_{3} \times \hat{R}_{2} \times \hat{R}_{1} \]

(11)

For the angular momentum the equivalent transformations are:

\[ J_{10.3} = J_{10.2} \hat{\Omega} \times \hat{R}_{3} \times \hat{R}_{2} \times \hat{R}_{1} \]

(12)

\[ J_{11.3} = J_{11.2} \hat{\Omega} \times \hat{R}_{3} \times \hat{R}_{2} \times \hat{R}_{1} \]

(13)

so that the Langevin eqn (1) in the rotating frame is

\[ J + \hat{\Omega} \times J + \beta \times \hat{J} = \hat{F}(t) \]

(14)

and the translational Langevin eqn (6) is

\[ \theta + 2 \hat{\Omega} \times \theta + \hat{R} \times \hat{R} = \hat{W}(t) \]

(15)

Eqs (14) and (15) are clearly interdependent through the angular velocity \( \hat{\Omega} \), which is the same in the laboratory and rotating frames of reference.

Therefore in both frames the rotational and translational Langevin equations for a diffusing asymmetric top are interdependent through the simultaneous presence in both equations of a deterministic dynamical variable or variables. It is not necessary, therefore, to link the equations with friction cross-terms. By imposing the various terms in eqs (14) and (15) and by using the technique of computer simulation to compute c.f.f. tensors among these terms selectivity rules and amplitude and time dependence can be determined for any molecular symmetry. This has the advantages described in the introduction, and also introduces into the analysis fundamental new accelerations such as the Coriolis and centrifugal accelerations which do not seem to have been investigated by analytical or experimental means in this context.

The Moving Frame (1, 2, 3)

Finally, in this analytical section we define the use of the moving frame (1, 2, 3) of the principal molecular moments of inertia in our analysis. The Euler equations of elementary dynamics are defined in this frame, because the moment of inertia tensor is diagonal. The origin of the moving frame is the molecular centre of mass, where the axes of the three principal moments of inertia intersect. Therefore the moving frame rotates and translates with the molecule, whereas the rotating frame does not translate, its origin being fixed at that of the laboratory frame. The moving frame is therefore generated from the rotating frame by a translation of the molecular centre of mass, and the two frames do not rotate relative to each other. The advantage of using the moving frame has been demonstrated by Ryckaert et al., and it is possible to define any vector in the moving frame, including the position vectors of the molecular centre of mass, by the set of equations:

\[ A_{1} = A_{e1} + A_{e2} + A_{e3} \]

(16)

\[ A_{2} = A_{e2} + A_{e2} + A_{e2} \]

\[ A_{3} = A_{e3} + A_{e3} + A_{e3} \]

Here \( e_{1}, e_{2}, \) and \( e_{3} \) are unit vectors in the axes 1, 2 and 3, and the subscripts 1, 2, and 3, 2, and 3 denote components in the laboratory frame. The c.f.f. illustrated for liquid methanol in this paper have been computed in frame (1, 2, 3). In this frame the definition employed for the position of the molecular centre of mass is eqn (16). Note that the translational Langevin equation in frame (1, 2, 3) is

\[ \theta + 2 \hat{\Omega} \times \theta + \hat{R} \times \hat{R} = \hat{W}(t)_{1,2,3} \]

(17)
where \( \beta \), the friction coefficient, is now a tensor; i.e., there is no direct reference to the position vector, in contrast to eqn (15) of the rotating frame (1, 2, 3). Similarly there is no direct reference to the position vector in the laboratory frame translational Langevin eqn (6). In both these cases the position vector appears only indirectly through the velocity \( \dot{a} \) and acceleration \( \ddot{a} \), as in Newton’s equation.

**Computer Simulation Methods**

It is worth providing a fairly detailed description of the computer simulation algorithm, called Tetra, which was used to integrate the classical equations of motion for 108 methanole molecules with a pairwise additive pair potential based on the ST2. This is necessary to avoid confusion with the quaternion algorithm also called Tetra; the latter was recently the subject of a communications to the CCPS newsletter to the effect that it was valid only for spherical tops. The algorithm used in this work is rigorously applicable to asymmetric tops, and a listing is available on request. It has been checked against a third, independent algorithm by Ferrario and Thompson (see 1981). Our algorithm Tetra does not use quaternions but operates in Cartesian coordinates. It is not a predictor corrector.

**Rotational Motion**

With reference to the rotational motion of the rigid asymmetric top the first step is the calculation of the torque \( T_\alpha(t) \) from the forces on each atom. The torque is evaluated at four points in time, and denoted symbolically in the algorithm as follows:

\[
\begin{align*}
TX1 &= T_{\omega_1}(t); \\
TXO &= T_{\omega_1}(t - 2h) \\
TX &= T_{\omega_1}(t - h); \\
TXA &= T_{\omega_1}(t - 3h).
\end{align*}
\]

The net molecular angular momentum is then calculated from the numerical integration of

\[
J(t) = \int_T T_\alpha(t) \, dt + J(0).
\]

The numerical integration proceeds in four stages as follows. With two points, an estimate of the torque derivative is possible with

\[
T_\alpha(t - h) = T_\alpha(t) - h \frac{d}{dt} T_\alpha(t) + O(h^2)
\]

(19)

\[
T_\alpha(t - h) = T_\alpha(t) - h \frac{d}{dt} T_\alpha(t) + O(h).
\]

(20)

With three points:

\[
T_\alpha(t - 2h) = T_\alpha(t) - 2h T_\alpha(t) + 2h^2 T_\alpha(t) + O(h^3)
\]

(21)

\[
T_\alpha(t - h) = T_\alpha(t) - h T_\alpha(t) + \frac{h^2}{2} T_\alpha(t) + O(h^3)
\]

(22)

\[
\frac{d}{dt} T_\alpha = \frac{3}{2} T_\alpha(t - h) + T_\alpha(t - 2h) + O(h^3).
\]

(23)

With four points:

\[
T_\alpha(t - 3h) = T_\alpha(t) - 3h T_\alpha(t) + \frac{3}{2} h^2 T_\alpha(t) - \frac{3}{2} h^3 T_\alpha(t) + O(h^3)
\]

(24)
Molecular Dynamics of Liquid Methanol

\[ T_d(t) = T_d(0) - 2h^2 T_s(0) + 2h^2 T_s^2(0) + \mathcal{O}(h^4) \]  

(25)

\[ \frac{d}{dt} T_d = T_d(t) - h T_s(t) + \frac{h^2}{2} T_s^2(t) + \mathcal{O}(h^4) \]  

(26)

Solving for the torque derivative gives

\[ \frac{d}{dt} T_d = -\frac{1}{6h^3} \left( 15 T_d - 18 T_s(0) - 9 T_s - 2 T_d - 3 T_s \right) + \mathcal{O}(h^2) \]  

(27)

with similar expressions for \( T_d^2(t) \) and \( T_d^2(t) \). Eqn (1) is then integrated with the numerical series approximation

\[ T_d(t) = a + b t + c t^2 + d t^3 + \mathcal{O}(t^4) \]  

(28)

which implies

\[ I(t) = a t + \frac{c t^2}{2} + \frac{d t^3}{4} + \mathcal{O}(t^4) \]  

(29)

\[ J(t) - J(0) = \int a + b r + c r^2 + d r^3 \, dr \]

\[ = \Delta(9 T_d(t) + 19 T_s(t) - 5 T_d(t) - 2h) + \mathcal{O}(t^4) \]  

(30)

The translational equations of motion in Tetra are integrated with the standard Verlet algorithm. The algorithm was originally developed by Prof. K. Sieger. This algorithm has been the basis for most of our simulation work in the past five years or so and additional technical description is available in the literature. It can also be used for the cationic and anionic mixtures of chiral asymmetric tops.

The pair potential for methanol was mimicked with atom-atom Lennard-Jones terms, situated on the methyl group (treated as a moiety) the oxygen atom and the hydrogen atom. Additionally, point charges, located as in Fig. 1 (the principal moment of inertia is defined), take into account the hydrogen bonding. The disposition and magnitude of the point charges was such as to reproduce the methanol dipole moment. As in ST2 some allowance was made for the fact that there is also a finite quadrupole moment in methanol, although the attempt was made to reproduce this in magnitude, because it does not seem to be known experimentally. (The original ST2 concept, by Stillinger and Ben-Naim, was designed to use point charges to account for the fact that water has a quadrupole moment.) The approximation of regarding the methyl group as a moiety of mass 15 has the effect of producing the following principal Cartesian coordinates (in Å):

<table>
<thead>
<tr>
<th>atom</th>
<th>x(Å)</th>
<th>y(Å)</th>
<th>z(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-0.974</td>
<td>1.20</td>
<td>0.16</td>
</tr>
<tr>
<td>O</td>
<td>-0.021</td>
<td>0.927</td>
<td>0.079</td>
</tr>
<tr>
<td>Me</td>
<td>0.000</td>
<td>-0.579</td>
<td>-0.0175</td>
</tr>
<tr>
<td>q</td>
<td>0.251</td>
<td>1.097</td>
<td>0.380</td>
</tr>
<tr>
<td>e</td>
<td>0.141</td>
<td>1.110</td>
<td>-0.401</td>
</tr>
</tbody>
</table>

The two charges marked q above are each of -0.123[e] disposed tetrahedrally with respect to the hydrogen and methyl groups around the oxygen atom, which carries no
charge, as in ST2 for water. The charge on the methyl group is 0.104[e] and that on the hydrogen atom is 0.143[e]. The O—Me bond length used was 1.5 Å and the O—H bond length 1.0 Å. The charges $\eta$ are located 0.3 Å from the oxygen atom. The disposition of charges was calculated on the basis of ST2 and the relative magnitudes estimated on information available from an ab initio self-consistent field computation used elsewhere.
Molecular Dynamics of Liquid Methanol

The atom-atom Lennard-Jones parameters were as follows:

\[ \sigma(H-H) = 2.4 \AA; \quad \epsilon(H-H) = 21.3 \text{ K}; \]
\[ \sigma(O-O) = 2.8 \AA; \quad \epsilon(O-O) = 58.4 \text{ K}; \]
\[ \sigma(Me-\text{Me}) = 3.6 \AA; \quad \epsilon(Me-\text{Me}) = 158.6 \text{ K}. \]

These were taken direct from independent literature estimates\(^{16}\) for hydrogen and oxygen, and those for the methyl group were initially based on carefully refined values used by Lasnier and Bred\(^{17}\) for t-butyl chloride. Adjustment was needed in the \( \sigma \) parameter of the methyl group from an initial value of 4.0 \( \AA \) to a value of 3.6 \( \AA \) in order to bring the pressure down to 1 bar for an input molar volume of 40.49 cm\(^3\) mol\(^{-1} \) at 293 K, the literature density.

With reference to fig. 1 it is clear that the moment of inertia distribution in this particular, simplified, model of methanol is very anisotropic. The three moments of inertia from our principal Cartesian coordinates are

\[ I_x = 1.75 \times 10^{-46} \text{ g cm}^2 \]
\[ I_y = 33.5 \times 10^{-46} \text{ g cm}^2 \]
\[ I_z = 33.6 \times 10^{-46} \text{ g cm}^2. \]

These compare with the experimental\(^{11}\) values of, respectively, 6.5762 \( \times 10^{-46} \) cm\(^2\), 35.3159 \( \times 10^{-46} \) g cm\(^2\) and 34.0790 \( \times 10^{-46} \) g cm\(^2\) so that the effect of replacing the three hydrogen atoms of the methyl group by a moiety of mass 15 is obvious. In this paper we aim to take advantage of this anisotropy in the course of computing various c.c.f. elements.

The time step employed was 5.0 \( \times 10^{-15} \) s and correlation functions were computed at equilibrium using a running time average over segments of ca. 1000 time steps each. The computer system used was the U.M.K.C.C. CDC 7600.

Some New Auto- and Cross-correlation Functions

We have computed the autocorrelation functions of the Coriolis acceleration, \( 2 \Omega \times R \), the centripetal acceleration \( \Omega \times (\Omega \times R) \), and the non-uniform acceleration \( \Omega \times (\Omega \times \Omega) \) both in the moving frame (1, 2, 3) and the laboratory frame (\( x, y, z \)). The existence of these a.c.f. for methanol immediately prove that translational and rotational motion are inextricably interrelated and also prove the reciprocity relations (8)–(11). Most contemporary papers on the molecular diffusion of methanol might attempt to use the Delboy theory, based on a greatly simplified version of eqn (14), and would not recognize the need to use both the translational and rotational Laguerre equations simultaneously. The result (demonstrated in fig. 2) also implies that all experimental sources of information on liquid methanol are affected by the inevitable presence of simultaneous translation and rotation. Very rarely does a scientific paper in this field try to deal with this quantitatively for the reason that the necessary theory is obscure or missing altogether.

Computer simulation provides a clear answer to this problem, in that it can be used to build up a particular experimental source of information, such as a spectrum, and then used self-consistently to look in great detail at the molecular dynamics. It must always be borne in mind that computer simulation is not in itself an experimental technique, but an interpretative method based on well defined numerical approximations. These become useful when analysis becomes difficult or so complex as to be obscure to experimentalists and non-specialists. The rest of the results in this paper are presented in this spirit.
Fig. 2. Illustration of the autocorrelation functions of the Coriolis acceleration, $2\Omega \times \mathbf{v}$, (a) and the non-uniform acceleration, $\mathbf{g} \times \mathbf{g}$, (b) in moving the frame of reference defined in fig 1 (---).

In (a) (---) denotes a.c.f. of $2\Omega \times \mathbf{v}$ in the laboratory frame.

The eqns (14) and (15) both contain the angular velocity $\Omega$ as a variable, dependent on time, but there is no contemporary analytical technique capable of solving them for auto- and cross-correlation functions such as the ones described in detail in this paper. It is possible of course to solve them separately, but that is not the point. The difficulty analytically is caused by the presence of vector products that make the stochastic differential equations non-linear. Add to this the well known limitations,\textsuperscript{1}... in molecular dynamics, of the class of Langevin equations in general, then the analytical approach becomes intractable very quickly. This seems to be a fundamental failure of the theory of diffusion in general, on a basic level, i.e. it cannot describe what it sets out to describe. In the face of this a method has been adopted and described elsewhere\textsuperscript{15} of simply inspecting the terms in eqns (14) and (15) and of constructing by computer simulation c.c.f. of many different types between these terms. Of these possibilities, only a few exist for $t > 0$, and the symmetry pattern governing this has been reported.\textsuperscript{15} The generally valid symmetry rules\textsuperscript{1} governing the existence in the moving frame and laboratory frame of the various c.c.f. could not be relied upon to recognize this pattern, is that some c.c.f. elements that are allowed by symmetry do not in fact exist above the noise of the simulation, and others do. Therefore it is necessary to compute each c.c.f. separately for the emergence of a recognisable symmetry pattern. This is a major computational task: for CH$_2$Cl, for example, over 400 varieties were investigated. For
Fig. 3. Curves 1, 2 and 3 illustrate the diagonal elements of the cross correlation function \( C_i \) (see text) in the frame (1, 2, 3).

In methanol we restrict ourselves to looking in detail at just two differem c.c.f. in frame (1, 2, 3). These are as follows:

\[
C_i(t) = \frac{\langle \Omega(t) \times \Omega(t) \Omega^T(0) \rangle}{\langle \Omega(0) \Omega(0) \Omega^T(0) \rangle^{1/2}}
\]  

(31)

\[
C_i(t) = \frac{\langle \Omega(t) \times \Omega(t) \times \Omega(t) \Omega(t) \Omega(t) \Omega^T(0) \rangle}{\langle 
\Omega^T(0) \Omega^T(0) \Omega^T(0) \Omega^T(0) \Omega^T(0) \Omega^T(0) \rangle^{1/2}}
\]  

(32)

These two c.c.f. are essentially the same type, i.e.

\[
(\Omega(t) \times \Omega(t) \Omega^T(0)) \overline{(\Omega^T(0))^{1/2}} (\Omega^T(0))^{1/2} (\Omega^T(0))^{1/2}
\]  

(33)

but fig. 3 and 4 show that they are different in sign. In each case only the diagonal elements in frame (1, 2, 3) of the tensor product survive. All elements vanish in frame (x, y, z) as for CH\(_3\)Cl\(_2\). This behaviour contrasts therefore with that of the simple tensor product between \( \sigma \) and \( \Omega \) first correlated by Ryckaert et al. in frame (1, 2, 3), where
only the off-diagonal elements may exist. Therefore in fig. 3 the curves 1, 2 and 3 denote, respectively, the diagonal elements:

\[ C_{ii}(t) = \frac{\langle R_i(t) \times \Omega_i(t) \rangle}{\langle R_i(0) \rangle^2 \langle \Omega_i(0) \rangle^2} \]  
\[ C_{ij}(t) = \frac{\langle R_i(t) \times \Omega_j(0) \rangle}{\langle R_i(0) \rangle^2 \langle \Omega_j(0) \rangle^2} \]  
\[ C_{ij}(t) = \frac{\langle R_i(0) \times \Omega_j(t) \rangle}{\langle R_i(0) \rangle^2 \langle \Omega_j(0) \rangle^2} \]  

These are very different in amplitude because the angular velocity component in this frame is inversely proportional to the appropriate molecular moment of inertia. Angular motion about the 1 axis is therefore relatively much faster than about the 2 or 3 axes. In contrast, the position vector \( R \) is the position vector of the molecular centre of mass in the laboratory frame projected into frame (1, 2, 3) with eqn (16) and, although the components \( R_1, R_2 \), and \( R_3 \) are not equal, their anisotropy is not as great as that in \( \Omega \). The net effect on the tensor product \( C_{ij} \) is therefore as in fig. 3. The amplitude of the maxima in each c.c.f. component is therefore understandable, approximately, in intrinsically molecular terms, but the positions of these maxima in time, and the overall shapes of the c.c.f. components, are all dependent also on intermolecular forces, i.e. on the ensemble dynamics, as for a.c.f. The overall picture that emerges from fig. 3 is that correlation between \( R \times \Omega \) and \( R \) about the 1 axis is strongest and shows that the motion of the centre of mass in axis measured through the component 1 of the linear velocity
Molecular Dynamics of Liquid Methanol

The correlation of the component $R_i(0)$ and depends on the angular motion of the molecule about axis 1 of the principal moment-of-inertia frame. The intermolecular forces do not seem to be effective in changing the order of angular velocity magnitudes in frame (1, 2, 3) from that expected in the freely rotating asymmetric top, i.e. the angular velocity about axis 1 is the greatest. As the methanol liquid freezes this situation might be expected to change as the molecules become locked into the crystal lattice.

The amplitude of the component 3 in fig. 3 is the smallest, and on three times smaller than that of component 1. This is despite the fact that the moment of inertia about axis 1 is roughly 30 times smaller than the other two which are nearly equal. Therefore the rate of intermolecular forces, namely hydrogen bonding, is clearly effective in tending to average out the angular velocity anisotropy in the condensed phase. In summary, correlation between $R_i(0)$ and $R$ is most effective in axis 1 and least effective in 3.

In fig. 4 this is accentuated considerably through the use of the c.c.f. $C_{21}$ which contains $v$ to the power three. In physical terms this c.c.f. correlates the centripetal acceleration in frame (1, 2, 3) to the linear velocity $vR$ in the same frame. The centripetal acceleration around axis 1 is much greater than around the other two axes, and fig. 4 shows that the 1 component of $C_{21}$ is 100 times greater in amplitude than component 3. In this respect, therefore, the motion of methanol involving the correlation between the vector $R$ and the vector $v$ in different ways, is highly anisotropic in the liquid. The reason for this can be traced directly to the anisotropy in the moment-of-inertia distribution of the free molecule. Cross-correlation functions of this type are therefore very sensitive to the finer detail of condensed-phase molecular dynamics.

Finally, it is necessary to note that there can be no objection to the introduction of the position vector $R$ directly in to the description of molecular dynamics in liquids, provided that the origin of the coordinate system is well defined. In the laboratory frame ($x, y, z$) the origin is defined through the equations

$$\langle R(t) \rangle \rightarrow \langle R(0) \rangle = 0$$

$$\langle R(t) \cdot R(0) \rangle \rightarrow 0 \text{ as } t \rightarrow \infty$$

i.e. the mean position of the ensemble is statistically stationary and is zero, and the autocorrelation function of $R$ vanishes as $t \rightarrow \infty$. In other words the molecules are symmetrically disposed on average with respect to the origin of the coordinate system. The components of $R$ in the moving frame are generated by a projection on to the three axes of the principal moments of inertia for each molecule, so that the definition of the origin of the laboratory frame is unimportant. This forestalls the possible criticism that the definition of the laboratory frame could be arbitrary, and therefore that the amplitudes of the c.c.f. involving $R$ would be dependent on an arbitrary laboratory frame origin.

The University of Wales is thanked for the award of the Fletcher Senior Fellowship.

References

2. Ref. (1), chap. 3.
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