Journal of Molecular Liquids, 37 (1988) 21–34
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

IRROTATIONAL AND VORTEX FIELDS IN THE THEORY OF MOLECULAR DYNAMICS

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(Received 12 November 1986)

ABSTRACT

The theory of molecular diffusion is extended to include consideration of the position vector $\underset{\sim}{r}$ of the centre of mass of each molecule in the ensemble. This implies automatically that the interaction of rotation and translation must be considered in the treatment of non inertial accelerations in the molecular ensemble. This leads to a consideration of vortex and irrotational fields in the theory of molecular dynamics in the laboratory frame (x,y,z) and in the moving frame (1,2,3) defined by the frame of the principal molecular moments of inertia. Computer simulations of supercooled liquid water are used to determine the nature of the time dependence of some of these autocorrelation functions involved in the development of the theory. This in turn might lead to a method of linking the ideas of molecular dynamics and hydrodynamics in the theory of fluids.

INTRODUCTION

The increasing power of digital computers means that a larger number of molecules per simulation can be used [1]. The borderline between molecular dynamics and hydrodynamics runs in the region where single molecule properties give way to multi-molecular ones, involving the collective motion of many thousands of molecular entities [2]. The collective motion may be a vortex flow with respect to a given axis in the sample or with respect to a given origin. This automatically brings into consideration the position vector of the molecular centre of mass, because the vortex field is made up of molecules in the sample rotating cooperatively with reference to the laboratory frame (x,y,z). This generates orbital angular momentum in the complete sample and leads to the problem of how vortex fields could be generated on a molecular level in a simulation. This paper introduces the vector $\underset{\sim}{r}$ into the analysis of molecular dynamics, where $\underset{\sim}{r}$ is the position of the centre of mass of a

0167-7322/88/$03.50

molecule with respect to an origin in the laboratory frame of reference (x,y,z). This introduces into consideration a method of analysing the way in which the rotation and translation of the molecule are inter-dependent [3-10]. After establishing the new terms that appear in this way directly in the laboratory frame it can be shown with a Taylor expansion that the number of new terms rapidly increases with the order of differentiation. An analysis of these terms is then pursued by taking the vector curl of each new field. This shows that some of the new fields are irrotational and some are vortex fields [11]. Furthermore it is possible to generate auto and cross correlation functions using the vortex and irrotational fields using the information available in the molecular dynamics simulation. This may all be achieved on a single molecule level by generating the trajectories in a simulation and systematically investigating the cross-correlation functions of importance. After establishing the relative importance in this way an attempt may then be made to extend the analysis to properties and correlation functions involving more than one molecule, i.e. to use cross-correlation functions among molecules as well as those correlating different vectors on the same molecules. This last stage of the analysis would need a very big molecular dynamics sample [2] and a supercomputer. In this paper the development is confined to evaluating the various molecular irrotational and vortex fields in terms of their auto and cross-correlation functions. In the end analysis it might be anticipated that some of the cross-correlation functions, generated from first principles, would be more important than others in the generation of observable macroscopic properties. Conversely the root cause of some of these well known phenomena, such as different types of vortex, might be traced to single molecule properties.

The position vector $\underset{\sim}{r}$ does not appear in the theory [12] of uncoupled rotational or translational diffusion, which is therefore incapable of producing vortex fields of the right type for generating hydrodynamical properties from single molecule properties, at least without assuming the intermediacy of a fluid medium, slip and stick conditions [13], rototranslational friction coefficients [14-18] and so on. It is not really valid to assume the presence of such a medium when it is known that true molecules interact through an intermolecular potential, and that a molecular liquid is, self evidently, made up of nothing but molecules. In other words the hydrodynamical principles are laws governing macroscopic properties whose origins are molecular dynamical. The computer power is now available to make the link between molecular dynamics and hydrodynamics, but only if the mutual influence of rotation upon translation is recognised from the start.

2. THEORY INVOLVING THE POSITION VECTOR

Consider a frame of reference (1,2,3)' which rotates with respect to the laboratory frame (x,y,z) at the angular frequency $|\underset{\sim}{\omega}|$. Each frame has the same origin. Let $\underset{\sim}{r}$ be the position vector of the centre of mass of a molecule in each frame. Let $\underset{\sim}{D}_f\underset{\sim}{r}$ be the linear velocity of the molecular centre of mass relative to (x,y,z) and $\underset{\sim}{D}_m\underset{\sim}{r}$ that relative to (1,2,3)'. This defines the differential operators $\underset{\sim}{D}_f$ and $\underset{\sim}{D}_m$. Let us now examine the Taylor expansion of $\underset{\sim}{r}$ in the rotating frame of reference, derivative by derivative. This examination generates terms in the laboratory frame which have their origins in the fact that the rotation and simultaneous translation of the molecule is in dynamical terms non-inertial. The velocities in the fixed and moving frames are linked through

$$\underset{\sim}{D}_f\underset{\sim}{r} = \underset{\sim}{D}_m\underset{\sim}{r} + \underset{\sim}{\omega} \times \underset{\sim}{r} \tag{1}$$

$$\underset{\sim}{D}_m\underset{\sim}{r} = \underset{\sim}{D}_f\underset{\sim}{r} - \underset{\sim}{\omega} \times \underset{\sim}{r} \tag{2}$$

where it is understood that all the terms on the r.h.s. are defined with respect to frame (1,2,3)', and that on the l.h.s. with respect to frame (x,y,z). The angular velocity $\underset{\sim}{\omega}$ is the same in both frames because it is the rate at which one frame rotates with respect to the other. Eqn (2) is the interesting link between rotating frame velocity (l.h.s.) and laboratory frame velocity (r.h.s). The r.h.s. automatically employs two velocities:

$$\underset{\sim}{v}_1 = [\underset{\sim}{\omega} \times \underset{\sim}{r}]_{(x,y,z)}; \tag{3}$$

$$\underset{\sim}{v}_2 = [\underset{\sim}{D}_f\underset{\sim}{r}]_{(x,y,z)}. \tag{4}$$

The velocity $\underset{\sim}{v}_1$ depends on the position vector $\underset{\sim}{r}$, and it is possible to show [11] that the vector curl of $\underset{\sim}{v}_1$ is $\underset{\sim}{\omega}$, i.e.

$$\underset{\sim}{\omega} = \tfrac{1}{2}\,\underset{\sim}{\nabla} \times \underset{\sim}{v}_1 \tag{5}$$

For each molecule therefore the curl of the linear velocity $\underset{\sim}{v}_1$ is the angular velocity $\underset{\sim}{\omega}$. The field $\underset{\sim}{\nabla} \times \underset{\sim}{v}_1$ is therefore provided with the rotational property $\underset{\sim}{\omega}$. In other words vortex rotation occurs in regions in the molecular ensemble where $\underset{\sim}{\nabla} \times \underset{\sim}{v}_1$ does not vanish. For a given $\underset{\sim}{\omega}$ the velocity $\underset{\sim}{v}_1$ is proportional to the position vector $\underset{\sim}{r}$. Therefore with respect to a given origin in the laboratory frame (x,y,z) the further out from this origin

the greater will be the velocity $\underset{\sim}{v}_1$. This is characteristic of a vortex field. In this picture, therefore, each molecule generates its own vortex field $\underset{\sim}{\nabla} \times \underset{\sim}{v}_1$. In a computer simulation the autocorrelation of this vortex field can be built up as

$$\langle \underset{\sim}{\nabla} \times \underset{\sim}{v}_1(t) \cdot \underset{\sim}{\nabla} \times \underset{\sim}{v}_1(o) \rangle \tag{6}$$

in the laboratory frame (x,y,z) and in the moving frame (1,2,3)'. This is possible and the running time average < > is well defined because the sample origin is fixed by the definitions $\langle \underset{\sim}{r} \rangle = \underset{\sim}{\rho}$; and $\langle \underset{\sim}{r}(t) . \underset{\sim}{r}(o) \rangle = o$; $t \to \infty$. i.e. the sample is defined to be isotropic and the a.c.f. of the position vector vanishes in frame (x,y,z) as $t \to \infty$. The origin of the laboratory frame is therefore not arbitrary with respect to $\underset{\sim}{r}$ for each molecule, but is defined in such a way as to ensure that the mean over the positions of all the molecules disappears in an isotropic sample.

Therefore for velocities the use of the moving frame and introduction of the position vector $\underset{\sim}{r}$ results in the appearance of an irrotational field and vortex field in the laboratory frame of reference.

Turning now to the next term in the Taylor expansion and therefore to a consideration of accelerations in the laboratory and moving frames there emerge the following results from two applications of the differential operators $\underset{\sim}{D}_m$ and $\underset{\sim}{D}_f$ in frames (1,2,3) and (x,y,z):

$$\underset{\sim}{D}^2_{fr} = \underset{\sim}{D}_f(\underset{\sim}{D}_f \underset{\sim}{r}) = \underset{\sim}{D}^2_m \underset{\sim}{r} + 2\underset{\sim}{\omega} \times \underset{\sim}{D}_m \underset{\sim}{r} + (\underset{\sim}{D}_m \underset{\sim}{\omega}) \times \underset{\sim}{r} + \underset{\sim}{\omega} \times (\underset{\sim}{\omega} \times \underset{\sim}{r}) \tag{7}$$

$$\underset{\sim}{D}^2_{mr} = \underset{\sim}{D}_m(\underset{\sim}{D}_m \underset{\sim}{r}) = \underset{\sim}{D}^2_f \underset{\sim}{r} - 2\underset{\sim}{\omega} \times \underset{\sim}{D}_f \underset{\sim}{r} - (\underset{\sim}{D}_f \underset{\sim}{\omega}) \times \underset{\sim}{r} + \underset{\sim}{\omega} \times (\underset{\sim}{\omega} \times \underset{\sim}{r}) . \tag{8}$$

These equations introduce the Coriolis acceleration, the centripetal acceleration, and the non uniform acceleration into both the moving frame (r.h.s. of eqn (7)) and the laboratory frame (r.h.s. of eqn (8)). In the classical Newtonian concept of force is equal to mass multiplied by acceleration these accelerations are not accounted for explicitly. For an object moving on the rotating earth's surface this is a good approximation but for rotating and translating molecules the acceleration terms on the r.h.s. of eqn (8) become just as important as the first (Newtonian) term on the r.h.s. of that equation. This implies that molecular dynamics are in this sense "non-Newtonian", simply because the translating molecules are simultaneously rotating and the frame of the laboratory is a non-inertial one with respect to the moving frame (1,2,3)' or indeed with respect to a frame defined by the principal molecular moments of inertia. In the numerical

technique of molecular dynamics simulation the mixing of rotation and translation occurs by writing the Newton equations for translation and the Euler equations for rotation. The mixing of rotation and translation then occurs through the presence in the classical hamiltonian of a pairwise additive intermolecular potential. This generates the individual molecular trajectories and these can be used to build correlation functions. It has been shown elsewhere [3-10] that correlation functions of the Coriolis, centripetal and non-uniform accelerations exist in both frames of reference used in equns (7) and (8) and also in the frame of the principal molecular moments of inertia. This is a direct proof of the non-Newtonian nature of molecular dynamics in terms of the new accelerations, whose correlation functions are now known in detail from computer simulation. Having shown this, it is possible then to examine each acceleration term to see whether it is an irrotational or a vortex field. This will show which of the new accelerations are potentially capable of generating a macroscopic vortex, and which do not. After this it is possible to show using cross-correlation functions generated by simulation whether the vortex fields are correlated to irrotational fields on the single molecule level. This should show whether this type of correlation would then be possible macroscopically. This type of mutual influence of one mode on another should finally be describable with the macroscopic, hydrodynamic equations of motion.

Taking the vector curl of each acceleration term on the r.h.s. of eqn (8) in the laboratory frame the only vortex field is that defined by $\underset{\sim}{\nabla} \times ((\underset{\sim}{D}_{rf}\underset{\sim}{\omega}) \times \underset{\sim}{r})$. The curl of the other three accelerations disappears in both frames of reference. Therefore the Newtonian field (the first term on the r.h.s. of eqn (8)) is an irrotational field and does not have a vector curl. This implies the natural result that translational diffusion does not generate a vortex on a single molecule level without the simultaneous presence of molecular rotation. The theory of translational diffusion cannot describe molecular vortex fields. Similarly the Coriolis acceleration has no vector curl, i.e. the $\underset{\sim}{\nabla}\times$ operator in this context means differentiation with respect to the components of r. Since $\underset{\sim}{v}$ and $\underset{\sim}{r}$ are conjugate variables the differentiation of one with respect to the other produces zero. The Coriolis acceleration is therefore an irrotational field on a single molecule level. The only time the Coriolis acceleration generates a vortex is when the molecular centre of mass velocity $\underset{\sim}{v}$ is explicitly dependent on the laboratory frame coordinates x,y, and z. In this case there must be an external macroscopic force on the molecular ensemble which acts in such a way that there is a gain of fluid (i.e. in the number of molecules) per unit volume per unit time. In hydrodynamic terms the fluid is compressible and the

divergence of the fluid velocity does not vanish. In molecular terms, more molecules must move systematically into a given volume, so that the external pressure on the molecular ensemble is increasing.

The vector curl of the molecular centripetal acceleration $\nabla \times (\omega \times (\omega \times r))$ vanishes and this is not a vortex field. There remains the non-uniform acceleration.

If the "orbital" velocity

$$v_l = \omega \times r$$

is differentiated with respect to time we obtain the "orbital" acceleration

$$\dot{v}_l = \dot{\omega} \times r + \omega \times \dot{r} \tag{9}$$

which is a sum of the non-uniform acceleration and the Coriolis acceleration. As we have seen the vector curl of the Coriolis acceleration vanishes in the absence of a pressure gradient across the molecular ensemble, which leads to the result:

$$\dot{\omega} = \tfrac{1}{2} \nabla \times \dot{v}_l \tag{10}$$

i.e. the vector curl of the orbital acceleration of each molecule is an angular acceleration, which is therefore an orbital angular acceleration, involving the position vector r. A number of individual molecular accelerations of this nature could act cooperatively to result in a macroscopic vortex.

Turning now to the third term in the Taylor expansion of the molecular centre of mass position vector, the differential operators in the moving and fixed frames are applied three times in the forward and back transforms, producing eight new terms in both frames which have the dimensions of derivative of acceleration. These are

$$D^3_{fr} = D^3_m r + D_m(2\omega \times D_m r) + D_m((D_m \omega) \times r) + D_m(\omega \times (\omega \times r))$$

$$+ \omega \times D^2_m r + \omega \times (2\omega \times D_m r) + \omega \times ((D_m \omega) \times r) + \omega \times (\omega \times (\omega \times r)) \tag{11}$$

$$D^3_{mr} = D^3_f r - D_f(2\omega \times D_f r) - D_f((D_f \omega) \times r) + D_f(\omega \times (\omega \times r))$$

$$-\omega \times D^2_f r + \omega \times (2\omega \times D_f r) + \omega \times ((D_f \omega) \times r) - \omega \times (\omega \times (\omega \times r)) \tag{12}$$

These equations reveal the existence of many higher order terms in the moving and laboratory frames, some of which are vortex fields. The autocorrelation

functions of all these terms can be constructed by computer simulation, and so can a large number of new molecular cross correlation functions between terms in both frames. Note that these are all essentially single molecule properties, the cross correlation is between a particular vector property at t = 0 and a time t later for the same molecule, an average being taken over the product for each molecule and for each time interval according to the standard rules of running time averaging. We have not yet started to take into account cross-correlations between molecules, because we are still at the point of establishing the single molecule dynamics. Essentially speaking, cooperativity of these single molecule auto and cross correlation functions would lead to the evolution of hydrodynamical modes of collective motion from the equations of molecular dynamics, essentially the equations of classical mechanics are used in computer simulation. This kind of investigation is possible with the fast array processors now being built. [1,2]

The vortex fields on the r.h.s. of eqn. (12) in the laboratory frame are those for which the curl exists, as usual. For example:

$$\nabla \times (\omega \times (\dot{\omega} \times r)) = \omega \times \dot{\omega} \tag{13}$$

and the irrotational fields are those for which the curl disappears, e.g.

$$\nabla \times (\omega \times (\omega \times (\omega \times r))) = 0 \tag{14}$$

A summary of these properties is given in table 1.

TABLE 1
Vortex and Irrotational Fields for Eqn. (12)

Field	Irrotational	Vortex
$\ddot{r}$	✓	
$3\dot{\omega} \times v$	✓	
$\omega \times \dot{v}$	✓	
$3\omega \times (\omega \times v)$	✓	
$-\omega \times (\omega \times (\omega \times r))$	✓	
$\ddot{\omega} \times r$		✓
$2\omega \times (\dot{\omega} \times r)$		✓
$\dot{\omega} \times (\omega \times r)$		✓

3 ANALYSIS INVOLVING THE MOLECULAR DIPOLE MOMENT $\underset{\sim}{\mu}$

If we now substitute the position vector of the molecular centre of mass ($\underset{\sim}{r}$) by the vector:

$$\underset{\sim}{\mu} = \underset{\sim}{r}_1 - \underset{\sim}{r}_2 \tag{15}$$

some useful results can be obtained, based on the analysis of the foregoing section. In eqn. (15) $\underset{\sim}{\mu}$ is the dipole moment vector of the molecule, which can be considered as the difference between the vectors $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ from either end of $\underset{\sim}{\mu}$ to the origin of the laboratory frame. Employing the kinematic relation:

$$\dot{\underset{\sim}{\mu}} = \underset{\sim}{\omega} \times \underset{\sim}{\mu} \tag{16}$$

it is seen from eqns. (3) to (5) that

$$\underset{\sim}{\omega} = \tfrac{1}{2} \underset{\sim}{\nabla} \times \dot{\underset{\sim}{\mu}} \tag{17}$$

In other words the curl of $\dot{\underset{\sim}{\mu}}$ with respect to the coordinates x,y and z (i.e.

$$\underset{\sim}{\nabla} \times \equiv \left(\frac{\partial}{\partial x}\, \underset{\sim}{i} + \frac{\partial}{\partial y}\, \underset{\sim}{j} + \frac{\partial}{\partial z}\, \underset{\sim}{k}\right) \times \tag{18}$$

is proportional to the molecular angular velocity $\underset{\sim}{\omega}$ at an instant t. The coordinates x,y and z in the partial derivatives of eqn. (18) are defined in the context of eqns. (15) to (18) by:

$$\begin{aligned} x &\approx x_1 - x_2 \\ y &\approx y_1 - y_2 \\ z &\approx z_1 - z_2 \end{aligned} \tag{19}$$

where (x_1, y_1, z_1) and (x_2, y_2, z_2) relate to $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ respectively.

With these derivatives one may similarly define:

$$\underset{\sim}{\nabla} \cdot \equiv \left(\frac{\partial}{\partial x}\, \underset{\sim}{i} + \frac{\partial}{\partial y}\, \underset{\sim}{j} + \frac{\partial}{\partial z}\, \underset{\sim}{k}\right) \cdot \tag{20}$$

$$\underset{\sim}{\nabla} \cdot \underset{\sim}{\nabla} \equiv \nabla^2 \equiv \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \tag{21}$$

the Laplacian operator.

It follows from eqn. (17) that $\underset{\sim}{\nabla} \times \dot{\underset{\sim}{\mu}}$ does not vanish, and that $\dot{\underset{\sim}{\mu}}$ generates a vortex field. Taking the a.c.f. of the molecular angular velocity $\underset{\sim}{\omega}$, using eqn. (17), it is seen that:

$$\langle \underset{\sim}{\omega}(t).\underset{\sim}{\omega}(o)\rangle = \langle \tfrac{1}{2}\underset{\sim}{\nabla} \times \dot{\underset{\sim}{\mu}}(t) \cdot \tfrac{1}{2}\underset{\sim}{\nabla} \times \dot{\underset{\sim}{\mu}}(o)\rangle \tag{22}$$

and using the vector identity

$$(\underset{\sim}{A} \times \underset{\sim}{B}) \cdot (\underset{\sim}{C} \times \underset{\sim}{D}) = (\underset{\sim}{A} \cdot \underset{\sim}{C})(\underset{\sim}{B} \cdot \underset{\sim}{D}) - (\underset{\sim}{A} \cdot \underset{\sim}{D})(\underset{\sim}{B} \cdot \underset{\sim}{C}) \tag{23}$$

produces

$$\langle \underset{\sim}{\omega}(t) \cdot \underset{\sim}{\omega}(o)\rangle = \tfrac{1}{4}\langle \nabla^2(\dot{\underset{\sim}{\mu}}(t) \cdot \dot{\underset{\sim}{\mu}}(o)\rangle - \tfrac{1}{4}\underset{\sim}{\nabla} \cdot \dot{\underset{\sim}{\mu}}(o)\ \underset{\sim}{\nabla} \cdot \dot{\underset{\sim}{\mu}}(t)\rangle \tag{24}$$

where the ∇ operators are defined as in eqns. (18) to (20). Because the l.h.s. of eqn. (23) cannot be negative the result is obtained that

$$\langle \nabla^2 (\dot{\underset{\sim}{\mu}}(t) \cdot \dot{\underset{\sim}{\mu}}(o))\rangle \neq o \tag{25}$$

and therefore

$$\nabla^2 (\dot{\underset{\sim}{\mu}}(t) \cdot \dot{\underset{\sim}{\mu}}(o)) \neq o \tag{26}$$

for each molecule of the ensemble. Therefore the product $\dot{\underset{\sim}{\mu}}(t).\dot{\underset{\sim}{\mu}}(o)$ does not obey Laplace's equation in general.

Eqn. (23) demonstrates the dependence of the angular velocity a.c.f. on the spatial derivatives of the vector $\dot{\underset{\sim}{\mu}}$, which is the derivative of $\underset{\sim}{\mu}$ with respect to time. This shows the inevitable interdependence of rotation upon translation providing the vortex field demonstrated in eqn. (17). For a system where the kinematic relation, eqn. (16), is not valid (e.g. in which there is no rotational motion) Laplace's equation

$$\nabla^2\phi = o \tag{27}$$

becomes valid for the appropriate scalar ϕ. One such system is an ensemble composed of atoms (where $\dot{\underset{\sim}{\mu}} = \underset{\sim}{\rho}$). Therefore it is concluded that Laplace's equation (27) is valid for an ensemble of atoms, but is not valid in an ensemble of molecules, where there is the additional degree of freedom represented by eqn. (16). It might, then, be argued that eqn. (26) is in the class of Poisson equations, so that the Laplace operator ∇^2 applied to the vector product $\dot{\underset{\sim}{\mu}}(t) \cdot \dot{\underset{\sim}{\mu}}(o)$ produces a Poisson equation.

EXTENSION TO HIGHER DERIVATIVES

Using the 'spatial definition" of the dipole vector $\underset{\sim}{\mu}$ (eqn. (15)) produces with eqn. (18), the laboratory frame result:

$$[\ddot{\underset{\sim}{\mu}}]_{(1,2,3)} = [\ddot{\underset{\sim}{\mu}} - 2\underset{\sim}{\omega} \times \dot{\underset{\sim}{\mu}} - \dot{\underset{\sim}{\omega}} \times \underset{\sim}{\mu} + \underset{\sim}{\omega} \times (\underset{\sim}{\omega} \times \underset{\sim}{\mu})]_{(x,y,z)} \qquad (28)$$

with the attendant vortex and irrotational fields as discussed for the fields generated from the centre of mass vector $\underset{\sim}{r}$. The equivalent of eqn. (9) is:

$$\ddot{\underset{\sim}{\mu}} = \frac{d}{dt} \ (\underset{\sim}{\omega} \times \underset{\sim}{\mu}) = \dot{\underset{\sim}{\omega}} \times \underset{\sim}{\mu} + \underset{\sim}{\omega} \times \dot{\underset{\sim}{\mu}} \quad , \qquad (29)$$

which is seen to be the sum of a "non uniform" acceleration $\dot{\underset{\sim}{\omega}} \times \underset{\sim}{\mu}$ and a Coriolis acceleration $\underset{\sim}{\omega} \times \dot{\underset{\sim}{\mu}}$. As in section (2)

$$\underset{\sim}{\nabla} \times (\underset{\sim}{\omega} \times \dot{\underset{\sim}{\mu}}) = \underset{\sim}{0} \qquad (30)$$

because there is no net translational flow in the molecular ensemble, and in consequence neither $\underset{\sim}{\omega}$ nor $\dot{\underset{\sim}{\mu}}$ are specifically functions of x,y and z of eqn. (19). From eqns (28) and (29)

$$\dot{\underset{\sim}{\omega}} = \tfrac{1}{2}\underset{\sim}{\nabla} \times \ddot{\underset{\sim}{\mu}}, \qquad (31)$$

and, following eqns. (21) and (23):

$$<\dot{\underset{\sim}{\omega}}(t) \ . \ \dot{\underset{\sim}{\omega}}(o)>$$

$$= \tfrac{1}{4}<\nabla^2(\ddot{\underset{\sim}{\mu}}(t) \ . \ \ddot{\underset{\sim}{\mu}}(o))> - \tfrac{1}{4}<\underset{\sim}{\nabla} \ . \ \ddot{\underset{\sim}{\mu}}(o)\underset{\sim}{\nabla} \ . \ \ddot{\underset{\sim}{\mu}}(t)> \qquad (32)$$

The processes leading to eqn. (24) and (32) can be continued naturally to higher derivatives of the molecular angular velocity $\underset{\sim}{\omega}$.

The terms on the r.h.s. of eqns. (24) and (32) can be expanded further using the vector identity, eqn. (23), again. The l.h.s. of eqn. (25) is therefore expanded as

$$<\nabla^2(\dot{\underset{\sim}{\mu}}(t) \ . \ \dot{\underset{\sim}{\mu}}(o))> \neq o$$

$$= <\nabla^2(\underset{\sim}{\omega}(t) \times \underset{\sim}{\mu}(t) \ . \ \underset{\sim}{\omega}(o) \times \underset{\sim}{\mu}(o))>$$

$$= <\nabla^2((\underset{\sim}{\omega}(t) \ . \ \underset{\sim}{\omega}(o))(\underset{\sim}{\mu}(t) \ . \ \underset{\sim}{\mu}(o)))>$$

$$- <\nabla^2(\underset{\sim}{\omega}(t) \ . \ \underset{\sim}{\mu}(o))(\underset{\sim}{\omega}(o) \ . \ \underset{\sim}{\mu}(t)))> \qquad (33)$$

Eqn. (33) implies the result:

$$<\underset{\sim}{\omega}(t) \ . \ \underset{\sim}{\omega}(o)\nabla^2(\underset{\sim}{\mu}(t) \ . \ \underset{\sim}{\mu}(o) > \neq o \qquad (34)$$

because $\underset{\sim}{\omega}(t) \ . \ \underset{\sim}{\omega}(o)$ is a constant with respect to the operator ∇^2 as defined by eqns (18) to (21). Finally, therefore, eqns. (34) gives the result

$$\nabla^2(\underset{\sim}{\mu}(t) \cdot \underset{\sim}{\mu}(o)) \neq o \ . \tag{35}$$

which is also obtained from the definitions in eqns. (15) to (21). Eqns. (35) and (26) show how the molecular vector products $\underset{\sim}{\mu}(t) \cdot \underset{\sim}{\mu}(o)$ and $\dot{\underset{\sim}{\mu}}(t) \cdot \dot{\underset{\sim}{\mu}}(o)$ respectively, obey a "Poisson equation" rather than a "Laplace equation" when operated upon by ∇^2, the one result (eqn. (26)) implying the other, eqn. (35).

This set of results proves that in equilibrium molecular ensembles the dynamics of position and rotation are always linked inextricably. This is for ensembles in which there is no net flow. If there is flow then the various $\underset{\sim}{\nabla}$ operators will produce non zero results when applied to the various molecular velocities, and there will be many implications. If there is an accelerated translational (or rotational) flow, the $\underset{\sim}{\nabla} \times$; $\underset{\sim}{\nabla}\cdot$ and $\underset{\sim}{\nabla}.\underset{\sim}{\nabla}$ ( ) operators will produce non zero results when applied directly to both velocities and accelerations, making possible many new results. This process can obviously be continued ad infinitum, depending on the nature of the flow, and therefore on the type of external field applied to the molecular ensemble.

4. ANALYSIS INVOLVING THE INTER MOLECULAR SEPARATION $\underset{\sim}{R}$

Define the vector between the centre of mass of molecules 1 and 2 by:

$$\underset{\sim}{R} = \underset{\sim}{R}_1 - \underset{\sim}{R}_2 \tag{36}$$

If the two molecules are moving in such a way that this vector remains constant then the motion can be defined as cooperative. Assuming that the motion of the two molecules is cooperative in this way then and are also rotating about a common axis (like planets at the opposite ends of a common orbit) then the orbital motion is that of a macroscopic vortex. The kinematic relation (16) applies in this case to the intermolecular vector $\underset{\sim}{R}$, and may be written

$$\dot{R} = \underset{\sim}{\Omega} \times \underset{\sim}{R} \tag{37}$$

where $\underset{\sim}{\Omega}$ is the angular velocity generated by the cooperative orbital motion of the two molecules. In analogy with equation (17) therefore:

$$\underset{\sim}{\Omega} = \tfrac{1}{2}\underset{\sim}{\nabla} \times \dot{\underset{\sim}{R}} \tag{38}$$

i.e. the curl of $\dot{\underset{\sim}{R}}$ exists and this is therefore a vortex field.

More generally, if the vortex angular velocity defined in this way exists by dint of the cooperative motion of two molecules, then an indication of the existence of a macroscopic vortex from a computer simulation might be obtained through the existence of correlation functions of the type (22), and

therefore of type (24), (32) and (33) with the dipole vector $\underset{\sim}{\mu}$ of these equations replaced by $\underset{\sim}{R}$ and the molecular angular velocity $\underset{\sim}{\omega}$ by the cooperative angular velocity $\underset{\sim}{\Omega}$. The existence of correlation functions of this type is therefore a direct test of the build up of a vortex using the dynamics of molecules, rather than the principles of fluid dynamics, which use no molecular concepts, but rather points in a fluid.

It is clear that this analysis, based on the cooperative motion of two molecules, can be extended to inlcude the motion of many molecules, given the computer power. Note that the swirling motion represented by eqn. (37), the kinematic equation for the intermolecular vector, need not be confined to a plane, and may be approximately valid even when the intermolecular distance is not rigidly constant, but fluctuates, as is the case in a true molecular liquid. The existence of the a.c.f. of the orbital angular velocity $\underset{\sim}{\Omega}$ is one way of testing for the existence of the cooperative vortex motion represented by eqn. (37). Using and adapting the results of section 3 many new correlation functions of this kind can be shown to exist theoretically and explored using simulation.

COMPUTER SIMULATION METHODS

In order to put some numbers on the sum of the above analytical theory a computer simulation of supercooled liquid water at 150 K; molar volume $0.06 \times 10^{27} cm^3$ was utilised to compute the sum autocorrelation functions of interest. The potential energy between two water molecules was modelled with a five by five site - site approximation consisting of Lennard Jones and partial charge terms described elsewhere [19]. Autocorrelation functions were generated from the trajectories held on tape and computed with running time averages in the usual way. In particular it is of interest to compute the autocorrelation functions in frames (x,y,z) and (1,2,3) of the orbital velocity $\underset{\sim}{v}_1$ and the spin angular velocity $\underset{\sim}{\omega}$. It is also interesting to compare the orbital linear velocity with the centre of mass linear velocity itself in order to measure the effect of the frame transformation from (x,y,z) to (1,2,3); a transformation basic to the methodology behind this paper.

The running time averages for these autocorrelation functions were computed with segments of about 1000 time steps each, recorded every two steps.

RESULTS AND DISCUSSION

In fig. (1) are summarised the results of the computer simulation of the

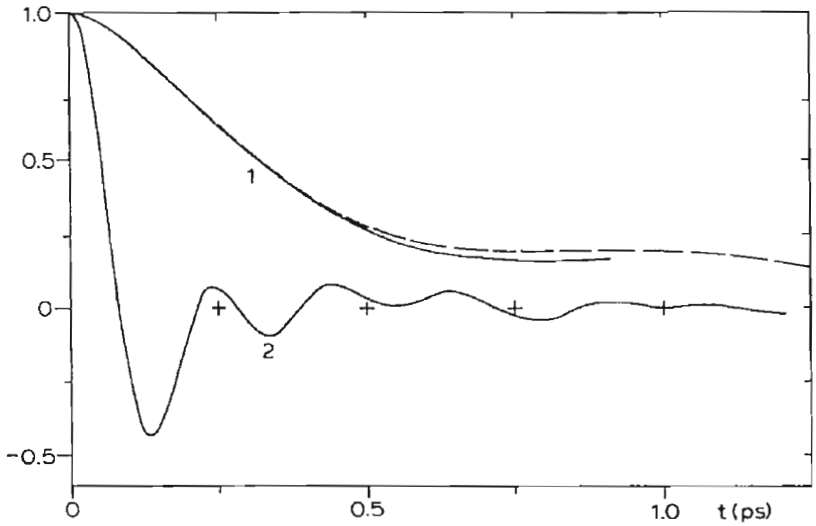

Fig. 1 Autocorrelation functions from a computer simulation of supercooled liquid water.

———— (1) Autocorrelation function of the orbital linear velocity

(2) Autocorrelation function of the angular velocity in both frames

— ——— Autocorrelation function of the linear velocity in both frames.

Abscissa time (ps).

orbital velocity autocorrelation function $\langle \underset{\sim}{v}_1(t) \cdot \underset{\sim}{v}_1(o) \rangle / \langle v_1^2 \rangle$ compared with the a.c.f. of the linear velocity correlaton function itself.

The interesting result emerges that the time dependence of the a.c.f. of the two quantities is approximately the same in both frames of reference; and also that the a.c.f. of the orbital velocity in frames (x,y,z) are virtually identical. This ensures that the analytical results of the foregoing section will be valid under conditions typified by those in supercooled water.

CONCLUSIONS

It has been established that non inertial accelerations play a fundamental role in the molecular dynamics of condensed matter and that consideration of these accelerations in the moving and fixed frames of reference leads to the classification of the various dynamical quantities in terms of vortex and irrotational fields. This might ultimately lead to a way of identifying some aspects of molecular dynamics with fluid dynamics in condensed media. The existence of the orbital linear velocity a.c.f. has been illustrated with computer simulation.

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