Molecular cross correlation functions in inertial and noninertial frames of reference

M. W. Evans
Department of Physics, University College of Swansea, Singleton Park, Swansea SA2 8PP, Wales, United Kingdom

(Received 22 December 1986; accepted 6 May 1987)

The dynamics of interacting molecules involve the translation and simultaneous rotation of each molecule in the ensemble. This means that the frame of reference defined by the principal molecular moments of inertia, frame (1,2,3), is a noninertial frame with respect to the laboratory frame (x, y,z). Furthermore, a rotating frame of reference (1,2,3)′ can be generated from (1,2,3) a by translation for each molecule from the center of mass of the origin of (x, y,z). The equations relating velocities, accelerations, and their derivatives in one of these frames to those of another are described and then used to calculate the cross correlation functions.

I. INTRODUCTION

One of the fundamental problems in molecular dynamics is to find ways of correlating statistically the interaction between rotational and translational motion. This is a problem which has thus far not been solved entirely by the analytical methods available.[1–8] This is because the theories depend fundamentally on approximations which leave out of consideration all single molecule cross correlations such as $\langle \mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$. This correlates the molecular center of mass velocity $\mathbf{v}$ and the same molecule's angular approximations results in over parametrization and confusion about frames of reference.

The state of uncertainty was finally resolved in 1981 by Ryckaert *et al.*[9] using computer simulation. This proved that the cross correlation $\langle \mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$ vanishes in frame (x, y,z) for all t in an isotropic sample, but exists for $t > 0$ in the frame (1,2,3) of the principal molecular moments of inertia. Subsequently, the time dependence of cross correlation functions (ccfs) of this type was confirmed by Evans *et al.*[10–22] for different molecular symmetries ranging from low symmetry chiral molecules to spherical tops of T_d symmetry.[22]

In 1985 the discovery of elements of $\langle \mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$ direct in the laboratory frame was reported by Evans[17] in a molecular liquid made anisotropic with a strong, uniaxial electric field. When applied in the z axis of the laboratory frame this promotes the existence[23] of the (x, y) and (y,x) elements of the ccf tensor direct in frame (x, y,z). Note that the off diagonal elements in frame (1,2,3) exist both in the presence and absence of the field depending on the molecular symmetry. Again the contemporary analytical theories had not predicted the outcome of these computer simulations because of the difficulties of over parametrization in essentially empirical description of molecular diffusion.

Papers in 1985 and 1986 reported the emergence of higher order cross correlation functions due to the realization that in the noninertial frame (1,2,3) the equations of motion contain additional terms which rarely if ever appear explicitly and clearly in the empirical theory of molecular diffusion. Examples of these are the Coriolis, centripetal, and nonuniform molecular accelerations, which exist in both frames of reference. These were cross correlated in a series of recent papers with velocities and several higher order one particle cross correlation functions discovered in the moving frame (1,2,3). These are fundamental in nature and, therefore, applicable in the statistical description of condensed phases of molecular matter.

The following sections attempt to provide a fairly rigorous and complete classification of the various new terms both in frames (1,2,3) and (x, y,z); and also provide a means of classifying and identifying the nonvanishing ccfs in both frames of reference.

II. DEFINITION OF FRAMES OF REFERENCE

The laboratory frame (x, y,z) is that of the static observer. An object that translates in this frame but does not rotate is said to be in an inertial frame of reference and obeys Newton's equations in classical nonrelativistic physics. In such a frame of reference the motion of a rigid body, e.g., a rod, is determined by the momentum of the center of mass of the rigid body and the angular momentum of that body about its center of mass. The combined motions complicate the trajectory of some point off the center of mass of the rod. In a molecule the trajectory of an atom in frame (x, y,z) is part of a rigid body whose center of mass motion is governed by Newton's equations. However, an object such as a rod or rigid molecule that both rotates and translates in frame (x, y,z) generates velocities and accelerations which are not present in the Newton equations.

The nature of these extra terms is revealed clearly by using as a vehicle of argument a frame of reference (1,2,3)′ (Fig. 1) whose origin is fixed at the origin of (x, y,z) but which rotates with respect to (x, y,z) with an angular velocity $\boldsymbol{\omega}$. For each molecule in the ensemble the frame (1,2,3) of the principal molecular moments of inertia is generated from frame (1,2,3)′ by a translation of the origin of the latter to the molecular center of mass. For each molecule in the ensemble, therefore, the angular velocity $\boldsymbol{\omega}$ of frame (1,2,3)′ with respect to (x, y,z) is the molecular angular velocity it-

 0021-9606/87/162257-06$02.10

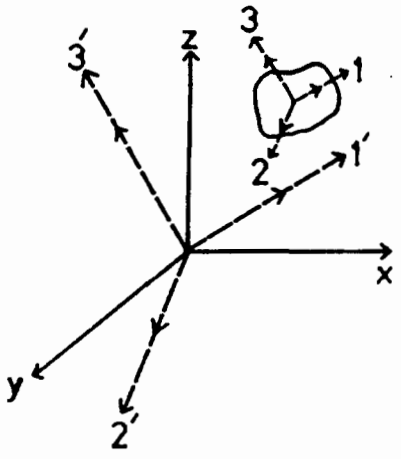

FIG. 1. Schematic of frames of reference. (x,y,z): laboratory frame. (1,2,3): moving frame. (1,2,3)': rotating frame.

self. Therefore, ω is a constant of frame transformation from (x,y,z) to (1,2,3)' or vice versa.

With these definitions, therefore, there is a basic theorem linking the differential operator D_f in the laboratory frame (x,y,z) to the equivalent in frame (1,2,3)'. This can be written as

$$D_f\mathbf{r} = (D_m + \boldsymbol{\omega}\times)\mathbf{r} \tag{1}$$

and conversely

$$D_m\mathbf{r} = (D_f - \boldsymbol{\omega}\times)\mathbf{r}. \tag{2}$$

In Eqs. (1) and (2) $\mathbf{r}$ is the position vector of the molecular center of mass. The operator D_f implies differentiation of $\mathbf{r}$ with respect to time in frame (x,y,z) and D_m the equivalent in frame (1,2,3)'. Equations (1) and (2) can, therefore, be written as

$$[\mathbf{v}]_{(x,y,z)} = [\mathbf{v} + \boldsymbol{\omega}\times\mathbf{r}]_{(1,2,3)'}, \tag{3}$$

$$[\mathbf{v}]_{(1,2,3)'} = [\mathbf{v} - \boldsymbol{\omega}\times\mathbf{r}]_{(x,y,z)}. \tag{4}$$

In Eq. (3) $[\mathbf{v}]_{(x,y,z)}$ is the linear center of mass velocity in frame (x,y,z), which is equivalent in the rotating frame (1,2,3)' to the sum on the right-hand side of this equation. The sum is made up of the Newtonian velocity $\mathbf{v}$ and the linear velocity $\boldsymbol{\omega}\times\mathbf{r}$ which is zero only when $\boldsymbol{\omega}$ is zero. This shows clearly the difference between the dynamics of an atom and a molecule, i.e., between a body which is translating but not rotating and molecular dynamics, where both terms on the right-hand side of Eq. (3) are important.

Equation (4) reverses the process, and shows that the center of mass linear velocity $\mathbf{v}$ in frame (1,2,3)' is equivalent to the difference on the right-hand side of Eq. (4). This equation shows, therefore, that the linear velocity exists directly in the lab frame (x,y,z). This means that the rotational motion of a body that is also translating imparts the linear velocity $\boldsymbol{\omega}\times\mathbf{r}$ to its translational center of mass motion in the laboratory frame (x,y,z).

The vector difference $[\mathbf{v} - \boldsymbol{\omega}\times\mathbf{r}]_{(x,y,z)}$ also exists in frame (1,2,3), the frame of the principal molecular moments of inertia, through the transformation, for any vector $\mathbf{A}$:

$$\begin{aligned} A_1 &= A_x e_{1x} + A_y e_{1y} + A_z e_{1z}, \\ A_2 &= A_x e_{2x} + A_y e_{2y} + A_z e_{2z}, \\ A_3 &= A_x e_{3x} + A_y e_{3y} + A_z e_{3z}, \end{aligned} \tag{5}$$

where the subscripts refer to the axes of the appropriate frame and where the unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ are in the principal moment of inertia axes 1, 2, and 3. Thus, $\mathbf{e}_{1x}$ is the x component in frame (x,y,z) of $\mathbf{e}_1$ and so on.

Using Eq. (5), therefore,

$$(\boldsymbol{\omega}\times\mathbf{r})_1 = (\boldsymbol{\omega}\times\mathbf{r})_x e_{1x} + (\boldsymbol{\omega}\times\mathbf{r})_y e_{1y} + (\boldsymbol{\omega}\times\mathbf{r})_z e_{1z} \tag{6}$$

and so on for the other components $(\boldsymbol{\omega}\times\mathbf{r})_2$ and $(\boldsymbol{\omega}\times\mathbf{r})_3$.

Equation (5), therefore, defines the existence of the linear velocity in the frame (1,2,3).

Similarly all the linear accelerations and their derivatives explored in the following sections exist in all three frames of reference.

A. The linear accelerations

These are generated by operating twice on the right-hand sides of Eqs. (1) and (2) with the appropriate differential operators, giving

$$D_f(D_f\mathbf{r}) = (D_m + \boldsymbol{\omega}\times)[D_m\mathbf{r} + \boldsymbol{\omega}\times\mathbf{r}] \tag{7}$$

and, conversely,

$$D_m(D_m\mathbf{r}) = (D_f - \boldsymbol{\omega}\times)[D_f\mathbf{r} - \boldsymbol{\omega}\times\mathbf{r}] \tag{8}$$

or in terms of velocities

$$[\dot{\mathbf{v}}]_{(x,y,z)} = [\dot{\mathbf{v}} + 2\boldsymbol{\omega}\times\mathbf{v} + \dot{\boldsymbol{\omega}}\times\mathbf{r} + \boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})]_{(1,2,3)'}, \tag{9}$$

$$[\dot{\mathbf{v}}]_{(1,2,3)'} = [\dot{\mathbf{v}} - 2\boldsymbol{\omega}\times\mathbf{v} - \dot{\boldsymbol{\omega}}\times\mathbf{r} + \boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})]_{(x,y,z)}. \tag{10}$$

All the terms on the right-hand side of Eq. (10) can be transformed into the principal molecular moment of inertia frame using Eq. (5).

Equation (9) shows the Newtonian linear acceleration $\dot{\mathbf{v}}$ supplemented in a simultaneously rotating and translating body by three more linear accelerations. These are real and exist in frame (x,y,z). Molecular dynamics requires the full consideration of all four accelerations, both in frames (x,y,z) and (1,2,3). They are:

(i) the Newtonian acceleration $\dot{\mathbf{v}}$;

(ii) the Coriolis acceleration $-2\boldsymbol{\omega}\times\mathbf{v}$;

(iii) the centripetal acceleration $\boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})$;

(iv) the nonuniform acceleration $-\dot{\boldsymbol{\omega}}\times\mathbf{r}$.

The last two of this list require explicit use of the position vector $\mathbf{r}$ and, therefore, definition of the coordinates of the center of mass of each molecule in the sample with respect to the origin of frame (x,y,z). These coordinates are defined with[21]

$$\langle\mathbf{r}(t)\rangle = \mathbf{0}; \tag{11}$$

$$\lim_{t\to\infty}\langle\mathbf{r}(t)\cdot\mathbf{r}(0)\rangle = 0; \tag{12}$$

in the laboratory frame (x,y,z).

B. Derivatives of the linear accelerations

These terms are derived by straightforward repeated application of the appropriate differential operators, so that

$$[\ddot{\mathbf{v}}]_{(x,y,z)} = [\mathbf{D}_m + \boldsymbol{\omega}\times][\dot{\mathbf{v}} + 2\boldsymbol{\omega}\times\mathbf{v} + \dot{\boldsymbol{\omega}}\times\mathbf{r} + \boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})]_{(1,2,3)'}, \quad (13)$$

$$[\ddot{\mathbf{v}}]_{(1,2,3)'} = [\mathbf{D}_f - \boldsymbol{\omega}\times][\dot{\mathbf{v}} + 2\boldsymbol{\omega}\times\mathbf{v} - \dot{\boldsymbol{\omega}}\times\mathbf{r} + \boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})]_{(x,y,z)}. \quad (14)$$

Therefore, there are, by Eq. (14), seven additional linear acceleration time derivatives to the Newtonian term $[\ddot{\mathbf{v}}]_{(x,y,z)}$, both in frames (x,y,z) and by Eq. (5) in frame (1,2,3).

Equations (13) and (14) illustrate that the set of linear velocities, linear accelerations, and their time derivatives to order n contains $1,3,7,15\ldots,(2^n-1)$ terms which all contribute in the laboratory frame and that of the principal molecular moments of inertia. A theory such as the original theory of rotational diffusion leaves out of consideration all these terms by definition. With advanced computer architecture, such as the Kingston ICAP1, there is no further need to approximate in this way. All the terms can be made available to monitor the dynamics of interacting molecules. One of the ways of implementing the extra information, and of controlling it systematically, is the construction and identification of nonvanishing time cross correlation functions that exist among the various linear velocities, accelerations, and higher time derivatives. These ccfs would then be available to monitor the dynamical behavior of any molecular ensemble in a very detailed way.

This is a great advance on the theories of molecular diffusion currently available.

C. Angular velocities accelerations, and time derivatives

1. Angular velocities

By definition,

$$[\boldsymbol{\omega}]_{(1,2,3)'} = [\boldsymbol{\omega}]_{(x,y,z)} \quad (15)$$

so there are no angular velocities other than the simple lab frame angular velocity itself. As mentioned in the introduction, the cross correlation exists between this and the Newtonian linear velocity in frame (1,2,3). This was the first ccf to be discovered by computer simulation,[9] viz.

$$\langle \mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle_{(1,2,3)}.$$

The next section aims to show that systematic consideration of the cross correlations in frame (1,2,3) between linear and angular terms should reveal many more possibilities, all fundamental to molecular dynamics in condensed matter. Whether or not these exist in frame (1,2,3) for an isotropic sample could be checked with group theory, based on the point group of the molecule under consideration, or, alternatively, with parity and time reversal symmetry. This provides a sound basis for checking the accuracy of the computer simulations of the ccfs, which should exist and which should just be noise, i.e., vanish by symmetry.

For example, the ccf between the linear velocity $\boldsymbol{\omega}\times\mathbf{r}$ and the angular velocity $\boldsymbol{\omega}$:

$$\langle \boldsymbol{\omega}(t)\times\mathbf{r}(t)\boldsymbol{\omega}^T(0)\rangle$$

vanishes for nearly all molecular symmetries in frame (1,2,3) by group symmetry for all t and vanishes in frame (x,y,z) by parity symmetry for all molecules. This has been checked independently by computer simulation,[26] which gave the expected results for a sample as small as 108 molecules of C_{2v} symmetry.

2. Angular acceleration

This is generated by the usual operators

$$[\dot{\boldsymbol{\omega}}]_{(x,y,z)} = [D_m + \boldsymbol{\omega}\times][\boldsymbol{\omega}]_{(1,2,3)'}, \quad (16)$$

$$[\dot{\boldsymbol{\omega}}]_{(1,2,3)'} = [D_f - \boldsymbol{\omega}\times][\boldsymbol{\omega}]_{(x,y,z)}, \quad (17)$$

which again give the simple result

$$[\dot{\boldsymbol{\omega}}]_{(x,y,z)} = [\dot{\boldsymbol{\omega}}]_{(1,2,3)'}. \quad (18)$$

Therefore, again, there are no noninertial angular accelerations in either frame. It follows that there are none in frame (1,2,3). By symmetry the only cross correlation function between linear and angular acceleration that survives in an isotropic molecular ensemble is

$$\langle \dot{\mathbf{v}}(t)\dot{\boldsymbol{\omega}}^T(0)\rangle_{(1,2,3)}$$

in frame (1,2,3). All the other possible ccf's between the three non-Newtonian linear accelerations and $\dot{\boldsymbol{\omega}}$ vanish by symmetry in both frames.[26] Again this has been checked individually by computer simulation for a 108 molecule sample of C_{2v} triatomic molecules.

3. Angular acceleration derivatives

At this stage in the development there appear the first angular terms from the operators

$$[\ddot{\boldsymbol{\omega}}]_{(x,y,z)} = [\mathbf{D}_m + \boldsymbol{\omega}\times][\dot{\boldsymbol{\omega}}]_{(1,2,3)'} = [\ddot{\boldsymbol{\omega}} + \boldsymbol{\omega}\times\dot{\boldsymbol{\omega}}]_{(1,2,3)'}, \quad (19)$$

$$[\ddot{\boldsymbol{\omega}}]_{(1,2,3)'} = [D_m - \boldsymbol{\omega}\times][\dot{\boldsymbol{\omega}}]_{(x,y,z)} = [\ddot{\boldsymbol{\omega}} - \boldsymbol{\omega}\times\dot{\boldsymbol{\omega}}]_{(x,y,z)}. \quad (20)$$

In total therefore, there are 16 possible ccfs between the linear and angular acceleration derivatives in frames (x,y,z) and (1,2,3) at this level of the development. All of these are accessible for computation in most simulation algorithms, which provide terms up to the second derivative of the acceleration.

III. CLASSIFICATION OF HIGHER ORDER CROSS CORRELATION FUNCTIONS

From consideration of symmetry the higher order ccf of the type

$$\langle \boldsymbol{\omega}(t)\times\mathbf{A}(t)\mathbf{A}^T(0)\rangle$$

exists in the moving frame of reference (1,2,3) but vanishes in the laboratory frame (x,y,z). This result originates in the general expression for the derivative of order n in the rotating frame (1,2,3)' and the laboratory frame (x,y,z):

$$[\mathbf{v}]^{(n+2)}_{(x,y,z)} = [\mathbf{D}_m + \boldsymbol{\omega}\times]_{(1)}[\mathbf{D}_m + \boldsymbol{\omega}\times]_{(2)}\cdots \times[\mathbf{D}_m + \boldsymbol{\omega}\times]_{(n)}[\dot{\mathbf{v}} + 2\boldsymbol{\omega}\times\mathbf{v} + \dot{\boldsymbol{\omega}}\times\mathbf{r} + \boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})]_{(1,2,3)'}, \quad (21)$$

$$[\mathbf{v}]^{(n+2)}_{(1,2,3)'} = [\mathbf{D}_f - \boldsymbol{\omega}\times]_{(1)}[\mathbf{D}_f - \boldsymbol{\omega}\times]_{(2)}\cdots \times[\mathbf{D}_f - \boldsymbol{\omega}\times]_{(n)}[\dot{\mathbf{v}} - 2\boldsymbol{\omega}\times\mathbf{v} - \dot{\boldsymbol{\omega}}\times\mathbf{r} + \boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})]_{(x,y,z)}. \quad (22)$$

A. The omega patterns

(1) It can be seen by inspection of Eqs. (21) and (22) that patterns of the type

$$\langle\boldsymbol{\omega}(t)\times\mathbf{A}(t)\mathbf{A}^T(0)\rangle_{(1,2,3)}, \quad (23)$$

$$\langle\boldsymbol{\omega}(t)\times[\boldsymbol{\omega}(t)\times\mathbf{A}(t)][\boldsymbol{\omega}(0)\times\mathbf{A}(0)]^T\rangle_{(1,2,3)}, \quad (24)$$

$$\langle\boldsymbol{\omega}(t)\times\{\boldsymbol{\omega}(t)\times[\boldsymbol{\omega}(t)\times\mathbf{A}(t)]\}\times\{\boldsymbol{\omega}(0)\times[\boldsymbol{\omega}(0)\times\mathbf{A}(0)]\}^T\rangle_{(1,2,3)}, \quad (25)$$

and so on exist in frame (1,2,3), where **A** denotes the vector generated in frame (1,2,3) from

$$[\dot{\mathbf{v}} - 2\boldsymbol{\omega}\times\mathbf{v} - \dot{\boldsymbol{\omega}}\times\mathbf{r} + \boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})]_{(x,y,z)}$$

through the frame transformation (5).

(2) Furthermore, patterns of the type

$$\langle\boldsymbol{\omega}(t)\times D_f\mathbf{A}(t)[D_f\mathbf{A}(0)]^T\rangle_{(1,2,3)}, \quad (26)$$

$$\langle\boldsymbol{\omega}(t)\times D_f^2\mathbf{A}(t)[D_f^2\mathbf{A}(0)]^T\rangle_{(1,2,3)}, \quad (27)$$

$$\langle\boldsymbol{\omega}(t)\times D_f^3\mathbf{A}(t)[D_f^3\mathbf{A}(0)]^T\rangle_{(1,2,3)}, \quad (28)$$

and so on exist in frame (1,2,3) using the same notation as Eqs. (23) to (25).

(3) Finally, in this group, cross patterns exist in frame (1,2,3) of the general type:

$$\langle\boldsymbol{\omega}(t)\times\mathbf{B}(t)\mathbf{B}^T(0)\rangle_{(1,2,3)};\quad \mathbf{B}\equiv\{\boldsymbol{\omega}\times D_f\mathbf{A}(t) + D_f[\boldsymbol{\omega}\times\mathbf{A}(t)]\}_{(1,2,3)}, \quad (29)$$

$$\langle\boldsymbol{\omega}(t)\times\mathbf{C}(t)\mathbf{C}^T(0)\rangle_{(1,2,3)};\quad \mathbf{C}\equiv\{(\mathbf{D}_f - \boldsymbol{\omega}\times)[\boldsymbol{\omega}\times D_f\mathbf{A}(t) + D_f(\boldsymbol{\omega}\times\mathbf{A}(t))]\}_{(1,2,3)}, \quad (30)$$

$$\langle\boldsymbol{\omega}(t)\times\mathbf{D}(t)\mathbf{D}^T(0)\rangle_{(1,2,3)};\quad \mathbf{D}\equiv\{(\mathbf{D}_f - \boldsymbol{\omega}\times)(D_f - \boldsymbol{\omega}\times)[\boldsymbol{\omega}\times D_f\mathbf{A}(t) + D_f(\boldsymbol{\omega}\times\mathbf{A}(t))]\}_{(1,2,3)}, \quad (31)$$

and so on.

B. The D_f patterns

In addition to the above nonvanishing cross correlation functions in frame (1,2,3), others exist in both frames (x,y,z) and (1,2,3) because of the general result for all correlation functions

$$\langle D_f\mathbf{A}(t)\mathbf{A}^T(0)\rangle \neq 0 \quad \text{for } t>0 \quad (32)$$

both in frames (x,y,z) and (1,2,3).

In one sense the result

$$\langle\boldsymbol{\omega}\times\mathbf{A}(t)\mathbf{A}^T(0)\rangle \neq 0 \quad \text{for } t>0 \quad (33)$$

in frame (1,2,3) is a special case of Eq. (32), which vanishes in frame (x,y,z) because of the parity symmetry difference imposed by the vector cross product $\boldsymbol{\omega}\times\mathbf{A}(t)$. Using the result (32), then both in frames (x,y,z) and (1,2,3) the following patterns of nonvanishing higher order cross correlation functions emerge from inspection of Eqs. (21) and (22),

(1) $\langle D_f\mathbf{A}(t)\mathbf{A}^T(0)\rangle$, $\langle D_f^2\mathbf{A}(t)(D_f\mathbf{A})^T(0)\rangle$, $\langle D_f^3\mathbf{A}(t)(D_f^2\mathbf{A})^T(0)\rangle$; (34)

(2) $\langle D_f[\boldsymbol{\omega}(t)\times\mathbf{A}(t)][\boldsymbol{\omega}(0)\times\mathbf{A}(0)]^T\rangle$, $\langle D_f\{\boldsymbol{\omega}(t)\times[\boldsymbol{\omega}(t)\times\mathbf{A}(t)]\}\times\{\boldsymbol{\omega}(0)\times[\boldsymbol{\omega}(0)\times\mathbf{A}(0)]\}^T\rangle$; (35)

and finally; analogous with Eqs. (29) and (31):

$\langle D_f\mathbf{B}(t)\mathbf{B}^T(0)\rangle$, $\langle D_f\mathbf{C}(t)\mathbf{C}^T(0)\rangle$, $\langle D_f\mathbf{D}(t)\mathbf{D}^T(0)\rangle$, (36)

where B, C, and D are defined as in Eqs. (29) to (31).

IV. DISCUSSION

The above classification schemes allowed the identification of nonvanishing higher order ccfs in the moving frame (1,2,3) which have not been considered hitherto in the theory of molecular diffusion because of its inherent approximations. Access to conventional pipeline processors has been limited but this situation is now rapidly changing, allowing the systematic exploration of new liquid state properties. In many respects the cross correlation function has advantages over the autocorrelation function, for example:

(i) there are many more ccfs than acfs, and they can be used to investigate the interrelation between different kinds of molecular motion in critical conditions such as phase changes.

(ii) the ccfs have the extra property of amplitude as well as time dependence. In other words the ccf is zero at $t=0$ and at long times but has finite maxima or minima in the intermediate interval which characterize the molecular dynamics. The amplitude and frequency of the oscillations are, in general, different for each element of the cross correlation matrix. Thus, the computation of these amplitudes is a new method of monitoring molecular dynamics which could prove fruitful in many different problems.

A. Monitoring of phase changes in the ices

The detection and description of phase changes by molecular dynamics computer simulation is a challenge which can be met adequately only with a sufficient number of molecules in the molecular dynamics sample. This is because a

phase transition, especially liquid to crystalline solid, is essentially a cooperative process, in regard to both rotational and translational motion. At some stage the motion in the molecular liquid must give way to cooperative rotation and translation in the solid, where lattice modes are observable in the Raman or far infrared. The implementation of single molecule ccfs of all types to monitor these transitions is a natural method of analysis when these functions are themselves made up both of rotational and translational variables, together with the center of mass coordinates $\mathbf{r}$.

The various experimentally identified phases of ice and the ice water transition itself present an interesting challenge because the intermolecular pair potential for water is known with increasing accuracy. Large molecular dynamics samples for water should, therefore, be capable of detecting the phase transitions in ice with careful monitoring of the molecular dynamics with ccfs. It should be particularly advantageous to use ccfs in solid-to-solid phase transitions, where spectral changes and changes in acfs are usually difficult to detect with certainty in the appropriate subpicosecond time interval.

B. Representations of flow phenomena on a molecular level

Recent molecular dynamics simulations[29] of two-dimensional flow around a circular obstruction, using upwards of 160 000 hard disks, have revealed the existence of eddies, and Reynolds number flow phenomena, using molecular dynamics computer simulation methods. This is an important step forward in our knowledge of the relation between molecular and hydrodynamics, and was achieved with a simple hard disk potential. With this, however, there is no scope for the investigation of ccfs of the type mentioned in this paper, because the angular motion of each individual disk is not accounted for. Nonetheless, the phenomena that can be seen with this system include many of the systems that are well known from continuum hydrodynamics, such as eddy pair formation downstream of the circular obstacle. In the region of the eddy pair the translation motion of the flow prior to its encounter with the obstacle is obviously transformed into rotational motion, clockwise in one eddy and counter clockwise in the other. In three-dimensional fully molecular systems the ccf in the region of the eddy, downstream of the cylindrical obstacle should be significantly different in time dependence on a molecular scale than those in the flow region outside the eddy.

The eddy and wake patterns downstream also change with time, and depend, as in the hydrodynamics of true flows, on the initial conditions. Therefore, the construction of ccfs by running time averaging would have to depend implicitly on the assumption that certain regions of the flow were statistically stationary for a long enough time interval over which to construct the running time averages. Nevertheless there is reason to believe that such a study would provide significant information on the behavior of three-dimensional flow around a cylindrical object in a three-dimensional molecular dynamics simulation.

Another possibility provided by large molecular dynamics samples is that of setting up vortices in the sample with the help of rotating external electric fields, or a circularly polarized electric field such as

$$E_y = E_0 \cos\left(\omega t - \omega \frac{x}{c}\right), \tag{37}$$

$$E_z = \pm E_0 \sin\left(\omega t - \omega \frac{x}{c}\right), \tag{38}$$

which is assumed to generate a torque of the form

$$\boldsymbol{\mu}\times\mathbf{E} = \mathbf{i}(\mu_y E_z - \mu_z E_y) - \mathbf{j}(\mu_x E_z - \mu_z E_x) + \mathbf{k}(\mu_x E_y - \mu_y E_x) \tag{39}$$

with

$$E_x = 0; \quad E_y = E_0 \cos \omega t; \quad E_z = \pm E_0 \sin \omega t. \tag{40}$$

Therefore, the torque will be dependent on whether the field is right or left polarized. The right polarized torque is

$$(\boldsymbol{\mu}\times\mathbf{E})_r = E_0 \sin \omega t(\mu_y \mathbf{i} - \mu_x \mathbf{j}) + E_0 \cos \omega t(\mu_x \mathbf{k} - \mu_z \mathbf{i}) \tag{41}$$

and the left polarized torque is

$$(\boldsymbol{\mu}\times\mathbf{E})_l = -E_0 \sin \omega t(\mu_y \mathbf{i} - \mu_x \mathbf{j}) + E_0 \cos \omega t(\mu_x \mathbf{k} - \mu_z \mathbf{i}). \tag{42}$$

If selected sample regions of the molecular dynamics cube are irradiated in a computer simulation with fields of type (41) or (42) vortices will be set up in a clockwise or counterclockwise direction. It would be interesting to check the effect these vortices would have on the rest of the sample; and to see if the subsequent effects could be monitored by computer simulation. The hydrodynamic theory of counter rotating vortices would be checked against the indications of the simulation. This would also be a situation accessible to experimental investigation with two strong laser fields, one right and one left circularly polarized. Particularly interesting effects would be seen with chiral molecules, because a strong circularly polarized field would rotate the chiral molecule, causing subsequent translation of the center of mass. Bigger or smaller regions of sample could be treated with the laser fields and the effects monitored.

C. Vibration/translation/rotation coupling

The introduction of bond vibration into the intermolecular potential energy representation will allow the consideration of cross correlation between vibrational coordinates, rotation, and translation of the molecule's own center of mass. In the context of quantum mechanics the cross correlation between vibration and rotation is already well known, and manifests itself in infrared and Raman spectra. In quantum mechanics the effect of rotation/translation cross correlation has been reviewed for HD liquid. If the center of mass translation is correlated to the molecular rotation then the usual selection rules are changed, extra absorption appear, and the overall spectrum is significantly affected.

The rules that govern the existence of these quantum mechanical cross correlations are expected to be the same as those governing the classical mechanical counterparts discussed in this paper. Similarly, whenever a classical ccf is

induced to exist directly in the laboratory frame (x, y, z) there will be analogous quantum effects directly visible in the laboratory frame spectra, i.e., the application of an external electric field to vibration rotation or rotation translation quantum lines of a gaseous sample for instance could result in the splitting of the observable quantum lines into further fine structure. This would be detectible with double resonance techniques at ultrahigh resolution and is roughly analogous to Stark splitting, where an external electric field is used to split quantum lines.

The cross correlation between center of mass translation and bond vibration has not been considered in terms of either classical cross correlation functions or their quantum mechanical equivalents in the theory of condensed phase molecular dynamics, and there is scope for considerable development in this area.

ACKNOWLEDGMENTS

IBM is acknowledged for the award of a Visiting Professorship and the University of Wales for a Pilcher Senior Fellowship.

[1]P. Debye, *Polar Molecules* (Chemical Catalog, New York, 1929).
[2]D. W. Condiff and J. S. Dahler, J. Chem. Phys. **44**, 3988 (1966).
[3]L. P. Hwang and J. H. Freed, J. Chem. Phys. **63**, 118, 4017 (1975).
[4]P. G. Wolynes and J. M. Deutch, J. Chem. Phys. **67**, 733 (1977).
[5]G. T. Evans, Mol. Phys. **36**, 1199 (1978).
[6]U. Steiger and R. F. Fox, J. Math. Phys. **23**, 296 (1982).
[7]G. van der Zwan and J. T. Hynes, Physica A **121**, 223 (1983).
[8]E. Dickinson, Annu. Rep. Chem. Soc. C **14**, 421 (1985).
[9]J. P. Ryckaert, A. Bellemans, and G. Ciccotti, Mol. Phys. **44**, 979 (1981).
[10]M. W. Evans, J. Chem. Soc. Chem. Commun. **1983**, 139.
[11]M. W. Evans, Phys. Rev. Lett. **50**, 371 (1983).
[12]M. W. Evans and G. J. Evans, J. Chem. Soc. Faraday Trans. 2 **79**, 767 (1983).
[13]M. W. Evans, J. Mol. Liquids **26**, 49 (1983).
[14]M. W. Evans, G. J. Evans, and J. Baran, J. Chem. Soc. Faraday Trans. 2 **79**, 1473 (1983).
[15]M. W. Evans, J. Mol. Liquids **26**, 229 (1983).
[16]M. W. Evans and G. J. Evans, in *Advances in Chemical Physics*, edited by M. W. Evans, series editors I. Prigogine and S. A. Rice (Wiley–Interscience, New York, 1985), Vol. 63.
[17]M. W. Evans, Phys. Lett. A **102**, 248 (1984).
[18]M. W. Evans, Phys. Rev. A **31**, 3947 (1985).
[19]M. W. Evans, J. Chem. Soc. Faraday Trans. 2 **81**, 1463 (1985).
[20]M. W. Evans, Phys. Rev. Lett. **55**, 1551 (1985).
[21]M. W. Evans, Phys. Rev. A **33**, 1903 (1986).
[22]M. W. Evans, Phys. Rev. A (in press).
[23]M. W. Evans, Physica B **131**, 273 (1985).
[24]L. D. Landau and E. M. Lifshitz, *Mechanics*, 3rd ed. (Pergamon, Oxford, 1976), p. 128ff.
[25]M. R. Spiegel, *Theory and Problems of Vector Analysis* (Schaum, New York, 1958), p. 53ff.
[26]M. W. Evans and G. J. Evans, Phys. Rev. A **34**, 468 (1986).
[27]M. Woijcik and E. Clementi, IBM Internal Report KGN 61.
[28]A. Laaksonen, IBM Internal Report KGN 41.
[29]D. C. Rapaport and E. Clementi, Phys. Rev. Lett. **57**, 695 (1986).